Società Chimica Italiana

SCI2021

XXVII CONGRESSO NAZIONALE DELLA SOCIETÀ CHIMICA ITALIANA

LA CHIMICA GUIDA LO SVILUPPO SOSTENIBILE

14–23 SETTEMBRE 2021

DID – ELE – MAS – TEO – TEC – TFA

BOOK OF ABSTRACTS
XXVII congresso della SCI, 2021

La chimica guida lo sviluppo sostenibile
14–23 settembre 2021

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Società Chimica Italiana | SCI2021

Benvenuti a SCI2021!

Il Congresso Nazionale della Società Chimica Italiana, giunto alla sua XXVII edizione, si svolgerà in modo virtuale da martedì 14 settembre a giovedì 23 settembre 2021. Come di consueto, sarà un punto di incontro e di confronto per tutto il mondo della chimica in Italia su argomenti di grande attualità.

Il congresso sarà aperto dalla ***plenary lecture*** **del Prof. Stanley Whittingham, premio Nobel per la Chimica 2019**, e prevede interventi di una serie di illustri oratori, fra cui **il premio Nobel per la Chimica 1981, Prof. Roald Hoffmann**. Il congresso si articolerà in sessioni plenarie di interesse generale e sessioni parallele, a cura delle Divisioni della Società Chimica Italiana. Nel pomeriggio di mercoledì 22 settembre sono previsti eventi satellite di interesse industriale, accessibili gratuitamente per gli iscritti al congresso.

Nelle attuali necessità di distanziamento sociale, il congresso si svolgerà tutto in modalità live telematica, con presentazioni, discussioni e tavole rotonde in diretta. Gli interventi verranno comunque registrati e resi disponibili ai partecipanti nelle due settimane successive alla chiusura del congresso, con possibilità di contatto e discussione con i presentatori.

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XXVII Congresso Nazionale della Società Chimica Italiana
“SCI 2021”, 14-23 settembre 2021

	14 settembre	15 settembre	16 settembre	17 settembre
09:30-10:30		**Lavori Divisioni** **14 Sessioni Parallele** 1 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 2 (TEC) + 3 (ELE) + 1 (TFA)	**Lavori Divisioni** **14 Sessioni Parallele** 3 (ANA) + 3 (FIS) + 2 (IND) + 3 (ORG) + 1 (CSB) + 1 (ELE) + 1 (TEC)	**Lavori Divisioni** **14 Sessioni Parallele** 2 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 1 (TEC) + 3 (ELE) + 1 (TFA)
10:30-11:00				
11:00-11:30				
11:30-12:00				
12:00-12:30			Break	
12:30-13:00			**ASSEMBLEE DIVISIONALI** **14 sessioni parallele** **(12:30 - 14:45)**	
13:00-14:00		**Break**		**Break**
14:00-14:30		ePoster Session		ePoster Session
14:30-15:00				
15:00-16:00	**APERTURA DEL CONGRESSO** *Saluti* **Maria Cristina MESSA** Ministro del MUR **Maria Chiara CARROZZA** Presidente CNR **Plenary Lecture del Prof. Stanley WHITTINGHAM** **PREMIO NOBEL PER LA CHIMICA 2019** Binghamton University, State University of New York, USA	**Lavori Divisioni** **14 Sessioni Parallele** 3 (ANA) + 2 (FAR) + 1 (IND) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 1 (TEO)	Sessione plenaria 2 ***La Chimica per il Benessere e la Qualità della Vita*** **Gunda I. GEORG** University of Minnesota, Department of Medicinal Chemistry, USA	**Lavori Divisioni** **14 Sessioni Parallele** 3 (ANA) + 1 (IND) + 1 (ABC) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 2 (TEO)
16:00-16:30	Sessione plenaria 1 ***Chimica, la Scienza al Centro*** **PREMIAZIONE DELLE MEDAGLIE SCI 2020**		**Juliane HOLLENDER** Swiss Federal Institute of Aquatic Science and Technology	
16:30-17:00			**Luis Liz MARZAN** CIC biomaGUNE, San Sebastián, Spain	
17:00-:17:30	Break		**Patrick COUVREUR** Université Paris-Sud France	
17:30-18:00	***Elsevier’s Lecture*** **Ralf METZLER** Theoretical Physics, University of Potsdam, Germany		**Mark NOE** vice-Presidente della Pfizer	
18:00-18:30	Live Q&A Sessione 1	Discussione	Live Q&A Sessione 2	Discussione
18,30-19,30	ePoster	e-poster	e-poster	e-poster

	20 settembre	21 settembre	22 settembre	23 settembre
09:30-10:30	**Lavori Divisioni** **3 Sessioni Parallele** 3 (ORG)	**Lavori Divisioni** **14 Sessioni Parallele** 2 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 1 (TEC) + 3 (ELE) + 1 (TFA)	Gruppo Giovani **Yan LIANG** University of Science and Technology of China	**Lavori Divisioni** **13 Sessioni Parallele** 3 (ANA) + 3 (FIS) + 1 (IND) + 3 (INO) + 3 (ORG)
10:30:11:00			**2 Sessioni Parallele**	
11:00-11:30				
11:30-12:30				
12:30-13:00	**Break**			

13:00-14:00	**ASSEMBLEA GENERALE** **(13:00 - 14:45)**	Break	Break	Break
14:00-15:00		ePoster Session	ePoster Session	ePoster Session
15:00-16:00	Sessione plenaria 3 ***La Chimica per la Cultura*** **Prof. Roald HOFFMANN** **PREMIO NOBEL PER LA CHIMICA 1981** Department of Chemistry Cornell University Ithaca USA	**Lavori Divisioni** **12 Sessioni Parallele** 3 (ANA) + 1 (IND) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 1 (TEO)	**Eventi Satellite** **5 Sessioni Parallele** **- Principi attivi e formulazioni in ambito cosmetico** **- Ruolo della Chimica nella produzione e controllo dei farmaci biotecnologici** **- Valorizzazione di scarti di filiere produttive** **- Sostenibilità di polimeri e compositi** **- La conversione e lo stoccaggio dell'energia chimica in energia elettrica, nella vita odierna e nella società futura**	Sessione plenaria 4 ***La Chimica per l'Industria del Futuro*** **Luigi NICOLAIS** Research Policy Advisor to MUR **Avelino CORMA** Institute of Chemical Technology Polytechnical University of Valencia, Spain
16:00-16:30	**Maria Perla COLOMBINI** Dipartimento di Chimica e Chimica Industriale, Università di Pisa			**Lidia ARMELAO** Direttore del Dipartimento di Scienze Chimiche e Tecnologia dei Materiali, CNR
16:30-17:00	Break			Break
17:00-18.00	TAVOLA ROTONDA **Divulgazione scientifica e immagine della Chimica** Partecipano: **Piero Angela** **Silvano Fuso** **Massimo Polidoro** **Luigi Campanella** Coordina: **Giorgio Cevasco**			**Nausicaa ORLANDI** Presidente Federazione Nazionale Ordini Chimici e Fisici **Mario MARCHIONNA** Corporate Head Technology Innovation Saipem
18:00-18:30	Live Q&A Sessione 3	Discussione	Live Q&A	Live Q&A Sessione 4
18:30-19:30	ePoster	e-poster	e-poster	**CONCLUSIONI E CHIUSURA DEL CONGRESSO**

Programma dei LAVORI di DIVISIONE - 15 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 01

09.30-09.35		**Antonio Marcomini**	*Opening*
09.35-10.00	**ABC IL001**	**Demetrios Anglos**	*Exploring heritage materials and objects via laser spectroscopies*
10.00-10.15	**ABC OR001**	**Gianluigi de Gennaro**	*Sars-CoV-2 airborne transmission: indoor and outdoor implications*
10.15-10.30	**ABC OR002**	**Eleonora Balliana**	*Silk and sanitizing solutions: the need to protect visitor and artworks*
10.30-10.45	**ABC OR003**	**Luca Ciacci**	*Combining the highest degradation efficiency with the lowest environmental impact in zinc oxide based photocatalytic systems*
10.45-11.00	**ABC OR004**	**Cecilia Velino**	*PROCRAFT project: conservation strategies of aircraft heritage from excavation to museum*
11.00-11.30	**break**		
11.30-11.45	**ABC OR005**	**Luca Ferrero**	*Airborne microplastics over the Baltic: influence of sea emissions*
11.45-12.00	**ABC OR006**	**Alessandra Bigogno**	*An indoor air pollution evaluation of the Quarto Stato museum*
12.00-12.15	**ABC OR007**	**Elena Badetti**	*Grafting on metal oxide nanoparticles surface reduces the toxicity of catechols*
12.15-12.30	**ABC OR008**	**Alessandro Ciccola**	*The new shades of the XX century: investigation of ACNA dyes through Raman spectroscopy and HPLC-MS*
12.30-12.45	**ABC OR009**	**Angelo Fenti**	*In Situ Electrochemical Oxidation for Destructive Treatment of PFAS*
12.45-13.00	**ABC OR010**	**Sabina Licen**	*Data fusion techniques based on Self-Organizing Map algorithm for the integration of different source/frequency instrumental data and ancillary information for environmental impact assessment*

Divisione CHIMICA FARMACEUTICA (FAR)

FAR 01

09.30 - 10.00	**FAR KN001**	**Giuseppe Campiani**	*Old but Gold: tracking the new guise of histone deacetylases as biomarkers and therapeutic targets in rare diseases. The role of isoform 6*
10.00 - 10.30	**FAR KN002**	**György M. Keserű**	*The role of the secondary binding pocket in GPCR pharmacology*
10.30 - 10.45	**FAR OR001**	**Agnese Pippione**	*Targeting prostate cancer with multiple-targeting ligands: activity on both AKR1C3 enzyme and androgen receptor*

15 settembre - mattina

10.45 - 11.00	**FAR OR002**	**Andrea Spinaci**	*Synthesis and characterization of new A3 adenosine receptors ligands as potential anti-cancer agents*
11.00 - 11.15	**break**		
11.15 - 11.45	**FAR KN003**	**Tracey Pirali**	*The power of multi-component reactions in drug discovery: soft drugs, PROTACs and more*
11.45 - 12.00	**FAR OR005**	**Simona Musella**	*Identification and characterization of a potent TRPM8 antagonists with in vivo analgesic properties*
12.00 -12.15	**FAR OR006**	**Letizia Crocetti**	*Synthesis of pyrazolo[1,5-a]quinazolines as ligand of α1β3γ2-GABAA receptor subtype and molecular modelling studies*
12.15 -12.30	**FAR OR007**	**Carmine Ostacolo**	*Discovery of CP86, a potent neuronal Kv7 channel activator with in vivo anticonvulsant effects*
12.30 - 13.00	**FAR KN004**	**Marco Radi**	*Navigating the antiviral drug discovery space: exploring different routes toward new broad-spectrum agents*

FAR 02

10.30 - 10.45	**FAR OR003**	**Francesca Musumeci**	*Design, synthesis, and biological evaluation of a new series of pyrazolo[3,4-d]pyrimidines active as SGK1 inhibitors. A lead optimization study*
10.45 - 11.00	**FAR OR004**	**Giuseppe La Regina**	*New pyrroles derivatives as anti-glioblastoma and anti-chronic myeloid leukemia agents*
11.00 - 11.45	**break**		
11.45 - 12.00	**FAR OR008**	**Laura Scalvini**	*N-Acylethanolamine acid amidase (NAAA): mechanism of palmitoylethanolamide hydrolysis revealed by mechanistic simulations*
12.00 -12.15	**FAR OR009**	**Leonardo Brunetti**	*Multiple causes, multiple targets: FAAH as a centerpiece for therapy of multifactorial pathologies*
12.15 -12.30	**FAR OR010**	**Rita Turnaturi**	*Influence of the N-substituent of (−)-cis-N-Normetazocine in the modulation of the functional profile at MOR, DOR and KOR: from agonist to antagonist through multitarget ligands*

15 settembre - mattina

Divisione CHIMICA FISICA (FIS)

FIS 01

Physical chemistry for Nanomaterials I

09:30-10:00	**FIS KN001**	**Marco Laurati**	*Blunt-end driven assembly of star-like dsDNA coated colloids*
10:00-10:15	**FIS OR001**	**Carlo Nazzareno Dibenedetto**	*Fabrication and spectroscopic investigation of Quantum Dots dimers*
10:15-10.30	**FIS OR002**	**Giovanni LiDestri**	*Forces between nanoparticels at the air/water interface: the role of the ligand chain length*
10:30-10.45	**FIS OR003**	**Davide Peddis**	*Interplay between inter- and intraparticle interactions in bi-magnetic core/shell nanoparticles*
10:45-11:00	**FIS OR004**	**Maryam Abdolrahimi**	*XAS Study of Molecular Coated Manganese Zinc Ferrite Nanoparticles*
11:00-11.15	**FIS OR005**	**Sawssen Slimani**	*Hybrid Spinel Iron Oxide Nanoarchitecture Combining Crystalline and Amorphous Parent Material*
11:15-11.30	**FIS OR006**	**Marco Fabbiani**	*Porous materials for hybrid functional nanocomposites: metal and organic nanowires confined in zeolites and mesoporous silica*
11.30-11.45	**break**		

Physical chemistry for Nanomaterials II

11:45-12:00	**FIS OR007**	**Grazia ML Messina**	*Surfactant vesicles and polysaccharides interactions with cellulose nanocrystals*
12:00_12:15	**FIS OR008**	**Simona Ricci**	*Highly efficient green inkjet printed nanostructured electrodes and SERS substrates*
12:15-12.30	**FIS OR009**	**Marcello Condorelli**	*Ag nanoflowers as single particle SERS active platform*
12:30-12:45	**FIS OR010**	**Valentina Mameli**	*57Fe Mössbauer Spectroscopy and DC magnetometry for the identification of Fe-bearing ultrasmall nanophases in inorganic ordered porous matrixes*
12:45-13:00	**FIS OR011**	**Giovanni Ferraro**	*Controlled decoration of plastic surfaces with metal nanostructures*
13:00-13:15	**FIS OR012**	**Roberta Ruffino**	*“Distorted” self-assembly of polymer thin films at nano-curved surfaces*

FIS 02

PhysicalChemistry for Biomedical Applications I

09:30-10:00	**FIS KN002**	**Paola Sassi**	*Spectroscopic markers of heart failure: a Raman and FTIR study*
10:00-10:15	**FIS OR013**	**Nunzio Tuccitto**	*Quantum Dots Enable Digital Communication Through Biological Fluids*

10:15-10.30	**FIS OR014**	**Elisabetta Fanizza**	*Plasmonic mesoporous silica coated copper sulfide nanoparticles as Near Infrared absorbing photothermal agents*
10:30-10.45	**FIS OR015**	**Rossella Labarile**	*Coating photosynthetic Rhodobacter sphaeroides with polydopamine*
10:45-11:00	**FIS OR016**	**Marco Fornasier (Vincitore del Premio Semerano)**	*A polyphosphoester analog of Pluronic F127 enhances the biocompatibility of monoolein-based cubosomes*
11:00-11.15	**FIS OR017**	**Alberta Terzi**	*X-ray Scattering Scanning Microscopies – novel diagnostic tools of pathologic tissues. A focus on aneurysms, breast cancer and diabetes*
11:15-11.30	**FIS OR018**	**Federica D'Aria**	*G-quadruplex within KRAS gene promoter: a physicochemical study*
11.30-11.45	**break**		

PhysicalChemistry for Biomedical Applications II

11:45-12:00	**FIS OR019**	**Vincenzo De Leo**	*Liposome/Polymer Assembly for Oral Delivery of Curcumin*
12:00_12:15	**FIS OR020**	**Monica Mura**	*Nanoantibiotics: design of multifunctional MSN nanosystems containing both antibiotic and copper ions to combat bone infection*
12:15-12.30	**FIS OR023**	**Elena Piacenza**	*Innovative and green synthesis of biocompatible Selenium nanoparticles in a confined environment with promising antimicrobial activity*
12:30-12:45	**FIS OR024**	**Jennifer Gubitosa**	*Green synthesis of Gold nanoparticles by using grape seeds wastewater: physico-chemical characterization and investigation of their related antioxidant features for cosmetic and biomedical applications*

Divisione CHIMICA INORGANICA (INO)

INO 01

9.30 - 10.30	**INO PZ001**	**Frank Neese**	*Deciphering Inorganic Chemistry Riddles Through a Combination of Spectroscopy and Quantum Chemistry*
10.30 - 10.45	**INO OR001**	**Roberto Gobetto**	*Innovative Mn and Re catalysts for CO2 Photo- and Electro-Reduction*
10.45 - 11.00	**INO OR002**	**Ilaria Barlocco**	*Disclosing the role of Gold on Palladium - Gold alloyed catalysts in formic acid decomposition*
11.00 - 11.15	**INO OR003**	**Cristina Pavan**	*Nearly free silanols on silica surface: a new paradigm for particle toxicology*
11.15-11.30	**break**		

11.30 - 11.45	**INO OR004**	**Massimo Christian D'Alterio**	*A combined theoretical and experimental investigation of a new class of [N,O-] imidazo[1,5-a]pyrid-3-yl)phenolate Zn(II) catalysts for the ring opening polymerization of lactide*
11.45 - 12.00	**INO OR005**	**Linda Leone**	*Highly selective indole oxidation promoted by a Mn-containing mini-enzyme*
12.00 - 12.15	**INO OR006**	**Javier Martí-Rujas**	*Synthesis and structural properties of isostructural Zn(II) M12L8 poly-[n]-catenane using the 2,4,6-tris(4-pyridyl)benzene (TPB) ligand*
12.15 - 12.30	**INO OR007**	**Francesco Fagnani**	*Three novel families of cyclometalated platinum(II) complexes with remarkable luminescence properties*
12.30 - 13.00	**INO IL001**	**Viktoria Gessner**	*Metallated Ylides: Powerful Reagents for the Stabilization of Reactive Main Group Species and Ligands in Catalysis*

INO 02

10.30 - 10.45	**INO OR008**	**Michele Benedetti**	*“NMR effective molecular radius” of coordinated ammonia*
10.45 - 11.00	**INO OR009**	**Chiara Salvitti**	*Redox reactivity of transition metal dioxide anions towards sulfur dioxide in the gas phase*
11.00 - 11.15	**INO OR010**	**Silvia Ruggieri**	*New chiral heteroleptic Eu(III)/Tb(III)/Yb(III)-based luminescent complexes designed for different applications*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR011**	**Tiziano Marzo**	*Oxaliplatin binds angiogenin and exerts high antiangiogenic effects in PC-3 cancer cells at non-cytotoxic concentration*
11.45 - 12.00	**INO OR012**	**Luca Spitaleri**	*Covalently conjugated gold–porphyrin nanostructures*
12.00 - 12.15	**INO OR013**	**Nicola Panza**	*Ferrate salts as stand-alone catalysts for chemical fixation of CO2 into epoxides and aziridines*
12.15 - 12.30	**INO OR014**	**Elena Lucenti**	*Cyclic triimidazole: an appealing and versatile ligand for the preparation of emissive d9 and d10 metal derivatives*

INO 03

10.30 - 10.45	**INO OR015 premio Wiley**	**Thomas Scattolin**	*Palladium organometallic complexes as promising anticancer agents*
10.45 - 11.00	**INO OR016**	**Caterina Damiano**	*Efficient and low-cost metal-free Porphyrin/TBACl system for the CO2 valorization into N alkyl and N aryl oxazolidin-2-ones*
11.00 - 11.15	**INO OR017**	**Carlo Nervi**	*Transition metal complexes as redox catalysts for CO2 conversion*
11.15-11.30	**break**		

11.30 - 11.45	**INO OR018**	**Cristina Tubaro**	*Gold(I) and gold(III) complexes with thioether- and phosphonium- functionalized N-heterocyclic carbene ligands*
11.45 - 12.00	**INO OR019**	**Marco Baron**	*Manganese(III) complexes with tetradentate O^C^C^O ligands: synthesis, characterization and preliminary catalytic studies on the CO2 cycloaddition with epoxides*
12.00 - 12.15	**INO OR020**	**Roberto Esposito**	*MOF catalyzed ketalization of glycerol into solketal*
12.15 - 12.30	**INO OR021**	**Francesco Ferretti**	*Heterocycles from nitro compounds: CO surrogates in the Pd catalyzed synthesis of carbazoles*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 01

09.30 - 10.00	**TEC IL001**	**Alberto Rainer**	*Nanogels as smart drug delivery systems*
10.00 - 10.15	**TEC KN001**	**Claudia Espro**	*Hydrothermal Carbonization as a sustainable approach for the single-step upgrading of industrial citrus processing waste into platform chemicals and biocarbon*
10.15 - 10.30	**TEC KN002**	**Fabrizio Monica**	*Chemistry of materials for energy technologies*
10.30 - 10.40	**TEC OR001**	**Virginia Venezia**	*Biowaste as valuable resource: humic acids valorization into multifunctional materials*
10.40 - 10.50	**TEC OR002**	**Francesco Mauriello**	*Sustainable Valorization of Anchovy Leftovers into Value Added Chemicals, Products and Energy*
10.50 - 11.00	**TEC OR003**	**Carlo Punta**	*Eco-design of Cellulose NanoSponges for water decontamination*
11.00 - 11.10	**TEC OR004**	**Ermelinda Bloise**	*CNSL components as green building-blocks for bio-based nanovesicles*
11.10 - 11.30	**Discussion**		
11.30 - 11.50	**Break**		
11.50 - 12.00	**TEC OR005**	**Manfredi Caruso**	*N-Hydroxyphthalimide role in Aerobic Oxidations: Homogeneous versus Heterogeneous Catalysis*
12.00 - 12.10	**TEC OR006**	**Laura Riva**	*Co-Polymeric Nanosponges from Cellulose Biomass as Heterogeneous Catalysts for Organic Reactions*
12.10 - 12.20	**TEC OR007**	**Serena Regina**	*Use of a bio-derived polymer as crosslinking agent for stable-polyvinyl alcohol membrane development*
12.20 - 12.30	**TEC OR008**	**Simona Sabbatini**	*Thermal-Oxidative Stability of PHBV/LDH Nanocomposites*
12.30 - 12.50	**Discussion**		

12.50 - 13.00	**TEC OR009**	**Angela Marotta**	*Furan as platform molecule in the production of greener epoxy-resins*
13.00 - 13.10	**TEC OR010**	**Franca Castiglione**	*Insights on Ionic Liquids structure and dynamics: NMR methods and recent advances*
13.10 - 13.20	**TEC OR011**	**Giselle de Araujo Lima e Souza**	*Ionic conductivity and thermal characterization of DBU-based protic ionic liquids*
13.20 - 13.30	**TEC OR012**	**Maria Enrica Di Pietro**	*Deep Eutectics: what is inside the solvents for the 21st century?*
13.30 - 13.50	**Discussion**		

TEC 02

10.30 - 10.40	**TEC OR013**	**Giulio Pota**	*Mesoporous Silica Nanoparticles: a powerful platform for biocatalysis*
10.40 - 10.50	**TEC OR014**	**Antonella Satira**	*Tandem Catalytic Upgrading of Limonene and Methyl Levulinate promoted by Pd-based Catalysts*
10.50 - 11.00	**TEC OR015**	**Francesco Parrino**	*Synthesis, characterization, and photocatalytic activity of Eu doped ZnO prepared by supercritical antisolvent precipitation route*
11.00 - 11.10	**TEC OR016**	**Cristina Leonelli**	*Microwave-assisted synthesis and isopropanol extraction in the preparation of TiO2 nanoparticle suspensions*
11.10 - 11.30	**Discussion**		
11.30 - 11.50	**Break**		
11.50 - 12.00	**TEC OR017**	**Aurelio Bifulco**	*Hybrid Strategies for the Improvement of the Flame Retardancy of in-situ Silica-Epoxy Nanocomposites cured with Aliphatic Hardener*
12.00 - 12.10	**TEC OR018**	**Isabella Lancellotti**	*Chemical stabilization in a single step process: geopolymerization of tannery wastewater pollutants*
12.10 - 12.20	**TEC OR019**	**Ambra M. Fiore**	*Hematite nanoparticles as promising catalyst*
12.20 - 12.50	**Discussion**		
12.50 - 13.00	**TEC OR021**	**Vincenzina Barbera**	*Functionalization of graphene related materials with biosourced C-3 and C-6 building blocks. From synthesis to applications*
13.00 - 13.10	**TEC OR022**	**Sabina Alessi**	*Polymer/rubber nanofibrous interleaves for the enhancement of delamination resistance of CFRP laminates*
13.10 - 13.20	**TEC OR023**	**Laura Tripaldi**	*Silica Hairy Nanoparticles in Rubber Nanocomposites*
13.20 - 13.30	**TEC OR024**	**Mariachiara Miceli**	*Titanosilicalite as Nickel Support for Methanation Reaction*
13.30 - 13.50	**Discussion**		

15 settembre - mattina

Divisione ELETTROCHIMICA (ELE)

ELE 01

09.30 - 10.00	**ELE_KN01**	**Patrizia Mussini**	*Enantioselective Voltammetry & Chiroptical Spectroscopy: Exploring Intriguing Analogies and Connections*
10.00 - 10.15	**ELE_OR02**	**Elisabetta Petri**	*Electrochemically responsive soft actuators*
10.15 - 10.30	**ELE_OR03**	**Carmelo Lo Vecchio**	*NiFe oxide co-catalyst for an enhanced water splitting in photo-electrochemical cells*
10.30 - 10.45	**ELE_OR04**	**Marco Piccinni**	*Synthesis and water dispersion of nickel-iron layered double hydroxides for energy storage applications*
10.45 - 11.00	**ELE_OR05**	**Daniele Rocco**	*Anodic Dimerization of New Donor-Acceptor Oligothiophenes: Electrochemical and Solvatochromic Behavior*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN06**	**Peter Fischer**	
11.45 - 12.00	**ELE_OR07**	**Giovanni Crivellaro**	*A complex electrochemistry triggering the operation of Vanadium Redox Flow Batteries*
12.00 - 12.15	**ELE_OR08**	**Giampaolo Lacarbonara**	*A spectroelectrochemical study of copper chloro-complexes for high performance copper redox flow batteries*
12.15 - 12.30	**ELE_OR09**	**Jorge Montero**	*Ferrocene and viologen derivatives as electrolytes for pH neutral aqueous organic redox flow batteries*

ELE 02

09.30 - 10.00	**ELE KN10**	**Giovanni Valenti**	*New Insights Into Electrogenerated Chemiluminescence Mechanism for the Enhancement of Bioanalytical Performance*
10.00 - 10.15	**ELE OR11**	**Sara Bonacchi**	*SpectroElectrochemistry of Metal Nanoclusters:new insights into the origin of the photoluminescence*
10.15 - 10.30	**ELE OR12**	**Marco Mazzucato**	*How Decisive is the Iron Precursor Ligand in Fe-N-C Single-Site Formation and Activity for Oxygen Reduction Reaction?*
10.30 - 10.45	**ELE OR13**	**Mattia Parnigotto**	*Water Loss Predictive Tests in Flooded Lead-Acid Batteries*
10.45 - 11.00	**ELE OR14**	**Mattia Reato**	*Electron Transfers in Films of Atomically Precise Metal Nanoclusters*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE KN15**	**Alessandro Minguzzi**	*In situ/operando X-ray absorption spectroscopy: a swiss-knife for studying (photo)electrodes*

11.45 - 12.00	**ELE OR16**	**Francesco De Bon**	*Para substituted pyridines ligands forms highly active catalysts for ATRP*
12.00 - 12.15	**ELE OR17**	**Danilo Dini**	*EQCM analysis of the process of electrochemical insertion in regioregular alkyl-susbtituted polyterthiophene during n-doping*
12.15 - 12.30	**ELE OR18**	**Matteo Grattieri**	*Bio-inspired intact bacteria-based biohybrid photoanodes*

ELE 03

09.30 - 10.00	**ELEKN19**	**Marc Koper**	*Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide*
10.00 - 10.15	**ELEOR20**	**Maruccia Elisa**	*Nitrogen-containing ordered mesoporous carbons applied as CO2 adsorbents and anode materials in energy storage devices*
10.15 - 10.30	**ELEOR21**	**Fortunati Alessia**	*Ionic liquids for capture and electrochemical Conversion of CO2*
10.30 - 10.45	**ELEOR22**	**Moro Miriam**	*Carbon Nanostructures decorated with Cerium Oxide as selective electrocatalysts for CO2 reduction*
10.45 - 11.00	**ELEOR23**	**Guzman Hilmar**	*CuZnAl-based oxide catalysts for the electrochemical CO2 conversion*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELEKN24**	**Monica Santamaria**	*Electrochemical surface treatments to improve corrosion resistance of light alloys*
11.45 - 12.00	**ELEOR25**	**Zoli Maddalena**	*Facile and scalable synthesis of Cu2O-SnO2 catalyst for the photoelectrochemical CO2 conversion*
12.00 - 12.15	**ELEOR26**	**Magni Mirko**	*Cathodic Plasma Electrolysis & Recovery of Zinc as Coating*
12.15 - 12.30	**ELEOR27**	**Poli Federico**	*Sustainable strategies to improve MFC power output by green supercapacitors and supercapacitive components*

Divisione TECNOLOGIA FARMACEUTICA (TFA)

TFA 01

09.30 - 10.00	**TFA IL001**	**Elias Fattal**	*Lipid and dendrimer-based nanomedicines for siRNA*
10.00 - 10.30	**TFA IL002**	**Stefano Colloca**	*Set up of large scale production process for GRAd-COV2 vaccine*
10.30 - 10.45	***Discussion***		
10.45 - 11.00	**break**		

15 settembre - mattina

11.00 - 11.15	**TFA OR001**	**Ilaria Arduino**	*Microfluidic preparation and characterization of iRGD-functionalized solid lipid nanoparticles for targeted delivery*
11.15 - 11.30	**TFA OR002**	**Angela Bonaccorso**	*Response Surface Methodology for the optimization of Nanogels Polyelectrolyte Complex intended for Ovalbumin nasal delivery*
11.30 - 11.45	**TFA OR003**	**Ilaria Filippin**	*Cellulase as active excipient in HPMC prolonged-release matrices: a novel approach to zero-order kinetics*
11.45 - 12.00	**TFA OR004**	**Stefania Petralito**	*Remote magneto-mechanical actuation of magnetoliposomes by alternating or pulsed magnetic fields*
12.00 - 12.15	**TFA OR005**	**Emma Piacentini**	*Controlled and tunable polymeric micro/nano particles production using membrane technology*
12.15 - 12.30	**TFA OR006**	**Giovanna Rassu**	*Crocetin as both neuroprotective agent and cross-linker for sericin for obtaining new nasal bioactive nanoparticles*
12.30 - 12.45	**TFA OR007**	**Federica Rinaldi**	*Rifampicin loaded liposomes for Mycobacterium abscessus infection treatement: intracellular uptake and antibacterial activity evaluation*
12.45 - 13.00	**TFA OR008**	**Mattia Tiboni**	*An affordable approach to scalable nanomedicine manufacturing: 3D printed microfluidics*
13.00 - 13.15	**TFA OR009**	**Siyuan Deng**	*Development and Characterization of a Novel Redox-responsive Core-shell Structure Nanohydrogel as Intracellular Delivery System*
13.15-13.30	***Discussion***		

Programma dei LAVORI di DIVISIONE - 15 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA 01

15.00 - 15.10	**ANA PL001**	**Claudio Minero**	*INTRODUZIONE*
15.10 - 15.30	**ANA PZ001**	**Luigia Sabbatini**	*Contaminarsi fa bene alla ricerca*
15.30 - 15.50	**ANA PZ002**	**Luigi Mondello**	*Recent Developments in Mass spectrometry and Cutting Edge Scientific Innovation to Characterize Complex Samples*
15.50 - 16.10	**ANA IL001**	**Susy Piovesana**	*New trends for the enrichment and liquid chromatography-mass spectrometry analysis of peptides with protein post-translational modifications*
16.10 - 16.30	**ANA KN001**	**Flavio A. Franchina**	*The value of multidimensional chromatography coupled to mass spectrometry for the non-targeted metabolite profiling of natural products*
16.30 - 16.45	**ANA OR001**	**Alessia Arena**	*Mineral oil investigation in omega-3 rich lipid supplements by using multidimensional liquid-gas chromatography*
16.45 - 17.00	**ANA OR002**	**Carmela Maria Montone**	*Untargeted characterization and quantitative analysis of underivatized fatty acids in Chlorella vulgaris microalgae*
17.00 - 17.15	**ANA OR003**	**Lorenzo Cucinotta**	*Simultaneous Enantiomeric and Isotopic Ratio evaluation of target terpenes in Cannabis sativa essential oils through Enantio-MDGC-C-IRMS*
17.15 - 17.30	**ANA OR004**	**Gemma De Grazia**	*Evaluation of cryogenic effect for target VOCs isolation by a preparative multidimensional gas chromatographic system*
17.30 - 17.45	**ANA OR005**	**Rosangela Elliani**	*DEVELOPMENT OF A RAPID AND SIMPLE PROTOCOL FOR THE ASSAY OF PARABENS AND BISPHENOLS IN HUMAN SALIVA BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY*
17.45 - 18.00	**ANA OR006**	**Antonio Ferracane**	*Simultaneous determination of 88 multi-class pesticide residues in four vegetable matrices using reduced QuEChERS extraction and flow-modulated comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry*
18.00 - 18.15	**ANA OR007**	**Micaela Galletta**	*Evaluation of use of hydrogen as carrier gas in flow-modulation comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry*

18.15 - 18.30	**ANA OR008**	**Anna Illiano**	*LC-MRM/MS assay for the quantification of some hormonal proteins in serum and follicular fluid of women undergoing in vitro fertilization*

ANA 02

15.50 - 16.10	**ANA KN002**	**Clemente Bretti**	*Removal of environmentally relevant cations: polymer inclusion membranes (PIMs)*
16.10 - 16.30	**ANA KN003**	**Francesco Pellegrino**	*A New Strategy for Overcoming the Volcano in Water Photosplitting: Controlled Periodic Illumination*
16.30 - 16.45	**ANA OR009**	**Raghav Dogra**	*Preliminary evaluation of Magnetic Nanoparticles for glyphosate contaminated water remediation*
16.45 - 17.00	**ANA OR010**	**Federico Girolametti**	*Evaluation of mercury content in red mullet (Mullus barbatus) muscle from the Adriatic Sea in relation to biological factors and sampling area: risk assessment for human consumption*
17.00 - 17.15	**ANA OR011**	**Marco Minella**	*Experimental evaluation of Fenton oxidation coupled with membrane distillation for produced water treatment: benefits, challenges and effluent toxicity*
17.15 - 17.30	**ANA OR012**	**Donatella Nardiello**	*Nanoconfined liquid phase nanoextraction: an innovative extraction technique for ex-situ and in-situ rapid and quantitative determination of benzene derivatives in seawater*
17.30 - 17.45	**ANA OR013**	**Gabriella Pinto**	*Characterization of polyphenolic compounds in food and industrial wastes*
17.45 - 18.00	**ANA OR014**	**Luca Rivoira**	*Iterative protocols for the extraction and quantitation of microplastics from marine sediments and oysters*
18.00 - 18.15	**ANA OR015**	**Saul Santini**	*Validation of a new method for the simultaneous determination of different classes of PBT chemicals in biota samples*
18.15 - 18.30	**ANA OR016**	**Davide Vivado**	*Study of iron speciation in coastal seawater samples of the Ross Sea (Antarctica) by CLE-AdSV*

ANA 03

15.50 - 16.10	**ANA IL002**	**Erika Scavetta**	*Organic Electrochemical Transistors as low cost chemical sensors*
16.10 - 16.30	**ANA IL003**	**Chiara Zanardi**	*Graphene-based electrodes for the detection of biomarkers in sweat*
16.30 - 16.45	**ANA OR017**	**Andrea Bonini**	*A Label-free impedance biosensing assay based on CRISPR/Cas12a collateral activity for bacterial DNA detection*

16.45 - 17.00	**ANA OR018**	**Tiziano Di Giulio**	*Molecularly imprinted polymers-based impedimetric sensor for metal-ion mediated recognition of a dipeptide*
17.00 - 17.15	**ANA OR019**	**Laura Fabiani**	*Magnetic beads combined with carbon black-based screen-printed electrodes for COVID-19: A reliable and miniaturized electrochemical immunosensor for SARS-CoV-2 detection in saliva*
17.15 - 17.30	**ANA OR020**	**Eleonora Macchia**	*Selective Single-Molecule Detection of clinically relevant biomarkers with an Organic Transistor*
17.30 - 17.45	**ANA OR021**	**Federica Mariani**	*Healthcare monitoring using wearable pH sensors*
17.45 - 18.00	**ANA OR022**	**Vincenzo Mazzaracchio**	*A TiO2 /KuQuinone modified screen-printed photoelectrochemical sensor for NADH detection*
18.00 - 18.15	**ANA OR023**	**Gheorghe Melinte**	*Enhancement of lysozyme detection process by using a gold clusters-based electrochemical aptasensor*
18.15 - 18.30	**ANA OR024**	**Filippo Silveri**	*Redox-active graphene film integrated into a smart device for pesticide biosensing*

Divisione CHIMICA FARMACEUTICA (FAR)
FAR 03

15.00 - 15.45	**FAR MD001**	**Kenneth A. Jacobson**	*Pratesi Medal Lecture - Design and Therapeutic Potential of Adenosine and P2Y Receptor Ligands*
15.45 - 16.00	**FAR PZ001**	**Ciro Milite**	*Modulators of Coactivator-Associated Arginine Methyltransferase 1 (CARM-1): There and Back Again*
16.00 - 16.15	**FAR PZ002**	**Mariateresa Giustiniano**	*Isocyanide Chemistry from the Ground (state) to the Star(s): what's the point for a medicinal chemist?*
16.15 - 17.00	**FAR MD002**	**Antonello Mai**	*Giacomello Medal Lecture - Lecture for the receipt of the "Giordano Giacomello" medal by the Medicinal Chemistry Division of the Italian Chemical Society*
17.00 - 17.15	**break**		
17.15 - 17.30	**FAR OR011**	**Marilia Barreca**	*Inhibition of non-Hodgkin lymphoma cell growth by pyrrolo[1,2]oxazole derivatives*
17.30 - 17.45	**FAR OR012**	**Laura Braconi**	*A new strategy to overcome multidrug resistance (MDR) in cancer cells: P-gp and hCAXII multitarget inhibitors*
17.45 - 18.00	**FAR OR013**	**Daniela Carbone**	*Synthesis and preclinical evaluation of a new generation of 1,2,4-triazine-based PDK modulators: a novel therapeutic approach to halt cancer growth.*

18.00 -18.15	**FAR OR014**	**Arianna Gelain**	*Unraveling the interaction mechanism of a benzothiadiazole-2,2-dioxide derivative with STAT3: towards novel direct inhibitors*

FAR 04

17.15 - 17.30	**FAR OR015**	**Lucia Tamborini**	*Flow-based redox biotransformations for food and pharma applications*
17.30 - 17.45	**FAR OR016**	**Federica Ianni**	*Stability of chlorogenic acid as model system after household microwave treatment*
17.45 - 18.00	**FAR OR017**	**Ilaria Frosi**	*Comparison of different extraction methods to recover bioactive compounds from corn waste (Zea mays L.)*
18.00 -18.15	**FAR OR018**	**Martina Contente**	*Valorization of food wastes and residues through glycosidases*

Divisione CHIMICA INDUSTRIALE (IND)

IND 01

Sessione congiunta con Gruppo Interdivisionale Catalisi

15.00 - 15.30	**IND KN001 Medaglia Piero Pino**	**Nicoletta Ravasio**	*Catalysis and Green Deal*
15,30 - 15,40	**IND OR001**	**Eleonora Aneggi**	*Solvent free selective oxidation of benzyl alcohol over supported Ru catalysts*
15.40 - 15.50	**IND OR002**	**Denise Cavuoto**	*The role of support wettability and acidity in the hydrogenation of γ-valerolactone over Cu/SiO2 catalyst*
15.50 - 16,00	**IND OR003**	**Tommaso Tabanelli**	*Improved Catalytic Transfer Hydrogenation of alkyl levulinates with alcohols over ZrO2 based catalysts*
16.00 - 16.10	**IND OR004**	**Eleonora Vottero**	*Reconstruction phenomena in a Pt/γ-Al2O3 catalyst under hydrogenation conditions*
16.10 - 16.20	**IND OR005**	**Maila Danielis**	*Structural Evolution and Enhanced Steam Deactivation Resistance of PtPd/CeO2 Methane Oxidation Catalysts Prepared by Dry Milling*
16.20 - 16.30	**IND OR006**	**Gabriella Garbarino**	*Effect of promoters on the performances of Ni-Al2O3 catalysts for CO2 hydrogenation*
16.30 - 16.45	**Discussion**		
16.45 - 17.00	**break**		
17.00 - 17.20	**IND KN002**	**Walter Cabri**	*The Twelve Principles of Green Chemistry Translation Guide for Palladium Catalyzed Cross Coupling Reactions for Active Pharmaceutical Ingredients Sustainable Productions”*
17.20 - 17.30	**IND OR007**	**Roberto Sole**	*The alkoxycarbonylation of protected propargyl alcohols*

17.30 - 17.40	**IND OR008**	**Aleksandr Voronov**	*Unexpected O-5-exo-dig Cyclization of Propargyl Ureas to Oxazoline-2-amines Catalyzed by Silver Salts*
17.40 - 17.50	**IND OR009**	**Francesco Taddeo**	*Kinetics of solketal synthesis promoted by Iron(III) complex*
17.50 - 18.00	**IND OR010**	**Vinayak. Botla**	*Palladium/Norbornene-Catalyzed Synthesis of 2-Iodobiaryls*
18.00 - 18.10	**IND OR011**	**Stefano Econdi**	*Heterogeneous catalysts for the liquid-phase degradation of simulants of organophosphorus chemical warfare agents*
18.10 -18.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)

ORG 01

15.00 - 15.30	**Benvenuto e premiazione (sessioni unificate)**		
15:30 - 16:00	**ORG PZ001**	**Anna Bernardi**	***Medaglia Adolfo Quilico*** *At the crossroad between Chemistry and Biology: interfering with the sugar code using glycomimetics*
16.00 - 16.15	**ORG OR001**	**Alessandro Ajo**	*Nanocages and capsules for drug and peptides delivery*
16.15 - 16.30	**ORG OR002**	**Silvana Alfei**	*Cationic Copolymers: A Promising Option in the Treatment of Drug Resistance in Neuroblastoma Cells*
16.30 - 16.45	**ORG OR003**	**Davide Audisio**	*Direct Carbon Isotope Exchange of Pharmaceuticals via Reversible Decyanation*
16.45 - 17.00	**ORG OR004**	**Sara Battista**	*Antibacterial and physicochemical properties of quatsomes formulated with L-prolinol-derived surfactants*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR005**	**Roberta Bernini**	*Hydroxytyrosol, much more than an antioxidant*
17.45 - 18.00	**ORG OR006**	**Andrea Calcaterra**	*Diels-Alder type adducts from Morus nigra as potent inhibitors of Micobacterium tuberculosis PtpB*
18.00 - 18.15	**ORG OR007**	**Fabrizio Chiodo**	*Carbohydrate-Mediated “Innate” Considerations in Designing Vaccine-Candidates*
18.15 - 18.30	**ORG OR008**	**Martina Cirillo**	*Selective Integrin Ligands Promote Cell Internalization of the antineoplastic agent Fluorouracil*

ORG 02

16.00 - 16.15	**ORG OR009**	**Mariapina D'Onofrio**	*Chemoselective disulfide-coupling for the semisynthesis of ubiquitinated forms of the Alzheimer’s associated protein tau*

15 settembre - pomeriggio

16.15 - 16.30	**ORG OR010**	**Maria Giulia Davighi**	*New potential carbonic anhydrase inhibitors based on mono and multivalent sugars and iminosugars*
16.30 - 16.45	**ORG OR011**	**Cristina De Castro**	*N-glycan from Paramecium bursaria Chlorella virus MA-1D: reevaluation*
16.45 - 17.00	**ORG OR012**	**Jenny Desantis**	*Design, synthesis, and evaluation of small molecules Proteolysis Targeting Chimeras (PROTACs) to induce androgen receptor degradation*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR013**	**Cristina Di Carluccio**	*Investigation of the molecular recognition of sialoglycans bound to Siglec-like adhesins of Streptococcus gordonii*
17.45 - 18.00	**ORG OR014**	**Rossella Di Guida**	*Structural characterization of the lipooligosaccharide and capsular polysaccharide from the psychrotrophic bacterium Pseudoalteromonas nigrifaciens Sq02*
18.00 - 18.15	**ORG OR015**	**Maria Funicello**	*Switching the anticancer effect to HIV protease inhibition: new heteroaryl-amidic compounds with a pseudo-symmetric core*
18.15 - 18.30	**ORG OR016**	**Dario Gentili**	*Synthesis of small molecules with potential antiviral acitivity against Sars-CoV-2*

ORG 03

16.00 - 16.15	**ORG OR017**	**Vincenzo Algieri**	*Regioselective Synthesis of 1,3,4,5-Tetrasubstituted Pyrazoles by Eliminative Enaminone-Nitrilimine 1,3-Dipolar Cycloaddition*
16.15 - 16.30	**ORG OR018**	**Michael Andresini**	*Nitrogen transfer to sulfenamides: synthesis of sulfinamidines and unexplored sulfinimidate esters as valuable precursors of protected sulfilimines*
16.30 - 16.45	**ORG OR019**	**Marco Ballarotto**	*Substituted 6H-benzo[c]chromenes: synthetic approach via a Diels-Alder/aromatization sequence and computational investigation*
16.45 - 17.00	**ORG OR020**	**Bruno Mattia Bizzarri**	*Aminomaleonitrile inspired prebiotic chemistry as a novel microwave assisted multicomponent tool for the synthesis of imidazole and purine derivatives with anti-influenza activity*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR021**	**Diego Caprioglio**	*The oxidation of phytocannabinoids: a systematic investigation*
17.45 - 18.00	**ORG OR022**	**Marco Colella**	*Use of flow technology for the development of a sustainable synthesis of azetines and azetidines*
18.00 - 18.15	**ORG OR023**	**Dario Corbisiero**	*Enantioselective Synthesis of Polyfunctionalized Isoxazoline Rings: Development of a Methodology for the preparation of Tumor-Oriented Small Molecules*

18.15 - 18.30	**ORG OR024**	**Massimiliano Cordaro**	*Synthetic Approaches to Molecular Diversity of BODIPY*

ORG 04

16.00 - 16.15	**ORG OR025**	**Vincenzo Mirco Abbinante**	*Highly-fluorinated aromatic diimides for organic electronics:from synthesis to thin-film preparation*
16.15 - 16.30	**ORG OR026**	**Rita Argenziano**	*Functional films from 5,6-dihydroxyindole oligomers and long chain diamines partnership*
16.30 - 16.45	**ORG OR027**	**Giacomo Biagiotti**	*Tailoring the structure of the BODIPY probe in the design of functional fluorescent materials*
16.45 - 17.00	**ORG OR028**	**Davide Blasi**	*Trityl-brominated radicals as building blocks for doublet CPL emitters*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR029**	**Alberto Bossi**	*Porphycenes, a lesser known tetrapyrrolic macrocycle with intriguing properties suitable for in situ sensing*
17.45 - 18.00	**ORG OR030**	**Adriano Parodi**	*Polyhydroxybutyrate as a sustainable platform for the production of chemicals and bio-polymers*
18.00 - 18.15	**ORG OR031**	**Simone Di Noja**	*Transfer of Axial Chirality to the Nanoscale Endows Carbon Dots with Circularly Polarized Luminescence*
18.15 - 18.30	**ORG OR032**	**Claudio Ferdeghini**	*Synthesis and thermal behavior of dicationic ionic liquids*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 01

15.00 - 15.05	**Opening Remarks Presidente Michael Assfalg**		
15.05 - 15.35	**CSB KN001**	**Rommie Amaro**	*Computational Microscopy of SARS-CoV-2*
15.35 - 16.00	**CSB PZ001**	**Luca Mazzei**	*Talking about urease: How the grasp on the molecular aspects of this enzyme can help in counteracting its role in microbiological pathogenesis and environmental issues*
16.00 - 16.15	**CSB OR001**	**Marta De Zotti**	*A pH-Induced Reversible Conformational Switch able to control the Photocurrent Efficiency in a Peptide Supramolecular System*
16.15 - 16.30	**CSB OR002**	**Ottavia Bellotto**	*Supramolecular hydrogels from unprotected dipeptides: a comparative study on stereoisomers and structural isomers the Photocurrent Efficiency in a Peptide Supramolecular System*
16.30 - 17.00	**Break**		
17.00 - 17.30	**CSB PZ002**	**Claudia Bonfio**	*Uncovering the emergence of modern cells*
17.30 - 17.45	**CSB OR003**	**Gianantonio Battistuzzi**	*Molecular basis of myoglobinopathy, a newly discovered molecular disease*
17.45 - 18.00	**CSB OR004**	**Lidietta Giorno**	*Selectivity and stability of biological macromolecules heterogenized to nanostructured artificial membranes*

18.00 - 18.15	**CSB OR005**	**Claudia Riccardi**	*Design, synthesis and characterization of cyclic TBA analogues*
18.15 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 01

15:00-16:00	**DID PL001**	**Jan Apotheker**	*Developments in chemistry education*
16:00-16:30	**DID IL001**	**Mariano Venanzi**	*Sustainable chemistry for a sustainable teaching. A proposal for a first level curriculum in Chemistry at University*
16:30-16:45	**DID OR001**	**Federica Branchini**	*Teaching the notion of chemical bonding: a didactic challenge*
16:45-17:00	**DID OR002**	**Maria Antonietta Carpentieri**	*A new didactic pathway to introduce Spectroscopy by historical-epistemiological/STEM laboratorial/distance learning blended approach*
17:00-17:15	**DID OR003**	**Maria Costa**	*Virtual Reality visualizations of complex molecular structures in chemistry education. The β-CD-ASA example*
17:15-17:30	**DID OR004**	**Sandro Jurinovich**	*A didactic sequence for teaching chromatography: observation, model and practical applications*
17:30-17:45	**DID OR005**	**Dora Stella Lombardi**	*'Light and Molecules': an experimental approach to the understanding of basic concepts of Quantum Mechanics*
17:45-18:00	**DID OR006**	**Alma Moretta**	*Additional Learning Requirements (OFA) in Math for Environmental Science degree course: a review for a better understanding of the difficulties of students entering university*
18:00-18:15	**DID OR007**	**Davide Peddis**	*From the astro to the nano scale: a learning by doing teaching pathway*
18:15-18:30	**DID OR008**	**Antonio Testoni**	*Chemistry, history and complexity*
18:30-18:45	**DID OR009**	**Sergio Palazzi**	*A colorful new morning - teaching applied chemistry in pandemic times*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 01

15.00 - 15.15	**Welcome**		
15.15 - 15.55	**MAS PL001**	**Giuseppina Maccarone**	*The Role of Mass Spectrometry in the – omics Era*
15.55 - 16.10	**MAS OR001**	**Daniela Cecconi**	*Integrated lipidomics and proteomics reveal cardiolipin remodelling, upregulation of HADHA and long chain fatty acids in pancreatic cancer stem cells*
16.10 - 16.25	**MAS OR002**	**Silvia Pedretti**	*Metabolomic approaches to investigate the role of the mitochondrial*
16.25 - 16.35	**Break**		

15 settembre - pomeriggio

16.35 - 17.15	**MAS PL002**	**John A. McLean**	*High dimensional molecular phenomics in systems, synthetic, and chemical biology*
17.15 - 17.30	**MAS OR003**	**Isabella Piga**	*Spatial proteomics to map tissue alterations during the progression of fibrosis in an IPF and Nintedanib-treated mouse model*
17.30 - 17.45	**MAS OR004**	**Federico Fanti**	*Quantitative analysis of resolvins in biological matrices by means LLE-µSPE-HPLC-MS/MS*
17.45 - 18.00	**MAS OR005**	**Elettra Barberis**	*A Combined GCxGC-MS and GC-MS Approach to Discovery and Validate New Potential Biomarkers for Prostate Cancer Diagnosis*

Divisione TEORICA E COMPUTAZIONALE (TEO)

15:00 -15:20	**TEO KN001**	**Emilia Sicilia**	*Computations for investigating anticancer activity of metal-based compounds beyond cisplatin*
15:20 - 15:40	**TEO PZ001**	**Greta Donati**	*Exploring Chemistry through Multiple Time and Size Scales*
15:40 - 15:50	**TEO OR001**	**Marco Bertani**	*Improving empirical force fields for molecular dynamics simulations of oxide glasses. The importance of three-body interactions in rigid-ion models*
15:50 - 16:00	**TEO OR002**	**Arianna Massaro**	*First-principles study of Oxygen redox activity in P2-type NaxNi0.25Mn0.68O2 high energy cathode for Na-ion batteries*
16:00 - 16:10	**TEO OR003**	**Mirko Vanzan**	*An atomistic insight on the hot-electron injection mechanism*
16:10 - 16:20	**TEO OR004**	**Sergio Tosoni**	*Computational characterization of single-atom species on metal-supported oxide thin films*
16:20 - 16:30	**TEO OR005**	**Ida Ritacco**	*Spontaneous Production of Ultrastable Reactive Oxygen Species on Titanium Oxide Surfaces Modified with Organic Ligands*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO PZ002**	**Alessandro Erba**	*The Role of Fock Exchange in Relativistic Density Functional Theory*
17:20 - 17:30	**TEO OR006**	**Luca Brugnoli**	*Development and application of a ReaxFF Reactive Force Field for Cerium Oxide/Water Interfaces*
17:30 - 17:40	**TEO PO005**	**Anna Ranaudo**	*Computational study on the structural stability of mutated Affitins*
17:40 - 17:50	**TEO OR008**	**Noelia Faginas-Lago**	*Molecular Simulations of CO2/N2/H2O Gaseous Mixture Separation in Graphtriyne Membrane*
17:50 - 18:00	**TEO OR009**	**Francesca Fasulo**	*Electrode-electrolyte interface in solid-state lithium batteries: new insights from density functional embedding theory*

15 settembre - pomeriggio

18:00 - 18:10	**TEO OR010**	**Mariagrazia Fortino**	*Multi-replica biased sampling for photoswitchable p-conjugated polymers*
18:10 - 18:30	**discussion**		

Programma dei LAVORI di DIVISIONE - 16 settembre mattina

Divisione CHIMICA ANALITICA (ANA)

ANA 04

09.30 - 09.50	**ANA IL004**	**Cosima Damiana Calvano**	*Allergenicity assessment of novel foods by identifying marker peptides using bioinformatics and LC-ESI-MS/MS*
09.50 - 10.10	**ANA OR024**	**Danilo Corradini**	*Separation and Detection of Charged and Neutral Biomolecules in Plants and Food Matrices by Capillary Zone Electrophoresis*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR025**	**Antonella Cavazza**	*Analytical approaches for safety assessment in the development of innovative packaging solutions*
10.30 - 10.45	**ANA OR026**	**Tatiana Chenet**	*Evaluation of the presence of plastics in two fish species of the Mediterranean Sea and potentially correlated harmful effects*
10.45 - 11.00	**ANA OR027**	**Paola Arena**	*A Holistic Approach to the Characterization of High-Value Generating Molecules from the Wastes of Tuna Fishery Industry*
11.00 - 11.15	**ANA OR028**	**Federica Dal Bello**	*Insects food for the future*
11.15 - 11.30	**ANA OR029**	**Debora fabbri**	*Integrated approach for the analysis of some pesticides in vegetables and food matrices fastidiosa*
11.30 - 11.45	**ANA OR030**	**Paola Agata E. Donato**	*Triacylglycerol Fingerprinting in Vegetable Oils by means of Subcritical Solvent Chromatography*
11.45 - 12.00	**ANA OR031**	**Marco Iammarino**	*Exploring the potentiality of capillary ion chromatography (CIC) as analytical technique for the determination of food additives*
12.00 - 12.15	**ANA OR032**	**Fabio Salafia**	*Use of ultra-high performance liquid chromatography to characterize non-volatile compounds in Italian beers*
12.15 - 12.30	**ANA OR033**	**Emanuela Trovato**	*Characterization of volatile and non volatile compounds in citrus beer to evaluate product quality for food frauds prevention.*

ANA 05

09.30 - 09.50	**ANA KN004**	**Alessandra Biancolillo**	*Variable selection with a focus on multi-way and multi-block data*
09.50 - 10.10	**ANA KN005**	**Cristina Malegori**	*Near infrared hyperspectral imaging combined with multivariate image analysis: potential and limitations for the identification of microplastics in aquatic samples*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR034**	**Giacomo Baccolo**	*Automate chemometric approach for peak identification and quantification in untargeted GC-MS data*

10.30 - 10.45	**ANA OR035**	**Denise Biagini**	*Oxylipin storm in COVID-19: a new perspective in classifying disease severity*
10.45 - 11.00	**ANA OR036**	**Francesca Di Donato**	*Authentication of donkey's milk by Near Infrared Spectroscopy coupled with chemometric classifiers*
11.00 - 11.15	**ANA OR037**	**Fabio Fornari**	*Connecting the dots between theory and practice: discovering new functional cocrystals through supervised pattern recognition*
11.15 - 11.30	**ANA OR038**	**Sabina Licen**	*SOMEnv: an R package for mining environmental monitoring datasets by Self-Organizing Map and k-means algorithms with a Graphical User Interface*
11.30 - 11.45	**ANA OR039**	**Lisa Rita Magnaghi**	*Optode & Chemometrics: Milk Freshness at a Glance*
11.45 - 12.00	**ANA OR040**	**Elisa Robotti**	*Optimization of the process of anaerobic digestion of FORSU by experimental design techniques*
12.00 - 12.15	**ANA OR041**	**Giorgia Sciutto**	*A chemometric strategy to exploit the complementary information from a combined XRF-Vis-NIR hyperspectral imaging system*
12.15 - 12.30	**ANA OR042**	**Federica Turrini**	*'Specialty' or 'Gourmet' oils: a multivariate statistical approach for the rapid identification of their botanical species*

ANA 06

09.30 - 09.50	**ANA KN006**	**Serena Arnaboldi**	*Unconventional Electrochemical Approaches for the Direct Readout of Chiral Information*
09.50 - 10.10	**ANA KN007**	**Isacco Gualandi**	*Electrosynthesis of Layered Double Hydroxides for analytical applications*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR043**	**Riccarda Antiochia**	*Wearable electrochemical microneedles-based nanoporous gold sensor for real time catecholamine detection*
10.30 - 10.45	**ANA OR044**	**Paolo Inaudi**	*Solid state electrochemical behaviour and spin multiplicity in charge transfer co-crystals of DBTTF:F4TCNQ*
10.45 - 11.00	**ANA OR045**	**Andreas Lesch**	*Large-scale production of electroanalytical sensors by combined inkjet printing and light-induced synthesis of metal nanoparticles*
11.00 - 11.15	**ANA OR046**	**Antonella Miglione**	*Combined paper-based substrates for electrochemical detection of copper ions in serum*
11.15 - 11.30	**ANA OR047**	**Patrizia R. Mussini**	*Enantiomer discrimination in voltammetry in media of high structural order at the electrochemical interphase implemented with chirality*

11.30 - 11.45	**ANA OR048**	**Laura Pigani**	*Cannabinoids fast detection in real matrices: an electrochemical sensors' approach*
11.45 - 12.00	**ANA OR049**	**Angelo Tricase**	*Electrochemical Characterization of supramolecular structure in Self-Assembled Monolayers*
12.00 - 12.15	**ANA OR050**	**Martina Vizza**	*Specific ion effect in electrochemistry: the deposition of copper in the presence of different background electrolytes*

Divisione CHIMICA FISICA (FIS)

FIS 03

Enerchem I

09:30-10:00	**FIS KN003**	**Emanuela Gatto**	*Photocurrent Generation in Supramolecular Bio-Inspired Nanoarchitectures on Gold Surface*
10:00-10:15	**FIS OR025**	**Cristina Artini**	*A novel approach for the evaluation of the defect clusters content in doped ceria through in-situ high pressure x-ray diffraction*
10:15-10.30	**FIS OR026**	**Chiara Milanese**	*Super activated biochar for solid state hydrogen storage and supercapacitors preparation*
10:30-10.45	**FIS OR027**	**Emanuela Sartori**	*Emissive Layered Perovskite Nanocrystals*
10:45-11:00	**FIS OR028**	**Giovanni Di Liberto**	*Theoretical Description Semiconductors Interfaces: insights from DFT*
11:00-11.15	**break**		

Enerchem II

11:15-11.30	**FIS OR029**	**Vanira Trifiletti**	*Synthesis of bismuth-based hybrid perovskites for thermoelectrics*
11.30-11.45	**FIS OR033**	**Mariarosaria Tuccillo**	*Operando study of a cobalt free Li-rich layered oxide materials (LRLO) in a lithium cell*
11:45-12:00	**FIS OR031**	**Simone Sansoni**	*Laser ablation in solution for a more sustainable perovskite-based optoelectronics*
12:00-12:15	**FIS OR030**	**GianLuca Chiarello**	*Photothermocatalytic steam reforming of methanol for H2 production*
12:15-12.30	**FIS OR032**	**Annalisa Polo (Vincitrice del Premio Semerano)**	*Effects of Mo6+ doping on the performance of BiVO4 photoanodes for solar water oxidation*

FIS 04

Physical Chemistry for Environment I

09:30-10:00	**FIS KN004**	**Luigi Gentile**	*Ecofriendly Isolation of Cellulose from buckwheat chaff*
10:00-10:15	**FIS OR039**	**Vito Rizzi**	*From agricultural wastes to a resource: Kiwi Peels as recyclable adsorbent to remove emerging pollutants from water*

16 settembre - mattina

10:15-10.30	**FIS OR035**	**Giuseppina Anna Corrente**	*Hydrochemical study of the Turbolo basin: evaluation of the spatial and seasonal variation of surface water quality*
10:30-10.45	**FIS OR036**	**Vanessa Miglio**	*Silica Monolith for the Removal of Pollutants from Gas and Aqueous Phases*
10:45-11:00	**FIS OR037**	**Gabriele Mulas**	*Investigation of mechanochemically driven CO2 conversion over Olivine powders*
11:00-11.15	**break**		

Physical Chemistry for Environment II

11:15-11.30	**FIS OR038**	**Pier Luigi Gentili**	*Establishing a link between Chemistry and Complexity Science to promote Sustainability*
11.30-11.45	**FIS OR034**	**Sebastiano Campisi**	*Tin-functionalized hydroxyapatite as an “ecofriendly bridge” joining water remediation and air protection processes*
11:45-12:00	**FIS OR040**	**Paolino Caputo**	*Use of Food Substances as chemical additives in the industrial field*
12:00_12:15	**FIS OR041**	**Alessio Zuliani**	*Environmentally friendly ZnO/Castor oil polyurethane composites for the efficient gas-phase adsorption of acetic acid*
12:15-12.30	**FIS OR042**	**Antonio Tursi**	*Synthesis and Enhanced Capture Properties of a New BioMOF@SWCNT-BP: Recovery of the Endangered Rare Earth-Elements from Aqueous Systems*

FIS 05

Spectroscopic Applications I

09:30-10:00	**FIS KN005**	**Elena Groppo**	*Revisiting the use of probe molecules in the characterization of heterogeneous olefin polymerization catalysts by IR spectroscopy*
10:00-10:15	**FIS OR043**	**Giampaolo Marcolin**	*Solvent-dependent Characterization of Fucoxanthin through 2D Electronic Spectroscopy Reveals New Details on the Intramolecular Charge Transfer State Dynamics*
10:15-10.30	**FIS OR044**	**Alessandra Forni**	*Multiple prompt and long-lived emissions from solid state purely organic materials*
10:30-10.45	**FIS OR045**	**Rosachiara Antonia Salvino**	*NMR in chiral partially ordered media: a tool for achieving conformational traits of small flexible enantiomers in solution*
10:45-11:00	**FIS OR046**	**Nicola Peruffo**	*Selective Switching of Multiple Plexcitons in Colloidal Materials: Directing the Energy Flow at the Nanoscale*

Spectroscopic Applications II

11:15-11.30	**FIS OR047**	**Elisabetta Collini**	*The effect of hydrogen bonds on the ultrafast relaxation dynamics of a BODIPY dimer*
11.30-11.45	**FIS OR048**	**Francesca Martini**	*Structure and dynamics of “cool” organic pigments by solid state NMR*

16 settembre - mattina

11:45-12:00	**FIS OR049**	**Margherita Bolognesi**	*Bidimensional black Phosphorus: surface functionalization, heterostructures with organic molecules, applications*
12:00_12:15	**FIS OR050**	**Annamaria Panniello**	*BODIPY-functionalized Quantum dots platform for high efficiency FRET processes*
12:30-12:45	**FIS OR093**	**Eleonora Vottero**	*C-H terminations in activated carbons and related catalysts:an Inelastic Neutron Scattering spectroscopy and DFT study*

Divisione CHIMICA INDUSTRIALE (IND)

IND 02

Sessione congiunta con Gruppo Interdivisionale Catalisi

09.30 - 9.40	**IND OR012**	**Annalisa Sacchetti**	*Bio-oils valorization by selective catalytic hydrogenation: a comparison between batch and continuous flow systems*
9.40 - 9.50	**IND OR013**	**Alessandra Toso**	*Pd/CeO2 as Passive NOx Adsorbers: key properties and NOx adsorption mechanism*
9.50 - 10.00	**IND OR014**	**Sebastiano Campisi**	*A green route to the catalytic nitrous oxide decomposition by transition metal doped hydroxyapatites*
10.00 - 10.10	**IND OR015**	**Luca Consentino**	*Ce doped WO3-TiO2 cordierite monoliths for Selective Catalytic Reduction of NOx by NH3*
10.10 - 10.20	**IND OR016**	**Roberto Fiorenza**	*The solar photothermo-catalytic approach for the VOCs degradation and the subsequent CO2 conversion*
10.20 - 10.30	**IND OR017**	**Melissa Greta Galloni**	*Cu, Fe, and CuFe exchanged hydroxyapatites as eco-friendly catalysts for NH3-SCR reaction*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.20	**IND KN003**	**Pierdomenico Biasi**	*From University to Industry: examples on how university-industry collaborations in catalysis can be effective and successful*
11.20 - 11.30	**IND OR018**	**Fabiana Vento**	*Photodegradation of Xenobiotics from Polluted Water Using a New PMMA-TiO2 Based Nanocomposite*
11.30 - 11.40	**IND OR019**	**Vincenzo Russo**	*Heterogeneous photodegradation for the removal of ibuprofen from water*
11.40 - 11.50	**IND OR020**	**Alessandro Allegri**	*Aquivion® PFSA-based spray-freeze dried composite materials for the conversion of furfuryl alcohol to levulinates*
11.50 - 12.00	**IND OR021**	**Somayeh Taghavi**	*Biomass-derived levulinic acid hydrogenation to GVL using bifunctional biochar-based catalysts*
12.00 - 12.10	**IND OR044**	**Giulia Zoppi**	*Green hydrogen production from wastewater derived from lignin-rich hydrothermal liquefaction*
12.10 - 12.30	**Discussion**		

16 settembre - mattina

IND 03

09.30 - 9.50	**IND KN004**	**Michele Laus**	*Polymer brush technology: the true and the false in grafting to processes*
9.50 - 10.00	**IND OR023**	**Stefano Gazzotti**	*1,3-Dioxolan-4-Ones as powerful tool for the synthesis of functionalized PLA-based materials with tailored properties*
10.00 - 10.10	**IND OR024**	**Carla Calabrese**	*Hybrid organic-inorganic materials based on polydopamine-like chemistry*
10.10 - 10.20	**IND OR025**	**Alessandro Piovano**	*β-ketoimine Cr complexes for the production of functional polyolefins: exploring the metal-ligand bond as a key point of the catalysts*
10.20 - 10.30	**IND OR026**	**Edoardo Podda**	*Self-Healing and Shape-Memory Hydrogels by Micellar Polymerization*
10.30 - 10.40	**IND OR027**	**Riccardo Chiarcos**	*Evidence of Preferential Grafting of Short Chains in Grafting To Reactions of Hydroxy-Terminated P(S-r-MMA) Copolymers*
10.40 - 10.55	**Discussion**		
10.55 - 11.10	**break**		
11.10 - 11.20	**IND OR028**	**Antonietta Cozzolino**	*Axially oriented guest induced crystallization in syndiotactic polystyrene unstretched fiber*
11.20 - 11.30	**IND OR029**	**Manohar Golla**	*Axially Oriented Co-crystalline Phases of Poly(2,6-dimethyl-1,4-phenylene)oxide and host-guest orientations*
11.30 - 11.40	**IND OR030**	**Camilla Parmeggiani**	*Liquid crystal elastomer based artificial muscles for cardiac repair*
11.40 - 11.50	**IND OR031**	**Daniele Martella**	*Cell instructive polymers based on liquid crystals*
11.50 - 12.00	**IND OR032**	**Nicole Mariotti**	*Bio-based and waste-derived polyurethanes for energy systems*
12.00 - 12.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)

ORG 05

10.00 - 10.30	**ORG PZ005**	**Marco Lucarini**	***Premio alla ricerca Chimica Organica nei suoi Aspetti Metodologici*** *Novel Spin-Labelled Mechanically Interlocked Molecules as Models for the Interpretation of Biradical EPR Spectra*
10.30 - 10.45	**ORG OR033**	**Fabio Buonsenso**	*Non-equilibrium dynamic chromatography: investigation of the reduction process of α-lipoic acid promoted by dithiothreitol*
10.45 - 11.00	**ORG OR034**	**Marta Da Pian**	*Combined use of forensic science in sexual assault: a case report*

11.00 - 11.15	**ORG OR035**	**Graziano Di Carmine**	*Aldol Reaction between Benzaldehyde and Hydroxyacetone Promoted by Silica SBA-15 supported proline: Unraveling the Solvent Effect on the Catalyst Behavior Using NMR Relaxation*
11.15 - 11.30	**ORG OR036**	**Elena Ermini**	*New 1-6 self-immolative spacer for the release of thiols under nitroreductase activation*

ORG 06

10.30 - 10.45	**ORG OR037**	**Germana Esposito**	*Molecular Networking: a powerful tool to dereplication of natural products*
10.45 - 11.00	**ORG OR038**	**Roberta Franzini**	*Chromatographic and spectroscopic investigation of chiral aza-dibenzocyclooctynes and their analogues obtained by azido-click reaction.*
11.00 - 11.15	**ORG OR039**	**Marco Galeotti**	*Hydrogen Atom Transfer based aliphatic C-H bond oxidation of hydrocarbons bearing cyclopropyl moieties. The role of hyperconjugation.*
11.15 - 11.30	**ORG OR040**	**Chiara Lambruschini**	*Photoisomerization of ferulic acid derivatives*

ORG 07

10.30 - 10.45	**ORG OR041**	**Francesca Ghirga**	*Development of ArnT-mediated colistin resistance diterpene-based inhibitors*
10.45 - 11.00	**ORG OR042**	**Laura Goracci**	*Exploring PROTACs metabolism: a structure-activity relationship study*
11.00 - 11.15	**ORG OR043**	**Concetta Imperatore**	*Toward marine inspired multitarget drugs for diabetes mellitus and its complications: design and synthesis of novel dual Protein Tyrosine Phosphatase 1B and Aldose Reductase ligands*
11.15 - 11.30	**ORG OR044**	**Marco Masi**	*Phytotoxins produced by fungal pathogens of legume crops*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 02

09.30 - 10.00	**CSB KN002**	**Paola Turano**	*Bioinorganic chemistry of ferritin nanocages*
10.00 - 10.15	**CSB OR006**	**Veronica Ghini**	*NMR as a tool to monitor the individual response of immunotherapy*
10.15 - 10.30	**CSB OR007**	**Luigi Russo**	*μs-ms conformational dynamics control the formation of prion protein intermediate states involved in amyloid fibrils*
10.30 - 10.45	**CSB OR008**	**Sabrina Elkhanoufi**	*New, highly sensitive off/on EPR probes to monitor enzymatic activity*
10.45 - 11.00	**CSB OR009**	**Alessia Distefano**	*A MS and SPR coupled approach to fully characterize IDE activity modulation*

11.00 - 11.15	**Break**		
11.15 - 11.30	**CSB OR010**	**Alessandro D'Urso**	*The increased thermodynamic stability of miRNAs might be the reason of stronger repressive activity*
11.30 - 11.45	**CSB OR029**	**Anna Di Porzio**	*Identification of a short peptide that preferentially binds to the G-quadruplex structure in the c-MYC oncogene promoter*
11.45 - 12.00	**CSB OR012**	**Chiara Platella**	*Targeting cancer-related DNA G-quadruplex structures by naphthalene diimide ligands*
12.00 - 12.15	**CSB OR013**	**Alessandra Romanelli**	*Self-assembly of PNA-peptide conjugates*
12.15 - 12.45	**Discussione**		

Divisione ELETTROCHIMICA (ELE)
ELE 04

09.30 - 10.00	**ELE IL28**	**Sara Rebeccani**	*PEDOT doped with Sulphonated Polyarylethersulphones as electroactive material in electroanalytical applications*
10.00 - 10.15	**ELE IL29**	**Cecilia Wetzl**	*Graphene-based functional materials for electrochemical imaging*
10.15 - 10.30	**ELE IL30**	**Lorenzo Ripani**	*Microkinetic modeling for the electrochemical CO2 reduction reaction in bicarbonate electrolyte*
10.30 - 10.45	**break**		
10.45 - 11.00	**ELE IL31**	**Riccardo Brandiele**	*Synthesis and characterization of materials for PEM-FC, based on Pt alloyed nanoparticles supported on next generation mesoporous carbon*
11.00 - 11.15	**ELE IL32**	**Annalisa Polo**	*Ternary Oxide Semiconductor Photoanodes for Solar Energy Conversion*
11.15 - 11.45	**ELE IL33**	**Laura Rotundo**	*Electroreduction of carbon dioxide by Re(I) and Mn(I) bipyridine complexes*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)
TEC 03

9.30 - 9.40	**TEC OR025**	**Paola Di Matteo**	*Phenolic compounds in alcoholic and low-alcoholic beer by fast HPLC-PDA-MS/MS analysis: impact of malt composition, hops and dealcoholization process.*
9.40 - 9.50	**TEC OR026**	**Elhussein M. F. M. H. Ahmed**	*Early-Detection of Xylella fastidiosa in Olive Trees by Hyperspectral Reflectance and Non-targeted Metabolomics*
9.50 - 10.00	**TEC OR027**	**Nazeeha Ayaz**	*Hydrophobin coated superfluorinated nanoparticles for 19F-MRI cell tracking*
10.00 - 10.10	**TEC OR028**	**Elena Dilonardo**	*S-PEEK membranes optimized for Vanadium Redox Flow Battery: the effects of sulphonation degree and filler content on operative conditions and set-up configurations*

16 settembre - mattina

10.10 - 10.20	**TEC OR029**	**Giuseppe Marcì**	*Selective photocatalytic partial oxidation of aromatic alcohols to aldehydes in aqueous suspensions of C3N4 obtained by polycondensation of melamine and cyanuric/barbituric acids*
10.20 - 10.40	**Discussion**		
10.40 - 10.50	**TEC OR030**	**Giancarlo Terraneo**	*Crystalline Molecular Rotors Assembled through Halogen Bonding*
10.50 - 11.00	**TEC OR031**	**Valentina Dichiarante**	*Multi-branched perfluoro-tert-butoxyl scaffolds for the functionalization of surfaces and nanomaterials*
11.00 - 11.10	**TEC OR032**	**Gabriella Munzi**	*A dinuclear Zn(II) Schiff-base complex as molecular tweezer: binding properties and sensing towards biogenic diamines*
11.10 - 11.20	**TEC OR033**	**Martina Lippi**	*Dynamic 1D Bispidine-based Coordination Polymers for Adsorption Applications*
11.20 - 11.30	**TEC OR034**	**Daniele Narzi**	*Mechanism of oxygen evolution and Mn4Ca cluster restoration in the natural water-oxidizing catalyst*
11.30 - 11.50	**Discussion**		

Programma dei LAVORI di DIVISIONE - 17 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 02

09.30-10.00	**ABC KN001**	**Edith Joseph**	*Green methods for metals conservation*
10.00-10.15	**ABC OR023**	**Francesco Abate**	*The evolving perspective on the study of ancient bronze coins*
10.15-10.30	**ABC OR024**	**Cecilia Velino**	*Investigation of the corrosive effects of ambient particulate matter on bronze through accelerated sampling and ageing*
10.30-10.45	**ABC OR025**	**Maria Labate**	*The leading role of diagnostics for cultural heritage in historic studies and conservation: Sarezzano reliquary busts as a case study*
10.45-11.00	**ABC OR026**	**Andrea Timoncini**	*Characterization of bacteria community on bronze and marble statues*
11.00-11.15			
11.15-11.30			
11.30-11.45	**ABC OR027**	**Roberta Zanini**	*Laser Ablation ICP-MS elemental imaging to investigate corroded surfaces of ancient glass*
11.45-12.00	**ABC OR028**	**Lucrezia Gatti**	*A new analytical strategy for the characterization of diagenetic pathways in ancient bones and teeth.*
12.00-12.15	**ABC OR029**	**Raffaella Lamuraglia**	*Archaeometric investigation on Roman frescoes from the archaeological site of Aquileia*
12.15-12.30	**ABC OR030**	**Francesca Porpora**	*Diammonium hydrogen phosphate and Ca (OH)2 nanoparticles for consolidation of ancient bones: evaluation of performances*
12.30-12.45	**ABC OR052**	**Serena Spadavecchia**	*Evaluation of the effectiveness of coatings for the protection of outdoor terracotta artworks through artificial ageing*
12.45-13.00	**ABC OR032**	**Giulia C. Lodi**	*The assessment of the organic composition of historical remedies and drugs through a multidisciplinary approach*

ABC 03

09.30-09.45	**ABC OR034**	**Antonino Fiorentino**	*New photo-Fenton like process for roof harvested rainwater disinfection*
09.45-10.00	**ABC OR035**	**Elisa Gaggero**	*Removal of contaminants of emerging concern by enzymatic treatment with fungal laccases*
10-10.15.00	**ABC OR036**	**Giulia Guerra**	*Zinc and Iron Based Metal-Organic Frameworks as Ofloxacin Adsorbents in Polluted Waters*
10.15-10.30	**ABC OR037**	**Giuseppe Mascolo**	*Biodegradability enhancement of non-ionic surfactants in industrial wastewater by UV/H2O2 pre-treatment*

17 settembe - mattina

10.30-10.45	**ABC OR038**	**Giuseppe Mascolo**	*Remediation of groundwater contaminated with PCBs and PAHs by photocatalysis employing nano-sized TiO2 supported onto steel mesh*
10.45-11.00	**ABC OR039**	**Mirco Volanti**	*Biogas to Syngas through the Combined Steam/Dry Reforming Process: An Environmental Impact Assessment*
11.00-11.15			
11.15-11.30			
11.30-11.45	**ABC OR040**	**Sapia Murgolo**	*Assessment of a sustainable biofilter technology for reducing the environmental spread of CECs and odour emissions*
11.45-12.00	**ABC OR041**	**Federica Piras**	*Vacuum-UV as pre- and post-treatment to biofiltration: a novel integrated treatment scheme for wastewater reuse*
12.00-12.15	**ABC OR042**	**Concetta Pironti**	*A study of the biocidal effectiveness of permaleic acid (PMA): new promising application in disinfection process*
12.15-12.30	**ABC OR043**	**Annarosa Gugliuzza**	*2D Materials Engineered Membranes for a New Vision on Water Desalination*
12.30-12.45	**ABC OR044**	**Giuseppe Vitola**	*Membrane biofunctionalization for pesticide removal in surface water and vegetative water*
12.45-13.00	**ABC OR045**	**Domenico Cipriano**	*Protocol implementation of odour Proficiency Tests (PTs)*

Divisione CHIMICA FARMACEUTICA (FAR)

FAR 05

09.30 - 10.00	**FAR KN005**	**Yimon Aye**	*Leveraging precision electrophile signaling toward drug discovery*
10.00 - 10.30	**FAR KN006**	**Antimo Gioiello**	*Enabling synthesis and technologies to develop bile acid-inspired lead compounds*
10.30 - 10.45	**FAR OR019**	**Francesca Ferlenghi**	*A sulfonyl fluoride derivative selectively inhibits EGFRL858R/T790M/C797S by covalent modification of the catalytic lysine*
10.45 - 11.00	**FAR OR020**	**Angelica Artasensi**	*Novel potential DPP IV/ CA II inhibitors for the treatment of Type 2 Diabetes*
11.00 - 11.30	**FAR KN007**	**Andrea Stevenazzi**	*The selective inhibition of histone deacetylase 6 (HDAC6)*
11.30 - 11.45	**FAR OR023**	**Giannamaria Annunziato**	*Investigational studies on cyclopropane− carboxylic acid derivatives targeting O acetylserine sulfhydrylase as colistin adjuvants*
11.45 - 12.00	**FAR OR024**	**Simone Lucarini**	*Phenotype screening of a bisindole chemical library identifies URB1483 as a new antileishmanial agent with topoisomerase IB as molecular target*

12.00 - 12.15	**FAR OR025**	**Santo Previti**	*Development of peptidyl Michael acceptors for S3 pocket investigation of rhodesain, cysteine protease of Trypanosoma brucei rhodesiense*
12.15 - 12.30	**FAR OR026**	**Valentina Straniero**	*Development of benzodioxane-benzamides inhibitors of FtsZ as potent broad-spectrum antimicrobial agents*
12.30 - 13.00	**FAR KN008**	**Anna K.H. Hirsch**	*Addressing underexplored anti-infective targets*

FAR 06

10.30 - 10.45	**FAR OR021**	**Maria Dichiara**	*Design, synthesis and pharmacological evaluation of 4-carbamothioylphenyl sigma-1 receptor antagonists for pain treatment*
10.45 - 11.00	**FAR OR022**	**Giacomo Rossino**	*Identification of novel Sigma 1 receptor antagonists based on arylalkanolamine scaffold for the treatment of neuropathic pain*
11.00 - 11.30			
11.30 - 11.45	**FAR OR027**	**Marilena Muraglia**	*To042: prospective lead compound for the treatment of myotonic syndromes*
11.45 - 12.00	**FAR OR028**	**Sebastiano Intagliata**	*Development of mutual prodrugs of 5-fluorouracil and heme oxygenase 1 inhibitor as anticancer agents*
12.00 -12.15	**FAR OR029**	**Luca Pinzi**	*LigAdvisor: a web server to perform in silico explorations on crystallographic ligands and known drugs for polypharmacology and drug repurposing*
12.15 -12.30	**FAR OR030**	**Lucilla Turco**	*NMR contributions to process chemistry sustainability in the pharmaceutical research area*

Divisione CHIMICA FISICA (FIS)

FIS 06

Physical Chemistry for Biomedical Applications III

09:30-10:00	**FIS KN006**	**Debora Scuderi**	*Free electron Laser and IRMPD spectroscopy*
10:00-10:15	**FIS OR052**	**Rita Gelli**	*Insights into biologically-relevant calciprotein particles: effect of stabilizing agents on the formation and crystallization mechanisms*
10:15-10.30	**FIS OR053**	**Alessandra Del Giudice**	*Regulation of the photosynthetic AB-GAPDH via self-assembly*
10:30-10.45	**FIS OR054**	**Davide Tocco**	*Investigation of Fe-BTC and Z MOFs as carrier for Aspergillus.sp Laccase*
10:45-11:00	**FIS OR055**	**Pasquale Sacco**	*Biopolymer-based platforms for cell mechanosensing and regenerative medicine*

17 settembe - mattina

11:00-11.15	**FIS OR057**	**Marta Penconi**	*Advancing near-IR phosphorescence with Ir(III) complexes bearing a single emitting ligand: properties and OLED applications*
11.15-11.45	**break**		

Sessione congiunta con TEO

11:45-12:00	**FIS OR058**	**Fabio Gabas**	*Divide and Conquer Semiclassical Initial Value Representation: a valuable theoretical tool for vibrational spectroscopy of biological systems*
12:00_12:15	**TEO OR011**	**Giacomo Saielli**	*A computational view of ionic liquid crystals*
12:15-12.30	**FIS OR060**	**Tommaso Giovannini**	*Energy-Based Molecular Orbital Localization in specific Molecular Regions*
12:30-12:45	**TEO OR012**	**Alessio Petrone**	*Electronic attosecond dynamics: Ab initio treatment of photo-induced excitonic states*
12:45-13:15	**FIS KN007**	**George Froudakis**	*Designing Novel Nanoporous Materials for Applications in Energy and Environment. From Multi-Scale Modeling to Materials Informatics*

FIS 07

Sessione congiunta con CSB

09:30-10:00	**FIS KN008**	**Roland Winter**	*Temperature, Pressure, and Cosolute Effects on Liquid–Liquid Phase Separation and Condensates of Proteins: Physical Chemistry and Biological Implications*
10:00-10:15	**FIS OR067**	**Francesca Baldelli**	*Superfluorinated Exosomes for Sensitive in Vivo Tracking by 19F-MRI*
10:15-10.30	**FIS OR063**	**Cristina Carucci**	*Drug loaded polymer coated silica nanoparticles as drug delivery route against bacteria*
10:30-10.45	**FIS OR064**	**Francesca Biscaglia**	*Engineered Peptides on Gold Nanostructures for Enhanced Targeting Activity in Cancer Diagnosis*
10:45-11:00	**FIS OR065**	**Ilaria Clemente**	*Cubic and lamellar mesophases obtained from algal biomass as drug carriers with high potentiality*
11:00-11.15	**CSB OR026**	**Angelo Spinello**	*Small-molecule modulators of spliceosome-mutant cancers as a new therapeutic strategy against hematologic malignancies*
11:15-11.30	**CSB OR027**	**Nunzia Iaccarino**	*Effects of sequence and base composition on the CD and TDS profiles of i DNA*
11.30-11.45	**break**		

Sessione congiunta con ELE

11:45-12:15	**FIS KN009**	**Maria Vittoria Dozzi**	*CuWO4-based photoanodes for solar energy conversion: effects of Mo6+ doping and coupling with BiVO4*
12:15-12:30	**ELE OR038**	**Gennaro Sannino**	*Development of SnO2 composites as electron transport layer in un-encapsulated CH3NH3PbI3 solar cells*

12:30-12:45	**FIS OR069**	**Guillermo Escolano Casado**	*Cu-functionalized hydroxyapatites: a study of their physico-chemical properties and their potential as electrocatalysts*
12:45-13:00	**ELE OR039**	**He Xiufang**	*Investigation of the mechanism of Pt3Fe3 clusters for the hydrogen evolution reaction and for the oxygen reduction reaction*
13:00-13:15	**FIS OR071**	**Simone Di Muzio**	*Thermodynamics of the hydrolysis of lithium salts: pathways to the inorganic SEI components*

Divisione CHIMICA INORGANICA (INO)
INO 04

9.30 - 9.50	**INO PZ002 (Premio Dottorato 2020)**	**Anna Dall'Anese**	*Palladium catalyzed copolymerizations: from ligand architecture to macromolecule microstructure*
9.50 - 10.10	**INO PZ003 (Premio Dottorato 2020)**	**Giacomo Picci**	*Novel supramolecular architectures based on weak interactions*
10.10 - 10.30	**INO PZ004 (Premio Dottorato 2020)**	**Fortuna Ponte**	*Anticancer drugs: a detailed computational analysis of “non classical” compounds mechanism of action*
10.30 - 10.45	**INO OR022**	**Andrea Biffis**	*Gold catalyzed direct alkyne hydroarylations in ionic liquids: a powerful tool in organic synthesis*
10.45 - 11.00	**INO OR023**	**Luca Conti**	*Ru(II) polypyridyl complexes as promising light-responsive agents for biological application*
11.00 - 11.15	**INO OR024**	**Filippo Campagnolo**	*Development of sustainable and green methodologies for homogeneous gold(I) catalysis*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR025**	**Matteo Atzori**	*Magneto-chiral dichroism in chiral molecular magnets*
11.45 - 12.00	**INO OR026**	**Stefano Scoditti**	*Anticancer and photophysical properties of a N^C^N-coordinated Pt(II) complex*
12.00 - 12.15	**INO OR027**	**Paolo Cleto Bruzzese**	*17O spin density studies of single-metal sites in Cu-CHA zeolites*
12.15 - 12.30	**INO OR028**	**Federica Santulli**	*A single catalyst for the synthesis and chemical depolymerization of polylactide*
12.30 - 13.00	**INO PZ005 (Premio Nasini 2020)**	**Enrico Ravera**	*Paramagnetic NMR in bioinorganic chemistry in the ‘twenties*

INO 05

10.30 - 10.45	**INO OR029**	**Mauro Ravera**	*Pt(IV) bifunctional complexes as anticancer agents: “is this true glory?”*

10.45 - 11.00	**INO OR030**	**Alessia Giordana**	*Solid acid catalysts for glucose hydrolysis: quantification of Lewis and Brønsted acid sites using 2,6-dimethylpyridine*
11.00 - 11.15	**INO OR031**	**Giorgio Facchetti**	*New sp3 diphosphine-based rhodium catalysts for the asymmetric addition of aryl boronic acids to azaarenes*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR032**	**Marco Chino**	*Design of a miniaturized FeS4 protein*
11.45 - 12.00	**INO OR033**	**Paolo Centomo**	*Selectivity enhancement of coordinating solvents on the direct synthesis of hydrogen peroxide*
12.00 - 12.15	**INO OR034**	**Tania Pecoraro**	*Luminescent self-assemblies of Pt(II) complexes in vivo*
12.15 - 12.30	**INO OR035**	**Cristiana Cesari**	*Homometallic and heterometallic ruthenium hydride carbonyl cluster*

INO 06

10.30 - 10.45	**INO OR036**	**Andrea Rossin**	*Thiazole-based Metal-Organic Frameworks for applications in CO2 storage/utilization and luminescence sensing*
10.45 - 11.00	**INO OR037**	**Patrizio Campitelli**	*Amino-decorated zinc bipyrazolate MOFs, an example of carbon dioxide capture and reuse (CCR)*
11.00 - 11.15	**INO OR038**	**Giorgio Tseberlidis**	*Sol-gel deposition of Cu2XYS4 thin-films with tunable bandgap as absorbers for photovoltaic applications*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR039**	**Francesca Deganello**	*Recycling inorganic waste into sustainable materials for energy and environment*
11.45 - 12.00	**INO OR040**	**Damiano Ricciarelli**	*Energy vs charge transfer in manganese doped lead halide perovskites*
12.00 - 12.15	**INO OR041**	**Marco Bellini**	*Electrocatalysis for energy: from nanostructured to molecular approach*
12.15 - 12.30	**INO OR042**	**Chiara Domestici**	*Novel mononuclear and dinuclear Ir-Cp* complexes bearing phosphonate and carboxylate ancillary and anchoring ligands as homogeneous and heterogenized water oxidation catalysts*

Divisione ELETTROCHIMICA (ELE)

ELE 05

09.30 - 10.00	**ELE_KN34**	**Matteo Bonomo**	*NiO/ZrO2 nanocomposites as photocathodes of tandem DSCs with higher photoconversion efficiency with respect to parent single-photoelectrode p-DSCs*
10.00 - 10.15	**FIS_OR068**	**Giuseppe Arrabito**	*Inkjet Printing Quasi-Miscible Droplets for Pseudo-Planar Organic Heterojunctions*
10.15 - 10.30	**ELE_OR35**	**Alessandro Facchin**	*Oxygen Reduction Reaction monitoring at Iron Single Site Catalyst: Electrochemical Scanning Tunnelling Microscopy of Iron Octaethylporphyrin*
10.30 - 10.45	**FIS_OR070**	**Mariangela Curcio**	*Laser irradiation of Bio-waste derived carbon as anode for Li-ion batteries*

17 settembe - mattina

10.45 - 11.00	**ELE_OR36**	**Barbara Vercelli**	*Doping or Aggregation: the case of Conjugated Polyelectrolytes PCPDTBT-2SO3K and PCPDTBT-SO3K*
11.00 - 11.15	**FIS_OR130**	**Elena Messina**	*Electrochemical study of Smart Nanocarriers forImproved Corrosion Protection of Reinforced Concrete*
11.15 - 11.30	**ELE_OR37**	**Marco Malferrari**	*Light-Induced Electrochemical Processes at Semiconductor-Films/Water Interface Modulate Cell Redox Balance*

ELE 06

09.30 - 10.00	**ELE_KN40**	**Stefania Rapino**	*Cancer Metabolic Profile Detected by Scanning ElectroChemical Microscopy*
10.00 - 10.15	**ANA_OR137**	**Ilaria Ragazzini**	*A simple and industrially scalable method for making a PANI-modified cellulose touch sensor*
10.15 - 10.30	**ELE_OR42**	**Nikolaou Pavlos**	*Ultrasensitive Hepatitis B Virus whole genome detection by Electrochemiluminescence*
10.30 - 10.45	**ANA_OR136**	**Cosimino Malitesta**	*Electrosynthesised ion imprinted polymers in development of sensor for Cd(II) ions determination in water*
10.45 - 11.00	**ELE_OR44**	**Patrik Sfragano**	*A bicyclic peptide-based biosensor for the electrochemical detection of a cancer-related protease*
11.00 - 11.15	**ANA_OR134**	**Veronica Caratelli**	*A Paper-Based Electrochemical Device for the Detection of Pesticides Inspired by Nature: a Flower-Like Origami Biosensor*
11.15 - 11.30	**ELE_OR43**	**Silvia Comis**	*Determination of emerging contaminants with electrochemical sensors based on titania nanoporous films: effect of sol aging on their electrochemical performances*
11.30 - 11.45	**break**		
11.45 - 12.00	**ANA_OR135**	**Noemi Colozza**	*A multiparametric electrochemical device for degradation monitoring in reinforced concrete*
12.00 - 12.15	**ELE_OR41**	**Alessanra Zanut**	*DNA-based Nanoswitches: insights into electrochemiluminescence signal enhancement*

ELE 07

11.30 - 12.00	**ELE_KN045**	**Marta Feroci**	*Solvent-supporting electrolyte system in electrolysis: not only chemical environment and charge carrier*
12.00 - 12.15	**ELE_OR04 6**	**Angeloclaudio Nale**	*Interplay between porosimetric parameters, densitometric parameters and catalytic activities of "Core-Shell" ORR Electrocatalysts*
12.15 - 12.30	**ELE_OR047**	**Gioele Pagot**	*Ion Coordination and Dynamics in Ionic Liquid-based Electrolytes for Hybrid Al/Mg Batteries*
12.30 - 12.45	**ELE_OR048**	**Carpanese Maria Paola**	*Copper-based perovskite electrodes for reversible solid oxide cells*
12.45 - 13.00	**ELE_OR049**	**Duranti Leonardo**	*Multi-functional Fuel Electrode for Reversible Solid Oxide Cells*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 04

9.30 - 10.00	**TEC IL002**	**Lvova Larisa**	*Recent advances in potentiometric sensors for environmental purposes: from single ion-selective electrodes to multisensor analysis*
10:00 - 10:10	**TEC OR035**	**Moulaee Kaveh**	*A new electrochemical platform for fast and efficient determination of dominant non-psychoactive cannabinoids in Cannabis Sativa*
10:10 - 10:20	**TEC OR036**	**Ferlazzo Angelo**	*Crown ether functionalized graphene quantum dots as electrochemical and fluorescence based sensors for the selective detection of potassium and sodium ions*
10:20 - 10:30	**TEC OR037**	**Zribi Rayhane**	*Electrochemical and sensing properties of 2D-MoS2 nanosheets produced via liquid cascade centrifugation at different rate*
10:30 - 10:40	**TEC OR038**	**Bella Federico**	*Hybrid solar cells operating in aqueous environment*
10:40 - 10:50	**TEC OR039**	**Grisorio Roberto**	*A new synthetic approach for size-tunable and stable CsPbBr3 nanocubes with near-unity photoluminescence quantum yield*
10:50 - 11:00	**TEC OR040**	**Bortolami Martina**	*BMIm-BF4: a versatile ionic liquid for BF3 generation and reactions*
11:00 - 11:15	**Discussion**		

Divisione TECNOLOGIA FARMACEUTICA (TFA)
TFA 02

09.30 - 10.00	**TFA IL003**	**Mauro Bonini**	*Release in oral solid nutraceutical forms: case studies.*
10.00 - 10.30	**TFA IL004**	**Marco Fidaleo**	*A lesson from Vitamin B12: from the biological issues to the design of a nutraceutical formulation*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.15	**TFA OR010**	**Annalisa Bianchera**	*Crystallization of stable doped mannitol polymorphs and in vitro assessment of their safety as carriers for lung delivery*
11.15 - 11.30	**TFA OR011**	**Luca Casula**	*Multicomponent nanosuspension for the bronchial asthma inhalation therapy*
11.30 - 11.45	**TFA OR012**	**Luca Cerri**	*Spray patch based on hyaluronic acid and chitosan microparticles medicated with olive leaf extract*
11.45 - 12.00	**TFA OR013**	**Maria Chiara Cristiano**	*EtoGel: combined systems for new ethosomes application in joint diseases treatments*
12.00 - 12.15	**TFA OR014**	**Tiziana Esposito**	*Castanea sativa waste as dermo-functional ingredient into a topical delivery system: from the design and development of the formulation to in vitro stability and in vivo skin tolerability and efficacy*
12.15 - 12.30	**TFA OR015**	**Diego R. Perinelli**	*Development of topical formulations using hydrolyzed keratin as an alternative to the commonly employed emulsifying agents*

17 settembe - mattina

12.30 - 12.45	**TFA OR016**	**Teresa Silvestri**	*Biodegradable microparticles for the treatment of the posterior eye segment diseases*
12.45 - 13.00	**TFA OR017**	**Elena Giuliano**	*Poloxamer– and poloxamine-based hydrogels as biocompatible systems for the delivery of active compounds*
13.00 - 13.15	**TFA OR018**	**Umberto M. Musazzi**	*Printing of cutaneous patches loaded with propranolol for the treatment of infantile hemangiomas*

Programma dei LAVORI di DIVISIONE - 17 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA 07

15.00 - 15.20	**ANA PZ003**	**Mariosimone Zoccali**	*Is There a Real Need for Multidimensional Chromatography Strategies with the Current Availability of Powerful Mass Spectrometry Platforms?*
15.20 - 15.40	**ANA KN008**	**Giovanni Ventura**	*AllerT: a Matlab-based workflow for putative allergens identification in novel foods via LC-ESI-MS/MS analysis*
15.40 - 16.00	**ANA OR051**	**Domenica Mangraviti**	*Differentiation and profiling of Morocco species belonging to Lamiaceae Family by Ambient Mass Spectrometry methods*
16.00 - 16.15	**ANA OR052**	**Nicole Marittimo**	*Advancements in Direct-MS using SPME coupled to Liquid-EI and CI*
16.15 - 16.30	**ANA OR053**	**Katia Arena**	*Characterization of bioactive compounds from natural products using focusing-modulated comprehensive two-dimensional liquid chromatography coupled to mass spectrometry*
16.30 - 16.45	**ANA OR054**	**Eleonora Oliva**	*Analysis of phenolic compounds in plant matrices by means of HPLC-MS/MS with targeted and semi-untargeted approach*
16.45 - 17.00	**ANA OR055**	**Tania Salerno**	*The Coupling of Gas Chromatography - Mass Spectrometry with Infrared Spectroscopy for Reliable Identification of Unknowns in Complex Samples*
17.00 - 17.15	**ANA OR056**	**Danilo Sciarrone**	*Reliability of monodimensional vs multidimensional GC-C-IRMS data: a critical evaluation*
17.15 - 17.30	**ANA OR057**	**Peter Q. Tranchida**	*Options of 1D GC, flow-modulation signal-enhanced 1D GC and flow-modulation comprehensive 2D GC in a single instrument: a proof-of-concept study*
17.30 - 17.45	**ANA OR058**	**Cecile Valsecchi**	*Enhanced LC-MS/MS spectra matching through multi-task neural networks and molecular fingerprints*

ANA 08

15.20 - 15.40	**ANA IL005**	**Alessandra Bianco Prevot**	*Organic Pollutant Removal using Photo-Fenton Processes in the presence of Fe(III) complexing agents*
15.40 - 16.00	**ANA IL006**	**Paola Fermo**	*In-situ and micro-destructive investigation for the analysis of degradation products present on marble surfaces*
16.00 - 16.15	**ANA OR059**	**Francisco Ardini**	*Evaluation of potential source areas for atmospheric lead reaching Ny-Ålesund (Svalbard) from 2010 to 2019*
16.15 - 16.30	**ANA OR060**	**Stefano Bertinetti**	*Strontium isotopic analysis of microsamples by inductively coupled plasma - tandem mass spectrometry*

17 settembre - pomeriggio

16.30 - 16.45	**ANA OR061**	**Luca Carena**	*Photochemistry of furfuryl alcohol in/on snow at -30°C: photoreactivity with singlet oxygen and by direct photolysis*
16.45 - 17.00	**ANA OR062**	**Silvia Illuminati**	*Year-round records of bulk aerosol composition over the Victoria Land (Antarctica)*
17.00 - 17.15	**ANA OR063**	**Elisa Calà**	*Identification of aloe and other dyes by means of SERS and HPLC-DAD-MS in the embroidery of a 15th century English folded almanac*
17.15 - 17.30	**ANA OR064**	**Emilio Catelli**	*Rediscovering the lost color. Advanced vector quantization algorithm and hyperspectral imaging for digital restoration of color films*
17.30 - 17.45	**ANA OR065**	**Giovanna Marussi**	*The Third-Century monetary crisis: chemical analysis of Denarii and Antoniniani*
17.45 - 18.00	**ANA OR066**	**Rosaria Anna Picca**	*Synthesis and spectroscopic characterization of synergistic nanomaterials for stone artwork protection*

ANA 09

15.20 - 15.40	**ANA KN009**	**Paolo Bollella**	*Enzyme based Amperometric Biosensors: From Direct Electron Transfer to Chimeric Enzymes*
15.40 - 16.00	**ANA OR067**	**Giuseppe Arrabito**	*Printing Biology: engineering analytical platforms by molecular inks*
16.00 - 16.15	**ANA OR068**	**Noemi Bellassai**	*Design of dual-functional polymer on plasmonic biosensor for detection of circulating tumor DNA point mutations*
16.15 - 16.30	**ANA OR069**	**Alessandro Bertucci**	*Artificial Biomolecular Communication Regulated by Synthetic DNA Translators*
16.30 - 16.45	**ANA OR070**	**Alessandra Maria Bossi**	*Soft molecularly imprinted nanoparticles for protein recognition in sensing and assays*
16.45 - 17.00	**ANA OR071**	**Stefano Cinti**	*A microfluidic paper-based chip patterned with Prussian Blue to determine sweat urea*
17.00 - 17.15	**ANA OR072**	**Erica Del Grosso**	*Transient control of DNA-based systems*
17.15 - 17.30	**ANA OR073**	**Marco Giannetto**	*Smart immunosensors for point-of-care serologic test to determine the level of immunity by Covid-19 infection or by SARS-CoV-2 vaccination*
17.30 - 17.45	**ANA OR074**	**Antonia Lopreside**	*Reagent-free paper biosensor based on genetically modified bioluminescent protein for cancer biomarker detection*
17.45 - 18.00	**ANA OR075**	**Lucia Sarcina**	*Selective detection of Xylella fastidiosa with a Surface Plasmon Resonance based immunoassay*

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 04

15.00-15.15	**ABC OR051**	**Dominique Scalarone**	*CAPuS project: research and higher education allied for the Conservation of Art in Public Spaces*

15.15-15.30	**ABC OR013**	**Ilaria Serafini**	*Advances in analytical methodologies applied to cultural heritage: first application of DLLME to characterize dyes in ancient textiles*
15.30-15.45	**ABC OR014**	**Slimani Sawssen**	*Caput Mortuum purple hematite pigment: Investigation of magnetic properties*
15.45-16.00	**break**		
16.00-16.15	**ABC OR015**	**Andrea Brunelli**	*Colloidal behavior of titanium dioxide nanoparticles in artificial and in Venice lagoon waters in the presence of standard or natural colloidal particles*
16.15-16.30	**ABC OR016**	**Felice Simeone**	*Assessment of the Cytotoxicity of Metal oxide Nanoparticles on the Basis of Immediately Available Physical-Chemical Parameters.*
16.30-16.45	**ABC OR017**	**Cristina De Ceglie**	*The effect of a karst-fractured aquifer on wastewater quality: an UHPLC-HRMS study*
16.45-17.00	**ABC OR018**	**Francesco Saliu**	*Plastic and its associated contaminants: determination of PAEs in coral reef invertebrates by in vivo SPME-LC-MS/MS*
17.00-17.15			
17.15-17.30	**ABC OR019**	**Armando Zarrelli**	*Characterization of degradation byproducts of Sartans: elucidation of their degradation pathway and ecotoxicity assessment*
17.30-17.45	**ABC OR020**	**Marco Mantovani**	*Microalgal treatment of the liquid fraction from hydrothermal carbonization process (HTC) in a circularity perspective*
17.45-18.00	**ABC OR021**	**Giulia Guidotti**	*Poly(diethylene 2,5-furanoate): a biobased promising candidate for compostable high-performant packaging*
18.00-18.15	**ABC OR022**	**Valeria D’Ambrosio**	*Lipids extraction from sewage sludge using green biosolvent for a sustainable production of biodiesel*

Divisione CHIMICA INDUSTRIALE (IND)

IND 04

Sessione congiunta con Gruppo Interdivisionale Energie Rinnovabili - Enerchem

15.00 - 15.30	**IND KN005** **Chini Lecture**	**Carlo Perego**	*CO2 utilization: from waste to resource*
15.30 - 15.40	**IND OR033**	**Martina Serafini**	*Nanostructured Cu-based Electrocatalysts on a Carbonaceous Gas Diffusion Layer for the Electrochemical Reduction of CO2*
15.40 - 15.50	**IND OR034**	**Simelys Hernandez**	*How to exploit thermochemical catalysts to make efficient & sustainable CO2 electroreduction to added value products*
15.50 - 16.00	**IND OR035**	**Ivan Grigioni**	*High rate CO2 electroreduction to formate with a InP colloidal quantum dots derived catalyst*
16.00 - 16.10	**IND OR036**	**Federico Bella**	*Preliminary investigation of anodic materials for potassium batteries*
16.10 - 16.20	**IND OR037**	**Maria Grazia Musolino**	*Solvothermal synthesis of doped hematite/reduced graphene oxide nanocomposites for sodium-ion batteries*

16.20 - 16.30	**IND OR038**	**Emilia Paone**	*Reductive Upgrading of Biomass Derived Furan promoted by Spent Lithium-Cobalt Batteries as an Efficient Heterogeneous Catalyst*
16.30 - 16.40	**IND OR039**	**Matteo Bonomo**	*Thermosetting polyurethanes resins: application as cheap, sustainable and scalable encapsulants for (flexible) Perovskite Solar Cells*
16.40 - 16.55	***Discussion***		
16.55 - 17.10	**break**		
17.10 - 17.20	**IND OR040**	**Andrea Fasolini**	*Low Temperature Methane Steam Reforming in a H2-selective Pd Membrane Reactor*
17.20 - 17.30	**IND OR041**	**Tiziano Montini**	*Visible-light-driven coproduction of diesel precursors and hydrogen from lignocellulose-derived methylfurans*
17.30 - 17.40	**IND OR042**	**Nicola Sangiorgi**	*Improved water stability of CsPbBr3 thin film photoelectrodes*
17.40 - 17.50	**IND OR043**	**Cosimo Micheletti**	*Luminescent Solar concentrators based on Aggregation-Induced Emission*
17.50 - 18.00	**IND OR022**	**Giuseppe Pipitone**	*Aqueous phase reforming of biorefinery by-products towards sustainable hydrogen production*
18.00 - 18.10	**IND OR045**	**Francesco Conte**	*H2 production by photoreforming of glucose*
18.10 - 18.30	***Discussion***		

Divisione CHIMICA ORGANICA (ORG)

ORG 08

15.00 - 15.30	**ORG PZ006**	**Daniela Montesarchio**	***Premio alla ricerca Chimica Organica per le Scienze della Vita*** *G-Quadruplexes to the fore: towards DNA-targeting magic bullets*
15.30 - 16.00	**Break**		
16.00 - 16.15	**ORG PZ014**	**Anna Esposito**	***Premio Tesi di Dottorato Chimica Organica per le Scienze della Vita*** *Exploring the therapeutic potential of L-deoxyiminosugars in rare diseases*
16.15 - 16.30	**ORG OR045**	**Cristina Minnelli**	*Epigallocatechin-3-gallate-based Inhibitors Targeting EGFR to Overcome Drug Resistance in Advanced NSCLC*
16.30 - 16.45	**ORG OR046**	**Lucía Morillas Becerril**	*Specific and nondisruptive interaction of guanidium-functionalized gold nanoparticles with neutral phospholipid bilayers*
16.45 - 17.00	**ORG OR047**	**Maria Luisa Navacchia**	*Dihydroartemisinin-bile acid hybridization as an effective approach to enhance dihydroartemisinin anticancer activity*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR048**	**Ferran Nieto Fabregat**	*Gram-negative bacteria LPS recognition by DC-SIGN*

17.45 - 18.00	**ORG OR049**	**Anna Notaro**	*Mimiviruses possess the biosynthetic pathways to produce bacteria-like sugars in a clade-specific manner*
18.00 - 18.15	**ORG OR050**	**Alessandro Palmioli**	*On-cell saturation transfer difference NMR for the identification of FimH ligands and inhibitors*
18.15 - 18.30	**ORG OR051**	**Daniela Perrone**	*Synthesis and preclinical evaluation of antisense oligonucleotides conjugated with ursodeoxycholic acid for the treatment of Duchenne muscular dystrophy*

ORG 09

16.00 - 16.15	**ORG PZ013**	**Mirko Maturi**	***Premio Tesi di Dottorato Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze*** *Advanced Functional Organic-Inorganic Hybrid (Nano)Materials: from Theranostics to Organic Electronics and Additive Manufacturing*
16.15 - 16.30	**ORG OR052**	**Mariacecilia Pasini**	*Sustainable by Design Carbon Dots as promising material for luminescent and biomedical applications*
16.30 - 16.45	**ORG OR053**	**Vincenzo Patamia**	*A new hybrid porous multifunctional material based on Loofah-Halloysite*
16.45 - 17.00	**ORG OR054**	**Marina Massaro**	*Synthesis and characterization of different mussel inspired materials for several applications*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR055**	**Giulia Neri**	*Fluorinated Polymers and Fluorescent Graphene as Innovative Nanotheranostic Materials*
17.45 - 18.00	**ORG OR056**	**Alessandra Operamolla**	*Cellulose nanocrystals for paper consolidation*
18.00 - 18.15	**ORG OR057**	**Luca Pettazzoni**	*Transamidation-based vitrimers from renewable sources*
18.15 - 18.30	**ORG OR058**	**Serena Riela**	*Improvement of properties of halloysite and some other «friends» by chemical modifications*

ORG 10

16.00 - 16.15	**ORG OR059**	**Claudio Curti**	*Merging Vinylogy with Organocatalysis: Direct, Asymmetric Entry to Chiral Fused Uracil Derivatives*
16.15 - 16.30	**ORG OR060**	**Daniele Fiorito**	*Synthetic studies towards Bastimolide B*
16.30 - 16.45	**ORG OR061**	**Paola Costanzo**	*Highly oleophilic and reusable polyurethane composites for the removal of oils from fresh water and seawater*
16.45 - 17.00	**ORG OR062**	**Andrea Mezzetta**	*Reactive Deep Eutectic Solvents (ReDESs): an underexploited option for organic chemistry*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR063**	**Lorenzo Di Terlizzi**	*Visible light-driven α-arylation of enol silyl ethers via arylazo sulfones.*

17 settembre - pomeriggio

17.45 - 18.00	**ORG OR064**	**Lucia Ferrazzano**	*Greening peptide synthesis: new options for a sustainable chemistry*
18.00 - 18.15	**ORG OR065**	**Valeria Nori**	*Organocatalysed Michael addition of masked acetaldehyde to nitroalkenes in water*
18.15 - 18.30	**ORG OR066**	**Rita Mocci**	*Mechanochemical Fischer Indolisation: Exploration of a Timeless Reaction in a New Guise*

ORG 11

16.00 - 16.15	**ORG OR067**	**Allegra Franchino**	*Merging organo- and Au(I) catalysis for asymmetric or silver-free reactions of alkynes*
16.15 - 16.30	**ORG OR068**	**Gianluigi Albano**	*Infrared irradiation-assisted solvent-free Palladium-catalyzed (hetero)aryl-aryl coupling via C-H bond activation*
16.30 - 16.45	**ORG OR069**	**Fabio Bellina**	*Pd/Ag-mediated dehydrogenative alkynylation of imidazoles*
16.45 - 17.00	**ORG OR070**	**Silvia Gaspa**	*Photocatalyzed amides synthesis from alcohols by visible light*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR071**	**Fabrizio Medici**	*Stereoseletive [2+2] photocycloaddition: a viable strategy for the synthesis of enantiopure cyclobutane derivatives*
17.45 - 18.00	**ORG OR072**	**Francesco Messa**	*Ligand-Free Cobalt-Catalyzed Cross-Coupling Reaction Between Organoaluminum Reagents and (Hetero)Aryl and Alkyl Bromides*
18.00 - 18.15	**ORG OR073**	**Giorgia Zanchin**	*Imino-pyridine Cr complexes as precatalyst for the polymerization of olefins: synthesis and catalytic tests with NEt3 as additive*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 03

15.00 - 15.30	**CSB KN003**	**Luc Brunsveld**	*Stabilization of Protein-Protein Interactions; from the fundamentals of cooperativity to applications in drug discovery*
15.30 - 15.45	**CSB OR014**	**Alessio Romerio**	*Design, synthesis and Biological evaluation of New, glycolipid-based Toll-Like Receptor 4 (TLR4) Modulators*
15.45 - 16.00	**CSB OR015**	**Giusy Tassone**	*Evidence of amino-thiadiazoles as innovative inhibitors of human glutaminyl cyclase, validated target for neurodegenerative disorders*
16.00 - 16.15	**CSB OR016**	**Francesco Tadini-Buonisegni**	*Modulation of Ca2+-ATPase transport activity by pharmacologically relevant compounds*
16.15 - 16.30	**CSB OR017**	**Michela Pisani**	*Insulin loaded in liquid crystalline mesophases: effects on carrier structure and insulin stability*
16.30 - 17.00	**Break**		

17.00 - 17.30	**CSB KN004**	**Elena Sgaravatti**	*Research and development of active ingredients from vegetable cells or crops to be used in the Health care, Food and Personal care sectors*
17.30 - 17.45	**CSB OR018**	**Valeria Romanucci**	*New curcumin mimics based on tyrosol scaffold: investigation of neuroprotective and anticancer activity*
17.45 - 18.00	**CSB OR019**	**Roberto Tira**	*Modulation of Tau aggregation with natural coffee compounds*
18.00 - 18.10	**CSB OR020**	**Rita Pagano**	*Phosphate-linked Silybin dimers: synthesis and investigation of biological activity*
18.10 - 18.20	**CSB OR021**	**Massimiliano Gaeta**	*Hybrid Porphyrin/DOPA-melanin Film as Versatile Biomaterial for Water Remediation*
18.20 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 02

15:00-15:30	**DID IL002**	**Carlo Fiorentini**	*The teaching of chemistry from the perspective of citizenship*
15:30-15:45	**DID OR010**	**Teresa Cecchi**	*Chemistry: a Precious Discovery in the Dantesque World*
15:45-16:00	**DID OR011**	**Maria Irene Donnoli**	*A Carbon atom journey*
16:00-16:15	**DID OR012**	**Elena Lenci**	*Peer review of scientific articles: a teaching experience*
16:15-16:30	**DID OR013**	**Silvia Prati**	*Increasing the engagement of non-chemistry major students: examples of didactic strategic*
16:30-18:30	**Panel Discussion**	**Silvia Bencivelli (coordinator)** **Pellegrino Conte** **Paola Govoni** **Piersandro Pallavicini** **Valentina Domenici**	*Chemistry: how, where, when and why*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 02

15.00 - 15.40	**MAS PL003**	**Nikolai Kuhnert**	*Mass spectrometry in coffee science: From bean to drink to human*
15.40 - 16.10	**MAS KN001**	**Tata Alessandra**	*Non-targeted authentication of food products: the synergic combination of ambient mass spectrometry, data fusion and machine learning"*
16.10 - 16.25	**MAS OR006**	**M.A. Acquavia**	*Influence of mixed starter cultures of Hanseniaspora osmophila and Saccharomyces cerevisiae on wine flavor profile explored through HS-SPME/GC-MS*
16.25 - 16.35	**Break**		

16.35 - 17.05	**MAS KN002**	**Linda Monaci**	*Future challenges in MS based technologies applied to the safety of foods.*
17.05 - 17.20	**MAS OR007**	**Rosalia Zianni**	*Lipidomic approach to evaluate the effect of X-ray irradiation treatment on the lipid profile of Camembert cheese*
17.20 - 17.35	**MAS OR008**	**Fabiola De Marchi**	*High-resolution mass spectrometry approaches finalized to identification of new glycoside compounds in grape*
17.35 - 17.50	**MAS OR009**	**Ciro Cannavacciuolo**	*Analysis by high-resolution mass spectrometry of polyphenolic alkaloids fraction from Portulaca oleracea*
17.50 - 18.05	**MAS OR010**	**Lucia Bartella**	*Paper Spray tandem mass spectrometry: an innovative approach to assess flavonoid content in citrus drinks*

Divisione TEORICA E COMPUTAZIONALE (TEO)

TEO 02

15.00 - 15.30	**TEO KN002**	**Alfonso Pedone**	*Exploiting Machine Learning Methods in Atomistic Simulations of Oxide Glasses*
15.30 - 15.45	**FIS OR059**	**Adriana Pecoraro**	*First-principles study of Mn and Fe co-doped BaZrO3 as PC-SOFC cathode for the Oxygen Reduction Reaction*
15.45 - 16.00	**TEO OR013**	**Leonardo Guidoni**	*Quantum Chemistry using Quantum Computers*
16.00 - 16.15	**FIS OR061**	**Marco Medves**	*TDDFT methods for large systems: new computational schemes and automatic generation of density fitting basis*
16.15 - 16.30	**TEO OR014**	**Elena Tocci**	*Molecular view on crystals nucleation and growth on different PVDF polymorphs*
16:30 - 17:00	**Discussion**		

TEO 03

15:00 - 15:10	**TEO OR015**	**Matteo Capone**	*Multi-Scale Charge-Transfer Modeling in Enzyme Catalysis*
15:10 - 15:20	**TEO OR016**	**Guelber Cardoso Gomes**	*Computational study of dicationic ionic liquids based on imidazole*
15:20 - 15:30	**TEO OR017**	**Elisa Bernes**	*An experimental and theoretical investigation on the electronic structure of indole, 2,3-dihydro-7- azaindole, and 3-formylindole in the gas phase by synchrotron-based spectroscopic techniques*
15:30 - 15:40	**TEO OR018**	**Yasi Dai**	*Addressing the Frenkel and charge transfer character of exciton states with a model Hamiltonian based on dimer calculations: application to large aggregates of perylene bisimide*

17 settembre - pomeriggio

15:40 - 15:50	**TEO OR019**	**Stefano Motta**	*Study of ligand binding to HIF-2α through Path-Metadynamics*
15:50 - 16:00	**TEO OR020**	**Alessandra Gilda Ritacca**	*The multifaceted roles of copper ion in human body explored by computational tools*
16:00 - 16:10	**TEO OR021**	**Anna Rovaletti**	*Unravelling the reaction mechanism of Mo/Cu CO dehydrogenase using QM/MM calculations*
16:10 - 16:20	**TEO OR022**	**Sara Del Galdo**	*How water density responds to the presence of a crowding agent*
16:20 - 16:30	**TEO OR023**	**Francesco Ferdinando Summa**	*SYSMOIC: A Program Package for the Calculation of Origin-Independent Electron Current Density and Derived Magnetic Properties in Molecular Systems*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO KN003**	**Fabrizia Negri**	*Modelling extended-core π systems and their aggregates: charge transport and optoelectronic properties*
17:20 - 17:40	**TEO PZ003**	**Giovanni Di Liberto**	*Rational Design of Semiconductor Interfaces for Photocatalysis*
17:40 - 18:00	**TEO PZ004**	**Eduardo Schiavo**	*First Principles Approaches for Heterogeneous Functional Materials*
18:00 - 18:30	**Discussion**		

Programma dei LAVORI di DIVISIONE - 20 settembre mattina

Divisione CHIMICA ORGANICA (ORG)

ORG 12

9.30 - 10.00	**ORG PZ004**	**Pierangelo Gobbo**	***Medaglia Giacomo Ciamician*** *A synthetic chemistry approach to the fabrication of protocells and protocellular materials*
10.00 - 10.30	**ORG PZ007**	**Francesco Giacalone**	***Premio alla ricerca Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze*** *Nanocarbon-based Hybrid Materials as Efficient and Sustainable Heterogeneous Catalysts*
10.30 - 10.45	**ORG OR074**	**Loredana Maiuolo**	*Polysubstituted 1,2,3-Triazoles: synthesis and biological application*
10.45 - 11.00	**ORG OR075**	**Michele Mancinelli**	*Atropisomeric Azaborines: Axial Chirality at the Boron-Carbon Bond*
11.00 - 11.15	**ORG OR076**	**Francesca Franco**	*Formal α-trifluoromethylthiolation of carboxylic acid derivatives via N-acyl pyrazoles*
11.15 - 11.30	**ORG OR077**	**Claudia Sciacca**	*Synthesis of nitrogenated analogues of honokiol as potential bioactive compounds*
11.30 - 11.45	**ORG OR078**	**Damiano Tanini**	*The unexpected role of Se(IV) vs Se(VI) species in the on water selenium-catalysed oxidation of anilines*
11.45 - 12.00	**ORG OR079**	**Claudio Zippilli**	*Double strategies for regioselective one-pot C-H oxidative functionalization of coumarins*

ORG 13

10.30 - 10.45	**ORG OR080**	**Chiara Liliana Boldrini**	*Eco-friendly deep eutectic solvent electrolyte solutions for dye-sensitized solar cells*
10.45 - 11.00	**ORG OR081**	**Gabriella Buscemi**	*Polydopamine/ethylenediamine nanoparticles embedding a bacterial photoenzyme for solar energy conversion*
11.00 - 11.15	**ORG OR082**	**Mattia Forchetta**	*Design of KuQuinone-Co3O4 nanoparticle hybrid dyads for photoelectrochemical applications*
11.15 - 11.30	**ORG OR083**	**Giulio Goti**	*Fluorescent Materials for the Enhancement of the Photosynthetic Efficiency*
11.30 - 11.45	**ORG OR084**	**Norberto Manfredi**	*Photo(electro)catalytic water splitting using Calix[4]arene-Based dyes*
11.45 - 12.00	**ORG OR085**	**Lorenzo Zani**	*Construction of tailored, donor-acceptor heterocyclic compounds for solar energy conversion*

ORG 14

10.30 - 10.45	**ORG OR086**	**Achille Antenucci**	*How do arenediazonium salts behave in Deep Eutectic Solvents? A combined experimental and computational approach*
10.45 - 11.00	**ORG OR087**	**Laura Baldini**	*Halogen-bonded architectures of multivalent calix[4]arenes*
11.00 - 11.15	**ORG OR088**	**Daniele Del Giudice**	*pH Transient Variation Triggered by Nitroacetic Acid Allowing Dissipative Control in Supramolecular Systems*
11.15 - 11.30	**ORG OR089**	**Oscar Francesconi**	*A tweezers-shaped receptor for the biomimetic recognition of the GlcNAc2 disaccharide in water*
11.30 - 11.45	**ORG OR090**	**Giorgio Olivo**	*Supramolecular Remote C(sp3)-H Oxidation*
11.45 - 12.00	**ORG OR091**	**Daniele Rosa-Gastaldo**	*Tuning the folding properties of synthetic recognition-encoded oligomers*

Programma dei LAVORI di DIVISIONE - 21 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 05

09.30-09.45	**Presentation**		
09.45-10.00	**ABC OR046**	**P. Guzmán García Lascurain**	*Agar foam for the cleaning of art surfaces: a new approach*
10.00-10.15	**FIS OR 129**	**David Chelazzi**	*pHEMA/PAA and pHEMA/PVP semi-IPNs: physico-chemical characterization and use for bronze cleaning*
10.15-10.30	**FIS OR128**	**Francesco Armetta**	*Unusual corrosion of bronze helmets discovered in Mediterranean seabed*
10.30-10.45	**ABC OR047**	**Francesca Ramacciotti**	*Advanced systems for the cleaning of Cultural Heritage*
10.45-11.00	**FIS OR 127**	**Leonardo Severini**	*Ultrasound-stimulated PVA microbubbles as removal tool for adhesive tapes from cellulose-based materials*
11.00-11.15	**ABC OR048**	**Elisabetta Zendri**	*Evaluation of a new setup to improve the electro-kinetic desalination of porous materials in Cultural Heritage*
11.15-11.30	**break**		
11.30-11.45			
11.45-12.00	**ABC OR049**	**Marco Valente Chavez Lozano**	*Deep Eutectic Solvents (DES) based on choline chloride and betaine for cleaning gelatin residues from cellulose nitrate cinematographic films.*
12.00-12.15	**ABC OR050**	**Giuseppe Lazzara**	*Halloysite nanotubes: a versatile material for conservation of cultural heritage*
12.15-12.30	**ABC OR012**	**Francesca Nardelli**	*Insights into the oil paint polymeric network by Solid State NMR*
12.30-12.45	**ABC OR031**	**Carolina Rigon**	*Discovering the Maya ritual practices through the study of pigmented human bones remains by Archaeometry investigation*
12.45-13.00		**Antonio Marcomini**	*Conclusioni*

ABC 06

09.30-09.50	**ABC KN002**	**Fabrizio Passarini**	*The tool of LCA to analyse and improve the sustainability of chemical processes*
09.50-10.00	**IND OR046**	**Prisco Prete**	*New biodegradable catalysts for photo-Fenton like process for wastewater treatment reuse in a circular economy perspective*

10.00-10.10	**ABC OR053**	**Damiano Sgherza**	*Integrating biodegradation and ozone-catalysed oxidation for treatment of biomass gasification wastewater*
10.10-10.20	**IND OR047**	**Stefano Andrea Balsamo**	*One-pot synthesis of TiO2-rGO photocatalysts for the degradation of groundwater pollutants*
10.20-10.30	**ABC OR054**	**Luisa Barbieri**	*An integrated system for a new controlled release fertilizer based on lightweight ceramic aggregates starting from waste materials and bio-products*
10.30-10.40	**IND OR048**	**Ermelinda Falletta**	*Efficient day-and-night NO2 abatement by polyaniline/TiO2 composites*
10.40-10.50	**ABC OR055**	**Pietro Calandra**	*Reutilization of residues from municipal wastes pyrolysis to improve and regenerate asphalts*
10.50-11.00	**Discussion**		

Modellazione ambientale e caratterizzazione chimica degli aerosol atmosferici/Environmental

11.15-11.30	**ABC OR056**	**Loris Calgaro**	*Exposure modelling of emerging contaminants in the Venice lagoon - a case-study on active pharmaceutical ingredients*
11.30-11.45	**ABC OR057**	**Federtica Zennaro**	*Modelling eutrophication processes in the Venice Lagoon: a multivariate Machine Learning approach*
11.45-12.00	**ABC OR058**	**Pierluigi Barbieri**	*Bioaerosol detection, pathogen airborne transmission and abatement studies: capacity building, experimental results and perspectives from the COVID-19 pandemic*
12.00-12.15	**ABC OR059**	**Manuel Amedeo Cefali**	*Evaluation of PMx chemical composition and planning of a vegetable-green barrier in a high traffic site in Milan*
12.15-12.30	**ABC OR060**	**Niccolo Losi**	*Aerosol characterization from the tropics to the North Pole*
12.30-12.45	**ABC OR061**	**Alessandro Mancini**	*X-Ray Diffraction of Non-Exhaust Emissions generated from Braking: How to Assess the Phase Composition of the Crystalline Fraction*
12.45-13.00		**Antonio Marcomini**	*Conclusioni*

Divisione CHIMICA FARMACEUTICA (FAR)
FAR 07

09.30 - 10.00	**FAR KN009**	**Anders Bach**	*Targeting protein-protein interactions involved in oxidative stress using fragment-based drug discovery*

10.00 - 10.30	**FAR KN010**	**Giancarlo Aldini**	*Chemical and molecular mechanisms of cellular and extra-cellular antioxidants*
10.30 - 10.45	**FAR OR031**	**Marco Catto**	*A second life for MAO inhibitors: from CNS diseases to cancer*
10.45 - 11.00	**FAR OR032**	**Stefano Sainas**	*Apoptotic and differentiating therapy for AML using potent human dihydroorotate dehydrogenase inhibitor*
11.00 - 11.30	**FAR KN011**	**Tiziano Bandiera**	*Discovery of a picomolar potency corrector of F508del-CFTR chloride channel*
11.30 - 11.45	**FAR OR035**	**Francesca Spyrakis**	*Identification of carbapenemase broad-spectrum inhibitors through in silico methodologies*
11.45 - 12.00	**FAR OR036**	**Serena Massari**	*1,2,4-Triazolo[1,5-a]pyrimidines: efficient one-step synthesis and functionalization as antiviral agents*
12.00 -12.15	**FAR OR037**	**Alessandra Altomare**	*An integrated metabolomic and proteomic approach for the identification of covalent inhibitors of the main protease (Mpro) of SARS- COV-2 from crude natural extracts*
12.15 -12.30	**FAR OR038**	**Antonella Messore**	*Discovery of non-DKA derivatives endowed of selective activity against ribonuclease H function of the HIV-1 reverse transcriptase*
12.30 - 13.00	**FAR KN012**	**Pedro Gois**	*Exploring B-complexes as likers for targeting drug conjugates*

FAR 08

10.30 - 10.45	**FAR OR033**	**Claudia Sorbi**	*Constrained 1,4-dialkylpiperazines as dopamine transporter (DAT) inhibitors to fight psychosis and cocaine addiction*
10.45 - 11.00	**FAR OR034**	**Elisa Uliassi**	*Psychotropic-based bifunctional compounds for neurodegenerative diseases*
11.00 - 11.30			
11.30 - 11.45	**FAR OR039**	**Salvatore Di Maro**	*Peptides from bench to clinical studies: our experience with CXCR4*
11.45 - 12.00	**FAR OR040**	**Azzurra Stefanucci**	*A novel β-hairpin peptide derived from the ARC repressor selectively interacts with the major groove of B-DNA*
12.00 -12.15	**FAR OR041**	**Stefano Tomassi**	*Shading the activity of a CXCR4-interacting peptide by 1,4- and 1,5-disubstituted [1,2,3]-triazole-based cyclization*

12.15 -12.30	**FAR OR042**	**Rosa Bellavita**	*Grafting Temporin L peptides: old tactics for new antimicrobial weapons*

Divisione CHIMICA FISICA (FIS)

FIS 08

Cultural Heritage and Environment

09:30-10:00	**FIS KN010**	**Gabriella Di Carlo**	*Corrosion protection in Concrete Heritage: from material design to in situ validation*
10:00-10:15	**FIS OR072**	**Lorenzo Lisuzzo**	*Pickering Emulsions Based on Wax and Halloysite Nanotubes for the Treatment of Archeological Woods*
10:15-10.30	**FIS OR073**	**Vanessa Rosciardi**	*Biocomposite Poly(Vinyl Alcohol)/Starch cryogels: green tailorable tools for the cleaning of painted artworks*
10:30-10.45	**FIS OR074**	**Rosangela Mastrangelo**	*Cleaning Pollock's and Picasso's masterpieces: the physical chemistry behind the scenes*
10:45-11:00	**FIS OR075**	**Giovanna Poggi**	*Adaptive castor-oil based organogels: synthesis, characterization and use for the selective and controlled cleaning of works of art*
11:00-11.15	**FIS OR076**	**Michele Baglioni**	*Nanostructured Fluids For Polymeric Coatings Removal: Surfactants Affect the Polymer Glass Transition Temperature*
11:15-11.30	**FIS OR077**	**Sara Morandi**	*Pd-promoted zeolites for low-temperature NOx adsorption*
11.30-11.45			**break**

Physical Chemistry of Sensors

11:45-12:00	**FIS OR078**	**Lucio Litti**	*Surface Enhanced Raman Scattering toward applications*
12:00_12:15	**FIS OR079**	**Stefano Toffanin**	*Organic optoelectronic components in highly integrated systems for plasmonics sensing in food security/quality*
12:15-12.30	**FIS OR080**	**Simona Bettini**	*SERS-SPR COUPLING FOR ULTRASENSITIVE DETECTION OF DOPAMINE IN ARTIFICIAL CEREBROSPINAL FLUID.*
12:30-12:45	**FIS OR081**	**Cristina Chirizzi**	*A bimodal imaging probe for combined Raman microscopy and 19F-MRI*
12:45-13:00	**FIS OR082**	**Giovanni De Filpo**	*Novel pressure sensors based on elastomeric PDLC films*
13:00-13:15	**FIS OR083**	**Francesco Tavani**	*Investigating the interfacial solvation properties of the Mg2+ ion by operando soft X-ray absorption spectroscopy at ambient pressure and simulations*

FIS 09

Physical Chemistry of Materials I

09:30-10:00	**FIS KN011**	**Luciano Galantini**	*From Molecules to Supracolloidal Atomium like Superstructures: Building from the Bottom-Up with Steroidal Amphiphiles*
10:00-10:15	**FIS OR084**	**Mario Prosa**	*Organic light-emitting transistors: advanced materials and innovative architectures towards a real-setting application*
10:15-10.30	**FIS OR085**	**Pietro Calandra**	*Mixing liquid amphiphiles to prepare organic fluids fully responsive to a magnetic field*
10:30-10.45	**FIS OR086**	**Valerio Loianno**	*A Hyphenated Approach Combining Pressure-Decay and In Situ FT-NIR Spectroscopy to Monitor Penetrant Sorption and Concurrent Swelling in Polymers*
10:45-11:00	**FIS OR087**	**Maria Rosaria Plutino**	*Design and development of multifunctional hybrid surface coatings for advanced and smart applications on textiles*
11:00-11.15	**FIS OR088**	**Federico Begni**	*Hyper Cross - Linked Polymers as additives for preventing aging of PIM1 membranes*
11:15-11.30	**FIS OR089**	**Chiara Nomellini**	*WO3-BiVO4 heterojunction: effects of WO3 nanostructuring on the photoelectrochemical performance*

Physical Chemistry of Materials II

11:45-12:00	**FIS OR090**	**Alberto Girlando**	*Charge-Transfer Soft Ferroelectrics*
12:00_12:15	**FIS OR091**	**Marco Sanna Angotzi**	*Designing Spinel Ferrite-Based Nano-Heterostructures Through Versatile Solvothermal Approaches*
12:15-12.30	**FIS OR092**	**Stefano Alberti**	*Physico-Chemical Characterization of Polydimethylsiloxane Electrospun Fibers*
12:15-12.30	**FIS OR051**	**Alessandro Piovano**	*A deep description of the electronic properties of Ti sites in Ziegler-Natta catalysts from advanced spectroscopic methods*
12:45-13:00	**FIS OR094**	**Matteo Busato**	*Structural Characterization of Deep Eutectic Solvents Mixtures with Water and Methanol*
13:00-13:15	**FIS OR095**	**Michele Porto**	*Use of REOBs and industrial by-products additives for new bitumen-like material formulation: chemical physical and mechanical characterization*

Divisione CHIMICA INORGANICA (INO)
INO 07

9.30 - 10.50	**INO PZ006 (Premio Dottorato 2021)**	**Fabio Pirro**	*De novo design of multi-domain metalloenzymes*
9.50 - 10.10	**INO PZ007 (Premio Dottorato 2021)**	**Matteo Vanni**	*Reactivity of Black Phosphorus with Pd Compounds*
10.10 - 10.30	**INO PZ008 (Premio Dottorato 2021)**	**Alessandra Barbanente**	*Targeted Delivery of Anticancer Platinum Complexes to Bone Tumors and Metastases “non classical” compounds mechanism of action*
10.30 - 10.45	**INO OR043**	**Rita Mazzoni**	*Cyclopentadienone-NHC Iron(0) electrocatalysts for water oxidation*
10.45 - 11.00	**INO OR044**	**Anna Pintus**	*Ammonium salts of oxalic acid derivatives: a new family of agents for the conservation of carbonate stone substrates of artistic value*
11.00 - 11.15	**INO OR045**	**Andrea Fermi**	*Visible-light activated metallaphotoredox catalysis enabled by TiIV complexes: new routes for C-C bond formation*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR046**	**Riccardo Pedrazzani**	*Correlating solid-state analysis and catalysis: exploring secondary π-interactions effects in Au(I) catalyzed reactions*
11.45 - 12.00	**INO OR047**	**Rossana Galassi**	*When metallaphilia makes the difference: the case of stacked coinage metals Trinuclear Cyclic Compounds*
12.00 - 12.15	**INO OR048**	**Alessia Belloni**	*FTIR-HSI analysis of triple-negative breast cancer (TNBC)*
12.15 - 12.30	**INO OR049**	**Francesca Gambassi**	*A Cu(II)-MOF based on a propargyl carbamate-functionalized isophthalate ligand*
12.30 - 13.00	**INO IL002**	**Anke Weidenkaff**	*Circular Materials for the Energy Transition*

INO 08

10.30 - 10.45	**INO OR050-ad hoc**	**Marzio Rancan**	*Hierarchical chiral transfer in bright lanthanides quadruple stranded helicate-cages by host-guest interaction*
10.45 - 11.00	**INO OR051**	**Giuseppe Ferrauto**	*Hydrophobic interactions between macrocyclic Gd-complexes and polyaromatic systems as route to enhance the longitudinal water relaxivity in Magnetic Resonance Imaging*

11.00 - 11.15	**INO OR052**	**Salvatore Impemba**	*Dinuclear Thioether-amide Aluminum Complexes in the Ring Opening Polymerization of Cyclic Esters*
11.15-11-30	**break**		
11.30 - 11.45	**INO OR053**	**Paolo Pelagatti**	*Put light on inside a microporous MOF to decipher the guest arrangement and guest- release properties*
11.45 - 12.00	**INO OR054**	**Francesca Garello**	*Biodegradable polyelectrolyte/magnetite capsules for MR imaging and magnetic targeting of tumors*
12.00 - 12.15	**INO OR055**	**Letizia Liccardo**	*CeOx/TiO2 Hollow Spheres as efficient photocatalyst for the degradation of organic pollutants in wastewater*
12.15 - 12.30	**INO OR056**	**Denise Lovison**	*Highly active ruthenium complexes: synthesis and evaluation of the anticancer activity through interaction with relevant biomolecules*

INO 09

10.30 - 10.45	**INO OR057**	**Gabriele Manca**	*Reactivity of imidazolate Au(I) cyclictrinuclearcompounds, CTCs, with iodine or MeI: a computational/experimental study*
10.45 - 11.00	**INO OR058**	**Luca Andreo**	*DFT and semi-empirical GFN2-xTB methods: experimental and computational characterization of an Iron(II) carbene complex*
11.00 - 11.15	**INO OR059**	**Mario Prejanò**	*How lanthanide ions affect the catalytic activity of methanol dehydrogenase: a computational point of view*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR060-ad hoc**	**Daniela Marasco**	*Transition metal complexes as neurodrugs: insights into their modulation of amyloid aggregation*
11.45 - 12.00	**INO OR061**	**Laura Del Coco**	*X. fastidiosa affecting olive trees in Salento: metal ions in soil, plants and treatment compounds*
12.00 - 12.15	**INO OR062**	**Antonino Famulari**	*Unveiling electronic and structural properties of, peroxygenase-like cytochrome P450, CYP116B5hd*
12.15 - 12.30	**INO OR063**	**Davide Corinti**	*Elusive intermediates in the reactivity of platinum(IV) prodrugs: a new perspective on their bioactivation*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 05

09.30 - 10.00	**TEC IL003**	**Alessandro Gori**	*Liquid biopsy at the crossroads of chemistry and technology: the extracellular vesicles case study*

21 settembre - mattina

10.00 - 10.15	**TEC KN003**	**Serena De Santis**	*Fourier transform IR micro-spectroscopy of biological tissues: a promising tool for diagnostic and assessment of tissue functionality.*
10.15 - 10.30	**TEC KN004**	**Andrea Melchior**	*Diclofenac adsorption on carbon-based nanomaterials: a molecular dynamics study*
10.30 - 10.40	**TEC OR041**	**Francesca Baldassarre**	*Utilization of biosourced materials in chemical nanotechnologies developing controlled release systems for human and plants health*
10.40 - 10.50	**TEC OR042**	**Paola Astolfi**	*Structural characterization and in-vitro anticancer activity of nanovectors for delivery of bioactive coumpounds*
10.50 - 11.00	**TEC OR043**	**Arianna Rossetti**	*3D integration of pH-cleavable drug-hydrogel conjugates on magnetically driven smart microtransporters*
11.00 - 11.10	**TEC OR044**	**Falcone Giovanni**	*Calcium Alginate hydrogels in Semi Solid Extrusion 3D printing: physico-chemical requirements for high printing performance*
11.10 - 11.30	**Discussion**		
11.30 - 11.40	**TEC OR045**	**Anita Ceccucci**	*Mixed oxide Cerium coating for improved titanium nanotubes bioactivity*
11.40 - 11.50	**TEC OR046**	**Clelia Dispenza**	*Adipose stem cell spheroids-laden hydrogels for minimally invasive bone and cartilage regeneration interventions*
11.50 - 12.00	**TEC OR047**	**Emanuela Muscolino**	*k- Carrageenan and PVA blends as bioinks to 3D print scaffolds for cartilage reconstruction*
12.00 - 12.10	**TEC OR048**	**Edoardo Testa**	*Adducts of functionalized graphene layers with Ag nanoparticles for antimicrobial applications*
12.10 - 12.30	**Discussion**		
12.30 - 12.50	**break**		
12.50 - 13.00	**TEC OR049**	**Martina Sanadar**	*A novel luminescent Europium(III) complexes for citrate detection*
13.00 - 13.10	**TEC OR050**	**Gaspare Varvaro**	*Co/Pd-based synthetic antiferromagnetic multi-stacks for biomedical applications*
13.10 - 13.20	**TEC OR051**	**Alessandra Vitale**	*Coupling electrospinning and photo-induced crosslinking to produce shape-stable rubber nanofibrous membranes*
13.20 - 13.30	**TEC OR052**	**Antonino Rizzuti**	*Analysis of the chemical profile of sparkling wines fermented with autochthonous yeast strains using a non-targeted metabolomic approach*
13.30 - 13.50	**Discussion**		

13.50 - 14.00	**CONCLUSIONE**

Divisione ELETTROCHIMICA (ELE)
ELE 08

09.30 - 10.00	**ELE_IL50**	**Piotr Zelenay**	*Oxygen Reduction at Platinum Group Metal-Free Fuel Cell Catalysts:Piotr Recent Progress*
10.00 - 10.15	**ELE_OR51**	**Alessandro Facchin**	*From Redox-like to Heterogeneous Electrocatalysis at Metal-Octaethylporphyrins@HOPG investigated by EC-STM*
10.15 - 10.30	**ELE_OR52**	**Lucia Mazzapioda**	*Non-stoichiometric Metal Oxide Particles as Active Electrode Component in PEM Fuel Cells*
10.30 - 10.45	**ELE_OR53**	**Simone Bonizzoni**	*Aquivion®-based Alkaline Membrane for Fuel Cell and Electrolyzer Applications*
10.45 - 11.00	**ELE_OR54**	**Antunes Staffolani**	*Identification of Solid Oxide Cells Processes by Distribution of Relaxation Times: Model Creation and Validation*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN55**	**Lior Elbaz**	*Design of Aerogel-based Electrocatalysts for ORR*
11.45 - 12.00	**ELE_OR56**	**Davide Cademartori**	*Anode-supporting substrates with hierarchical porosity manufactured with freeze tape casting for reversible solid oxide cells*
12.00 - 12.15	**ELE_OR57**	**Vincenzo Baglio**	*Electrospun MnCo2O4/CNF as Oxygen Electrode for Alkaline Zn-Air Batteries*
12.15 - 12.30	**ELE_OR58**	**Eleonora Pargoletti**	*Disclosing the Electrocatalytic Behavior of Doped-MnO2 for Lithium-Air Batteries*

ELE 09

09.30 - 10.00	**ELE_IN59**	**Doron Auerbach**	
10.00 - 10.15	**ELE_OR60**	**Keti Vezzù**	*Innovative Olivine Cathodes for High-Voltage Lithium Batteries*
10.15 - 10.30	**ELE_OR61**	**Akiko Tsurumaki**	*Highly Versatile Gel Polymer Electrolytes for High Voltage Lithium Batteries*
10.30 - 10.45	**ELE_OR62**	**Marisa Falco**	*Protic ionic liquid electrolytes in lithium metal cells*
10.45 - 11.00	**ELE_OR63**	**Lorenzo Mezzomo**	*Long life lithium metal batteries employing dendrite-eating nanocomposite solid-state electrolytes based on hybrid fillers.*
11.00 - 11.15	**break**		

11.15 - 11.45	**ELE_KN64**	**Michele Pavone**	*Heterogeneous functional materials for post-Li energy storage devices, new insights and design principles from quantum chemistry*
11.45 - 12.00	**ELE_OR65**	**Ernestino Lufrano**	*Study of lithiated Nafion-based nanocomposites membranes as single lithium-ion conducting electrolytes for lithium batteries*
12.00 - 12.15	**ELE_OR66**	**Anna Mangini**	*Li-ion Batteries with Innovative Silicon Anodes: Study of Electrolytes Based on Carbonates*
12.15 - 12.30	**ELE_OR67**	**Alessandro Brilloni**	*Novel methods for increasing energy and reducing environmental impact of lithium batteries.*

ELE 10

09.30 - 10.00	**ELE_KN68**	**Tealdi Cristina**	*Fast but not so fast: can we improve intercalation in cathode materials for rechargeable batteries?*
10.00 - 10.15	**ELE_OR69**	**Toigo Christina**	*Rheological properties of aqueous sodium alginate slurries*
10.15 - 10.30	**ELE_OR70**	**Leonardo Sbrascini**	*Enhanced Performance of a Sustainable Si/C Anode for High Energy Density Lithium-ion Batteries*
10.30 - 10.45	**ELE_OR71**	**Daniele Versaci**	*Carbon nitride based double layer approach for enhancing Li-S battery performances*
10.45 - 11.00	**ELE_OR72**	**Hamideh Darjazi**	*Improvement of NMC layered cathode materials by combined doping/coating and evaluation of electronic-ionic transport properties by electrochemical impedance spectroscopy*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN73**	**Teofilo Rojo**	*Recent progress in electrode materials for next generation sodium ion batteries*
11.45 - 12.00	**ELE_OR74**	**Giovanna Maresca**	*Sodium-conducting, ionic liquid electrolytes for Na battery systems*
12.00 - 12.15	**ELE_OR75**	**Shahid Khalid**	*Aqueous sodium battery enabled by super-concentrated binary electrolyte.*
12.15 - 12.30	**ELE_OR76**	**Michele Tribbia**	*Improved zinc electrodeposition in mild-acidic aqueous Zn-ion batteries*

Divisione TECNOLOGIA FARMACEUTICA (TFA)

TFA 03

09.30 - 10.00	**TFA IL005**	**Manuela Estima Gomes**	*Using magnetic stimulus to bioengineer tendon tissue and tissue models: new tools to understand and stimulate regenerative pathways*

21 settembre - mattina

10.00 - 10.30	**TFA IL006**	**Marco Romanelli**	*Inflammation in wound healing: the role of drug delivery*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.15	**TFA OR019**	**Giuseppina Sandri**	*Polysaccharides based scaffolds for skin tissue engineering*
11.15 - 11.30	**TFA OR020**	**Giulia Vanti**	*Development and Optimisation of a Locally- acting Microemulgel to Improve the Biopharmaceutical Properties of Cannabidiol for Dermatological Delivery*
11.30 - 11.45	**TFA OR021**	**Silvia Pisani**	*Engineered tubular scaffold for full-thickness esophageal replacement*
11.45 - 13.30	**Tavola Rotonda**	**Michele Schlich**	*Valorizzazione del dottorato in tecnologia farmaceutica al di fuori dell'accademia. Cosa si aspetta un’azienda da un dottore di ricerca rispetto ad un laureato?*

Programma dei LAVORI di DIVISIONE - 21 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA10

15.00 - 15.20	**ANA PZ004**	**Martina Catani**	*Boosting the downstream processing of biopharmaceuticals by means of multicolumn continuous chromatography*
15.20 - 15.40	**ANA IL007**	**Maurizio Quinto**	*Rotating Magnetic Chromatography, a new technique for micro-particle and cell separation*
15.40 - 16.00	**ANA IL008**	**Roccaldo Sardella**	*Role of mobile phase composition in enantioselective liquid chromatography*
16.00 - 16.15	**ANA OR076**	**Federica Bianchi**	*Nanomaterials for improved sensitivity in sample treatment*
16.15 - 16.30	**ANA OR077**	**Irene Coralli**	*Secondary reactions in the analysis of microplastics by Py-GC-MS*
16.30 - 16.45	**ANA OR078**	**Simona Felletti**	*Investigation of the chemoselectivity of normal phase stationary phases towards the separation of cannabinoids*
16.45 - 17.00	**ANA OR079**	**Giuseppina Gullifa**	*Potential Health Impact Assessment of New Pocket Pen- Vaporizers: Vapor Characterization Using SPME-GC/MS*
17.00 - 17.15	**ANA OR080**	**Jacopo La Nasa**	*Analytical pyrolysis coupled with gas chromatography/mass spectrometry and solvent extraction for the characterization of microplastics and polymer additives*
17.15 - 17.30	**ANA OR081**	**Roberta La Tella**	*Evaluation of carbon - clad zirconia columns as stationary phases for superheated water liquid chromatography*
17.30 - 17.45	**ANA OR082**	**Marcello Locatelli**	*Fabric Phase Sorptive Extraction: an innovative tool for TDM and pharmacotoxicological studies using unconventional biological matrices*
17.45 - 18.00	**ANA OR083**	**Sara Palmieri**	*Molecular imprinted polymer coupled to LC-MS/MS for maleic hydrazide determination in food samples*
18.00 - 18.15	**ANA OR084**	**Marco Roverso**	*Determination of lactose in low-lactose milk by direct liquid injection and high-resolution mass spectrometry*

ANA11

15.20 - 15.40	**ANA KN010**	**Silvia Berto**	*Study and application of chemical models to measure the urine saturation with calcium salts*
15.40 - 16.00	**ANA OR085**	**Chiara Abate**	*Sequestering ability of carnosine towards some potentially toxic divalent metal cations in aqueous solution*

21 settembre - pomeriggio

16.15 - 16.30	**ANA OR087**	**Denise Bellotti**	*Understanding the thermodynamics and coordination chemistry of metal-binding proteins: the common thread to elucidate metal acquisition processes at host/pathogen interface*
16.30 - 16.45	**ANA OR088**	**Rosita Cappai**	*Complex formation equilibria of a kojic acid derivative with different metal ions*
16.45 - 17.00	**ANA OR089**	**Salvatore Cataldo**	*CYCLODEXTRIN-BASED NANOSPONGES FOR LEAD(II) ION ADSORPTION FROM AQUEOUS SOLUTIONS*
17.00 - 17.15	**ANA OR090**	**Ottavia Giuffrè**	*O-phosphorylethanolamine and O-phosphorylcholine in aqueous solution: acid-base behavior and speciation with Mg2+*
17.15 - 17.30	**ANA OR091**	**Anna Irto**	*Thermodynamic parameters on the interaction of divalent and trivalent metal cations with 3-hydroxy-4-pyridinones*
17.30 - 17.45	**ANA OR092**	**Luana Malacaria**	*Studies on the complexation between quercetin and some first-row transition metal cations in aqueous solution*
17.45 - 18.00	**ANA OR093**	**Rossella Migliore**	*Recognition of antibiotics by calixarene-based micellar aggregates in aqueous solution: binding features and driving forces*
18.00 - 18.15	**ANA OR094**	**Davide Spanu**	*On-line ion trapping by frontal chromatography ICP-MS: a low-cost strategy for the fast speciation of inorganic pollutants*

ANA12

15.20 - 15.40	**ANA KN011**	**Flavio Della Pelle**	*2D Nanomaterials: among functional natural compounds and affordable sensor designs*
15.40 - 16.00	**ANA KN012**	**Barbara Roda**	*Celector(R): the cell chromatography for quality control of living cells*
16.00 - 16.15	**ANA OR095**	**Jessica Brandi**	*Identification of protein biomarkers responsible for meat tenderness in bovine Longissumus dorsi muscle by Kohonen self-organizing maps and multivariate analysis*
16.15 - 16.30	**ANA OR096**	**Simone Cavalera**	*Anti-Retroviral Drugs Monitoring in Urine and Saliva: A Rapid and Sensitive Lateral Flow Immunoassay for Tenofovir*
16.30 - 16.45	**ANA OR097**	**Andrea Cerrato**	*An innovative analytical platform for cannabis chemovar differentiation based on untargeted metabolomics and chemometrics*

16.45 - 17.00	**ANA OR098**	**Angela Di Capua**	*Use of online buffer exchange coupled to native-mass spectrometry to elucidate the stoichiometry of the Salmonella FraR (transcriptional repressor)-DNA complex*
17.00 - 17.15	**ANA OR099**	**Fabio Di Nardo**	*Exploiting silver nanoplates as colorimetric label in Lateral Flow Immunoassay*
17.15 - 17.30	**ANA OR100**	**Nicolò Interino**	*UPLC-Q-TOF-MS/MS analysis of bile acids and their main metabolite profile in farm animal faeces and species-specific correlation with gut microbiota*
17.30 - 17.45	**ANA OR101**	**Valentina Marassi**	*Nanosphere, polymer, self-assembled material? Clearing up the confusion on polydopamine through multidetection-FFF*
17.45 - 18.00	**ANA OR102**	**Monica Mattarozzi**	*Insights into aptamer-protein interactions for analytical applications: egg white lysozyme as case study*
18.00 - 18.15	**ANA OR103**	**Lapo Renai**	*Untargeted metabolomics reveals different postprandial serum metabolome profiles after single intake of Vaccinium myrtillus and Vaccinium corymbosum*

Divisione CHIMICA INDUSTRIALE (IND)
IND 04

Sessione congiunta con Gruppo Interdivisionale Green Chemistry - Chimica Sostenibile

15.00 - 15.20	**IND KN006**	**Rafael Luque**	*Benign by design strategies for a more sustainable future: the valorisation concept*
15.20 - 15.30	**IND OR049**	**Anna Gagliardi**	*Upgrading of Ethanol: Boosting the Guerbet Reaction with a Redox Co-Catalyst*
15.30 - 15.40	**IND OR050**	**Ilenia Rossetti**	*Sustainable process design for the valorization of bioethanol as platform chemical*
15.40 - 15.50	**IND OR051**	**Maela Manzoli**	*Enabling technologies to boost cellulose selective valorisation over bifunctional catalyst*
15.50 - 16.00	**IND OR052**	**Silvia Tabasso**	*Green deep eutectic solvents and microwave technology towards a closed loop biorefinery*
16.00 - 16.10	**IND OR053**	**Nicola Di Fidio**	*Microwave-assisted FeCl3-catalysed production of glucose from giant reed and cardoon cellulose fraction and its fermentation to new generation oil by oleaginous yeasts*
16.10 - 16.20	**IND OR054**	**Alessia Ventimiglia**	*Theoretical study of glucose oxidation to glucaric acid using gold based catalyst*
16.20 - 16.35	***Discussion***		
16.35 - 16.50	**break**		
16.50 - 17.10	**IND KN007**	**Volker Hessel**	*Sustainability as Process Design Guidance for Flow and Plasma Chemistry*
17.10 - 17.20	**IND OR055**	**Valeria Pappalardo**	*Heterogeneous catalysis in the esterification of natural antioxidants*

17.20 - 17.30	**IND OR056**	**Carmelina Rossano**	*Amberlite IR120 as catalyst for the levulinic acid esterification reaction in batch and continuous operation*
17.30 - 17.40	**IND OR057**	**Silvia Giorgi**	*Synthesis of new biopolymers by biomasses valorization*
17.40 - 17.50	**IND OR058**	**Riccardo Bacchiocchi**	*Innovative heterogeneous catalysts for the reduction of levulinic acid derivatives to γ-valerolactone and consecutive reduction products*
17.50 - 18.00	**IND OR059**	**Francesco Mauriello**	*Hydrogenolysis of aromatic ethers under lignin-first conditions*
18.00 - 18.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)

ORG 15

15.00 - 15.30	**ORG PZ002**	**Paolo Tecilla**	***Medaglia Angelo Mangini*** *Self-organized Supramolecular Systems for Catalysis, Sensing and Transport*
15.30 - 16.00	**ORG PZ009**	**Elena Lenci**	***Premio alla ricerca Chimica Organica per le Scienze della Vita Junior*** *Combining Diversity-Oriented Synthesis and chemoinformatics to generate small molecules libraries*
15.50 - 16.00	**Break**		
16.00 - 16.15	**ORG OR092**	**Molly Pither**	*Elucidation of the Chemical Structure of Lipopolysaccharides Isolated from the Commensal Bacteria Veillonella parvula*
16.15 - 16.30	**ORG OR093**	**Debora Pratesi**	*The glycomimetic approach for selective inhibition of Carbonic Anhydrases*
16.30 - 16.45	**ORG OR094**	**Deborah Quaglio**	*Resorc[4]arene-based site directed immobilization of antibodies for immunosensors development*
16.45 - 17.00	**ORG OR095**	**Roberto Rossi**	*Problem solving in Pharmaceutical processes: isolation,* *characterization and synthetic preparation of unknown impurities in 4-piperidinepropanol manufacture*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR096**	**Laura Russo**	*Chemoselective synthesis of triple-functionalizes nanoparticles for multimodal in vivo imaging of pancreatic β-cells*
17.45 - 18.00	**ORG OR097**	**Giovanni Sacco**	*Affinity enhancement of peptide ligands for tumor overexpressed receptors*
18.00 - 18.15	**ORG OR098**	**Cristina Manuela Santi**	*Synthesis of an analogue of Neisseria meningitidis A capsular polysaccharide for the development of a glycoconjugate vaccine*
18.15 - 18.30	**ORG OR099**	**Federica Santino**	*Rational Design of Pseudoproline-Containing K-Opioid Receptor-Selective Peptidomimetics*

21 settembre - pomeriggio

ORG 16

15.30 - 16.00	**ORG PZ010**	**Manuel Orlandi**	***Premio alla ricerca Chimica Organica nei suoi Aspetti Metodologici Junior*** ***Catalyst Design via Computational Means:*** *Correlations Bridge Experiments and Calculations*
16.00 - 16.15	**ORG OR100**	**Valentina Pirota**	*Selective hydrolysis of water-soluble naphthalene diimides driven by core-substitution*
16.15 - 16.30	**ORG OR101**	**Simone Potenti**	*4-Fluorothreonine as a test case: the effects of fluorination on molecular properties*
16.30 - 16.45	**ORG OR102**	**Michele Ricci**	*Application of ASCA modelling tools on a PDO hard cheese: Analysis of the effects on physical parameters of Trentingrana*
16.45 - 17.00	**ORG OR103**	**Federica Sabuzi**	*Computational study of substituted phenols pKa*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR104**	**Carla Rizzo**	*New supramolecular fluorescent NDI-gels as bioimaging materials*
17.45 - 18.00	**ORG OR105**	**Maria Sologan**	*Functionalized gold nanoparticles for MRI applications*
18.00 - 18.15	**ORG OR106**	**Benedetta Maria Squeo**	*Thiophene substituted aza-BODIPY as promising metal-free, pure NIR emitter for OLEDs*
18.15 - 18.30	**ORG OR107**	**Kristian Vasa**	*Design and synthesis of macromolecular and nanostructured carbonic anhydrases-based materials*

ORG 17

15.30 - 16.00	**ORG PZ011**	**Sara Meninno**	***Premio alla ricerca Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze Junior*** *Powerful Strategies to Functionalized Molecules in One- Pot, Mild Conditions and Benign Solvents*
16.00 - 16.15	**ORG OR108**	**Giulio Bertuzzi**	*Novel Visible-Light Mediated Protocols for the Synthesis of N Heterocycles and Site-Selective Functionalizations*
16.15 - 16.30	**ORG OR109**	**Tommaso Bortolato**	*Radical α-Trifluoromethoxylation of Ketones by Means of Organic Photoredox Catalysis*
16.30 - 16.45	**ORG OR110**	**Mattia Di Maro**	*A ball-milling green synthetic procedure for the preparation of novel macromolecular stabilizers for polyolefinic-based materials*
16.45 - 17.00	**ORG OR111**	**Salvatore Marullo**	*Cholinium-based ionic liquids as catalysts for the glycolysis of post-consumer PET waste*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR112**	**Angelica Mero**	*Treatment of biomass food waste by exploiting Natural Deep Eutectic Solvents and bio based-Ionic Liquids*

17.45 - 18.00	**ORG OR113**	**Elisabetta Monciatti**	*Hydroaminomethylation of terminal alkenes in water: microwave and micellar catalysis roles*
18.00 - 18.15	**ORG OR114**	**Matteo Tiecco**	*Organocatalytic activity of chiral L-Proline-based Deep Eutectic Solvents*
18.15 - 18.30	**ORG OR115**	**Federica Valentini**	*Catalytic biomass valorization towards hydrogen transfer reactions using formic acid and derivates as safe H-source*

ORG 18

15.30 - 16.00	**ORG PZ012**	**Nicolas D'Imperio**	***Premio alla ricerca Chimica Organica per lo Sviluppo di Processi e Prodotti nell' Industria Junior*** *Olefins from carbonyls. Development of new phosphorus-based cross-coupling reactions*
16.00 - 16.15	**ORG OR116**	**Valerio Fasano**	*How Big is the Pinacol Boronic Ester as a Substituent?*
16.15 - 16.30	**ORG OR117**	**Susanna Bertuletti**	*From carbonyls to chiral alcohols via asymmetric biocatalysis: exploiting the substrate promiscuity of hydroxysteroid dehydrogenases (HSDHs)*
16.30 - 16.45	**ORG OR118**	**Denisa Bisag**	*Catalyst- and substrate- dependent chemodivergent reactivity of stabilised sulfur ylides with salicylaldehydes*
16.45 - 17.00	**ORG OR119**	**Giulia Brufani**	*Imidazolium based heterogenous catalyst for the synthesis of cyanohydrintrimethylsylil ether and β-azido ketones*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR120**	**Emanuela Calcio Gaudino**	*Highly Efficient Microwave-assisted synthetic protocols under Pd based β-cyclodextrin heterogeneous catalyst*
17.45 - 18.00	**ORG OR121**	**Francesco Calogero**	*Photoredox allylation and propargylation of aldehydes catalytic in titanium*
18.00 - 18.15	**ORG OR122**	**Vincenzo Campisciano**	*Al(III) Porphyrin–Imidazolium Salt Copolymer onto Carbon Nanotubes as Catalyst for the Synthesis of Cyclic Carbonates*
18.15 - 18.30	**ORG OR123**	**Francesca Foschi**	*Copper-Catalyzed/Hypervalent Iodine(III)-Mediated Dimerization/Cyclization of 2-Benzylamino-phenols: Synthesis of Fluorescent Oxazolo-phenoxazines*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 04

15.00 - 15.30	**CSB KN005**	**Angela Casini**	*Gold-templated reactions in biological systems: from medicine to catalysis*

15.30 - 15.45	**CSB OR022**	**Francesco Bellia**	*Hyaluronate–Carnosine conjugates: copper(II) complexes and antioxidant properties*
15.45 - 16.00	**CSB OR023**	**Daniele Vitone**	*The speciation of zinc complexes with chloroquine ligand*
16.00 - 16.15	**CSB OR024**	**Valentina Oliveri**	*8-Hydroxyquinoline Hybrids Differentially Interact with α-Synuclein*
16.15 - 16.30	**CSB OR025**	**Giancarlo Terraneo**	*Halogenation Dictates Architectures and Properties of Amyloid Peptides*
16.30 - 17.00	**Break**		
17.00 - 17.30	**CSB KN006**	**Amedeo Caflisch**	*Fragment-based drug design*
17.30 - 17.45	**FIS OR066**	**Federica Rizzi**	*Role of the FZD10 delivering exosomes in cellular proliferation of gastrointestinal cancer*
17.45 - 18.00	**FIS OR062**	**Ivana Miletto**	*Functionalized Upconversion Nanoparticles for Theranostic*
18.00 - 18.15	**CSB OR028**	**Gabriele Travagliante**	*Spectroscopic study on interactions of porphyrins and micro-RNA*
18.15 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 03

15:00-15:30	**DID IL003**	**Eleonora Aquilini**	*Caring for yourself, the environment and others in primary school*
15:30-15:45	**DID OR014**	**Sergio Palazzi**	*Towards a material archive of dyestuffs from the XX century*
15:45-16:00	**DID OR015**	**Ugo Cosentino**	*The School-University joint interventions provided in the National Recovery and Resilience Plan*
16:00-18:00	**Panel Discussion**	**Riccardo Iacona (Coordinator)** **Vincenzo Balzani** **Andrea Segrè** **Vittorio Maglia** **Giovanni De Feo**	*360-degree sustainability*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 03

15.00 - 15.40	**MAS PL004**	**Encarnación Moyano**	*Mass spectrometry for the environmental analysis of halogenated organic pollutants*
15.40 - 16.10	**MAS KN003**	**Sara Bogialli**	*Mass spectrometry for the monitoring and protection of the environment*
16.10 - 16.25	**MAS OR011**	**Carolina Barola**	*Temporal trend of per- and polyfluoroalkyl substances in air samples collected at the rural site of Monte Martano (Central Italy)*
16.25 - 16.35	**Break**		

21 settembre - pomeriggio

16.35 - 17.15	**MAS PL005**	**Antony Memboeuf**	*How can energetics in CID MS/MS help the analytical chemists?*
17.15 - 17.30	**MAS OR012**	**Angela Tartaglia**	*Fabric Phase Sorptive Membrane Array: A Novel Approach for Non-Invasive In Vivo Sampling*
17.30 - 17.45	**MAS OR013**	**Raffaella Pascale**	*An interplay between FT-ICR MS and LC-LTQ MS/MS for Metabolic Profiling of Peperoni di Senise PGI Bell Peppers*
17.45 - 18.00	**MAS OR014**	**Eugenio Aprea**	*Volatile organic compounds in Gorgonzola cheese and their relationship with sensory descriptors and consumers' liking*
18.00 - 18.15	**MAS OR015**	**Flaminia Vincenti**	*New Synthetic Opioids: Development of Analytical Methods for Their Characterization and Determination by Means of HPLC-HRMS/MS*

Divisione TEORICA E COMPUTAZIONALE (TEO)

TEO 04

15:00 -15:20	**TEO KN004**	**Mauro Stener**	*Predictive optical photoabsorption of metal clusters via efficient TDDFT simulations*
15:20 - 15:40	**TEO PZ005**	**Lorenzo Cupellini**	*Multiscale investigation of chlorophyll fluorescence quenching in plant light-harvesting complexes*
15:40 - 15:50	**TEO OR024**	**Chiara Aieta**	*Quantum nuclear densities from semiclassical on-the-fly molecular dynamics*
15:50 - 16:00	**TEO OR025**	**Filippo Lipparini**	*An easy and efficient strategy to compute an accurate SCF guess for ab-initio molecular dynamics simulations*
16:00 - 16:10	**TEO OR026**	**Marco Mendolicchio**	*Accuracy and Reliability in the Simulation of Vibrational Spectra: A Comprehensive Benchmark of Generalized Vibrational Perturbation Theory to the Second Order (GVPT2)*
16:10 - 16:20	**TEO OR027**	**Fulvio Perrella**	*Improving accuracy and efficiency of ADMP Extended Lagrangian Molecular Dynamics*
16:20 - 16:30	**TEO OR028**	**Diego Sorbelli**	*Probing the electronic structure of gold dihydride with state-of-the-art relativistic approaches*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO PZ006**	**Nicola Tasinato**	*Computational Strategies for Environmental Chemistry*
17:20 - 17:30	**TEO OR029**	**Francesco Di Maiolo**	*Theoretical Approaches to Quantum Molecular Dynamics in Out of Equilibrium Environments*
17:30 - 17:40	**TEO OR030**	**Lorenzo Donà**	*Extending and assessing composite electronic structure methods to the solid state*
17:40 - 17:50	**TEO OR031**	**Federica Lodesani**	*An in-depth look into the mechanism of crystallization of lithium disilicate: a metadynamics study*

21 settembre - pomeriggio

17:50 - 18:00	**TEO OR032**	**D. K. Andrea Phan Huu**	*Molecular spectroscopy in condensed phases: an antiadiabatic approach to the medium polarizability*
18:00 - 18:10	**TEO OR033**	**Pierpaolo Pravatto**	*Tunneling splitting and the stochastic description of activated processes*
18:10 - 18:30	**discussione finale**		

Programma dei LAVORI di DIVISIONE - 23 settembre mattina

Divisione CHIMICA ANALITICA (ANA)

ANA13

09.30 - 09.50	**ANA IL009**	**Anna Laura Capriotti**	*The progress in peptidomics: new strategies for purification and untargeted identification of short peptides*
09.50 - 10.00	**break**		
10.00 - 10.15	**ANA OR104**	**Adriana Arigò**	*Analytical methods in clinical lipidomics: HPLC and SFC comparison for the analysis of lipid mediators in clinical samples*
10.15 - 10.30	**ANA OR105**	**Alfonsina D'Amato**	*nLC-MS/MS data integration of quantitative proteomics and lipidomics to study the effects of bioactive compounds*
10.30 - 10.45	**ANA OR106**	**Chiara De Luca**	*Multicolumn Countercurrent Solvent Gradient Purification (MCSGP) process for the intensification of the polishing step of a bioactive peptide mixture*
10.45 - 11.00	**ANA OR107**	**Dounia El Fadil**	*Enzyme inhibition coupled to Molecular Imprinted Polymers for acetazolamide determination in biological samples*
11.00 - 11.15	**ANA OR108**	**Alessio Lenzi**	*Determination of salivary short chain fatty acids and hydroxy acids in heart failure patients by in-situ derivatization and Hisorb-probe sorptive extraction coupled to thermal desorption and gas chromatography- tandem mass spectrometry*
11.15 - 11.30	**ANA OR109**	**Marcello Manfredi**	*Metaproteomics and metabolomics investigation of microbiome alterations in pediatric obese subjects*
11.30 - 11.45	**ANA OR110**	**Francesca Merlo**	*A simple and Fast Multiresidue Method for determination of hormones in vegetables and fruits*
11.45 - 12.00	**ANA OR111**	**Giuseppe Micalizzi**	*Microwave distillation technique for the isolation of Cannabis Sativa L. essential oils and GC-MS/FID analysis for terpenes and terpenoids characterization.*
12.00 - 12.15	**ANA OR112**	**Daniele Naviglio**	*“Cholesterol is not considered a nutrient of concern for overconsumption” (Dietary Guidelines for Americans 2015)*

ANA14

09.30 - 09.50	**ANA IL010**	**Nicola Cioffi**	*Analytical Challenges in the Fight Against Biological Threats. The case of Nanoantimicrobials Inhibiting the Persistency of SARS-CoV-2*
09.50 - 10.00	**break**	**break**	
10.00 - 10.15	**ANA OR113**	**Maria Luisa Astolfi**	*A rapid analytical method for the determination of 45 elements in extra-virgin olive oils*

23 settembre - mattina

10.15 - 10.30	**ANA OR114**	**Laura Barone**	*Innovative spectroscopic approach for bloodstains identification*
10.30 - 10.45	**ANA OR115**	**Deborah Biggio**	*Surface characterization of CuZn37 alloys in contact with artificial saliva: the role of organic compounds*
10.45 - 11.00	**ANA OR116**	**Beatrice Campanella**	*A multi-analytical approach for the study of immortalized hippocampal neurons after mild heat shock*
11.00 - 11.15	**ANA OR117**	**Roberta D'Agata**	*Ultrasensitive plasmonic assay and specifically-designed PNA probes for circulating microRNAs detection: towards a liquid biopsy*
11.15 - 11.30	**ANA OR118**	**Danilo Donnarumma**	*Identification and quantification of toxic compounds and essential molecules in the context of tuna fishery industry waste valorization*
11.30 - 11.45	**ANA OR119**	**Walter Giurlani**	*Film thickness determination of metal multilayers by XRF multivariate analysis using Monte Carlo simulated standards*
11.45 - 12.00	**ANA OR120**	**Giulia Gorla**	*Low-cost miniaturized NIR spectrometer as an analytical tool for monitoring kefir fermentation process*
12.00 - 12.15	**ANA OR121**	**Min Li**	*XAS study of Manganese Hexacyanoferrate cathode material in aqueous Zn-ion batteries at three K-metal edges*
12.15 - 12.30	**ANA OR122**	**Maria Chiara Sportelli**	*Analytical characterization of laser-ablated silver nanoparticles for safe and biodegradable food packaging applications*

ANA15

09.30 - 09.50	**ANA OR123**	**Raffaela Biesuz**	*SAFER Smart Labels at work on fish*
09.50 - 10.00	**break**		
10.00 - 10.15	**ANA OR124**	**Sara Gaggiotti**	*Liquid phase exfoliated Transition Metal Dichalcogenides for gas sensing*
10.15 - 10.30	**ANA OR125**	**Laura Montali**	*A clover-like paper biosensor for mercury (II) on-site monitoring with a combined bioluminescent-colorimetric detection*
10.30 - 10.45	**ANA OR126**	**Andrea Pastore**	*pH Colorimetric sensor Arrays based on acid-base indicators enhanced by surfactants*
10.45 - 11.00	**ANA OR127**	**Angela Punzo**	*Application of whole-cell analytical bioassay based on turn-on chemiluminescence dioxetane probe sensing to quantify intracellular H2O2 in nutraceutical and biomedical fields*
11.00 - 11.15	**ANA OR128**	**Simona Ranallo**	*Non-natural antibody-protein communication mediated by a synthetic DNA responsive device*

11.15 - 11.30	**ANA OR129**	**Annalisa Scroccarello**	*Colorimetric paper-based analytical device for direct evaluation of olive oil phenols*
11.30 - 11.45	**ANA OR130**	**Francesca Torrini**	*A competitive microplate bioassay to detect gonadorelin in urine samples via a polynorepinephrine-based molecular imprinted polymer*
11.45 - 12.00	**ANA OR131**	**Mohamad Ahmad**	*A spatial perspective to retrieve spatial-spectral signatures from overlapped components in spectroscopic imaging data*
12.00 - 12.15	**ANA OR132**	**Rosalba Calvini**	*Quantification of rind percentage in grated Parmigiano Reggiano cheese by NIR-hyperspectral imaging and evaluation of the effect of factors related to sample preparation and composition*
12.15 - 12.30	**ANA OR133**	**Eleonora Mustorgi**	*Multivariate online monitoring of a powder blending process using a miniaturized near infrared sensor*

Divisione CHIMICA FISICA (FIS)

FIS 10

Physical Chemistry of Biomaterials

09:30-10:00	**FIS KN012**	**Roberto De Santis**	*Design for biointerface engineering*
10:00-10:30	**FIS KN013**	**Julietta Rau**	*New trends in the development of biomedical implants with multifunctional surfaces*
10:30-10.45	**FIS OR096**	**Monica Dettin**	*Chitosan covalently functionalized with peptides mapped on Vitronectin and BMP-2 for bone tissue engineering*
10:45-11:00	**FIS OR097**	**Angela De Bonis**	*Study of the bioactivity of thin glass-ceramic films deposited on electrospun polymeric scaffolds by nanosecond PLD*
11:00-11.15	**FIS OR021**	**Lorenzo Degli Esposti**	*Crystallization of amorphous calcium phosphate to hydroxyapatite nanoparticles: new insights in the field of biomaterials and biomineralization*
11:15-11.30	**FIS OR099**	**Alessio Carmignani**	*Study of the impact of size on the properties of polydopamine nanoparticles and their interaction with glioblastoma multiforme cells*

Computational and Applied Chemistry

11.45-12.00	**FIS OR100**	**Laura Orian**	*Methylmercury toxicity: insight from a theoretical physical-chemical description*
12:00_12:15	**FIS OR101**	**Marta Corno**	*Ab-initio modelling of Fe2NiP-H2O interaction: a phosphate factory for Early Earth*
12:15-12.30	**FIS OR102**	**Mirko Leccese**	*First-principles study of the C/Si interface: the influence of graphene corrugation on the H adsorption and abstraction reactions*

23 settembre - mattina

12:30-12:45	**FIS OR103**	**Brunella Bardi**	*Excited-state symmetry breaking in an aza-nanographene dye*
12:45-13:00	**FIS OR104**	**Rosangela Santalucia**	*HCN adsorption and reactivity at the Mg2SiO4 surface:a laboratory model of the chemistry on interstellar dust grains*

FIS 11

Physical Chemistry for Environment and Materials I

09:30-10:00	**FIS KN014**	**Cataldo Simari**	*Reversible and low-cost CO2 capture by quaternary-ammonium-functionalized aromatic polymers*
10:00-10:15	**FIS OR105**	**Claudio Cara**	*High value-added mesostructured silica from hexafluorosilicic acid (FSA): from a hazardous waste to precious silicon source.*
10:15-10.30	**FIS OR106**	**Rodolfo Esposito**	*A sustainable approach to formulation chemistry:structure and dynamics of bio-based complex mixtures*
10:30-10.45	**FIS OR107**	**Mariafrancesca Baratta**	*Photocatalytic degradation of organic pollutants in water using an innovative TiO2/SWNT membrane*
10:45-11:00	**FIS OR108**	**Chiara Lo Porto**	*Plasma deposition of TiO2-based nanocomposite coating for photocatalytic degradation of organic pollutants in water*
11:00-11.15	**FIS OR110**	**Stefano Marchesi**	*The NMR relaxometry as a powerful tool to study the uptake of paramagnetic ions from water by synthetic saponite clays*
11:15-11.30	**FIS OR109**	**Giulia Siciliano**	*Synthesis and characterization of polydopamine coated SPIONs for Cu2+ ions removal of from water*
11.30-11.45	**break**		

Physical Chemistry for Environment and Materials II

11:45-12:00	**FIS OR111**	**Nicola Blangetti**	*Template assisted sol-gel synthesis of Fe-doped TiO2 with photocatalytic activity under visible light*
12:00_12:15	**FIS OR112**	**Chiara Nannuzzi**	*Physico-chemical characterization of high surface area TiO2*
12:15-12.30	**FIS OR113**	**Massimo Dell'Edera**	*Nano-TiO2 based material for environmental and antibacterial application*
12:30-12:45	**FIS OR114**	**Marco Montalbano**	*Combining Morphology, Surface Fluorination and Au Nanoparticles Deposition on TiO2: Effects on Rhodamine B Photodegradation*
12:45-13:00	**FIS OR115**	**Maria Francesca Colella**	*Chemical-physical methods to investigate properties of vegetable oils and fats*
13:00-13:30	***Conclusioni***		

23 settembre - mattina

FIS 12

Thermodynamics and Kinetics I

09:30-10:00	**FIS KN015**	**Andrea Scorciapino**	*Development of a thermodynamic and kinetic model for passivemigration of ion carriers across lipid bilayers*
10:00-10:15	**FIS OR116**	**Marco Paolantoni**	*When the Solute is Completely Slaved to the Solvent:Jump Reorientation of Formamide in Water*
10:15-10.30	**FIS OR117**	**Federico Rossi**	*Shape Transformation of Artificial Vesicles Induced by an Interplay between Osmosis and pH Change*
10:30-10.45	**FIS OR118**	**Martina Maria Calvino**	*Shelf-life prediction of paracetamol formulations by non-isothermal thermogravimetry*
10:45-11:00	**FIS OR119**	**Chiara Pelosi**	*Stability of protein-polymer conjugates in solution*
11:00-11.15	**FIS OR120**	**Stefano Salvestrini**	*Kinetics and mechanism of 4-hydroxybenzoic acid degradation by persulfate/MnO2 oxidation*
11:15-11.30	**FIS OR121**	**Valentina Migliorati**	*Unraveling the solvation properties of Lanthanide (3+) ions: from molecular solvents to Ionic Liquid based systems*

Thermodynamics and Kinetics II

11:45-12:00	**FIS OR122**	**Marcello Budroni**	*Between dissipative structure and applications: chemical oscillations*
12:00_12:15	**FIS OR123**	**Olga Russina**	*NATURE OF SOLVATION OF CYCLODEXTRINS IN (PROTIC) IONIC LIQUIDS AND DEEP EUTECTIC SOLVENTS*
12:15-12.30	**FIS OR124**	**Duccio Tatini**	*Specific ions effects in green oleate-based formulations: how salts can influence the structure and rheology of viscoelastic systems*
12:30-12:45	**FIS OR125**	**Marianne Moedlinger**	*Structures and phase equilibria in the ternary Cu-As-Sb system (a preliminary investigation)*
12:45-13:00	**FIS OR126**	**Alessandro Damin**	*Cu+ bi-pyridine based homoleptic complexes as catalysts for partial oxidation reactions: a Raman study*

Divisione CHIMICA INDUSTRIALE (IND)

IND 06

09.30 - 10.00	**IND KN008 Medaglia Mario Giacomo Levi**	**Siglinda Perathoner Gaetano Iaquaniello**	*Waste-to-chemicals: a low-carbon innovative solution for circularity*
10.00 - 10.10	**IND OR060**	**Stefania Lucantonio**	*Experimental study of interactions between biomass pellets and oxygen carriers for chemical looping gasification in fluidized beds*

10.10 - 10.20	**IND OR061**	**Lucia Fagiolari**	*Electrodes and electrolytes for aqueous dye-sensitized solar cell*
10.20 - 10.30	**IND OR062**	**Francesca Rosso**	*Carbon Dioxide Absorption Mechanism in Biocompatible Ionic Liquids Solutions*
10.30 - 10.40	**IND OR063**	**Giuliano Giambastiani**	*“To Dissipate or not to Dissipate extra-Heat? This Is the Question!” How to Reduce Energy Wastes in a Challenging Process at the Heart of P2G Chain*
10.40 - 10.50	**IND OR064**	**Matteo Borella**	*A study of Kraft lignin conversion and possible upgrading to valuable compounds*
10.50 - 11.05	***Discussion***		
11.05 - 11.20	**break**		
11.20 - 11.40	**IND KN009**	**Paolo Vacca**	*New generation of specialty zeolites for sustainable chemistry*
11.40 - 11.50	**IND OR065**	**Giorgio Ferrari**	*Multifunctional Hardening Accelerator for Low-Clinker Binders*
11.50 - 12.00	**IND OR066**	**Rosa Vitiello**	*Optimization of HASE polymers effect in formulation of cement using Design of Experiment*
12.00 - 12.10	**IND OR067**	**Matteo Guidotti**	*Are Aqueous Hydrogen Peroxide and Sodium Percarbonate Efficient in the Inactivation of SARS-CoV 2?*
12.10 - 12.20	**IND OR068**	**Carlo Pirola**	*Chemical Plants Active Learning by Virtual Immersive Laboratory: the Eye4edu Project*
12.20 - 12.30	**IND OR069 Premio Tesi di Dottorato**	**Veronica Papa**	*Manganese- and Cobalt Based Catalysts for Homogeneous Hydrogenation*
12.30 - 12.40	**IND OR070**	**Elena Ghedini**	*Biomasses, Drug Delivery and Hi-Tech formulative protocols*
12.40 - 12.50	**IND OR071**	**Maryam Hmoudah**	*Assessment of the robustness of iron-based metal organic framework (MIL-88A) in aqueous environment*
12.50 - 13.00	***Discussion***		

Divisione CHIMICA INORGANICA (INO)
INO 10

9.30 - 10.00	**INO PZ009 (Premio Malatesta)**	**Roberta Sessoli**	*The contribution of coordination chemistry to the second quantum revolution*
10.00 - 10.30	**INO PZ010 (Premio Nasini 2021)**	**Edoardo Mosconi**	*Computational Modeling of Perovskite for Photovoltaic Applications*
10.30 - 10.45	**INO OR064-ad hoc**	**Iole Venditti**	*Functionalized silver nanoparticles for water pollution monitoring: sensitivity, selectivity and the challenge of eco-safe behavior*

23 settembre - mattina

10.45 - 11.00	**INO OR065**	**Diego Tesauro**	*New aromatic NHC-gold complexes as anticancer agents: protein target evaluation and cytotoxic activity*
11.00 - 11.15	**INO OR066**	**Farid Hajareh Haghighi**	*Silane-functionalized TiO2 nanoparticles decorated with Ag nanoparticles for dual antimicrobial effects*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR067**	**Francesca Tessore**	*Porphyrins for second order nonlinear optics*
11.45 - 12.00	**INO OR068**	**Annaluisa Mariconda**	*Sulfonated N-heterocyclic carbene silver(I) and gold(I) water soluble complexes: catalytic and cytotoxic activity*
12.00 - 12.15	**INO OR069**	**Riccardo Freccero**	*Widening the tin solid-state chemistry: unusual bonding scenario in the LaMgSn2 rare-earth stannide*
12.15 - 12.30	**INO OR070**	**Veronica Ghini**	*NMR reveals the metabolic changes induced by Auranofin in ovarian cancer cells*
12.30 - 13.00	**INO IL003**	**David P. Giedroc**	*Metals, molecules and metabolism: Molecular mechanisms of bacterial metallostasis*

INO 11

10.30 - 10.45	**INO OR071**	**Antonio Zucca**	*Advances in Pt(II) rollover chemistry*
10.45 - 11.00	**INO OR072**	**Marco Lunardon**	*Hybrid transition metal dichalcogenide/graphene microspheres for hydrogen evolution reaction*
11.00 - 11.15	**INO OR073**	**Silvia Mostoni**	*Porphyrin functionalized ZnO/SiO2 hybrid nanoparticles as scintillator agent*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR074**	**Alfonso Annunziata**	*Square-planar vs. trigonal bipyramidal molecular geometry in glucoconjugate triazole Pt(II) complexes: synthesis, in-solution behaviour and anticancer properties*
11.45 - 12.00	**INO OR075**	**Giada Mannias**	*Iron(III) trimesate xerogel by ultrasonic irradiation*
12.00 - 12.15	**INO OR076**	**Christian Rossi**	*Exploiting the transformative features of metal halides for the synthesis of CsPbBr3@SiO2 core-shell nanocrystals*
12.15 - 12.30	**INO OR077**	**Luciano Marchiò**	*Supramolecular assemblies in silver bispyrazolylmethane complexes: phase transitions and the role of the halogen bond*

INO 12

10.30 - 10.45	**INO OR078**	**Adolfo Speghini**	*Fine-tuning of the size of luminescent CaF2 nanoparticles*
10.45 - 11.00	**INO OR079**	**Antonio Santoro**	*Responsive Self-Assembled Dynamic Helicates*
11.00 - 11.15	**INO OR080**	**Chiara Mazzariol**	*Synthesis in confined space of luminescent nanostructures of undoped and Eu(III)-doped calcium molybdate*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR081**	**Marta Stucchi**	*The synergistic and photochromic effect of Au nanoparticles on a Silver-waste derived TiO2 photocatalyst*

11.45 - 12.00	**INO OR082**	**Diego Olivieri**	*Efficient palladium catalyzed bis-alkoxycarbonylation of olefins for the synthesis of useful succinic acid derivatives*
12.00 - 12.15	**INO OR083**	**Luca Rigamonti**	*Multivariate approach to the analysis of structural data of iron(II) spin crossover complexes and cobalt(II) single molecule magnets*
12.15 - 12.30	**INO OR084**	**Simonetta Geninatti**	*Histidine containing PLGA nanoparticles as novel theranostic agents for Boron Neutron Capture Therapy*

Divisione CHIMICA ORGANICA (ORG)

ORG 19

9.30 - 10.00	**ORG PZ003**	**Pierangelo Metrangolo**	***Medaglia Giorgio Modena*** *A Journey through the Word of Halogen Bonding*
10.00 - 10.30	**ORG PZ008**	**Jacopo Roletto**	***Premio alla ricerca Chimica Organica per lo Sviluppo di Processi e Prodotti nell'Industria*** *The art of Process Development in API manufacturing*
10.30 - 10.45	**ORG OR124**	**Andrea Sartori**	*Dual Conjugates Targeting αVβ3/αVβ6 Integrins and Tyrosine Kinase Receptors as antifibrotic agents*
10.45 - 11.00	**ORG OR125**	**Angela Scala**	*Synthesis and biological profile of novel three-arms star-shaped PLA-PEG amphiphilic copolymers*
11.00 - 11.15	**ORG OR126**	**Monica Scognamiglio**	*Isolation and structural elucidation of oleanane saponins from Bellis sylvestris Cyr. involved in plant-plant chemical interactions*
11.15 - 11.30	**ORG OR127**	**Alba Silipo**	*Herbaspirillum Root189 LPS glycan chain decorations affect LPS bioactivity, membrane properties and prevent plant immune recognition*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR128**	**Laura Siracusa**	*Secondary metabolic profiles and anticancer actions from fruit extracts of immature pomegranates*
12.15 - 12.30	**ORG OR129**	**Rachele Stefania**	*Enhanced relaxivity by hydrophobic interactions of macrocyclic Gd-HPDO3A complexes linked to pyranine*
12.30 - 12.45	**ORG OR130**	**Luca Valgimigli**	*Oxygen Uptake Kinetics as a Powerful Tool to Investigate Tyrosinase Enzyme Inhibition*
12.45 - 13.00	**ORG OR131**	**Danilo Vona**	*Enzyme immobilization on polydopamine-coated living microalgae cells for bioremediation*

ORG 20

10.30 - 10.45	**ORG OR132**	**Matteo Corrieri**	*Metal-Free Synthesis of Azacarbolines Enabled by Hypervalent Iodine-Promoted Intramolecular Oxidative Cyclization*

23 settembre - mattina

10.45 - 11.00	**ORG OR133**	**Federico Frateloreto**	*Functionalization of C-H bond using self-assembling supramolecular iron(II) complexes*
11.00 - 11.15	**ORG OR134**	**Andrea Gualandi**	*Photoredox allylation of aldehydes mediated by bismuth and cobalt*
11.15 - 11.30	**ORG OR135**	**Marco Lombardo**	*Visible Light Photocatalytic Synthesis of Oxygenated Heterocyclic Compounds*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR136**	**Michela Lupi**	*A Hydrogen Bond Donor / Lewis Base (HBD/LB) catalytic route to enantioenriched hetero[4]helicenes*
12.15 - 12.30	**ORG OR137**	**Giulia Martelli**	*Fast Heck-Cassar-Sonogashira Cross-Coupling Reactions with Palladium Catalyst Recycling and Green Solvent/Base recovery*
12.30 - 12.45	**ORG OR138**	**Silvia Gazzola**	*2- and 6-Purinylmagnesium Halides in Dichloromethane: Scope and Insights Into the Solvent Influence on the C- Mg Bond*
12.45 - 13.00	**ORG OR139**	**Angelo Nacci**	*Nanostructured catalysts for a circular economy*

ORG 21

10.30 - 10.45	**ORG PZ015**	**Gabriele Laudadio**	***Premio Tesi di Dottorato Chimica Organica nei suoi Aspetti Metodologici*** *New synthetic methods enabled by photochemistry and electrochemistry in flow*
10.45 - 11.00	**ORG OR140**	**Andrea Francesca Quivelli**	*Mild Approaches for Copper-Catalysed Coupling Reactions: Ligand-Free Ullmann-type C–N and C–O Bond Formation in Deep Eutectic Solvents*
11.00 - 11.15	**ORG OR141**	**Marco Rabuffetti**	*Stereoselective monoreduction of bulky 1,2-dicarbonyls catalyzed by a benzyl reductase from Pichia glucozyma (KRED1-Pglu)*
11.15 - 11.30	**ORG OR142**	**Daniele Ragno**	*Regiodivergent Isosorbide Acylation by Oxidative NHC-Catalysis in Batch and Continuous-Flow*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR143**	**Giorgio Rizzo**	*Palladium anchored on Silk Fibroin as suitable catalyst for Suzuki-Miyaura Cross-Coupling Reactions*
12.15 - 12.30	**ORG OR144**	**Patrizio Russo**	*Novel Synthesis of Thienofuranone Derivates by Pd-Catalyzed Carbonylation Reaction*
12.30 - 12.45	**ORG OR145**	**Gabriele Lupidi**	*Vitamin B2 Promoted Tandem Nef-Henry Reactions for the synthesis of Symmetrical β-Nitro Alcohols from Nitroalkanes*

12.45 - 13.00	**ORG OR146**	**Ida Ziccarelli**	*Synthesis of Isobenzofuranones, Isochromenones and Thienopyranones by a Pd-Catalyzed Oxidative Carbonylation Approach*

DIDATTICA CHIMICA (DID)

- Orals
- Posters

Sustainable chemistry for a sustainable teaching. A proposal for a first level curriculum in Chemistry at University

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Green and Sustainable Chemistry (GSC) has been generating a new way of thinking about the development, design and employment of chemical processes, representing a holistic, integrative and interdisciplinary approach that may constitute the core of an innovative curriculum for a first degree course in Chemistry.

Teaching practices based on GSC are most suitable for the design of a curriculum which address the UN Sustainable Development Goals (SDG), promoting an integrate cultural vision linking Chemistry to ecology, economy and society [1].

GSC involves knowledge about the basics of inorganic and organic chemistry, the equilibrium and kinetics of chemical reactions, the detection, analysis and remediation of pollutants, to cite only a few central issues of SDG.

From a more fundamental point of view, GSC may foster a systemic approach, that leads to a deeper understanding of Chemistry and her links to social, ecological and economical dimensions. This naturally promotes citizenship skills at the local and global level through an ethics- and values-driven comprehension of the discipline. In a learner-centered system, this approach requires innovation in the methods of teaching Chemistry, encouraging participatory learning, systems-based thinking, inquiry-based learning, problem-solving skills [2].

An innovative Chemistry curriculum based on GSC should aim to deepen chemical knowledge, translate knowledge into useful applications and prepare chemists to meet the SDG challenges.

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[2] P.G. Mahaffy, A. Krief, H. Hopf, G. Mehta, S.A. Matlin *Nat. Rev. Chem.* **2018**, *2*, 0126.

The teaching of chemistry from the perspective of citizenship

Carlo Fiorentini

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School can contribute significantly to the development of a conscious and complex citizenship, provided that it is not only a place of preparation for the adult life, but above all a vital place for socio-cultural growth.

This implies that the acquisition of new knowledge takes place in every disciplinary area on the basis of the principle of motivational and cognitive adequacy, which allows all students to be active in a social dimension, in the construction of knowledge and in the development of their thinking and their cognitive structures.

The cognitive adequacy of knowledge and a problematic, constructive methodological-relational approach can contribute effectively to the development of citizenship skills. Both allow some essential aspects of the democratic education to be lived constantly and in depth first of all the recognition of the equal dignity of each student in the process of building knowledge. To that recognition follow in a more analytical way: mental openness, emotional involvement, the value of confrontation and dialogue, the attribution of importance to provisional hypotheses, the assumption of non-dogmatic and rigid attitudes, learning to cooperate in the construction of knowledge, the ability to evaluate the degree of certainty that can be attribute the development of self-discipline to the statements made.

In this context, reflections will be developed relating to the important contribution that can be provided by the teaching of chemistry in the first two years of upper secondary school.

Caring for yourself, the environment and others in primary school

Eleonora Aquilini [a,b]

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Environmental education aims to relate each of us with the Earth, with other human beings and with all living beings in a perspective of solidarity and responsible participation that leads to recognition and respect for all differences. Environmental education fit into one of the goals of the 2030 Agenda for Sustainable Development, which is "an action program for people, the planet and prosperity signed in September 2015 by the governments of the 193 UN member countries. It incorporates 17 Sustainable Development Goals, SDGs, into a large action program for a total of 169 'targets' or milestones. The official launch of the Sustainable Development Goals coincided with the beginning of 2016, guiding the world on the way to go over the next 15 years: the countries, in fact, are committed to achieving them by 2030. The Goals for Development follow up on the results of the Millennium Development Goals that preceded them, and represent common goals on a set of important development issues: the fight against poverty, the elimination of hunger and the fight against to climate change, to name just a few." [1] The goal that most directly concerns the school is the fourth SDG "Providing quality, equitable and inclusive education, and learning opportunities for all" [2] that can also be pursued through environmental education that is closely linked to the curriculum. [3]

The environment therefore must not be considered as something external to us but as a part of us and this relationship must also be built in the classroom, starting at least from primary school. In this sense, the various disciplines should all contribute to this sense of unity with the environment. In the case of science, the links with environmental education seem to be more evident. It is important that environmental education is part of the school curriculum and that it is seen as an integrated part of the knowledge, methods and behavioral values that constitute the focus of the training.

[1] Centro Regionale di informazione delle Nazioni Unite: http://www.unric.org/it/agenda-2030
[2] Indicazioni nazionali e nuovi scenari:
https://www.miur.gov.it/documents/20182/0/Indicazioni+nazionali+e+nuovi+scenari/
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Teaching the notion of chemical bonding: a didactic challenge

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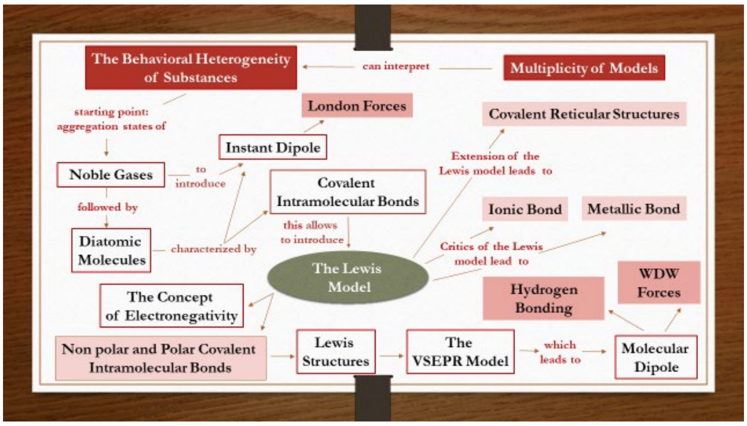
Teaching chemical bonding effectively is a challenge, as this notion raises numbers of didactic and conceptual problems, that are well highlighted in the literature [1]. Students are reported to misapprehend the nature of intra- and inter-molecular bonds, to overlook their involvement in physical and chemical transformations, to neglect energetic aspects, to misunderstand the relationship between the macroscopic properties and the microscopic structure of substances, etc. As a reaction to these conceptual and didactic problems, we designed a teaching sequence on chemical bonding whose conceptual structure is reported in the figure: the sequence is preferentially addressed to students of the first two years of secondary school. A main feature of this teaching sequence is the alternation between intra- and inter-molecular bonding models, aimed at emphasizing their common nature of electrical interaction and their position along the energy scale [2-3]. The issue of the stability of the resulting systems justifies the formation of all kinds of bonds and serves as logical common thread throughout the sequence. Other pivotal steps aspects are:



- The choice of discussing weak intermolecular forces (London forces) in monoatomic substances (noble gases) and to construct the notion of instant dipole, first.
- The emphasis on the non-directional character of ionic bond as a consequence of its very nature of Coulombian interaction between point electric charges, which is the key to understanding the reticular nature of ionic substances.
- The choice of introducing the ionic and metallic bonding models as critics of the covalent bond model. This is aimed at stressing both the modelling nature of bond descriptions and the limits of each bonding model. In fact, different bonding models are gradually introduced throughout the sequence, every time that previous models do not fit the explanatory needs raised by new phenomena [4].

Parts of this teaching sequence have been tested in a second-year classroom of a technical institute between January and May 2021. The results of this experience will be discussed.

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[3] A. Bergqvist, M. Drechsler, S.-N. Chang Rundgren, *Int. J. Sci. Educ.* **2016,** *3,* 298
[4] E. Roletto, "La scuola dell'apprendimento. Didattiche disciplinari, modelli e applicazioni operative" Erickson **2005**

A new didactic pathway to introduce Spectroscopy by historical-epistemiological/STEM laboratorial/distance learning blended approach

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Spectroscopy is undoubtedly a powerful instrument for investigating the Structure of Matter. Among Italian High Schools, Spectroscopy is systematically studied in Chemical Technical Institutes, while it rarely appears in Scientific and Applied Sciences High School called *Licei*. In the last ten years, one of the authors has proposed and experimented interactive laboratories to introduce Spectroscopy to high school students, mainly during special programs (i.e. "Alternanza Scuola Lavoro"), called "*Fare Chimica con la luce*" [1,2]. In the present work, we are reporting a new didactic pathway to introduce UV-Visible Spectroscopy in Italian High Schools. During a first step of the work [3], a didactic pathway concerning optical phenomena was developed and tested in two classes at 'Cattaneo Technical Institute' of San Miniato (Pisa) by applying two main teaching methodologies: (i) experimental demonstrations designed *ad hoc* supported by short videos, (ii) laboratorial experiments based on the *Inquiry-Based Learning* method, followed by a collective discussion. All the experiments were collected as audio-video materials with explanatory pictures and they were made available for distance learning, too. These digital materials were also collected and presented during the Researcher's Night (Bright) organized by the Department of Chemistry and Industrial Chemistry of the University of Pisa, which was an on-line event due to the Covid-19 pandemic [4]. During second step of the work, a website was created [5] implemented with additional resources, such as instructional materials in order to help students build home-made spectroscopes; presentations and interactive materials to better understand the instrumental design and functionality of UV-Vis Spectrophotmeters; description of historical instruments with relevant educational values. The web-site (#DADSpectroscopy) was presented in the first part of the Chemical Educational National School "Giuseppe Del Re", organized by Chemical Educational Division of Italian Chemical Society (2020 edition). One of the innovative aspects of this work is related to its modular form and to the amount of original materials, which was available to teachers of any kind of High Schools. During the teacher training school, the teachers could use the available resources or select just few parts of the proposed pathway, and test them in face-to-face or distance modality teaching with their students. Reports and feedbacks from the school teachers were discussed and analyzed in the second part of the School and this was very important to implement this new didactic approach to Spectroscopy. The ongoing step of this work involving further testing in classroom and implementation will be presented during the Congress.

Bibliography:

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Virtual Reality visualizations of complex molecular structures in chemistry education. The β-CD-ASA example.

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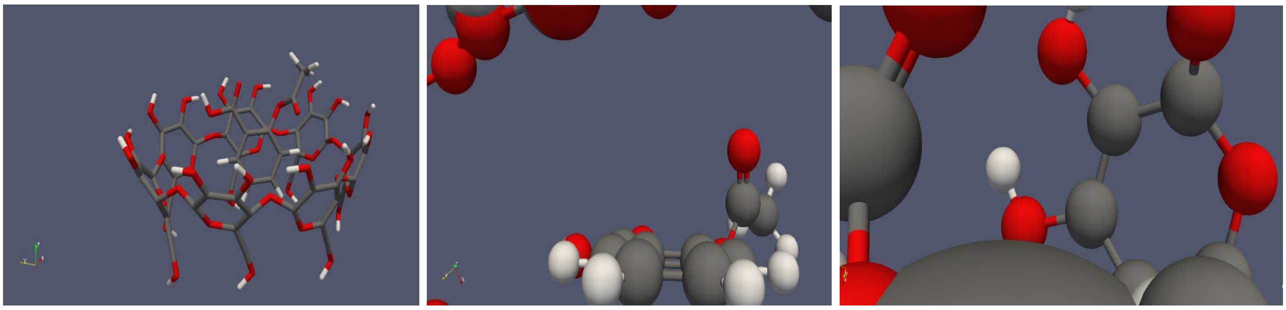
Chemistry can be a very difficult topic to understand for students, because it requires to think in an abstract way both about the existence of atoms, molecules, and ions, and about their structural and dynamic behaviors and interaction. In this context, realistic multimedia visualization tools (visual, audio and interactive learning) are very helpful. Virtual Reality (VR) molecular scenarios have been recently developed in order to enhance 3D molecular structure visualizations.

Virtual reality implies designing and immersive reality in which simulated real objects, such as a virtual laboratory, and/or molecules can be explored and/or manipulated. In this way complex molecular structures can be elucidated more readily and make it possible to focus on specific portions.

In order to demonstrate the advantage of using VR visualizations, in this work we report an example of host-guest interactions in the β-cyclodextrin (β-CD) - acetylsalicylic acid (ASA) complex whose pharmacological properties and structure have been reported. [1][2] In this study, the preferential orientation of ASA in β-CD has been suggested and we have adopted it for our visualization.

In the above figure different views of the β-CD-ASA complex are shown. Different types of atoms are indicated by different colors: H, ○ C, ● O. ●

In the left figure, an overall view of the complex is displayed; it can be seen that the ASA molecule is arranged so the carboxylic and acetylic groups stick out the secondary β-CD ring thus optimizing different kinds of H- bond intermolecular interactions. [1][2] This situation can be further explored in VR. For example, if we imagine to over tune the complex on its side and virtually enter through the β-CD's primary ring (middle figure), it is possible to observe more closely the arrangement and the relative positions of the substituents on the ASA benzene ring. At this point (right figure) the VR environment makes it possible to turn around and observe the ASA's surroundings. In this way, along with other panoramic views, a more realistic and detailed view of the complex can be obtained with important advantages in chemistry education.



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A didactic sequence for teaching chromatography: observation, model and practical applications

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Chromatography is a fundamental separation and analytical technique in chemistry. The principles of chromatography and the application of this tool in the laboratory practices are core knowledges of the Italian national curriculum of chemistry technical high schools. Moreover, the use of chromatography in many different fields makes this topic suitable for students of general science courses in scientific high school curricula.

In the last two years the author has experimented didactic activities involving chromatography in the framework of the analytical chemistry courses of *Istituto Tecnico "C. Cattaneo"* in San Miniato (Pisa). The activities have been conducted using both face-to-face and on-line learning, as required during the Covid-19 pandemic. In this work, the past experiences have been arranged into a complete didactic sequence made of three main modules. The didactic approach includes theoretical lessons, in-class discussions and laboratory experiences; these strategies are inserted in a general *inquiry-based* learning framework. Furthermore, the didactic sequence involves the construction of models and theoretical simulations that develop mathematical and computational skills in students, and it encourages abstract and symbolic thinking.

The didactic sequence starts from the macroscopic observations of a simple column chromatography separation process of a blue food colorant and the collection of different fractions. In this first step, the main goals are building the first chromatogram and understanding the concepts of chromatographic run and of chromatographic band, as well as introducing the basic terminology.

In the second step, a separation model based on the distribution equilibrium is elaborated with the students by means of in-class discussion and brain storming. The proposed separation model is based on the classic plates' theory by Martin and Synge [1]. From an historical point of view, such theory has played a significant role as the first model to understand the chromatographic process.

Our simplified model can be used to simulate a chromatographic run with a single component or with a mixture, by using a spreadsheet that has been compiled following a tutorial approach with videos and slides. The result of the virtual experiment is a chromatogram that can be analyzed in the same way as a real one. The simulation is important for understanding the dependence of the chromatogram (retention time and peak broadening) from the input parameters (distribution constant, phase factor, number of plates ecc…). The self-reflection and the reworking of basic chromatographic concepts are promoted by structured worksheets that can be solved by using the students' simulation program.

The last part of the didactic sequence is constituted by laboratory practical activities in which students face to a real problem: the separation and the identification of leaves pigment extract by using both the thin layer chromatography (TLC) e the column chromatography.

The *inquiry-based* approach and the different didactic tool and methodologies allow a successful student engagement in the learning process and an overall satisfying result. The connection between observation, model and simulations and practical activities is the strength of this didactic sequence. All the educational materials (video-tutorial, presentation, notebooks, and worksheets) are free available from the website "*Percorsi di chimica*" edited by the author [2]. The materials facilitate other teachers in replicating the sequence in their classes.

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‘Light and Molecules’: an experimental approach to the understanding of basic concepts of Quantum Mechanics

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Physics Curricula for the fifth year of Liceo Scientifico are expected to introduce basic concepts of Quantum Mechanics (QM). There is an evident conceptual gap with respect to the teaching of Chemistry, that since the first years is bound to introduce some issues the physical basis of which lies on QM (electronic configuration of atoms and molecules, physical basis of Periodic Table, nature of chemical bond, atomic and molecular orbitals).

Unfortunately, QM is generally introduced in a rather formal way, that requires mathematical tools to be managed (at the very end, the Schroedinger equation is a second order differential equation, and such equations are not part of the background of a secondary school student). However, we firmly believe that some very basic ideas of QM can be introduced via an experimental approach, minimizing the formal apparatus of presentation. Among the others: the quantum nature of energy exchange, the wave property of matter, the probabilistic nature of the QM laws.

In this regard, optical spectroscopy seems to us the most suitable instrument to pursue an experimental approach for the understanding of the QM foundations of molecular properties. It should be noted that from an historical point of view, spectroscopic experiments represented the most evident proof of the failures of classical physics (black body spectrum, Rydberg spectral series).

With this aim, a joint activity, connected to the Piano Lauree Scientifiche/PCTO, was established between the Department of Chemical Science and Technologies of the University of Rome Tor Vergata (UTOV) and the I.I.S. Liceo Scientifico Lucio Anneo Seneca (LS Seneca) of Rome. The laboratory, denoted as ‘Light and Molecules’, was dedicated to the study of the interaction between the electromagnetic radiation (the electric field component) and some simple molecular systems [Carbon Monoxide (IR), $CHCl_3$/$CDCl_3$ (IR) acetone (UV), cyanines (Vis)].

Four teams of students (5R class - LS Seneca) participated to the PLS/PCTO Lab, working on general aspects of the radiation-matter interaction and on two case studies:

1. General Theory: *Radiation-Matter Interaction*. Team: Lorenzo Rocca, Emanuele Soave, Gianluca Stati, Alessandro Tripodi.
2. Case study: *Vibrorotational spectrum of Carbon Monoxide*. Team: Alessio Chelli, Emilio Di Salvo, Arabella Lacap, Lia Pagotto, Aurora Seri.
3. Case study: *Solvatochromism of the UV spectrum of Acetone. Determination of the energy of Hydrogen Bonding*. Team 1: Denise Albertin, Giovanni Cianciusi, Valeria Cianciusi, Enrico Roncucci; Team 2: Sara Brunetti, Flavia Del Monaco, Giulia Forgione, Simone Mastrogiacomo, Luca Sbriccoli.

Due to COVID-19 emergence, the students analysed the spectra measured in the spectroscopy laboratory at UTOV (Rita Cimino, Gabriele Rossi) under the supervision of Prof. Dora Stella Lombardi (LS Seneca) and Mariano Venanzi (UTOV). All the activities were carried out applying group learning and peer training methods.

Additional Learning Requirements (OFA) in Math for Environmental Science degree course: a review for a better understanding of the difficulties of students entering university

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Enrolled freshmen in Environmental Science Bachelor's degree course at University of Salerno must certify the minimum required skills in math and logics by obtaining at least 15 points (out of 30) in the compulsory national CISIA TOLC-S entry test (sections Basic math and Logics/Problems). If not, students can apply to the degree course but they are assigned Additional Learning Requirements (OFA) and must attend a preliminary remedial math/logics course in order to be admitted to the Math exam of the degree course. From a review of the last three academic years data it has been observed that only a tiny percentage of students fit the entry test requirement: 7.6% in 2018/19; 2.2% in 2019/20; 6.1% in 2020/21; consequently, high numbers of students must attend remedial courses every year and many of them fail to pass the relevant exam, sometimes after several attempts. Therefore, in order to get better understanding of the reasons of students' difficulties, a critical review has been performed of the whole process, from the entry competence requirements to the OFA rationales and outcomes.

In detail, the seven OFA exam sessions held in the last two years have been considered, involving 150 students. The percentages of students passing the test at first attempt constantly stand between 40% and 60%. The test questions have been grouped in topic categories and for each of them the results have been analyzed, as percentage of correct, incorrect and not given answers. The category representing the major challenge for students, with percentages of correct answers always well below 50%, is relevant to "*Problems*", intended as application of basic math notions to solve simple reasoning problems. All the 150 students, including the ones who had precociously left the degree course for another course or another university or have just abandoned studies, have been asked to answer a survey questionnaire for acquiring information regarding: school background (i.e. type of high school attended, favorite subjects, attitude to apply problem solving in the different subjects, etc.), motivations and expectations regarding the degree course, difficulties encountered in the OFA courses and exams, perception of the OFA impact on development of students' academic career. Among the aspects that emerged it is worth highlighting one as surprising as it is worrying, which concerns the apparent disconnection, at high school, between the Basic Science studies (Biology, Chemistry, Earth Science) and Math studies. Despite the good attitude and preference of these students towards Science (which positively influenced their choice of pursuing a study career in the environmental sciences) mathematical tools and approaches are poorly regarded as the basis of science, which suggests there is a widespread belief that mathematical skills are not fundamental to scientific studies.

Moreover, a further important finding of the survey is the marginal role of high school teachers in advising students in choosing Environmental Science degree program.

Finally, the results of this study indicate that further insights into the difficulties encountered by incoming students are needed, but at the same time careful reflection to define, as a matter of urgency, more effective orientation strategies, possibly cooperative between universities and high schools, to increase awareness and motivation towards choice of university course is certainly necessary.

From the astro to the nano scale: a learning by doing teaching pathway

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From the nano-world to solar systems length-scales span over several orders of magnitude. In young student it is therefore hard to fully understand the relative proportions among different objects even belonging to the same level of complexity. Resizing to human related distances is an effective way to understand the relative distances in astronomic scales or the amount of information contained in a single cell. In general, the use of imagination is essential in educational research as well as the use of different skills in interdisciplinary works. Some appealing examples will be given and the result of a pilot learning by doing teaching pathway involving hundreds of young students will be presented. Clues will give indications for future directions in educational research.

[1] M. Salvador, D. Lago-Cachón, P. Calandra , A. Malito And D. Peddis, Atti Accad. Pelorit. Pericol. Cl. Sci. Fis. Mat. Nat., **2021** In press

Chemistry, history and complexity

Antonio Testoni

Divisione di Didattica della Società Chimica Italiana

The issue of sustainability is inextricably linked to the issue of complexity. Chemistry, and more generally science, is something more than a "corpus" of knowledge: it is a way of thinking, it is a way of operating, it is a particular way of relating to the world and understanding its complexity. Therefore, in the teaching / learning of a scientific discipline, such as chemistry, not only specific disciplinary knowledge / skills must be considered, but also the knowledge of the processes and strategies used for the construction of knowledge. Knowledge and processes are inseparable as they are two sides of the same coin, which is that of culture. For this reason we believe that it is important, from the didactic point of view, to put in place a narrative that takes into due consideration the evolutionary process of growth and innovation of knowledge. Therefore we cannot decontextualize knowledge, divide it from its origin and from the network of problems that generated it. Without the didactic reconstruction of this problematic context (theoretical and experimental), concepts and theories are meaningless for the student, they remain mere verbal definitions, lifeless and do not affect pre-existing conceptual schemes, that is, they do not become a "way of thinking disciplinary ".We will exemplify these considerations by taking into consideration some aspects of “Lavoisier's Chemistry”, in particular the issue of the quantification of chemical phenomena.

A colorful new morning - teaching applied chemistry in pandemic times

Sergio Palazzi

ISIS di Setificio "Paolo Carcano", Como

Colour is one of the most effective stimuli to capture the attention and elicit the fantasy of learners, and this is especially true for those who are not primarily interested in "hard sciences".
The world of textile chemistry offers a lot of didactic chances that could be helpful even for those not directly involved in that sector of applied chemistry [1].

We are teaching at a historic *Istituto Tecnico* devoted to the study of textile production (weaving, finishing, printing…). During the pandemic periods, laboratory practice had several limits and normal lessons were often given via web, so it was hard to keep the concentration on experimental observations and on the subsequent theoretical interpretations.

The occasional aim of this job was already introduced elsewhere [2]; here we would like to stress the scientific and operational part of the job as a didactic approach for future works.

This presentation will discuss how we organized our lab practice dividing the tasks among different classes, where the younger students (3rd class, 16-17 yo) were "leading" and the older ones (4th-5th classes) were more or less acting as consultants to better explain several points.
We also decided to collect our materials in a bound catalogue to be kept at our school museum, to remember this terrible period.

Both in research and in daily life, one of the most relevant differences between fibres of different chemical nature or different structure is the ability to be dyed by substances grouped in the traditional *dye classes,* and within each of them by the structural peculiarities of related molecules. Dyeing conditions (e.g. temperature, time, pH, salinity…) can differentiate those behaviours.

In order to save time, we simply used two not-so-different dyes, a blue and a magenta from the *direct* and *acid* classes, to simultaneously dye fibres like viscose, silk, nylon and wool; dyes where then partly stripped by washing. The only instrument used to study their behaviour was the reflection spectrophotometer. From the graphs in the "old" chromaticity diagram and in k/s vs. λ it is possible to argue the different ideas of equilibrium; numbers do not require physical presence.

A study of the chemical composition of the dyes and of the auxiliaries introduced to the topics of ecotoxicological evaluations and sustainability issues, relevant not only in textile production. Students also realized that the distinction between "natural" and "man made" fibres is an artefact of our traditional prejudices, whereas the understanding of chemical properties and microstructural features is quite more relevant also to design new and more acceptable technological processes.

[1] S. Palazzi, *CnS – La chimica nella scuola*, **2012**, XXXIV-3, 284-289
[2] S. Palazzi, *A Campione*, AICTC, **2021**, *58*, 1/21, 12-13

Chemistry: a Precious Discovery in the Dantesque World

Teresa Cecchi, Arianna Giuliani

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This didactic path celebrates the 700th anniversary of Dante Alighieri's death with a STEAM approach through a chemical reading of the Divine Comedy. The outcome of our journey to Hell, Purgatory, and Paradise is both a theater performance which will be held in Torino and Fermo, (next Fall), and 15 video pitches in English available on YouTube (next July) which can also be shown during the Congress.

Chemistry interprets various specific cultural aspects relating to the souls placed by Dante in otherworldly places with surprising and never explored scenic effects. Chemical reactivity underpinning the show is both theoretically and practically studied. It is demonstrated that an aesthetically fascinating scientific experiment promotes learning thanks to the emotions related to it [1]. In the realization of the show important relational aspects come into play that are crucial in cooperative learning: self-confidence and trust in the group of peers are needed to face the stage. Deep and significant understanding of the chemical reactivity is needed to explain it on the stage.

In common parlance, art and technique belong to different categories, usually antithetical. Our didactic path aims to recompose this dichotomy. In Greek “tecnè” means “art”! The Latins indicated the science of matter as "Ars Chimica" and this is another motivation for bringing the most spectacular chemical technique to the stage.

The show is a significant stimulus for the spread of chemical culture even in humanistic environments normally impenetrable to it: the proper chemical actions are not only clearly explained but also accompanied by readings of appropriate extracts from the Divine Comedy, philosophical reflection and music that cause pleasant synaesthesias.

The didactic strategy and the continuous evaluation of learning try to develop in the students not only LOTS but also HOTS through brainstorming, Inquiry based learning, and rationalization of every chemical aspect connected to every cultural feature dealt with.

In the following we detail 5 excerpts from the theater performance (corresponding to 5 YouTube video pitches)

1-In Hell, the avarice is represented by marvelous oscillating reactions whose electric potential is transformed into a sound with a fluctuating pitch.

2-In Hell, in the circle of the lustful the wind of passion, made of oxygen (developed from the reaction of potassium permanganate with hydrogen peroxide) and of liquid nitrogen, safely overwhelms Paolo and Francesca and the audience.

3-The alchemist wizards in Malebolge will show us the wonderful alchemy of breathtaking reactions, accompanied by the notes of Paul Dukas's Apprentice Sorcerer. The 9th circle of Lucifer is displayed with the chemistry of sulfur, the demonic element par excellence, whose spectacular reactions are accompanied by Paul Bonneau's Dance of the Demons.

4-The ascent to Purgatory is mimicked by ascending chromatography, the purification chemical technique par excellence, on paper folded in the shape of a cone, with a breathtaking scenic effect

5-The ascent to Paradise passes through the 7 heavens of the Ptolemaic Aristotelian universe, each associated with a metal, whose spectacular reactivity is the "chemical track" of the brief reading that exemplifies the cultural aspect linked to the specific sky. The journey through Dante's skies is accompanied by the musical scales written by Kepler in his book “Harmonices Mundi” for the celestial bodies. The theology of light (Love that moves the sun and other stars) to represent the divine is interpreted with the lighting of the magnesium circles, as per the exact Dantesque description.

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A Carbon atom journey

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IPASR "Giustino Fortunato" Potenza – sede di Lagopesole

This is the synopsis about the teaching experience of First class students of the IPASR "Giustino Fortunato" high school of Lagopesole (Potenza, Italy). This activity was inspired by the "Carbon" story of the book "The periodic system" written by Primo Levi. There, the author claimed a final end of the book reporting the story of a carbon atom.

The atom, after being stored for millions of years in the form of $CaCO_3$ in a limestone rock, is brought to the Earth's surface by a miner, and then becomes CO_2 freed by the action of a furnace. The journey continues, time after time, as in an eternal present: always equal to itself, and yet in completely different forms. In fact, it becomes glucose with the process of chlorophyll photosynthesis, and thus migrate to humans, plants and animals. Finally, tied in a long chain, it is ingested, assimilated, and finally transported by the blood until it reaches a nerve cell, the same one that is responsible for Levi's writing who concludes the book in this way.

The carbon cycle is the biogeochemical cycle through which carbon is exchanged between the geosphere (among which sediments and fossil fuels are considered), the hydrosphere (rivers and oceans), the biosphere (including fresh waters), and the Earth's atmosphere. In order to provide a full understanding of this process, the school teachers of the "Giustino Fortunato" high school were inspired by the author's suggestions. Together with the student, they carried out basic chemical reactions in the laboratory involving carbon compounds ($CaCO_3$, CO_2, $C_{12}H_{22}O_{11}$) that manifest macroscopic variations (precipitate formations, color variations, gas production), which represent experimental evidence of chemical transformations.

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Peer review of scientific articles: a teaching experience

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Frontiers for Young Minds is an open access, non-profit scientific journal for which young people are both the target audience and critical participants in the review process [1]. An innovative and engaging peer review process allowed researchers to confront with young minds, with positive results for both sides. From one side, kids are encouraged in asking questions, they can learn how to distinguish between true science facts and "fake news" and they have the chance to interact for the first time with the "modus operandi" of the research world and of the publishing process. From the other side, researchers, with the aim of describing their work in a more comprehensible fashion, are stimulated in looking at their data from a broader perspective, gaining inspirational and motivational glimpse from students' comments. In this process, Science Mentors play a key role. The Science Mentors guide the Young Reviewers through the review process, serving as a direct connection to the scientific community. They assist them in navigating through a cutting-edge science manuscript, and empower them as young experts to provide feedback to authors about communicating science to their peers. Finally, as the entire process is carried out in English, this teaching experience represents an interesting opportunity for the application of the CLIL (Content and Language Integrated Learning) methodology [2].

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Increasing the engagement of non-chemistry major students: examples of didactic strategic

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In recent years, many educational institutions have focussed the attention to the evaluation of the students' engagement.
The engagement is a measure of the level of attention, and interest that a student develope for a subject [1] and can be considered as a benchmark of the quality of the teaching activities [2]. Moreover, several studies have shown that there is a strict connection between student engagement and student performance [3].
Increasing the students' engagement towards a subject which is not related to their major may be a challenge [4]. Referring to chemistry, some aspects may be particularly critical such as the varying degrees of chemistry backgrounds and the different perception of self-efficacy [4].

This contribution is aimed at presenting the experimentation performed in the frame of a course on chemistry applied to cultural heritage held for students at the second year of a five year degree programme in restoration.
To increase the students' engagement and their self-efficacy 's perception, different didactic strategies have been applied considering that students learn using different cognitive styles. Pro-active learning has been promoted proposing activities which allowed students to make connections between theory and practise, both in classroom and in laboratory and using interactive quiz to allow the students to gain awareness of their comprehension level and to acquire metacognitive skills about their own learning process.

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Towards a material archive of dyestuffs from the XX century

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The preservation of material archives of substances is a relatively recent issue, relevant in the field of cultural heritage preservation.

Although since the start of large-scale industrial chemistry (first half of XIX century) many artists experimented new pigments and ligands, along XX century the use of commercially available new materials in art production reached a general diffusion, at a level that in many cases the study and the conservation of works of art have to face many problems. Most pigments, and often the totality of other ingredients, are practically unknown and/or require expensive chemical analysis, when it is not possible to find traced samples.

Something alike happens with all the textile materials present in many kinds of collections, if we think of the mind-blowing number of synthetic dyestuffs that followed the lucky intuition by William Perking in the spring of 1859.

The availability of dye material archives could also be useful for researchers involved in other fields: the synthetic dyestuffs revolution has led to exceptional advantages to the lifestyle of all mankind, but was characterised by tragic consequences for the health and the environment, still present in many places around the world. As we know, most of the early introduced substances were of high ecotoxicological concern. Having an archive of industrial grade formulates, often rich in by-products and raw materials residuals, can give an added value also to these researches.

At international level, the publicly accessible material archives of dyes and pigments are very few. This communication outlines an early feasibility stage for the creation of a new archive, or an addition to existing collections, starting from a considerable number of dyestuff samples, in their original packaging, almost all from the second half of last century.

The were "rescued" some years ago from a clean-up of old didactic warehouses of the former Istituto Nazionale di Setificio (now, ISIS Paolo Carcano), Como. Until now they have been preserved in a confined storage. Most of them are in the range 10 – 100 g.

For many of them, there is also a documentation in a large collection of bound catalogues, mostly with original dyed fabric samples.

Possible research lines could include the complete cataloguing starting from the Colour Index tracing, the chemical characterisation of some representative formulates, but also a controlled use to prepare new textile samples as references.

Further developments could include a cooperation with other schools (analogue "relics" can be still present in the storages of many other historic Istituti Tecnici) and with a large number of firms, both chemical producers and finishing factories.

The School-University joint interventions provided in the National Recovery and Resilience Plan

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The National Recovery and Resilience Plan (*Piano Nazionale di Ripresa e Resilienza*, PNRR) [1] provides for a series of interventions concerning: student orientation; initial and in-service training of teachers; strengthening of the STEM disciplines in the schools. For the realization of these actions it is necessary that the University and the School work closely together. Implementation of these measures, their monitoring and evaluation on the basis of appropriate indicators constitute a characterizing element of this Plan: it is necessary to spend well and within the established times.

The *Piano Lauree Scientifiche* (PLS), which involves all classes of scientific degrees, has been operating for 15 years on the topics previously indicated [2, 3] and in these years has created a solid network of relations between the universities and the schools. Since 2018, the University and Research Mystery (MUR) has also launched the *Piani Orientamento e Tutorato* (POT) [4] that share the same objectives of the PLS in the technological, social and humanistic disciplines. Finally, the three-year programme 2021-2023 of MUR provides for the reprocessing of national PLS and POT projects, extending the latter to all graduation classes.

The objectives set out in the PNRR can be achieved by using the network of the national PLS and POT projects and the community of colleagues that has ensured the quality of the actions and results in these projects. In addition, student orientation, in-service teacher training and strengthening of STEM disciplines are addressed in the PNRR as “separate chapters” while the experience gained in the PLS has shown that these elements are closely interconnected with each other and play a significant role in reducing drop-out and improving the careers of university students. Experience shows that these issues can and should be addressed within a common reference framework.

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Developments in chemistry education

Jan Apotheker

Chair of the Committee on Chemistry Education of IUPAC

The recent pandemic has caused a changeover from face-to-face teaching to using on line methodology in teaching. Responsibility for the learning process is shifting from teacher to student.
This changeover is simply an acceleration of a process that has started up in (chemistry) education over the past 25 years. Recent research in chemistry education, based on research on teaching and learning from the beginning of the twentieth century, indicates the need for a more individual approach of the learning process. Both Maria Montessori and Lev Vygotsky demonstrated the need for such an approach.

This changeover in chemistry education from teacher centered education to student centered education is also illustrated in the changeover in content of the chemistry curriculum. In order to solve societal problems like climate change, the energy transition, and more recently health issues connected to the covid-19 pandemic, society needs scientists and specifically chemists. Chemists are the experts in molecular processes, that are able to connect with biology as well as physics.

One of the major challenges of teaching chemistry in secondary schools is catching the interest of enough students in science and chemistry in particular. The ultimate goal will be that more students will become interested enough to take up a study in chemistry.

In order to demonstrate the fascinating world of molecules to students, the curriculum needed to change. Two things were needed in this change over. The first was demonstrating the role of chemistry and chemical research in society. The other thing needed was linking school chemistry with chemical research. The content of the curriculum in secondary schools had no relation with the chemistry at the universities. This needed to change and has been changed over the past twenty years.

Società Chimica Italiana SCI2021

ELETTROCHIMICA (ELE)

- Orals
- Posters

PEDOT doped with Sulphonated Polyarylethersulphones as electroactive material in electroanalytical applications[#]

[#]Premio di Laurea Metrohm della Divisione di Elettrochimica

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Poly(3,4-Ethylendioxythiophene) (PEDOT) is a conductive polymer formed by the polymerization of the bicyclic monomer 3,4-ethylenedioxythiophene and largely applied in the sensors, capacitors and fuel cells fields. It has high and quite stable conductivity, high optical transmittance, good biocompatibility and low toxicity. However, PEDOT is insoluble in many organic solvents and, as other conductive polymers, it presents a facile but slow interconversion between redox states.[1] To improve PEDOT conductivity different dopants has been used and in particular molecules and polymers carrying sulfonic functionalities. Herein, a new polymer, Sulphonated Polyarylethersulphones (SPAES), with different degrees of sulfonation was tested as dopant.[2]
The co-polymers are dissolved in four organic solvent and deposited onto a Glassy Carbon electrode (GC), studying physic-chemical and electrochemical properties. A strong dependence of polymers electrochemical performance and features from different properties of solvents emerged in these analyses and in studies upon their morphology, structure, and solvatochromic behavior.[3]
The combination of these proprieties and the non-toxic behavior makes PEDOT_SPAES a perfect candidate for the electroanalytical applications, also in potable water and biomedicine. Therefore, we also tested this novel conductive polymer for the quantification of inorganic and organic molecules. Pb^{2+}, ascorbic acid, caffeine, dopamine, and uric acid is detected by the best performing new polymer-solvent combination.[4] A new kind of conducting polymers with interesting sensors application and performance could be available for several research fields, such as environmental application and early disease diagnosis.

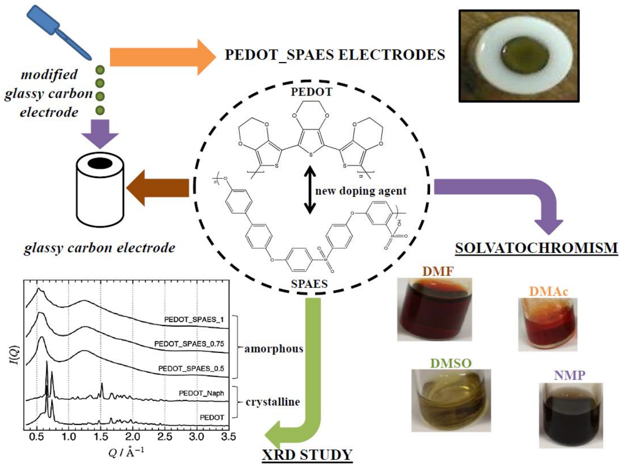

Figure 1. Scheme of physic-chemical and electrochemical analyses on PEDOT doped with SPAES.

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Graphene-based functional materials for electrochemical imaging*

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Premio di Laurea **"Anton Paar"**

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In the last years electrochemical techniques were successfully applied to imaging of several systems, having some interesting advantages as high spatio-temporal resolution, great sensitivity and chemical specificity.[1] In general, the electrochemical imaging is based on the detection of electroactive species related with morphology and functionality. Among others, scanning electrochemical microscopy (SECM) and electrochemiluminescence (ECL) are two promising techniques widely applied to the study of biological environments. In SECM an ultramicroelectrode is used to record electrochemical signals from the sample, giving information on both topography and electrochemical activity[2]. On the other hand, ECL is an analytical technique based on the detection of luminescence signals produced upon application of an electrochemical stimulus offering low backgrounds, high sensitivity ($\leq 10^{-11}$ M), good temporal and spatial resolution, robustness, and low fabrication costs.[3–5] Graphene-based nanomaterials, known for their peculiar conductivity properties, can be employed to build hybrid systems enhancing the electrochemical imaging performances.[6] Herein, we present a new synthetic strategy and material characterization studies where graphene oxide (GO) is used as a scaffold for a dual functionalization with: i) a targeting unit, specific for cell membranes and ii) $Ru(bpy)_3^{2+}$ as ECL luminophore. In our design, this system will allow anchoring the graphene-based material to the cell membrane and performing electrochemical imaging based on the two different techniques. Indeed, in SECM imaging the graphene label will act as a conductive discriminating agent between labeled and unlabeled cells, while the anchoring of the ECL probe on a conductive layer will enhance the ECL imaging performances.

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Microkinetic modeling for the electrochemical CO_2 reduction reaction in bicarbonate electrolyte

Premio di Laurea "**Photoanalytical s.r.l.**"

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Since the industrial era, human activities have been perturbating the equilibrium of the Earth atmosphere releasing great amount of CO_2 from fossil fuel combustion and agriculture. In the last decades, the electrochemical CO_2 reduction reaction (CO_2RR) has aroused great interest as a way to store the excess of renewable energy by converting CO_2 into valuable chemicals.

In this work, we developed a microkinetic model (Fig. 1) to study the CO_2RR to carbon monoxide (CO) in bicarbonate buffer. Digital simulation was carried out through numerical computation of partial differential equations for the diffusion-convective mass transport in presence of the bicarbonate equilibria, in such a way to ultimately understand how to enhance the efficiency towards CO_2RR over the competing hydrogen evolution reaction (HER). We investigated the influence of the bicarbonate acid/base reactions on the concentration profile of the species and pH, as well as the role of bicarbonate as a buffer and a possible proton donor for CO_2RR and HER. We also evaluated the effect of forced convection on the surface concentration of the species and pH. Lastly, from the simulation of linear sweep voltammetry curves for different bicarbonate buffers we showed the central role of the homogeneous reactions in determining the diffusion limiting current for CO_2RR.

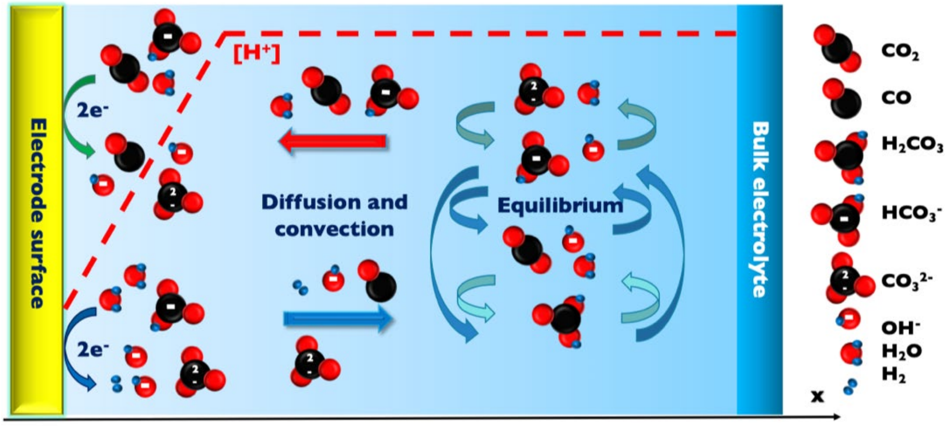

Fig. 1 Illustration of the kinetic model, which includes mass transport effects (diffusion and convection) coupled with electrochemical and homogeneous chemical reactions.

Synthesis and characterization of materials for PEM-FC, based on Pt alloyed nanoparticles supported on next generation mesoporous carbon.

Premio di Dottorato "**Fondazione Oronzio e Niccolò De Nora**"

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Proton exchange membrane fuel cell is a promising green alternative to the internal combustion engines for the automotive sector. Platinum and its alloys are the most performing catalysts for PEMFC, although they suffer from multiple drawbacks, including poisoning, durability issues which hinder the penetration into the automotive market. In recent years, huge efforts have been made in the research for improving Pt catalyst performance, which led to the development of many types of Pt alloys with Ni, Co or as Y or Gd.

My PhD was focused on the understanding the interaction between the platinum NPs and the support and how the carbon proprieties (in terms of morphology, porosity, doping, conductivity) can influence the catalytic performance of the catalysts vs. the ORR.

The metal-support interaction can, generally, affect the catalytic activity by influencing the NP shape and size, inducing strain on the NP due to lattice mismatch and changing the electronic structure via electro transfer. A method for increasing the catalyst activity and stability involves the using of carbon supports doped with heteroatoms such as nitrogen (N) or sulfur (S), Figure 1. [1,2]

A promising way to increase the performance of Pt catalysts is the preparation of bimetallic systems based on Pt as Pt_xY alloys, because the amount of Pt could be reduced while the catalytic activity and stability may be improved. Pt_xY alloy was synthetized on different carbon supports, with different surface area, porous distribution, conductivity, and surface functional groups. The idea is understanding how the support influences growth, shape of the NPs and the alloy formation. [3,4]

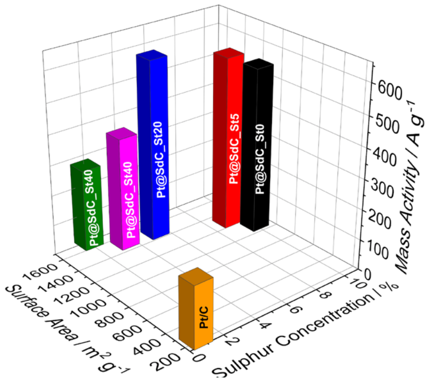

Figure 1: Hystogram Sulphur Concentration vs. Surface Area vs. Mass Activity for ORR for the Pt@Sulphur doped Carbon

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Ternary Oxide Semiconductor Photoanodes for Solar Energy Conversion

Premio di Dottorato “Fondazione Oronzio e Niccolò De Nora”

Annalisa Polo

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Solar energy conversion and storage into hydrogen is a valuable approach to capture the energy that is freely available from sunlight and to turn it into a clean fuel. Photoelectrochemical (PEC) water splitting is an established powerful technology to this aim. In my PhD thesis I focused on the development and optimization of efficient oxide-based semiconductor photoanodes for water oxidation, the kinetic bottleneck of the overall PEC water splitting process. Films of the desired materials were prepared through spin coating deposition, and their intrinsic properties as photoanodes were successfully improved by means of a comprehensive PEC study carried out in parallel with a thorough structural, morphological, and spectroscopic characterization.

Three different classes of promising ternary metal oxides, able to absorb a large portion of the solar spectrum, were investigated, namely *i)* $BiVO_4$ (E_g = 2.4 eV), known for its excellent solar light to hydrogen conversion efficiency, *ii)* the copper tungstate-based materials $CuWO_4$ (E_g = 2.3 eV) and $CuW_{(1-x)}Mo_{(x)}O_4$ (E_g = 2.0 eV), as visible-light active alternatives to wide band gap WO_3, and *iii)* $ZnFe_2O_4$ (E_g = 2.0 eV) belonging to the spinel ferrites class, possessing excellent photothermal and chemical stability.

$BiVO_4$ was employed as visible light sensitizer towards the more reductive TiO_2 in the $TiO_2/BiVO_4$ heterojunction, to produce highly reducing electrons under visible light irradiation, suitable for overall water splitting without any external bias [1]. The multifaceted role of Mo^{6+} doping onto both the bulk and surface properties of $BiVO_4$ was successfully identified in the improved bulk conductivity or interfacial charge transfer of the optimized Mo^{6+} doped photoanodes, with an enhanced photoactivity towards water oxidation with respect to pure $BiVO_4$ [2]. The fundamental issue of $CuWO_4$, consisting in a severe bulk charge recombination due to intra-gap states acting as electron traps, was revealed through an in-depth electrochemical investigation coupled with ultrafast transient absorption measurements [3], and addressed through the development of $CuW_{0.5}Mo_{0.5}O_4$ photoanodes exhibiting a greatly enhanced visible light-induced photoactivity, in addition to a significantly improved photogenerated charge carriers separation [4]. Finally, the photoelectrocatalytic activity of $ZnFe_2O_4$ photoanodes, compromised by a poor electron conductivity, was effectively improved by optimizing synthesis parameters such as the annealing temperature, the film thickness, and a post-synthesis hydrogen treatment [5–6]. The interplay between the superior film crystallinity ensured by the optimum annealing treatment at the higher temperature and the efficiency of hydrogenation, which proved effective in maximizing charge separation in the thickest photoactive layers, led to record performances in the frame of this study.

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Electroreduction of carbon dioxide by Re(I) and Mn(I) bipyridine complexes

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Global warming coupled to a severe climate change is threatening our ecosystem: amongst greenhouse gas emissions, CO_2 levels must be kept under control and Carbon Capture, Storage and Utilization must be widely implemented. The shift from a linear C-economy to a circular C-economy would be highly desirable. CO_2 is a highly stable molecule; thus, a large energy input is required for its transformation. In my PhD thesis I have been focusing on homogenous Re and Mn bipyridine electrocatalysts for CO_2 reduction, with an in-depth electrochemical investigation, aiming at a clear understanding of the pivotal role of the second coordination sphere and the different metal involved.[1-3] The transition from the homogeneous to the heterogeneous approach, which in some cases displays superior stability and durability, can find considerable support whenever the intimate molecular mechanism responsible for the catalysis is initially deeply investigated in the homogeneous phase: the Mn bipyridine complex in which the bpy ligand was modified with an aniline moiety allowed the formation of a stable C-C covalent bond with carbonaceous electrode surfaces. The C-C bond was obtained through electrochemical reduction of the corresponding diazonium salt.

A dramatic increase of TONs when passing from the homogeneous conditions ($TON_{CO} = 12$) to the catalyst heterogenized on Carbon Cloth (CC) employed as GDL (Gas Diffusion Layer) was observed. The Mn functionalized CC in a complete gas-fed electrolysis cell TON_{CO} reached more than $1.6\ 10^5$ over 16 hours of operation. Additionally, a TON_{HCOO^-} of $1.9\ 10^4$ was afforded too, witnessing the importance of the experimental setup for tuning the catalyst selectivity.[4-5]

The studies reported herein suggest that a close connection between homogeneous and heterogeneous CO_2RR electrocatalysis would be beneficial for both fields. The knowledge of traditional coordination chemistry and molecular catalysis may be extremely useful to overcome the limiting factors of the state-of-the-art heterogeneous catalysts, especially in terms of selectivity. On the contrary, approaches used in materials science and heterogeneous catalysis applied to molecular systems would contribute to extend their applicability.

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Oxygen Reduction at Platinum Group Metal-Free Fuel Cell Catalysts: Recent Progress

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The performance of platinum group metal-free (PGM-free) electrocatalysts for oxygen reduction reaction (ORR) in the polymer electrolyte fuel cell (PEFC) cathode, especially that of materials obtained via the most successful to date and thus widely used high-temperature treatment approach, has improved very significantly over the past two decades. However, the activity and durability of PGM-free catalysts continues to trail that of the incumbent precious metal-based formulations. In particular, the PGM-free catalysts typically lose 40-80% of their initial activity during the first 100 hours of operation in low-temperature fuel cells, falling way short of the 8,000-hour lifetime target established by U.S. Department of Energy (DOE) for automotive PEFCs. Consequently, significant improvements to the performance durability are required before PGM-free catalysts can be considered for practical systems.

In this presentation, we will summarize the present state of the PGM-free catalyst durability, introduce methods of assessing the catalyst performance and performance metrics, as well as summarize recent progress in the development of PGM-free catalysts at Los Alamos National Laboratory. We will introduce a novel ‘dual-zone’ approach to the high-temperature synthesis of PGM-free catalysts that has already led to very significant improvements to their durability. In H_2-air fuel cell testing, the ‘dual-zone’ catalyst has recently shown negligible performance loss during up to 80,000 voltage cycles using a standardized PGM-free durability test protocol, developed in the ElectroCat consortium, and later approved by DOE. The ‘dual-zone’ catalyst has also retained 70% of its initial activity in a 600-hour fuel cell test at a constant reference voltage of 0.70 V. While the origins of these very significant enhancements in PGM-free catalyst durability are subject to ongoing studies, we will attempt to summarize in the final part of this presentation the likely reasons for the observed benefits brought about by this novel approach.

Enantioselective Voltammetry & Chiroptical Spectroscopy: Exploring Intriguing Analogies and Connections

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UV-Vis absorption spectroscopy, involving intramolecular electron transitions triggered by light, and voltammetry, involving electrode-to/from-molecule electron transfers triggered by the electrode potential, have well known analogies and connections, and are usually exploited in sinergy for the investigation of electronic properties of advanced molecules and materials. In our recent investigations of "inherently chiral" electroactive molecules of axial stereogenicity to be exploited as chiral selectors in electroanalysis and electrochemistry, we realized that, fascinatingly, the two techniques also share many connections and analogies at a superior complexity level, adding chirality to the involved actors, *i.e.* considering *chiral* molecules interacting with the left-handed and right-handed helicoidal components of *polarized* light, (in circular dichroism CD spectroscopy) as well as *chiral* molecules undergoing electron transfer at a *chiral* electrode surface (in enantioselective voltammetry). [1]

In particular we will discuss with appropriate examples the following shared features:

(i) *Top enantioselection with inherently chiral molecules:* "inherently chiral" molecules of helical or axial stereogenicity result in top enantiodiscrimination performances both in chiroptical spectroscopy, in terms of neat differences in absorption of the above L- and D-polarized light components, [2,3] and in enantioselective voltammetry, in terms of neat differences in the electron transfer potentials for (*R*)- or (*S*)-molecular probes; [4]

(ii) *Loss of energy level degeneration for interacting chromophores/redox sites:* chiral electroactive molecules of axial stereogenicity, consisting of two equal moieties, behave as equivalent, reciprocally interacting chromophores in CD, and as equivalent, reciprocally interacting redox centres in CV, in both cases resulting in loss of degeneration of energy levels. This implies absorption wavelength difference and consequent "Davydov splitting" in the CD pattern, [3] as well as a twin peak system in the CV pattern; [1,5]

(iii) *Pseudochiral manifestations with achiral molecular probes+magnetic fields:* CD spectra can also be obtained from polarized light absorption by *achiral* molecules *in a magnetic field*, and peak potential differences have been observed on a chiral electrode for *achiral* molecules *in a magnetic field* [6]; both phenomena are modulated by the magnetic field intensity and orientation.

Support to our chiral electroanalysis research line by Fondazione Cariplo/Regione Lombardia as well as by Università degli Studi di Milano is gratefully acknowledged.

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From all-vanadium redox flow battery to next generation redox flow battery systems – how can stationary energy storage become cost-efficient

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Vanadium flow batteries are widely acknowledged as long duration storage for stationary applications. Nevertheless, a huge variety of flow battery technologies have been published in literature during the last recent years. In this talk the advantages and disadvantages of vanadium flow battery technology will be presented. The main downside are: a) high costs of the electrolyte, b) lack of reliable State of Charge (SOC)/ state of health (SOH) detection, c) proper regeneration systems to maintain state-of-health (SOH) [1]. New approaches developed by Fraunhofer ICT and partners to circumvent the downsides will be shown.

In the second part of the talk, the conventional VRFB will be contrasted with different new emerging flow battery chemistries. Examples of current research on iron-iron, hydrogen bromine and zinc slurry air batteries at Fraunhofer ICT will be presented. Each of these emerging systems has one advantage over conventional VRFB, like higher power density (H_2-Br_2-RFB) [2], higher energy density (Zn-Slurry Air RFB) [3] and better environmental sustainability (all-iron RFB) [4]. Recent findings and typical potential applications for such systems will be provided.

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New Insights Into Electrogenerated Chemiluminescence Mechanism for the Enhancement of Bioanalytical Performance

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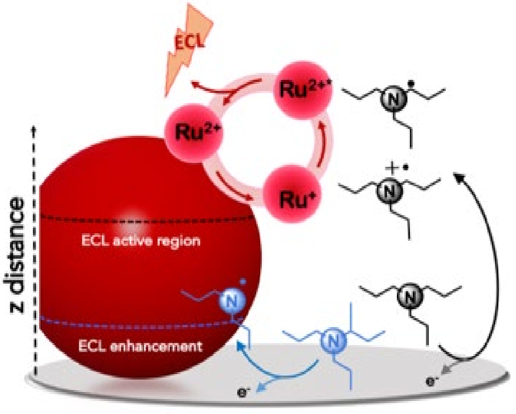
Electrochemiluminescence (ECL) is a leading technique in bioanalysis.[1] Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background. The most challenging breakthrough in the development of analytical electrochemiluminescence (ECL) applications was reported from Bard and co workers that presented for the first time the generation of ECL with a coreactant.[1] This finding opened the application of ECL to large literature and transformed ECL from an academic curiosity to a real application and industrial success. In this context, the only real used materials for the ECL analytical and commercial application are tripropylamine (TPrA) as sacrificial "oxidative-reductant" coreactant and Ruthenium(II)-tris(2,2'-bipyridine) ($[Ru(bpy)_3]^{2+}$) as emitting species. In this case the mechanism for the ECL generation was proposed by Bard and still nowadays the only one accepted.[2],[3]

Here we show an additional, and very efficient, mechanism pathway for the generation of ECL by using TPrA as coreactant. Thanks to our molecular approach and the combination between ECL and microscopy we experimentally prove the alternative mechanism with the standard $[Ru(bpy)_3]^{2+}$/TPrA system.[3],[4] These mechanistic findings allow us to propose alternative amines as coreactant enhancing the ECL signal of more than one order of magnitude. Our mechanism and the signal-enhancing effect were applied also to commercially available immunoassay analyzer demonstrating the impact of electrochemical molecular approach on electroanalytical instrumentation. The reported results, besides contributing to a better understanding of the mechanisms operating in the chemiluminescence generation, also pave the way for the development of very highly efficient ECL coreactants for ultrasensitive bioanalysis.[5],[6]



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In situ/operando X-ray absorption spectroscopy: a swiss-knife for studying (photo)electrodes

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A deep understanding of reaction mechanisms is required for the rational design of catalysts by better defining structure/activity relations. To do this, we need to picture the active site under operative conditions: local structure, oxidation state, nature of neighbouring atoms.

Operando (or *quasi*-operando) X-ray absorption spectroscopy (XAS) represents the technique-of-choice [1] and we have adopted it to study materials for fuel cells, water electrolysis, photoelectrochemicl water splitting as well as photochemical H_2 production.

This was possible after the design of new cells and the development of novel methods and experimental approaches to better fit its capabilities in (photo)electrochemistry. Among these, Fixed Energy X-Ray Absorption Voltammetry (FEXRAV) represents a novel tool for fast and easy preliminary characterization of electrodes and photoelectrodes. It consists in recording the absorption coefficient at a fixed energy while varying at will the electrode potential. Still, FEXRAV gives important information by itself and can serve as a preliminary screening of the potential window or for choosing the best experimental conditions for a better targeted XAS analysis. This led to new insights in the mechanisms of the oxygen evolution reaction [2,3].

Other time-resolved techniques will be described, including those based on energy dispersion [4], and the overview is completed by considering time-resolved studies on photoelectrodes [5,6,7].

Thanks to the intrinsic element selectivity of XAS, this technique also becomes a powerful "microscope" to selectively study specific interfaces within highly complex semiconductor/overlayer/electrolyte systems [8].

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Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide

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The electrocatalytic reduction of carbon dioxide is a promising approach for storing (excess) renewable electricity as chemicalenergy in fuels. Here, I will discuss recent advances and challenges in the understanding of electrochemical CO_2 reduction. I will summarize existing models for the initial activation of CO_2 on the electrocatalyst and their importance for understanding selectivity. Carbon–carbon bond formation is also a key mechanistic step in CO_2 electroreduction to high-density and high-value fuels. I will show that both the initial CO_2 activation and C–C bond formation are influenced by an intricate interplay between surface structure (both on the nano- and on the mesoscale), electrolyte effects (pH, buffer strength, ion effects) and mass transport conditions. This complex interplay is currently still far from being completely understood.

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Electrochemical surface treatments to improve corrosion resistance of light alloys

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Light metals and light alloys have low density and high strength-to-weight ratios. They are generally characterized by low toxicity in comparison to heavy metals and include aluminium, magnesium and titanium alloys. Light metals and alloys can form native oxide films on their surfaces that offer only limited protection to corrosion, thus it is often necessary to carry out surface treatments aimed to improve their resistance in aggressive environments.

Anodizing and hard anodizing are among the most used surface treatments to enhance the corrosion resistance of light metal alloys. They are both electrochemical processes that allow the growth of an oxide layer on the surface of metals, whose compositional and morphological features greatly depend on the process operating conditions, such as applied voltage/current density, electrolyte temperature and composition. Anodic oxide can be further functionalized for tailoring the physico-chemical properties of the material in view of the target application.

In this work we discuss the effect on corrosion resistance of oxides layers grown by anodizing or hard anodizing of three selected light metal alloys, i.e. AA5083 aluminium alloy used for ship building, AZ31 magnesium alloy proposed for the fabrication of biodegradable implants, and Ti-6Al-4V alloys for orthopaedic implants.

Anodizing of AA5083 alloy was carried out in a tartaric and sulfuric acid solution at 37°C. Corrosion resistance was investigated by corrosion potential measurements and by Electrochemical Impedance Spectroscopy (EIS) in 3.5% NaCl aqueous solution soon after anodizing as well as after the electrodeposition of a superhydrophobic layer on top of the anodic oxide grown to reduce the contact time between the material and the aggressive environment.

Anodizing of AZ31 was carried out in a hot glycerol based electrolyte with the aim to influence the Pilling Bedworth ratio of the anodic layer and thus its adhesion to the alloy beneath. Corrosion resistance was investigated in simulated body fluid at 37°C by corrosion potential measurements and by EIS. Accurate evaluation of the hydrogen evolution was obtained by a method based on the measurement of the hydrostatic force resulting from the accumulation of hydrogen in a submerged container. In vitro studies were carried out to evaluate the cytocompatibility of the anodized AZ31 samples.

Cast and additive manufactured Ti-6Al-4V alloys were anodized in calcium acetate glycerophosphate aqueous solution to induce the growth of a porous oxide layer suitable to favour the formation of hydroxyapatite and thus to improve osteointegration. The anodizing process was optimized taking into account the different microstructure of alloy as a function of the production process. Corrosion resistance was investigated in simulated body fluid at 37°C by corrosion potential measurements and by EIS.

NiO/ZrO2 nanocomposites as photocathodes of tandem DSCs with higher photoconversion efficiency with respect to parent single-photoelectrode p-DSCs

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The nanocomposites of nickel oxide (NiO) and zirconia (ZrO_2) (NZNCs)[1] are particularly effective photocathodic materials in p-type dye-sensitized solar cells (p-DSCs) and tandem DSCs (t-DSCs).[2] The t-DSCs obtained from P1-sensitized NZNC as photocathode and nanostructured titania (TiO2) sensitized with squaraine VG10-C8 as photoanode display overall efficiencies of ca. 2 % at their best and, more importantly, produced photocurrents that surpassed systematically the values obtained from the parent devices having one photoelectrochemical interface. Such a finding is a consequence of the diminished resistance of the electrolyte the thickness of which is systematically smaller in t-DSCs with respect to parent DSCs with a single photoelectrochemical junction and same interelectrodic separation. The results here reported demonstrate that a careful combination of photoelectroactive electrodes can lead to an increase in current density of more than 15% in the t-DSC with respect to single-junction DSCs employing the same photoelectrodes provided that the whole thickness of the t-DSC is the same as in the single photoelectrode DSC and the photoelectrodes in the t-DSC do not incur in short-circuit phenomena through the electrolyte. For the successful realization of t-DSCs another important aspect is the complementarity of the absorption properties of the chosen colorants with the sensitized electrodes having similar absorbance in their respective ranges of optical absorption.[3] The latter condition in t-DSCs makes possible the achievement of photoactivity spectra with a uniform efficiency of conversion in the whole visible range. For the attainment of efficient t-DSCs the two different photoelectrodes from parent DSCs (i.e. the devices at a single photoeletrochemical interface), should generate anodic and cathodic photocurrent densities with very similar values. Such a matching of photocurrents requires a careful selection of the thickness values for the photoelectrodes especially in case of materials with considerably different characteristics of charge injection. The approach here considered is a promising one for the assembly of quasi-transparent photoelectrochemical tandem devices operating as smart windows that convert light into electrical power. [4]

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Cancer Metabolic Profile Detected by Scanning ElectroChemical Microscopy

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Metabolic alterations characterize cancer; nevertheless, how these alterations track or even contribute to disease progression is still an open issue. Metabolic activity can be highly dynamic over time and spatially very heterogeneous. The majority of oncogenic signaling pathways converge to adapt cancer cell metabolism to sustain the energetic and biosynthetic demands of uncontrolled cell proliferation. The real time and in situ imaging of small molecules and metabolites, such as glucose and lactate, is a real challenge as these molecules are too small to be tagged without altering their functioning in the cell.

Early breakthrough in the identification of the roles of key molecular players were only possible thanks to innovative experimental technologies. In this contribution the potentiality of Scanning Electrochemical Microscopy (SECM) to provide information about the cancer metabolism will be shown. SECM can be used to map in real-time the local concentration and time evolution of key player molecules in close proximity of cell membranes. [1-4]

We demonstrated that the scanning electrochemical approach is a highly informative tool in the cancer related bio-analytical challenge. Cell functional imaging allows identifying cancer cells and helps to elucidate mechanisms of cancer initiation and progression.

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Solvent-supporting electrolyte system in electrolysis: not only chemical environment and charge carrier

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When carrying out an organic reaction, the choice of the solvent is mainly affected by its polarity, boiling point, density, etc. (*i.e.*, by physical properties), along with its solubilizing ability. Likewise when carrying out an electrolysis in electro-organic synthesis, with the addition of the ability as charge carrier. In other words, the main task entrusted to the solvent-supporting electrolyte system is to be a suitable chemical environment and ensure the conductivity of the solution.

Nonetheless, in some cases the solvent-supporting electrolyte system is the real actor, being the salt (anion and/or cation) the electroactive species. And this is true in "classical" organic solvent-supporting electrolyte solution as well as in the more recently exploited ionic liquids.

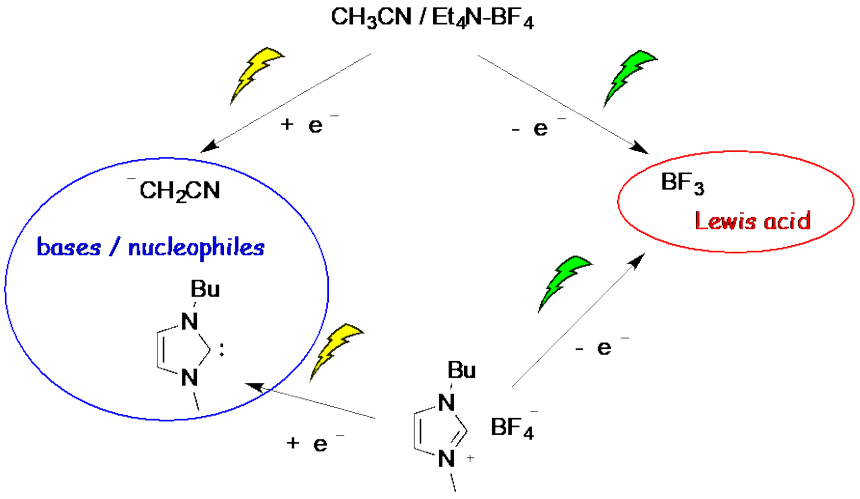
The cathodic reduction of a tetraalkylammonium cation leads to the formation of a very strong base (probably an alkyl anion) which immediately deprotonates the solvent, yielding the corresponding anion. When the solvent is acetonitrile, the cyanomethyl anion is formed (but also the anions of DMF, DMSO, EtCN and $MeNO_2$ can be obtained using this methodology).

On the other hand, when an imidazolium ionic liquid acts as both solvent and supporting electrolyte, the corresponding N-heterocyclic carbene (NHC) is produced at the cathode.

Both species (cyanomethyl anion and NHC) can act as bases and/or nucleophiles and the competition between these two reactivities relies on both the chemical environment (*i.e.*, the parent system) and the reaction partners.

On the other side, the anion of the supporting electrolyte is usually the electroactive species at the anode. As an example, when using a tetrafluoroborate salt, the tetrafluoroborate anion is oxidized to fluorine and boron trifluoride, which is a Lewis acid and as such behaves.

In this communication, an overview of the results obtained in LEOS* (Sapienza University) using such electrogenerated species will be reported.



* LEOS: Laboratory of Electrochemistry & Organic Synthesis.

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Design of Aerogel-based Electrocatalysts for ORR

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In the past couple of decades great advancements have been made in the development of PGM-free catalysts based on earth-abundant elements, nitrogen, carbon and transition metals (usually Fe or Co), inspired by biological systems such as porphyrins and phthalocyanines.[1-6] In order to overcome the poor stability and low catalytic activity of transition-metal complexes, a new class of high temperature-treated (HT-treated) catalysts, composed of the same elements, i.e., a transition metal, carbon and nitrogen, was developed. Although HT-treated PGM-free catalysts exhibit improved activity and stability, their performance remains inferior to PGM catalysts, calling for further improvements to make them a viable alternative to the state-of-the-art materials.

In this work, we designed, synthesized and characterized ORR catalysts based on iron, carbon and nitrogen in a well-defined, high surface-area covalent framework (COF) of aerogels. Aerogels are ultralight, porous materials, with ultra-low density and high void volume (> 97%), also known for their unique physicochemical properties such as high porosity, controllable pore size and surface area, low thermal conductivity, just to name a few.[7] The variety of precursors used for aerogel synthesis makes them promising candidates for a wide range of applications in catalysts, capacitors, insulators, absorbents, and many more.[8-9] In the context of electrocatalysis of fuel cell reactions, carbon-aerogels have been mostly used so far as catalyst supports for PGM and PGM-free catalysts.[10-11]

In their inorganic form, aerogels can have ultra-high catalytic site density, high surface area, and tunable physical and chemical structures – all very important features for a heterogeneous catalyst. In this talk, we will discuss the synthesis and electrocatalytic properties of an iron-porphyrin aerogel. 5,10,15,20-(tetra-4-aminophenyl)porphyrin (H2TAPP) and Fe(II) were used as the building blocks of the aerogel, which was later heat-treated at 600 °C to enhance electronic conductivity and catalytic activity while preserving its macro-structure. The resulting material has a very high concentration of atomically dispersed catalytic sites ($4.01 \cdot 10^{19}$ sites cm^{-3}), capable of catalyzing the oxygen reduction reaction in alkaline solution (Eonset = 0.93 V vs. RHE, TOF = 0.2 e^{-} $site^{-1}$ s^{-1} at 0.8 V vs. RHE). At the end of the talk I will also show some of our recent results with other types of aerogels, some for different applications.

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Heterogeneous functional materials for post-Li energy storage devices, new insights and design principles from quantum chemistry

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Energy storage technologies for current and foreseeable applications must rely on widespread and sustainable resources, with a particular attention on performances and safety issues [1]. The grand challenge is to control at the atomic level all the physico-chemical and electrochemical features at play. The objective is an effective implementation of a new paradigm of materials development based on solid scientific knowledge. To this end, first-principles modelling can provide an in-depth understanding of battery working mechanisms by offering an unbiased atomistic perspective on structure, stability and electron/ion transport. In this context, we present here our latest results on electrode systems, with a special focus on the outlined design strategies that can encourage the effective development of high-performing devices, including Li-ion, Na-ion and Li-air batteries. On the anode side, we address the capability of TiO_2 nanoelectrodes toward the reversible Na^+ uptake and storage and dissect the origin of Na^+ insertion activity at anatase nanocrystal facets [2-4]. Structural interfacial features are also shown to be key in determining migration efficiency in MoS_2/Graphene heterostructure [5]. DFT-based investigations on high-energy cathodes allows to unveil key features in their electrochemical behavior, such as the role of antisite defects in the capacity loss of $LiTMPO_4$ (TM = Co, Fe, Mn) [6] and the anionic redox activity in P2-type $Na_xNi_{0.25}Mn_{0.68}O_2$ layered oxide [7]. We also show the need of more accurate theoretical tools (within post-HF methods) for the detailed description of chemical processes involving highly correlated systems, such as the reversible formation of Li_2O_2 and the singlet O_2 release occurring along the Li-air battery functioning. All these results provide a new perspective on how materials design can be driven by theoretical tools, overcoming old trial-and-error approaches, and it is now essential to speed up the large-scale exploitation of advanced technology beyond lithium.

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Fast but not so fast: can we improve intercalation in cathode materials for rechargeable batteries?

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Energy storage technologies, in particular rechargeable batteries, are already widely used in portable electronic devices and are predicted to increase their importance in the electric vehicle sector and as storage technology for the integration of renewable intermittent energy resources in the grid. Enabling the partial diversification of energy storage's chemistries from the technology of choice for portable applications, *i.e.* Li-ion batteries (LIBs), allows to meet important targets in terms of cost and resource exploitations, environmental sustainability and safety. It is for this reason that research in the field of Na-ion batteries as well as multivalent ion batteries, such as those based on Mg^{2+}, Ca^{2+} and Zn^{2+}, is growing in importance together with the continuous efforts to improve LIBs performances.

Computational modeling has a key role in predicting and understanding material properties and atomistic modeling techniques offer important possibilities in the investigation of materials for batteries applications. The optimization of the intercalation behavior of ions in a particular structure is of great importance in the development of cathodes materials for rechargeable batteries. This can be achieved through the comprehension of the relationship between the materials' structural and defect properties at the basis of their intercalation mechanism, with the idea that computational modeling results can guide materials syntheses.

Over the last years, we have applied a range of computational modeling techniques (mainly static lattice energy minimization, classic molecular dynamics) to the investigation of cathode materials for rechargeable batteries. In this contribution we present an overview of the results obtained for representative classes of cathode materials for rechargeable batteries, including olivine-type $LiFePO_4$, spinel-type $ZnCo_2O_4$ and the tunnel oxide $Na_{0.44}MnO_2$. The computational results are discussed in comparison to experimental evidences, whenever available.

Recent progress in electrode materials for next generation sodium ion batteries

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The path to a more sustainable society requires urgent action to combat climate change and its consequences. To meet the goal people are turning to renewable energies and other solutions that favor the reduction of greenhouse gas emission. Still, this global challenge requires the development of energy storage systems that facilitate the progress towards a low-carbon economy by complementing renewables and reducing the impact of intermittent generation. In this scenario, sodium ion batteries (NIBs) may be the key that opens the door to a more energy-sustainable future.[1,2] NIBs are based on the chemistry of sodium, which is more abundant and cheaper than lithium, they are Co and Ni free, and they are also more stable and safer than their lithium analogues, which overall makes them a more eco-friendly choice. Through the correct selection and optimization of materials, accompanied by the manufacture and integration of the components in the different cell configurations, it will be possible to exploit the full potential of this technology.[3]

In this talk, an overview of the state of the art of this technology will be given in order to decipher the recipes that lead to the design of the most efficient electrodes. The materials used in the electrodes are key components of NIBs, as their nature will establish the battery performance. Regarding cathode materials, the pros and cons of the most used compounds will be presented, with special emphasis on polyanionic systems, Prussian Blue analogs and the family of layered oxides.[1,4] Regarding the anodic side, carbon-based compounds remain as the most promise materials, although in recent years there has been a growing interest in the use of phosphorus as active material in the negative electrode.[5-7] Finally, research directions leading to the prediction and design of highly functional and durable electrodes will be proposed to enable the development of the next generation NIBs.

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Electrochemically responsive soft actuators.

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The emulation of human skeletal muscles has brought to the idea of actuators and several materials have been studied so far, with different contractile mechanism [1, 2]. Ionic electroactive polymers contain ions inside the polymer chain that migrate along the structure under the application of a low voltage (few volts). The applied voltage enables the formation of two double layers near the electrodes and, in turn the bending of the actuator [3]. Also, the dielectric electroactive polymer acts as a capacitor in which the dielectric elastomer is placed between two compliant electrodes, and the application of high voltage modifies the geometry of the actuator [4]. Electronically conducting polymers insert/deinsert counter ions upon the faradaic doping/undoping reactions occurring at low voltage, and the polymer undergoes reversible bending [5]. The idea of a linear actuation is fascinating, especially if it can be performed electrochemically at low voltage. To this aim, the introduction of molecular machine in polymeric nanofibers through electrospinning has been envisioned [6]. Electrospinning is a suitable technique to produce bundles of fibers, with hierarchical structure, resembling the skeletal muscle myofibrils and myofibers [7, 8]. In this work, we present and discuss electrochemical results by using model molecules of molecular machines with the same redox couple. The purpose is to demonstrate that it is possible to electrochemically stimulate the active molecule inside the polymer fibers, thus opening a new scenario in electrochemically responsive soft actuators.

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NiFe oxide co-catalyst for an enhanced water splitting in photo-electrochemical cells

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Photoelectrochemical splitting of water was widely investigated in the last decades, in order to obtain "green" H_2 as energy vector. Hydrogen is evolved at the cathode, and O_2 at the anode of the photoelectrochemical (PEC) cell, by converting renewable resources from nature, such as sun light and water, which are abundant almost everywhere in the earth.

For a large-scale commercialization of these devices, the main drawbacks of this technology, which need to be overcome, could be summarized in the following points: expensive electrode materials and components, difficulty of separating pure H_2 from the output stream, too low solar to hydrogen (STH) efficiency and the use of corrosive electrolytes limiting the durability of the PEC.

In this study, an innovative concept of tandem cell architecture [1, 2] using a transparent polymer electrolyte membrane is further implemented compared to our previous studies by introducing a co-catalyst for the anode based on earth abundant metal oxide semiconductors.

This tandem PEC cell is able to capture a significant portion of the solar energy. The photoanode (PA), based on Fe_2O_3, directly exposed to the solar irradiation absorbs higher energy photons according to its energy gap of 2.1 eV, whereas the underlying CuO photocathode (PC), exposed to the light transmitted or diffused through the transparent polymer electrolyte membrane, absorbs lower energy photons (band gap of 1.2 eV). Herein, a Ni-Fe oxide co-catalyst was deposited over a phosphorus-modified Fe_2O_3 (hematite) photoanode and annealed at 450 °C. Ni-Fe oxide-based PEC cell was compared with various co-catalysts including $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ and IrRuOx [3]. The loading of NiFeOx was optimized to maximise conversion efficiency. It appears that NiFeOx deposition on hematite at a suitable mass loading (12 $\mu g\ cm^{-2}$) enhances the efficiency of a PEC based on Fe_2O_3 and CuO semiconductors containing a membrane separator.

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Synthesis and water dispersion of nickel-iron layered double hydroxides for energy storage applications

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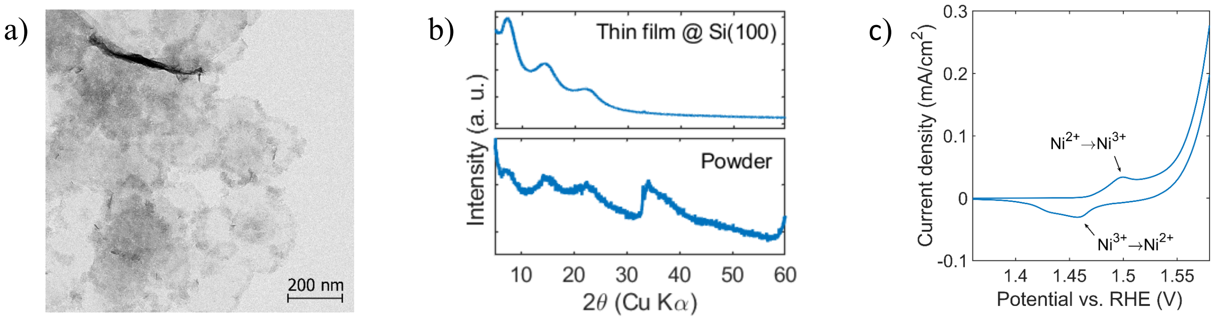
Layered double hydroxides (LDHs) are a class of anionic clays consisting of positive charged brucite-like layers spaced by water molecules and counterbalancing anions [1]. In particular, LDHs based on the first row of transition metals have recently drawn attention due to their (electro)photocatalytic properties [2]. Contrarily to other layered materials (graphene, boron nitride, TMDs, MXenes, …) [3], LDH layers are held together by both: the electrostatic forces between layers and anions amid them, and a dense network of hydrogen bonds that involves interlayered water molecules and hydroxyl terminations on layer surfaces [1]. For these reasons, an optimal solvent/surfactant mixture, suitable for LDH exfoliation, should be capable to break hydrogen bonds and weaken electrostatic interactions between ions (*i.e.*, solvents with high dielectric constant). Nowadays, formamide is the most used and effective solvent to achieve the exfoliation of LDHs [2]. However, since formamide has toxicity issues and a high boiling temperature (210°C), other solvents (water or alcohols) are recommended to exfoliate LDHs [2]. In our work, we report that citrate intercalated nickel-iron layered double hydroxide (NiFe-LDH), which are synthesized by carefully tuning the solution pH, spontaneously exfoliate when placed in contact with distilled water or ethanol. The formation of single-layer nanosheets is confirmed by X-ray diffraction and atomic force microscopy analysis. Lastly, NiFe-LDH are showing promising performances as cathode material for asymmetrical supercapacitors and as electrocatalyst for the oxygen evolution reaction.



Figures. a) Transmission electron microscopy image of NiFe-LDH nanosheets. b) X-ray diffraction profiles of NiFe-LDH thin film and powder. c) Cyclic voltammetry profile of NiFe-LDH@graphite paper.

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Anodic Dimerization of New Donor-Acceptor Oligothiophenes: Electrochemical and Solvatochromic Behavior

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The term Organic Electronics is used to indicate the vast field regarding the use of organic materials (either "small" molecules, oligomers or polymers) in electronic devices. Oligothiophenes (OTs) are among the most studied organic semiconductors. Their well-defined structures allow to investigate more accurately several physico-chemical properties such as optical absorption and emission, charge transport, electrochemical behavior and so on. The design of push-pull systems, resulting from the combination of electron rich and electron deficient moieties, enables to simultaneously optimize all parameters. However, the syntheses of OTs are often characterized by a high number of reaction steps, impacting negatively on the final product overall yield. In addition, toxic organometallic compounds based on nickel and tin are often used for some necessary reaction steps, such as Stille and Kumada reactions.[1] In this research project we performed electrochemical studies on donor-acceptor (D-A) OTs in order to shortening their classical synthetic routes. The obtained results gave us the possibility to develop a new synthetic strategy including anodic dimerization of small D-A OTs to longer A-D-A ones with an approach more environmentally friendly.[2] Moreover, we investigated the solvatochromic behavior of OTs, obtained from chemical and mixed chemical/electrochemical syntheses.

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Long life lithium metal batteries employing dendrite-eating nanocomposite solid-state electrolytes based on hybrid fillers.

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The need for energy storage devices able to deliver higher amounts of specific capacity and energy densities has recently renewed the interest towards lithium metal batteries (LMBs), i.e. secondary batteries employing metallic lithium as anodic material. However, despite the incredible theoretical performances of lithium anode as an incredibly negative working potential and a specific capacity ten times higher than graphite, the implementation of these systems is currently hindered by many detrimental issues such as the uncontrolled growth of Li dendrites on the anodic surface [1]. Among all the possibilities that can be exploited to tackle this specific problem, the use of mechanically strong solid-state electrolytes (SSEs) is particularly showing its good effectiveness. Consequently, dispersing strengthening ceramic fillers into a soft polymeric matrix, otherwise prone to dendrite piercing, can hinder dendrite growth and enable stable cycling into LMBs [2]. Anyway, the addition of high amount of inorganic particles into a polymer usually results in strong aggregation and low homogeneity of the final product while reduced loading of ceramic are not able to effectively prevent dendrite penetration. Therefore, different strategies have to be tailored to improve the compatibility between these two phases.

Following an approach already successfully exploited for titania [3], we anchored short chains of poly ethyleneglycol (PEG) with different molecular weight on the surface of porous silica nanoparticles (NPs) exploiting (3-aminopropyl)triethoxysilane (APTES) as intermediate grafting agent. These hybrid fillers were then dispersed into high-M_w polyethylene oxide (PEO) in order to produce nanocomposite SSEs with ceramic loading up to 23% with a satisfying ionic conductivity and very high homogeneity endowed by the presence of the grafted PEG. Such electrolytes were able to sustain over 350 hours of continuous stripping-plating, tens of times more that pure polymeric membranes, in Li/Li symmetric cells both due to their increased mechanical toughness and to the ability of silica fillers to react with lithium dendrites, that also enabled some of these cells to autonomously restart their operation after short-circuit. Such dendrite-eating phenomenon of silica has been already reported for coated separators soaked in liquid electrolytes [4] but this is the first time that a similar behaviour is observed for all solid-state devices, also enabled by the high superficial area of our porous NPs. Additionally, implementing this electrolyte into Li/LFP full cells permitted the stable cycling at 70°C for over 50 cycles of lithium metal anodes and the delivery of discharge specific capacity values up to 156 mAh g^{-1}, with better results than liquid electrolyte analogue.

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A complex electrochemistry triggering the operation of Vanadium Redox Flow Batteries

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The latest advancements in Vanadium Redox Flow Battery (VRFB) technology claim that performance degradation can be mainly ascribed to the high crossover of the electrolyte species through the Ion Exchange Membrane (IEM) separating the anode and cathode compartments [1]. In this work, we explored with a comprehensive modelling study how the possible solution equilibria and redox-active vanadium species complexes into a VRFB are established, and their influence on both the cell voltage and the self-discharge. This analysis reveals previously unforeseen pathways for performance degradation in the VRFB involving parasitic processes taking place at the electrodes. The results of the model indicate that, in Open Circuit Voltage (OCV) conditions, the VOH^{2+}/V^{2+} and $H_2VO_4^-/VO^{2+}$ redox couples contribute negatively to capacity retention. Furthermore, upon charging, the parasitic processes involving the VOH^{2+}/V^{2+} and $H_2VO_4^-/VO^{2+}$ redox couples lower the total kinetic current by up to 22% and 4.7%, respectively. Thus, in accordance with the model described herein, these latter pathways give rise to non-negligible performance losses due to electrode processes, that are completely unrelated to the most commonly assumed sources of VRFB performance loss (*i.e.,* the crossover of electroactive species through the separator). In conclusion, it is demonstrated that the approach outlined herein could open the door for a completely new way of studying the performance losses taking place in a redox flow battery (RFB) as related to its specific chemistry.

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A spectroelectrochemical study of copper chloro-complexes for high performance copper redox flow batteries

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In order to satisfy the different needs of an increasingly electric-based society, Redox Flow Batteries (RFB) are promising candidates for large energy scale application due to the dependency of the energy storage capacity from the volume and the concentration of the electrolytes used [1].

The three different oxidation states of copper (Cu(0), Cu(I) and Cu(II)) can be used in aqueous RFB taking advantage of complexing agents to stabilize the Cu(I) [2]. In chloride-rich aqueous solution, both Cu(I) and Cu(II) are present as chloro-complexes. Cu(II) shows at least five species ($CuCl_n^{(2-n)}$ with $0 \leq n \leq 4$); while Cu(I) exhibit mainly four complexes ($CuCl_n^{(1-n)}$ with $0 \leq n \leq 3$). The equilibria involving these complexes strongly depends on the concentration of copper and chloride with respect to the solvent. Hence, the copper chloro-complexes distribution, determines the thermodynamics and the kinetics of the electrochemical reaction [3-5].

In this work, we pursue a deeper study of the stability of the copper chloro-complexes in real solutions. Different supporting electrolytes influence the copper chloro-complexes stability. UV-Vis spectroscopy tests on copper electrolytes combined with electrochemical techniques give information on the electrochemical behaviour of electrolytes with different chloro-complexes distribution. The impact on electrochemical performances of different supporting electrolytes was studied for the employment in CuRFB's positive half-cell.

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Acknowledgements

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Ferrocene and viologen derivatives as electrolytes for pH neutral aqueous organic redox flow batteries

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Recently aqueous organic redox flow batteries (AORFBs) have attracted increasing interest because water soluble organic molecules combine the advantages of low price and environment friendliness of water with versatility of organic species. However, the widespread diffusion of AORFBs is still hindered by the need of identifying suitable redox couples to achieve high performance, in terms of delivered electrical power, stored energy, and stability.
In this work we synthesized 1,1'-disulphonic ferrocene disodium saltand the bis(3-trimethylammonio)propyl viologen tetrachlori for application as catholyte and anolyte, respectively, for a AORFBs operating at neutral pH.
Ferrocenes consist in two cyclopentadienyl rings bound on opposite sides of a central iron atom.[1] This type of complexes have good stability and high electrochemical reaction rates, but their solubility and stability in aqueous solvents are quite low. To solve this, ferrocenes have been modified by addition of polar groups on the cyclopentadienyl ring to enhance water solubility and avoid degradation[2], obtaining 1,1'-disulphonic ferrocene disodium salt (DS-Fc).
Moreover 4,4'-bipyridinium ions, also called as viologens, are highly soluble in water and possess great redox activity in aqueous solutions. Viologens exist in three oxidation states, Vi^{2+} ↔ Vi^{+*} ↔ Vi^{0}, where the first reduction step is highly reversible, while the second reduction is irreversible. The irreversibility of the second reduction results in the complete inactivation of the viologen based electrolyte.[3] To fix this problem, alkylation of the viologen can avoid the second reduction step and therefore, the inactivation of the electrolyte. The alkylated viologen synthesized in this work was the bis(3-trimethylammonio)propyl viologen tetrachloride (BTMAP-Vi).
DS-Fc and BTMAP-Vi were characterized by cyclic voltammetry (CV) (Figure 1) and linear sweep voltammetry (LSV) in neutral electrolyte. Diffusion coefficients were determined by the Koutecky-Levich theory, obtaining $2.11\cdot10^{-6}$ cm^2/s for BTMAP-Vi and $2.8\cdot10^{-6}$ cm^2/s for DS-Fc. Furthermore, the redox flow cell assembled with DS-Fc and BTMAP-Vi, as catholyte and anolyte respectively, achieved a open circuit voltage of 1.15V and a theoretical capacity of 26.8 Ah/L with 1M electrolyte concentration.

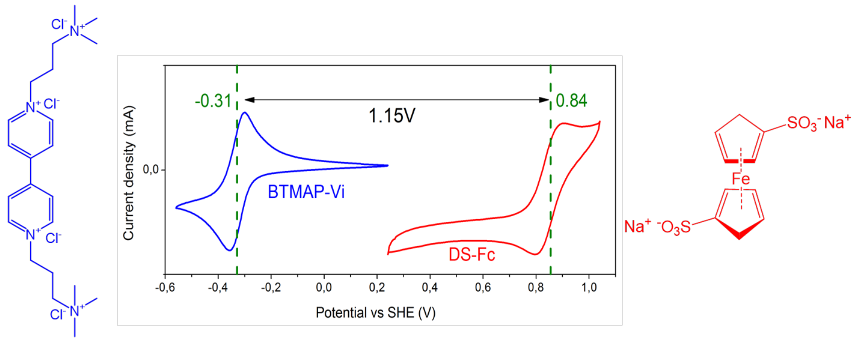

Figure 1. Cyclic voltammograms of DS-Fc (red trace) and BTMAP-Vi (blue trace) in aqueous solution 2mM with $NaNO_3$ 0.5M as electrolyte support, cycled at a scan rate of 10 mV/s.

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SpectroElectrochemistry of Metal Nanoclusters: new insights into the origin of the photoluminescence

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Atomically precise thiolate-protected metal nanoclusters (NCs), with metallic (Au, Ag, etc.) core of less than 2 nm and tailored capping monolayer, are emerging as ideal candidates to introduce controlled features useful in applications such as catalysis, energy conversion and nanomedicine.[1] In particular, insights into the NC composition-structure-properties relationship have recently highlighted vast opportunity for the design of systems with tunable proprieties, as each atom counts in defining new structures and functionalities.[2] It is worth noting that, whereas the electronic and structural properties of most NCs are well understood, the origin of the peculiar near-infrared photoluminescence (PL) of these ultrasmall NCs remains an open question.[3] Intraband and interband transitions, surface or 'semi-ring' states, or ligand-metal charge transfer states have been indeed alternately assigned to justify the mechanism of the NCs emission. [4]

In this framework, we describe *in situ* absorption and photoluminescence spectroelectrochemical analysis of gold [$Au_{25}(SPh)_{18}$] and metal-doped NCs [$Au_{24}Cd(SPh)_{18}$] as straightforward method to shed light on the dependence of the optical properties of the NCs on their electronic charges [i.e. (+1), (0), (-1)], thereby giving an important contribution to resolve the physical origins of the NCs emission. In particular, a remarkable red shift of the emission band has been observed upon the electrochemical reduction of gold NPs suggesting a larger perturbation of their excited states than upon oxidation.[5] Our experimental results, also supported by X-Ray analysis and theoretical investigation of NCs electron and nuclear dynamic, highlight how the coupling of the electrochemical and optical investigations is essential to fully exploit the unique properties of the NCs and to design novel structures with enhanced optical properties.

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How Decisive is the Iron Precursor Ligand in Fe-N-C Single-Site Formation and Activity for Oxygen Reduction Reaction?

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Iron-nitrogen-doped carbon materials (Fe/N/C) have emerged as one of the best non-PGM alterative to Pt/C catalysts for the electrochemical reduction of oxygen (ORR). A lot of different iron and nitrogen precursors and porous carbonaceous supports have been studied, but the type of the active sites in these catalysts and the correlation between site formation and carbon morphology are still not well understood. Specific surface area and porous structure of the support (micro-, meso- and macropore ratio) are fundamental for functionalization, namely nitrogen and iron fixation and not less important for the transport of reactant and product [1]. Another aspect is the structure of metal source, which may induce different catalytic activity due to different affinity to form Fe-N_x sites or due to carbonification of organic part of precursor, which could lead to pore occlusion. BET analysis could help regarding this aspect. One easy and wildly used approach to synthetize those material is by pyrolysis of metal salt and nitrogen precursors or metal complexes containing iron with carbon at high temperature. Aminic ligand has been seldom explored in literature with worst result compare with heterocyclic organic compound ligand [2], like 1,10-phenantroline (*phen*) or 2,2-bipyridyl (*bpy*), which are the most common choice because the aromatic nature that could help to form N-doped carbon. We considered also other ligand containing pyridinic group, like TPMA or BPMA and imidazole that has a different cyclic structure and which are rarely used in literature [2]. In addition, different complexes with different ligand (*phen* or *bpy*)/metal ratio have been considered.

RRDE technique in 0.5 M H_2SO_4 shows that 1,10-phenantroline is the best precursor for high activity (figure 1) with the 3:1 and 1:1 ligand:metal ratio, while with 2:1 we observe the worst activity, in this case probably due to the nature of counterion (SCN^-). Also SD of each catalyst was obtained via NO_2 stripping to understand the ability of each complexes to form Fe-N_x sites and comparing that with activity. Surprisingly in alkaline environment the worst catalyst became one of the best (figure 1) suggesting that the role of Fe-N functionalities is less determinant in catalyze the reaction, in contrast peroxide production grows suggesting a mixed 4/2x2 electron reduction pathway.

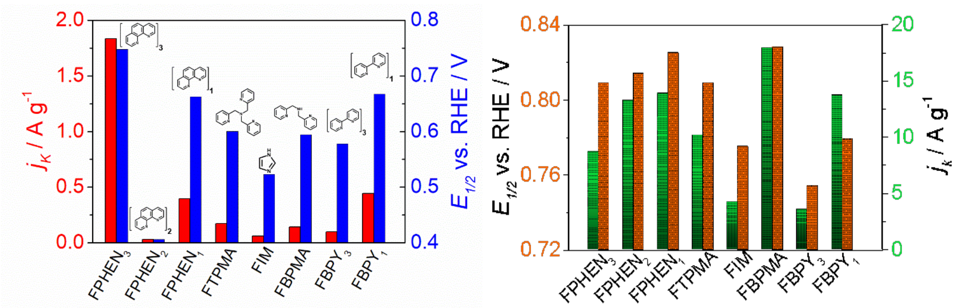

Figure 1: Ligand and activity in term of kinetic current at 0.8 V_{RHE} and half-wave potential in acid (left) and alkaline (right) media

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Water Loss Predictive Tests in Flooded Lead-Acid Batteries

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A recent study on the *European Union Battery Demand and Supply,* shows that in the next decade both lead and lithium batteries are critical to clean energy transition. Specifically, the Lead Acid battery (LAB) industry will maintain a strong position in European Union and it will be able to meet projected growth, but ongoing investments in R&D and production enhancement are required. Water loss and corrosion of the positive plate grid represent two of the main aging processes in LAB are strictly interdependence.[1] To date, the most widely used industrial method to determine the water consumption in LAB is the weight loss test, however this method poses significant experimental difficulties, both in obtaining sufficient gravimetric sensitivity and in being assured that the weight loss was due solely to hydrogen and not a combination of gases, including water vapor itself.[2] Alternative ways to characterize the water consumption exploit the detection and analysis of gas vented from the batteries with a pressure sensor[3] or with a Gas-Chromatography system;[4] while effects of impurities and additives on the kinetics of oxygen evolution reaction and hydrogen evolution reaction are relieved with electrochemical analysis (linear and cyclic voltammetry) on a single positive or negative LAB plate, respectively.[5]

Despite the large number of studies concerning water consumption, there are no studies in the literature that combines the information deducible from voltammetric techniques, with the determination of gassing rates in floating overcharging tests. Therefore, the purpose of this study is the definition of a measurement set-up which allows the comparison between the kinetics parameters deducible by voltammetry tests, with the gas rates quantification collected at increasing floating overcharging currents. The effectiveness of the experimental set-up is verified through the measures of nine sample plates originated from nine different production batches.

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Electron Transfers in Films of Atomically Precise Metal Nanoclusters

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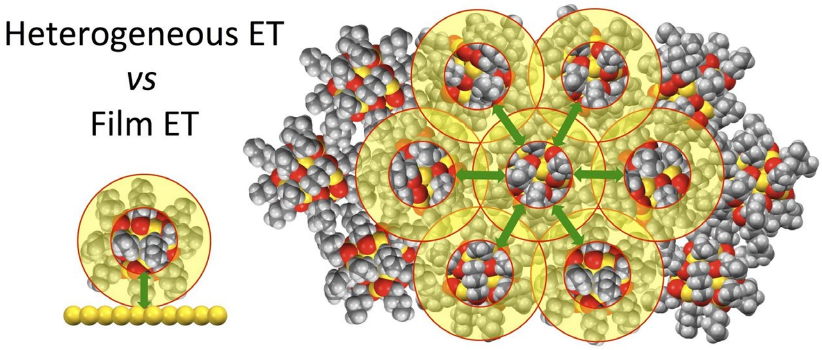
Gold Monolayer Protected Clusters (MPCs) are unique materials since they merge toghether properties of nanoparticles and molecular features, at least for metal core diameters lower than 1.6 nm. The interest in this systems grow a lot during the last years and nowadays they represent promising materials in different application fields [1-3]. If understanding the redox properties of MPCs in solution is of special interest in areas such as redox catalysis [2,4,5], obtaining insights into how MPCs transfer electrons in the solid state is fundamental to tailor properties in electronic devices. Indeed, providing an example, MPC films could find application as sensors for the detection of vapor-phase analytes, whose sorption affects the conductivity of the film itself [6]. Within this topic, assessing the dynamic behavior of the capping monolayer is crucial, as this determines the cluster's effective size and electron-transfer (ET) properties.

In this communication, a systematic study on the effect of the monolayer thickness on the ET between molecular $Au_{25}(SR)_{18}^0$ nanoclusters in films will be presented. The length of the ligands protecting the Au core was varied by using a series of linear-chain thiolate (SC_nH_{2n+1}) protected Au_{25} clusters, where n = 3, 4, 5, 6, 7, 8, and 10. Conductivity measurements were carried out on dry films obtained by drop-casting $Au_{25}(SR)_{18}^0$ solutions onto interdigitated gold electrodes. By using electrochemically determined Stokes radii, the conductivity results were transformed into the corresponding ET rate constants (k_{ET}) between neighboring clusters. The effect of branching was assessed by using the 2-methyl-1-butanethiolate-protected Au_{25} cluster. ET in films was also studied as a function of temperature, and the results were analyzed in the framework of the ET theory [7].

Recently, the chemoresistive properties of these materials have been also tested and the results will be evaluated in relation to the previous electron transfer study. On this occasion, preliminary results on the sensing response of drop casted films on the reversible absorption of selected aromatic organic vapors will be shown.



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Para substituted pyridines ligands forms highly active catalysts for ATRP

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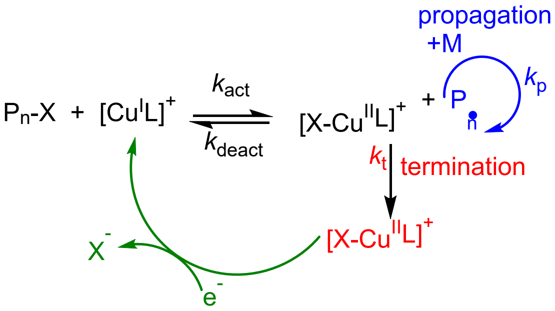
Sustainable chemistry is of utmost importance in this century, especially in polymer chemistry. Atom Transfer Radical Polymerization (ATRP) is the predominant Reversible deactivation Radical Polymerization (RDRP), used in both academia and seminally in the industry. One of the recurrent drawbacks often pointed out about ATRP is the need of a metal catalyst, which is typically a Cu/*N*-multidentate amine complex. Starting from the normal ATRP introduced in 1995, where $>10^4$ ppm of Cu was required, the latest ATRP variants such as *e*ATRP, photoATRP, ICAR ATRP, SARA ATRP and ARGET ATRP use drastically less Cu, down to tens of ppm (with respect to monomer).
To balance the needed metal reduction while ensuring a proper polymerization rate, ligand engineering has arisen as a valuable tool to tailor the electronic properties of such amines, hence the activity of the catalyst. 4-chloropyridines are very useful ligand precursors. The para position of the aromatic ring is the most valuable one due to resonance, and replacing the chlorine atom by nucleophilic aromatic substitution with electron donating amines is a key step to boost the electronic density.[1] The synthesis of the 4-chloro building block is a multistep synthesis with overall moderate yields and inexpensive reagents. It can be used to generate a series of precursor ligands like tris(4-chloropyridylmethyl)amine (TPMA-3Cl), bis(4-chloropyridylmethyl)amine (BPMA-2Cl), bis(4-chloropyridyl)ethaneamine, 4,4'-dichlorobipyridine and bis(4-chloropyridyl)dimethylethaneamine. Nucleophilic aromatic substitution, exploiting divergent chemistry, finally provide highly active and tailored *para*-substituted ligands. With the linear 2-aminomethylethanol and the cyclic pyrrolidine, seven new *para*-substituted ligands for ATRP have been synthesized.
Binary ($[\mathrm{Cu^{II}L}]^{2+}$) and ternary ($[\mathrm{XCu^{II}L}]^{+}$) Cu complexes were characterized by cyclic voltammetry in DMSO and H_2O. For some selected catalysts, which exhibited the kinetic regime of "total catalysis", k_{act} has been calculated by cyclic voltammetry at relatively low scan rate, using ethyl-2-bromoisobutyrate (EBiB) or 2-hydroxyethyl-2-bromoisobutyrate (HEBiB) as model initiators.
These very active catalysts may be used in low ppm ATRP, like ICAR ATRP or *e*ATRP, when a low amount of Cu is desired or emulsion polymerizations.



Scheme 1. Mechanism of ATRP with electrochemical (re)generation of the catalyst.

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EQCM analysis of the process of electrochemical insertion in regioregular alkyl-susbtituteo *Dini*[a], Elisabetta Salatelli [b]*d polyterthiophene during *n*-doping

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The material produced through the electrochemical polymerization of 3′4′-DDTT has been characterized with the EQCM during the process of *n*-doping. The supporting electrolyte (SE) was chosen considering mainly the two characteristics of hydrophobicity (to avoid the presence of water as potential contaminant) and chemical affinity with the alkyl and aromatic moieties present in poly-3′4′-DDTT. On these bases the salt $(n\text{-}C_4H_9)_4NClO_4$ was selected as SE since it contains the organic molecular cation $(n\text{-}C_4H_9)_4N^+$ that is expected to represent the charge compensating species in poly-3′4′-DDTT during *n*-doping. The feature of the reversibility of the electrical current profiles originated by the process of injection/extraction of electronic charge carriers in poly-3′4′-DDTT, is not encountered in the associated EQCM data. The interpretation of the EQCM data requires the consideration of phenomena of different nature. In the present work a thorough discussion of the factors influencing the EQCM response during polymer *n*-doping is provided taking into account the spontaneous adsorption of cations, the eventual reorientation of poly-3′4′-DDTT on the substrate and the consequences of the chains rearrangement on the electrical polarizability of poly-3′4′-DDTT during the cycles of electrochemical *n*-doping and undoping.

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Bio-inspired intact bacteria-based biohybrid photoanodes

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Coupling intact photosynthetic organisms and abiotic electrodes enables converting solar energy into electrical (and/or chemical) energy while providing the enzymatic machinery for self-repair and replication of the biocatalysts. Photosynthetic bacteria can be both oxygenic (that produce oxygen by performing the light driven water splitting) or anoxygenic (that oxidize various organic compounds present in water utilizing light as energy source). Among the latter, purple bacteria have one of the most versatile metabolisms among all bacteria. This versatility led to an increasing interest in interfacing these organisms with abiotic electrodes to mimic photosynthesis in a biohybrid system [1, 2] However, various challenges remain prior to implement such technology in the field, including enhancing photoexcited electron transfer from the biocatalyst to the electrode and maximizing stability of the biohybrid architecture.

In this context, a mussel-inspired approach to achieve a firmly anchored layer of purple bacteria on the electrode is reported. Polydopamine (PDA), containing both catechol and amine groups, is a polymer presenting similar characteristic to the adhesive plaque of mussel byssus, and it has been recently utilized to encapsulate isolated photosynthetic apparatus [3, 4]. Here, PDA was modified with a quinone-based redox mediator providing an artificial redox mediating system. The intact bacteria-based biohybrid photoanode was obtained by a one-pot preparation of the composite, followed by drop casting and electrochemical modification of carbon-based electrodes. Electrochemical and spectroscopic evidence for the obtained biohybrid photoanodes will be discussed together with future research possibilities.

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Nitrogen-containing ordered mesoporous carbons applied as CO_2 adsorbents and anode materials in energy storage devices

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Porous carbons, thanks to their easily tunable features (porosity, surface chemical properties, etc.), can be employed for several applications: separation processes [1], as catalyst supports [2] as well as electrode components in electrochemical energy storage/conversion devices [3].
Among these, in the framework of strategies for the mitigation of global warming and climate changes, nitrogen-containing ordered mesoporous carbons (NOMCs) are proposed as CO_2 adsorbents, thanks to their outstanding adsorption ability and selectivity. NOMCs can be synthesized with different pore architectures as nano-replications of a silica hard template, using a three-step procedure: i) infiltration of the carbon/nitrogen source inside the pore channels of silica, ii) pyrolysis of the hybrid system, and iii) template removal (see Fig. 1a). This method is particularly useful for achieving the optimal textural properties, i.e. a hierarchical pore architecture composed of both micro- and mesopores able to promote at the same time improved capture performances and fast kinetics of gas diffusion, respectively.

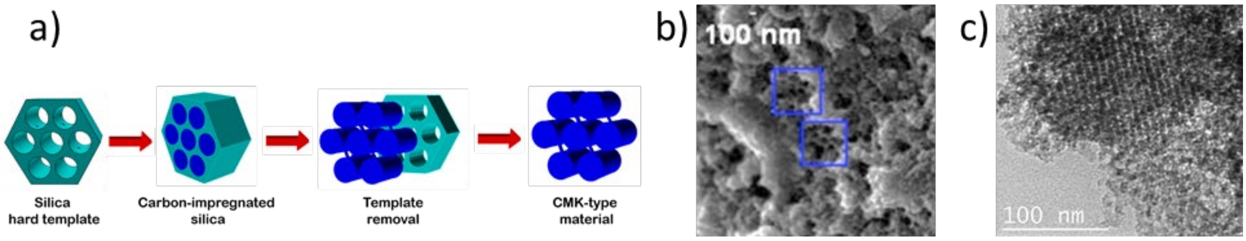

Figure 1: a) Synthesis procedure of CMK-type materials via the nanocasting approach, b) FESEM and c) HR-TEM images of N-containing CMK-8 sample.

In this work, the aforementioned approach, known for the preparation of the so-called CMK-type materials, is exploited for tuning the textural features of the carbonaceous adsorbents. Moreover, a natural occurring nitrogen/carbon source was chosen as a precursor, in order to introduce basic sites useful to promote the interaction of the carbon framework with the acidic CO_2 molecule, thus also fostering a selective adsorption in a gas mixture. Therefore, the regular, ordered mesoporous architecture (Fig. 1b-c) and the chemical surface properties were investigated to unveil their effect on the CO_2 capture performances.
In addition, the described NOMCs can be applied not only for CO_2 up-take, but also in energy storage and conversion devices (e.g., lithium or sodium-based batteries), photocatalysis or electrocatalytic reduction of CO_2. For these applications, they can be used as-synthesized or eventually decorated with specifically selected metal oxides, and related results are here shown.

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IONIC LIQUIDS FOR CAPTURE AND ELECTROCHEMICAL CONVERSION OF CO_2

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The exponential increase in the concentration of greenhouse gasses in the atmosphere is considered one of the most important reasons for climate change. Carbon Dioxide is the most significant anthropogenic gas that contributes to global warming. CO_2 capture and storage (CCS) has been proposed as one of the most important invention to mitigate CO_2 emissions. Moreover, conversion of carbon dioxide into energy-rich chemicals is a viable approach to reducing the global carbon footprint. The most common techniques to remove CO_2 from gas streams are the chemical and physical adsorption by liquid solvents. Traditionally, aqueous amine solutions have been used as chemical solvents because of their high selectivity, high reactivity and low price. Unfortunately, they present also many disadvantages associated with the high energy demand required for the solvent regeneration, corrosion issues and loss of solvent because of their high volatility. Hence, in the need to find more efficient solvents for CO_2 capture and conversion, Ionic Liquids (ILs) have been highlighted as very good alternatives to common amine solution.[1] Within this field lies this research, which in turn is part of a much broader European project called SunCoChem. For this project we are testing the stability and performance of various ionic liquids, provided by Iolitec, Ionic Liquids Technologies GmbH, and in particular their ability to capture and electrochemically convert a pure CO_2 stream to CO with high efficiencies. The ionic liquids were tested in a two-compartment H-type electrochemical cell. In the anodic chamber a nickel mesh electrode was immersed in a solution of potassium hydroxide and in the cathodic one a silver foil cathode was employed in a solution of acetonitrile and ionic liquid. An organic solvent was used to favor the dissolution of the ionic liquid and the homogenization of the solution. Other organic solvents such as propylene carbonate, ethylene glycol and 1-butanol were also tested with the aim of finding the best compromise between low viscosity, good conductivity and high electrochemical stability window. The Ionic Liquids (ILs) tested so far have a cationic part based on imidazole, which is expected to stabilize and lower the activation energy for the reduction of CO2. During Linear Sweep Voltammetry (LSV) tests this trend was confirmed by a shift to more positive potentials of the onset (~ 0.5V) for the CO_2 reduction reaction in the presence of these Ionic Liquid and interesting value of current density were reached. Throughout the Chronopotentiometry (CP) studies, some ILs evidenced a decrease in the applied potential indicating the increase of the electrolyte conductivity. Our results evidence relevant current density values, a good stability during chronopotentiometry (CP) tests and a high selectivity towards the target product: CO, which however change depending on the used IL.

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Carbon Nanostructures decorated with Cerium Oxide as selective electrocatalysts for CO_2 reduction

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The electrocatalytic reduction of CO_2 is a captivating strategy for the conversion of CO_2 into fuels, to realize a close loop for carbon footprinting. The research has focused on the development of new materials and technology capable of capturing and converting CO_2 into useful products.[1] Among all reduction products, formic acid is particularly attractive for its high volumetric hydrogen density, low toxicity, and liquid state, that make it a valuable hydrogen storage vector. The design of new electrocatalysts that reduce CO_2 in a selective and efficient fashion is a key step for future exploitation of this technology. Here we present how the combination of different building blocks in a single nanostructure might be a good strategy to achieve a good selectivity in the CO_2 reduction process. Combining the unique physico-chemical properties of functionalized nanomaterials (such as carbon nanotubes and carbon nanohorns) and nanocrystalline cerium dioxide (CeO_2) we revealed faradaic efficiency for formic acid production as high as 55% at an overpotential as low as 0.02V in acid solutions. These performances have been possible by the formation of partially reduced ceria ($Ce^{4+/3+}O_{2-x}$) responsible of an increased CO_2 adsorption and a more efficient electron transfer at the surface.[2] In the nanocomposite, the carbon nanostructures are used as support and they have a fundamental role in to counteracting the insulating effect of oxide nanoparticles and promoting the generation of Ce^{3+} sites. Their elevated surface area and high electrical conductivity guarantee a greater process efficiency.[3] In particular, the nanohorns have a unique conical geometric, where the nano-tips terminals act as "electron collector", increasing the charge mobility.[4] We demonstrated that the interconnections between various components are fundamental for the efficient CO_2 reduction to formic acid and opens new possibilities in the design of optimized electrocatalytic materials.

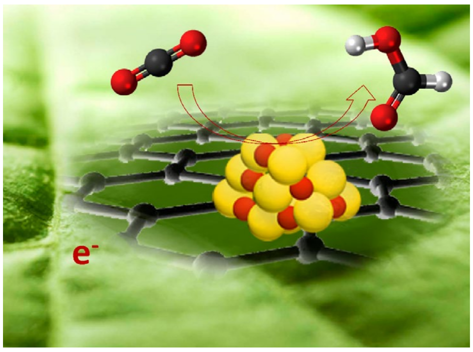

Figure SEQ Figure * ARABIC 1. Schematic CO_2 reduction into formic

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CuZnAl-BASED OXIDE CATALYSTS FOR THE ELECTROCHEMICAL CO_2 CONVERSION

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Electrochemical Reduction of CO_2 (ER-CO_2) is a very attractive alternative to tackle Global Warming.[1] Cu-based materials have shown increased yields of hydrocarbon and oxygenate products, while its selectivity towards CO is low.[2] Inspired by the thermocatalytic process, co-precipitation method was employed to synthesize CuZnAl-based oxide catalysts with nonpyramidal and mesoporous structure. The Physico-chemical properties of the catalysts were studied by several characterization techniques (e.g., XRD, XPS, BET, SEM, TEM) and electrochemical impedance spectroscopy at different applied-potentials to understand the role of the modification of the catalyst components during operation in the final selectivity and activity. Results revealed that adding ZnO and Al_2O_3 to the CuO-based catalyst contributed to promote CO formation over H_2. XPS measurements on the fresh samples revealed that the ternary CuZnAl catalyst stabilize the superficial Cu-oxidized species, being mainly constituted by Cu^{+2} (95%). This material reached a Faradaic efficiency towards syngas of almost 95% at -0.89 V vs. RHE and the highest syngas production rate was obtained at the most negative applied potential (~ 17 $\mu mol\ h^{-1}\ cm^{-2}$ at -1.14 V vs. RHE). A tunable H_2/CO ratio was achieved by applying different potentials, reaching lower values by increasing applied negative potential (CO current density increased). For instance, a H_2/CO ratio of ~ 2 was obtained at -0.89 V vs. RHE, which is a suitable raw material for further methanol synthesis. The enhanced performance for syngas production of the tricomponent catalyst is ascribed to its surface properties, i.e., alkalinity and the oxidation state on the surface, its lowest diffusional mass transfer resistance, its highest total pore volume, and the lowest Cu crystals size among the prepared catalysts.

Acknowledgments

This work has received funding from the EU's Horizon 2020 Research and Innovation Action program under the Project SunCoChem (Grant Agreement No 862192).

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Facile and scalable synthesis of Cu_2O-SnO_2 catalyst for the photoelectrochemical CO_2 conversion

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Since natural CO_2 sink cannot keep up with the constant anthropogenic emission, a renewable and green approach to CO_2 recovery is increasingly necessary to minimize the worrying impact of its emission to the environment. Within the depicted scenario, electrochemical and photoelectrochemical CO_2 reduction are being widely investigated as promising methods to transform CO_2, under mild reaction conditions, into useful chemicals or fuels. [1,2] Cu_2O is a cheap, abundant, and intrinsically p-type semiconductor. Due to its narrow band gap (~ 2.1 eV) and the suitable positioning of conduction and valence bands, Cu_2O is an ideal photocatalyst for CO_2RR. Simultaneously, SnO_2 is an n-type direct band-gap semiconductor with noticeable electron mobility together with an intrinsic stability. The role of SnO_2 coupled with Cu_2O as catalyst for syngas production was recently investigated [3], therefore it follows the stabilization mechanism induced by Sn(IV) onto the Cu(I) oxidation state, by acting as a barrier for further reduction of copper species, avoiding photoactivity losses. The synthesis of photoactive copper-tin-oxide-based catalyst was optimized by an ultrasound assisted co-precipitation method. The significant advantages of the sonochemical synthesis approach [4] guided the choice of coupling of the two methods. The characterization steps included Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX), UV-Visible Spectroscopy, X-ray photoelectron spectroscopy (XPS) analyses and X-rays Diffraction (XRD), allowing the morphological assessment, the crystalline phase evaluation and the composition of the surface species. The cubic crystalline phase (cuprite) of Cu_2O was noticed in the XRD pattern, which is evident from the most intense peak (111) at 2θ values of 36.52°. No traces of other phases related to Copper were observed in the diffraction pattern, which points out the suitability of the chosen synthesis methods and that the reduction process has been successfully carried out towards the cubic phase of Cu_2O. The study on specific surface area and porosimetry of the material, measured from N_2 adsorption/desorption isotherms, revealed a mesoporous structure with a BET surface area value of 142 m^2/g, a pore volume of 0.12 cm^3/g and an average pore width of 5.9 nm, which were detected via BJH method. The high surface area and pore volume of the compound is beneficial for the photocatalytic activity. From UV-Visible Spectroscopy analysis, the band gap energy value of 2.5 eV was calculated via Tauc plot method. The composition of a catalyst-based ink was optimized to avoid the Cu(I) oxidation during the electrodes preparation and preserve the catalyst photoactivity, which was assessed for the photo-electrocatalytic CO_2 reduction in an H-cell system, leading to the formation of value-added C-compounds like syngas and Formate, among others.

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Cathodic Plasma Electrolysis & Recovery of Zinc as Coating [Elsevier Award]

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Galvanized steel, resulting from coating steel with a deposit of zinc, finds extensive use in several fields, from construction to automotive as well as for metal fittings and home appliances. Although the steelmaking industry has long understood the challenges of the circular economy (ca. 30% of the world output being secondary steel), further efforts should be done to improve the steel recycling processes, for example making more profitable the powdery waste obtained in the production of steel by electric arc furnaces (AEFs). In fact, when galvanized scrap is used to feed furnaces, about 30 wt.% of the AEF dust is made of zinc, the fourth more used metal worldwide.

Combining the Regenerative and Circular Economy vision with the real needs of steelmaking companies, our research group has started a feasibility study aimed at proposing a *direct strategy* to regenerate galvanized steel with two main goals: *i*) shortening the current multi-step processes for the recovery/reuse of zinc; *ii*) offering a possible process innovation in galvanizing. The rationale is to galvanize secondary steel by cathodic plasma electrolysis (CPE), by using directly Zn-containing aqueous solutions resulting from the leaching of EAF dust. The project aims also at improving scientific knowledge on CPE that is an electrochemical approach much less investigated [1] with respect to its anodic counterpart (plasma electrolytic oxidation, PEO).

In the present talk, some preliminary lab-scale data will be discussed concerning the employment of CPE for both *surface pre-treatment* and *galvanizing* of steel, in the form of plate and wire rod. Considering the good performance of NH_4Cl as zinc leaching agent of EAF dust (by preventing some drawbacks of the conventional approach with sulfuric acid), special attention will be devoted to ammonium-based solutions, as a still unexplored medium for CPE (Figure 1). After preliminary screening of electrolytes and operative parameters aimed to obtain a stable plasma by minimizing the power supplied, the effects of CPE on *i*) the surface morphology of the treated steel and *ii*) the features of the zinc deposit have been investigated by combining electrochemical and microscopic techniques. Finally, real leaching solutions have been implemented for CPE galvanizing, to identify any interfering species.

Collected data support the feasibility of the CPE process that allows to obtain zinc deposit with corrosion protection performance comparable to that of commercially available benchmarks (*i.e.*, hot dip galvanizing and electrogalvanizing processes).

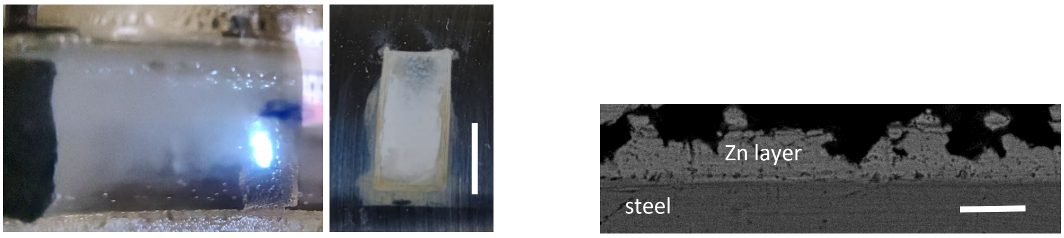

Figure 1. *Left: electrolytic plasma regime in 1.3 M NH_4Cl solution and effect of the treatment on a steel plate (marker = 0.5 cm). Right: BS-SEM micrograph of a cross section after CPE galvanizing (marker = 10 μm).*

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Sustainable strategies to improve MFC power output by green supercapacitors and supercapacitive components

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The inextricable link between the water needed for energy production and the energy needed for water purification is the key concept of the Water-Energy-Nexus (WEN). Microbial Fuel Cells (MFCs) play a central role, in this context. Indeed, in MFCs microorganisms are exploited as biocatalysts capable to convert chemical energy stored in wastewater's organic matter into electricity with the possibility of degrading a plethora of simple organics that are present in complex civil and industrial wastewaters. Sustainability is intrinsic in this system since no critical raw materials such as rare earth or lithium are needed. Despite this, the low power produced by MFCs makes the direct use for practical applications difficult. Usually, MFCs are coupled with an external energy storage system that accumulates the energy produced and delivering it when needed. Electrical double-layer capacitors (EDLCs) store electric energy by fast and highly reversible electrostatic processes. Therefore, a further step to improve the sustainability of this system and engage the WEN challenges is the valorization of wastes by their transformation into functional materials to be implemented in technologies that enable efficient energy management together with the design of green, sustainable EDLC to be couple with MFCs that do not exploit harmful components. Here we report about strategies to further push the concept of system sustainability, while improving the power output of microbial fuel cells with sustainable supercapacitive features. Biochar has been used as the main component of electrode component for EDLCs and MFCs fed with simple agricultural by-products. The lignin-derived activated carbon (LAC) was generated by a one-step carbonization route using $KHCO_3$ as mild activating agent. The chemical-physical characterization of LAC biochar and the electrochemical investigation of LAC-EDLCs and LAC-MFCs is here presented and discussed

Acknowledgments

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Oxygen Reduction Reaction monitoring at Iron Single Site Catalyst: Electrochemical Scanning Tunnelling Microscopy of Iron Octaethylporphyrin

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Metal-porphyrins and -phthalocyanines become are good model systems of MN_4 sites, which are implied in many reactions involving both inorganic and organic applications [1]. In particular, MNx sites, where usually M= Fe, are nowadays employed as valid alternative to platinum-group materials (PGM) in PEM-fuel cells [1].

FeN_4 sites exert the so-called "redox-catalysis", since the catalytic effect is provided by the redox properties of the metal atom, which can easily access different oxidation states. In this paper, H_2-octaethyl porphyrin (H_2-OEP) and Fe(III)-octaethyl porphyrin chloride (Fe(III)-OEP) were characterized in their ability to adsorb on an HOPG substrate, studying their self-assembly capability at the solid/liquid interface, as well as their behaviour and stability at the solid/electrolyte interface. This was accomplished by means of Electrochemical Scanning Tunnelling Microscopy, allowing the Fe-OEP/HOPG (or H_2-OEP, or mixed) layers to behave as working electrode in the "four-electrode setup". We found 5 surface supercells that can fit the experimental observation within the error bars ±1Å on lengths and ±5° on angles (Figure 1a). Physical chemical changes and adlayer stability were probed by potentiodynamic imaging, namely recording STM images at a precise working electrode potential. By lowering the applied potential, the adlayer retains a good stability and the iron atoms undergo the expected redox transition Fe(III)→Fe(II).

Thanks to the redox properties exhibited by Fe-OEP, its behaviour was further studied in O_2 saturated electrolyte: a high-current density cathodic peak was found at E_p= 0.28 V vs RHE, indicating a net catalytic activity of the Fe-OEP adlayer. In EC-STM images, a spot is visible in a shifted position from the center of some molecules, indicating the presence of an O_2 molecule adsorbed on the Fe catalytic site. Furthermore, we modeled the oxygen reduction process catalyzed by FeOEP adsorbed on HOPG and estimate the Gibbs free energies of each elementary step combining DFT, MD and thermodynamics data.

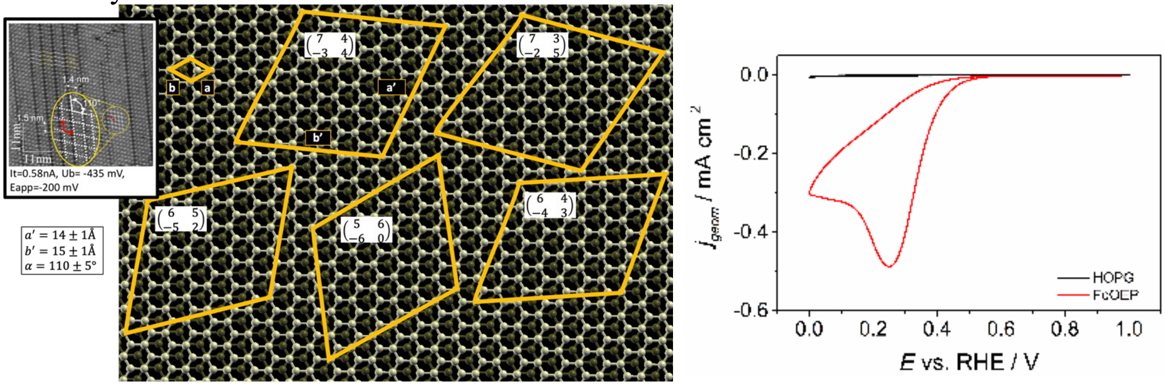

Figure 1: a) high-resolution EC-STM images of FeOEP adlayer in Ar purged electrolyte and 5 model supercells on graphite (0.0.1) surface b) cyclic voltammetry of FeOEP@HOPG in O_2 saturated electrolyte.

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Doping or Aggregation: the case of Conjugated Polyelectrolytes PCPDTBT-2SO$_3$K and PCPDTBT-SO$_3$K

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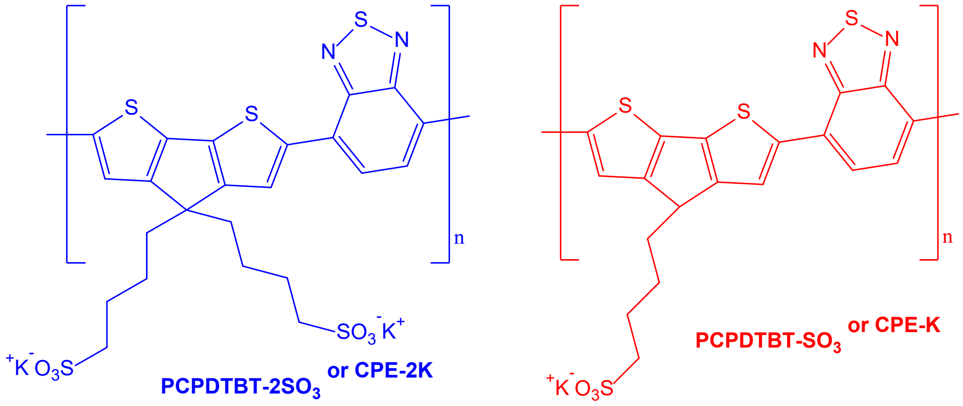
Conjugated polyelectrolytes (CPEs) are defined by a backbone that contains a π-conjugated electronic structure with pendant ionic functionalities, which make the polymer soluble in water and in polar solvents[1]. CPEs combine the optical and charge transport properties of organic semiconductors with the possibility of modulating physical properties by electrostatic interactions. Furthermore, the solubility in water and in polar solvents makes CPEs appealing materials both as optical reporters in bio-sensors and bio-imaging applications and as charge regulating layers in organic solar cells[2], organic light-emitting diodes and organic thin-films transistors. Recently, the CPE poly[2,6-(4,4-bis-potassium butanylsulfonate-4*H*-cyclopenta-[2.1-b;3,4-b’]dithiophene)-*alt*-4,7-(2,1,3-benzothiazole)] (PCPDTBT-2SO$_3$K or CPE-2K) has become object of interest because is soluble in water and become doped in presence of a proton source[3]. In fact, it has been reported that the dopant is H$^+$ and that the addition of sodium hydroxide to CPE-2K solutions reverses the process and de-dopes the polymer. The proposed “doping” mechanism consists in an initial double protonation of the polymer backbone, followed by comproportionation with a non-protonated chain, ultimately leading both to the formation of polarons (radical cations), which are stabilized by the pendant sulphonate groups[4]. Starting from these considerations, here we present a deep study of the di-alkylated CPE-2K in comparison with mono-alkylated CPE-K (Scheme 1). Through combined spectroscopic (UV-vis-NIR) and electrochemical (cyclic voltammetry) analyses we aim to look into the doping mechanism trying to show how protons cause the organization of both polymers in aggregates, which then stabilize the polarons. A comparison with other CPE systems is also performed.



Scheme 1: Structures of the molecules.

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Light-Induced Electrochemical Processes at Semiconductor-Films/Water Interface Modulate Cell Redox Balance

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Reactive oxygen species (ROS) are known to play a main role in several cellular processes [1,2,3]. It has been showed that organic polymers can be employed to modulate cellular processes and stimulate cell proliferation [4,5]. We previously showed, by employing Scanning Electrochemical Microscopy (SECM), that poly-3-hexyl-thiophene (P3HT) films upon photostimulation produce reactive oxygen species (ROS) in water solutions at the electrolyte/organic polymer liquid/solid interface [6]. We obtained a spatially-controlled production of hydrogen peroxide as determined by SECM at the micrometric scale. As a proof of principle of the possibility to directly modulate cellular protein factors, we investigated the interaction of a model redox protein, Cytochrome C, with photostimulated P3HT films; by employing an SECM/fluorescence microscope apparatus, we showed that Cytochrome C is reduced at the photostimulated organic semiconductor/liquid interface [6].
Here we report on the effects of controlled production of ROS on physiologically relevant parameters of HL-1 cells, a cardiac muscle cell line, when grown on the top of the organic polymer films. The organic semiconductor films were illuminated with an high spatial control and SECM was employed to investigate the effects of the ROS local production on single cardiac muscle cells.

Acknowledgements
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Development of SnO_2 composites as electron transport layer in un-encapsulated $CH_3NH_3PbI_3$ solar cells

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Improving morphological and electronic properties of the electron transport layer (ETL) is one of critical issue to fabricate highly efficient perovskite solar cells. Tin dioxide is used as ETL for its peculiarity such as low-temperature solution-process[1] and high electron mobility[2] and several handlings have been tested to increase its performances[3-5]. Herein, SnO_2:ZnO and SnO_2:In_2O_3 composites are studied as ETL in planar n-i-p $CH_3NH_3PbI_3$ solar cells fabricated in ambient air, starting from glass/ITO substrates. Morphological, electrical and optical properties of these films are investigated. First-principle calculations are also reported and help to further explain the experimental evidences. Photovoltaic performances of full devices show an improvement in efficiency for SnO_2:In_2O_3–based solar cells respect to pristine SnO_2, probably due to a suppression of interfacial charge recombination between ITO/ETL and ETL/perovskite.

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Investigation of the mechanism of Pt_3Fe_3 clusters for the hydrogen evolution reaction and for the oxygen reduction reaction

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With the fast-growing developing economies and the acceleration of industrial development, the demand for renewable, sustainable, and environmental-friendly energy sources is severely increasing [1]. Hydrogen, as a green fuel, attracts our attention and Pt stands out for its good performance in electrochemical production of hydrogen and for its use in fuel cells. However, the price of Pt limits its application and reducing the amount of Pt used in fabricating the electrodes becomes an urgent problem. According to our previous work [2], "Pt-based" clusters are an interesting option to reduce the loading of Pt and they are very stable thanks to a strong bond with the carbon support. Thence, we are studying Pt-X clusters (where X is a second metal) to further reduce the loading and to improve the activity. Therefore, we use Pt-X clusters as the electrode material and deposited it on the *rotating ring-disk electrode* (RRDE) tip to test the performance for the hydrogen evolution reaction (HER) and for the oxygen reduction reaction (ORR), in both alkaline and acidic media. We explored cyclic voltammetry curves (CV) by controlling the rotating speed of RRDE and the scan rate, using different working potential windows as well as N_2 and O_2 condition, in basic and acid media, to illustrate both reactions. Besides, we adopted X-ray absorption spectroscopies (XAS) to investigate the oxidation state and local structure changes of Pt and Fe under operative conditions. From above, we want to study structure-activity relations and provide rational design instructions related to Pt-based clusters and, more in general, to the electrode material for both the ORR and the HER.

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DNA-based Nanoswitches: insights into electrochemiluminescence signal enhancement

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Electrochemiluminescence (ECL) is a powerful transduction technique that has rapidly gained importance as a powerful analytical technique [1]. Since ECL is a surface-confined process, a comprehensive understanding of the generation of ECL signal at a nanometric distance from electrode could lead to several highly promising applications [2]. In this work, we explored the mechanism underlying the ECL signal generation at the nanoscale using luminophore-reporter-modified DNA-based nanoswitches (i.e. molecular beacon) with different stem stability [3,4]. ECL is generated according to the "oxidative-reduction" strategy using tri-n-propylamine (TPrA) as co-reactant and $Ru(bpy)_3^{2+}$ as luminophore. Our findings suggest that by tuning the stem stability of DNA-nanoswitches we can achieve different ECL signal profiles and, in specific conditions, a "digital-like" association curve, showing an extremely steep transition after the addition of increasing concentrations of DNA target and a large signal variation. This suggests the co-presence of two different ECL generation mechanisms at the nanoscale and open the way for the design of customized DNA-devices for highly efficient dual-signal-output ratiometric-like ECL systems.

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Ultrasensitive Hepatitis B Virus whole genome detection by Electrochemiluminescence

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According to the pandemic infection of Covid-19, the determination of viruses has become a crucial topic for our society. Hepatitis B Virus (HBV) is one of the major worldwide infect agents that in 2015 World Health Organization estimates the infection of 257 million people.[1] A PCR-free sensor is developed for the determination of HBV whole double stranded genome (ds-DNA) based on electrochemiluminescence (ECL). However, the ECL is an electrochemical technique with a simple instrumentation which is based on a luminescent phenomenon, produced from an electron-transfer reaction taking place on the surface of the electrode and yielding light-emitting excited states. The most know luminophores/coreactant system in aqueous media is tris(2,2'-bipyridine) ruthenium(II) ($[Ru(bpy)_3]^{2+}$)/tri-n-propylamine with important analytical application in commercial assays for the detection of biomarkers such as TSH and troponin T. [2,3] The ds-DNA of HBV has been immobilized and remained anchored between two monoclonal oligonucleotide chains probes (P1 and P2), thus the same time the triplex formation is created via Hoogstern H-bonds.[4] The space between the two probes is blocked using thiol. Both thiol and specific probes are immobilized in the surface of the gold electrode according to Au-S chemistry. (Figure 1a) The ECL-active $[Ru(phen)_2dppz]^{2+}$ complex is used as luminophores group for the detection of HBV genome and as luminophore for generate ECL. The $[Ru(phen)_2dppz]^{2+}$ can be intercalated in the grooves of ds-DNA according of the nature of -dppz ligand (π-π* stalking intercalation).[5] This ECL based DNA sensor has been tested in a large HBV concentration range (between 0 to 10000 copies mL^{-1}) and the high sensitivity of the techniques allow a very low limit of detection (LoD) of 2.7 copies mL^{-1}.

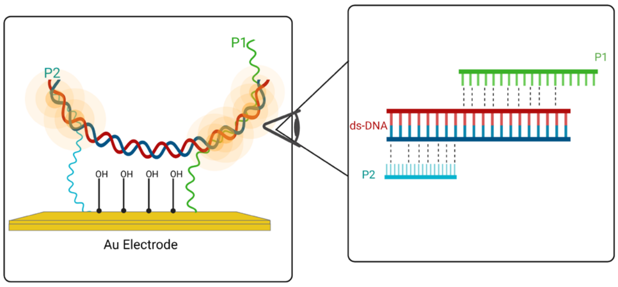

Figure 1: Immobilization of specific probes and triplex formation between ds-DNA of HBV and P1, P2 probes.

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Determination of emerging contaminants with electrochemical sensors based on titania nanoporous films: effect of sol aging on their electrochemical performances.

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Thanks to their properties and characteristics, such as high active surface area, increased surface/volume ratio, increased selectivity, lower limits of detections, electroanalytical sensors based on nanomaterials have been broadly used in the last years. [1]

More recently, the study of new devices based on hybrid systems composed of metal nanoparticles and nano-titania for electroanalytical applications has increased because of their ability to prevent or to overcome the fouling and passivation of the electrode, due to the presence of the photoactive nanoporous titania layer. [2-5]

These devices have already demonstrated their ability to detect analytes for different applications (emerging pollutants detection, biomolecule detection, …), but the complete understanding of the reasons of their increased properties, has still to be clarified in depth.

In this context, the aim of this presentation is to show the effect of the aging time of the TiO_2 sol on the electrochemical behaviour of the devices. In particular, it seems that the aging time affects the structure of the final coverage resulting in a change in the diffusional mechanism, from convergent to linear. This effect suggests an evolution of the particles that results in a difference of the pore size and distribution. Controlling this effect could allow the researcher to design the sensor according to the analytical need.

The photo-renewable ad-hoc designed sensors composed by Au nanoparticles coated with nanoporous TiO_2 are further used for the electrochemical determination of other emerging contaminants, enlarging the spectrum of applications.

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A bicyclic peptide-based biosensor for the electrochemical detection of a cancer-related protease

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Malignant cancer cells invade the surrounding tissues by exploiting their ability to degrade the extracellular matrix through the activation of an intense proteolytic cascade. The human urokinase-type plasminogen activator (h-uPA) converts plasminogen, an abundant proenzyme in plasma, into plasmin. This latter proteolytic enzyme induces the lysis of the basement membrane and the extracellular matrix, thus promoting the diffusion of cancer throughout the organism. Evidences showed that high levels of h-uPA in biological fluids are often linked to metastatic evolutions of neoplasia and adverse prognoses for the patient. Thus, h-uPA may represent an interesting and minimally-invasive biomarker for the diagnosis and prognosis of such conditions.

With this in mind, we employed a chemically constrained bicyclic peptide that presents a large interaction surface for h-uPA and used it as bioreceptor to develop a simple peptide-based biosensing platform. The bicyclic peptide was immobilised onto the surface of superparamagnetic microbeads *via* streptavidin-biotin interactions. A sandwich-type electrochemical assay on disposable screen-printed carbon electrodes allowed the detection of h-uPA at concentrations of clinical interest. Many optimizations of the operative conditions were introduced to obtain a straightforward analysis.

Moreover, experiments in complex biological samples were also carried out, owing to the simplification of sample treatment achieved by using magnetic microbeads.

Acknowledgements

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Interplay between porosimetric parameters, densitometric parameters and catalytic activities of “Core-Shell” ORR Electrocatalysts

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Critical bottlenecks of Proton Exchange Membrane Fuel Cell operation are the sluggish kinetics of the oxygen reduction reaction (ORR) [1] and mass transport issues at the cathode electrode [2]. The development of new ORR electrocatalysts (ECs) with suitable morphology and activity is aiming to address both shortcomings. The ECs reported in this research work exhibit a *“core-shell”* morphology: a hierarchical graphene-based support (H-GR) *“core”* is covered by a carbon nitride *“shell”*. The latter stabilizes the Pt-based active sites in *“coordination nests”* [3]. The *“core”* comprises highly defected graphene nanoplatelets [4] and carbon black nanoparticles; Ni is introduced in the EC as a *“co-catalyst”* to raise the ORR kinetics of the ECs [3]. Morphology and especially porosity of the innovative support of the proposed ECs are very different from that typically adopted in the state of the art. Thus, to fully exploit the potential of such support and guide the synthesis of new and improved ECs, the morphological features of ECs need to be studied in detail. Physisorption of N_2 is carried out to evaluate the specific surface area of the ECs, together with the profiles of their micro- and mesopores. The real density of the ECs is evaluated and a new parameter is proposed, namely the surface area per volume *“Σ”* (expressed as m^2/cc). This latter is of paramount importance to design efficient membrane-electrode assemblies (MEAs) for implementation in practical devices. The results of morphologic/porosimetric studies are correlated with the outcome of both bulk and surface chemical characterizations carried out by CHNS microanalysis and X-ray photoelectron spectroscopy (XPS). Finally, the morphologic studies are correlated with the *“ex-situ”* intrinsic ORR performance and selectivity in the 4-electron mechanism determined by cyclic voltammetry with the thin-film rotating ring-disk method (CV-TF-RRDE).

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Ion Coordination and Dynamics in Ionic Liquid-based Electrolytes for Hybrid Al/Mg Batteries

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Electrochemical energy storage devices based on novel chemistries are required in order to sustain the demand set by the automotive (*e.g.*, electric vehicles) and the stationary (*e.g.*, peak shaving, electricity production from renewable energy sources) fields. Indeed, lithium and lithium technology-related metals (*e.g.*, Co) are suffering from the critical issues associated to their supplying. In this context, magnesium and aluminum are considered as a valid alternative, due to their: (i) light multivalent nature; (ii) low reduction potential (-1.66 and -2.37 V *vs*. SHE for Al^{3+}/Al and Mg^{2+}/Mg, respectively); (iii) high volumetric and gravimetric theoretical capacities (2980 $Ah\cdot kg^{-1}$ and 8046 $Ah\cdot dm^{-3}$ for Al, and 2205 $Ah\cdot kg^{-1}$ and 3832 $Ah\cdot dm^{-3}$ for Mg); and (iv) high abundance in the Earth's crust and low cost (1'925 and 2'700 $\$\cdot ton^{-1}$ for Al and Mg, respectively) [1, 2]. Mg- and Al-based secondary batteries are suffering from the unavailability of suitable stable and high-performing electrolytes. In the most recent years, electrolyte systems based on ionic liquid (IL) have gained the attention of scientists due to their high efficiency in the multivalent metal deposition and stripping processes and to their high thermal and electrochemical stabilities [3-5]. Nevertheless, the complexity of multivalent metal coordination in solution is blocking the full understanding of the nature of these compounds, thus limiting their optimization.

In this work, we have investigated the characteristics of a series of IL-based hybrid Al/Mg electrolytes of the type $[Pyr_{14}Cl/(AlCl_3)_{1.5}]/(\delta\text{-}MgCl_2)_x$ ($x = 0$, 0.056, 0.091 and 0.146). A full detailed understanding on ion coordination, complex geometries, structures and dynamics is achieved combining advanced thermal analyses, vibrational, electric and nuclear magnetic spectroscopies. It is demonstrated the presence of $AlCl_4^-$ and $Al_2Cl_7^-$ building blocks that are able to efficiently coordinate $\delta\text{-}MgCl_2$ units, establishing a circular equilibrium which is modulated by both the temperature and the magnesium concentration. This equilibrium influences the reorganization of cationic and anionic nanodomains and the host medium dynamics of the IL matrix. Thus, the long-range charge migration process is the result of the exchange of anionic active species between adiacent delocalization bodies, and it is activated by the host dynamics which depend on temperature and magnesium concentration.

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Copper-based perovskite electrodes for reversible solid oxide cells

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Chemically substituted perovskite oxides constitute the most widely studied electrode materials for oxygen reduction and evolution in Solid Oxide Cells (SOCs). Although the most promising and widely studied perovskite-based electrode materials contain Cobalt in B-site, the presence of Co leads to very high values of TEC (moving from 15.3 × 10^{-6} K^{-1} for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ to 24 × 10^{-6} K^{-1} for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$), leading to mismatch with doped-ceria typically used electrolyte [1]. Moreover, Cobalt is classified as critical raw material to the European Commission, as ratified in [2]. Some years ago, considerable efforts have been carried out to develop a new class of Co-free systems, to be used at the oxygen side of solid oxide cells. Very high conductivity of 238 S cm^{-1} and interesting polarization resistance of 0.070 Ω cm^2 at 800 °C were found out for $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LSCuF) perovskites [3]. More recently, other authors investigated $La_{1-x}Sr_xFe_{0.8}Cu_{0.2}O_{3-\delta}$, confirming a renewed interest towards these electrodes, despite degradation mechanisms due to Cu migration [4]. The aim of this study is to investigate different stoichiometric composition of $La_{1-x}Sr_xFe_{1-y}Cu_yO_{3-\delta}$, produced by solid combustion synthesis from nitrate precursors, to be used as electrodes both for oxygen reduction and evolution. The final aim is to infiltrate the solution directly in a porous scaffold, in order to produce a discrete nanolayer on the electrolyte, so that improve long-term chemical stability. Preliminary results obtained in electrolyte-supported cell and three-electrode configuration showed an interesting polarization resistance of 0,015 Ω cm^2 a 700 °C, as reported in Fig. 1, where electrochemical impedance spectra are shown at open circuit voltage (OCV) and under $\pm 0.52\ V\ bias$. These latter showed a decrease in polarization resistance, suggesting improved kinetics both in anodic and cathodic conditions, with respect to OCV. Further investigation has been dedicated to long-lasting behaviour of LSCuF-infiltrated electrodes and anode-supported cells as well, whose results will be discussed in detail.

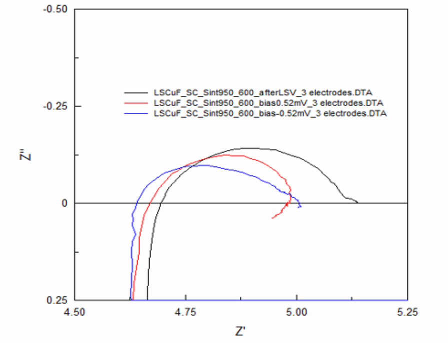

Fig. 1: Impedance spectroscopy spectra of a three-electrode LSCuF/GDC/LSCuF electrolyte-supported cell: black plot: OCV; red plot; +0.52 V; blue plot: -0.52 V.

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Multi-functional Fuel Electrode for Reversible Solid Oxide Cells

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Increasing the efficiency of energy storage and conversion is a crucial step towards enabling a deeper penetration of renewables into the existing system. Reversible Solid Oxide Cells (RSOCs) have the potential to play a fundamental role in the upcoming energy transition. RSOCs are electrochemical devices that can work both in electrolysis mode (Solid Oxide Electrolyzer, SOEC) and in fuel cell mode (Solid Oxide Fuel Cell, SOFC), ensuring high efficiency. A key aspect of these devices is the optimization of the fuel electrode, since this cell compartment must withstand high-temperature switch from reducing to oxidizing atmospheres, being at the same time catalytically active towards fuel oxidation and H_2O or CO_2 reduction [1, 2]. Using a coking tolerant material as RSOC fuel electrode increases the fuel flexibility in SOFC mode, with the possibility to fully exploit methane-containing fuels like natural gas or biogas [3, 4]. Moreover, RSOCs run in fuel cell mode and fed with hydrocarbon-based fuels allow for easy CO_2 capture in the exhaust lines. Using the same device in electrolysis mode, the stored CO_2 can be reconverted into CO, syngas (if H_2O is added to the CO_2 inlet stream) and O_2.

The state-of-the-art fuel electrode, Ni-8YSZ cermet has unrivalled catalytic activity both as SOFC anode and SOEC cathode. Nevertheless, when used as SOFC anode, Ni-YSZ suffers from two main drawbacks: mechanical instability due to NiO/Ni volume changes upon redox cycles, and Ni passivation due to coking when carbon-containing fuels are used [3,4]. In SOEC mode, ZrO_2 reduction can occur at high cathodic potential, resulting in Ni-Zr formation and performance degradation [5].

Here we present a recently developed [6] composite material, made up of $La_{0.6}Sr_{0.4}Fe_{0.8}Mn_{0.2}O_{3-\delta}$ (LSFMn) [7] and 5wt% Ni-containing $Ce_{0.58}Sm_{0.15}O_{2-\delta}$ (NiSDC), tested as fuel electrode for LSGM-electrolyte supported cells, with an LSFCo+GDC air electrode. The composite is designed to be resistant to carbon deposition. Upon reduction, Fe exsolved from LSFMn forms a Fe-Ni alloy with Ni present on SDC. The *in-situ* formed alloy, supported onto a Mn-containing oxide backbone, activates CH_4 molecules while SDC increases the O^{2-} supply at the anode to get rid of any carbonaceous deposits. The same cell configuration was also tested for CO_2 reduction in different CO_2:CO ratios.

LSFMn+NiSDC was used in SOFC-mode for hydrogen, dry methane and carbon monoxide oxidation and showed power density outputs of 657, 668 and 527 mW/cm^2 at 850 °C, respectively. The fuel electrode delivered 2.66 A/cm^2 when it was used as cathode for CO_2 electrolysis.

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From Redox-like to Heterogeneous Electrocatalysis at Metal-Octaethylporphyrins@HOPG investigated by EC-STM

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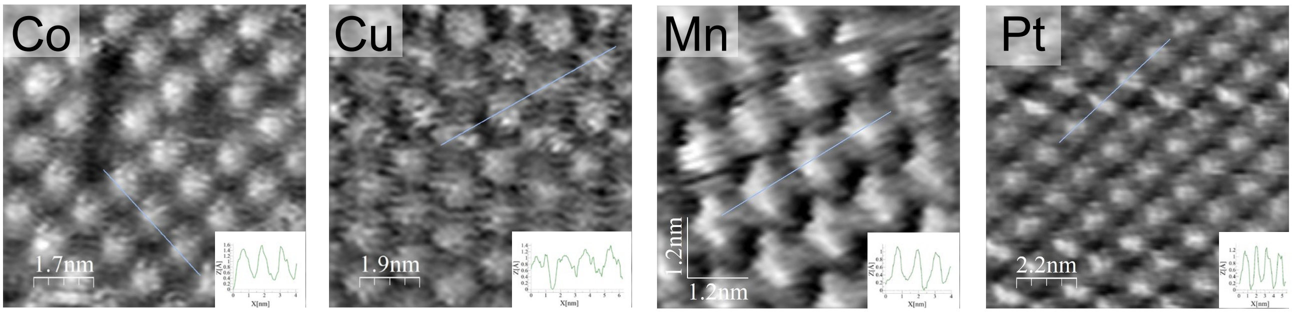
Oxygen reduction reaction (ORR) is a vital reaction, not only for the process of respiration of almost all biological systems on earth, but also in the electrocatalysis field of fuel-cells and metal-air batteries. In these devices, O_2 is entailed at the cathode, and it undergoes reduction, with H_2O or H_2O_2 being produced. Unfortunately, ORR needs to be catalyzed [2], and platinum group materials (PGM) should be avoided, though representing still the most performing catalysts for ORR. Among non-PGM alternatives, carbonaceous matrixes embedding MN_x (M=metal, N_x= x nitrogen atoms) sites exhibit good catalytic properties [3]. To further understand how the catalysis is exerted by MN_x sites, model systems like metal porphyrins can be taken into exam, since they provide a unique source of MN_4 sites. Metal porphyrins are regarded as catalysts for both homogeneous and heterogenous reactions [1]. If conductive substrates are properly functionalized with metal porphyrins, an electrode surface can be obtained and studied under electrochemical condition, gaining exact information about the electrocatalytic properties of the active site. In this paper, octaethylporphyrin carrying different metals (M= Fe, Co, Mn, Cu, Pt and Ru) was functionalized on a HOPG substrate and characterized by means of electrochemical scanning tunnelling microscopy (EC-STM), which has the capability to monitoring the active site while catalysis is ongoing [4,5]. Additional information is gained by cyclic voltammetry (CV) and rotating ring and disk electrode techniques (RRDE). Different electrocatalytic behaviors were discovered, with Fe and Co returning the most positive ORR peak, and Pt and Ru giving the worst performances. For first-raw transition metal atoms, it is recognized that the catalytic activity is mainly mediated by the redox couple possessed by the metal [6]. For heavier metal atoms, like Pt and Ru, although being less active, the mechanism is still uncertain. This work is therefore aimed to classify metal elements on the basis of their activity towards ORR, thereby providing the explanation of the catalytic mechanism.



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Non-stoichiometric Metal Oxide Particles as Active Electrode Component in PEM Fuel Cells

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Platinum scarcity and its high cost have led to the need of alternative materials catalyzing the oxygen reduction reaction (ORR), which is the main rate-determining step occurring in low-temperature proton exchange membrane fuel cell (PEMFC) devices, causing a rise in the fuel cell overpotentials. Developing improved catalysts with higher ORR activity is challenging[1].

To this purpose, we propose the modification of conventional Pt/C catalysts using appropriate non-stoichiometric oxides to be used as co-catalysts for the ORR to reduce the Pt loading and improve its electrocatalytic activity.

In particular, a sub-stoichiometric calcium titanate perovskite, ($CaTiO_{3-\delta}$)[2] and cerium oxide (CeO_2) are here proposed as Pt/C promoters for ORR.

Fundamental physical chemical characterizations by means of X-ray diffraction, infrared spectroscopy, morphological and thermal analysis, for the understanding of functional features of the proposed materials will be presented.

Composite catalysts based on Pt/C, containing different amount of the oxide additives, were prepared and their activity was studied by either rotating disk electrode (RDE) and fuel cell tests, performed at high temperatures (80°C and 110°C) and low relative humidity (30%). The composite catalysts were compared to a bare Pt/C used as reference.

Interestingly, both cells adopting the composite catalytic materials show the best electrochemical performances, as a result of enhanced ORR kinetic mainly due to an improvement of the Pt-metal oxide interface[3]. Indeed, the presence of oxygen vacancies in the lattice of these oxides lead to produce a new oxygen ion conducting pathway in the electrode, promoting the oxygen reduction reaction.

This approach could indicate a new strategy to develop materials functionality.

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Aquivion®-based Alkaline Membrane for Fuel Cell and Electrolyzer Applications

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The increased interest in hydrogen, as energy vector, puts Fuel Cell (FC) and Electrolyzer (El) devices under a new light. Actuality, commercial low temperature FCs and Els are based on a Proton Exchange Membrane (PEM). However, the high cost of these technologies, chiefly due to the use electrocatalysts based on Platinum and Platinum Group Metals, prevents their wide spread and large-scale applications. Anion Exchange Membranes (AEMs) are largely investigated because the use of an alkaline pH environment opens the possibility to exploit cheaper ECs, based on Fe, Ni, Ag. Moreover, the alkaline environment facilitates the Oxygen Reduction Reaction at the cathode with respect to PEM working conditions.

Here we present a synthetic strategy to convert commercial protonic membranes into AEM. In particular, the polyfluorinated PEM Aquivion® EW=980 g/mol (Solvay) is functionalized by reaction with aqueous diamine solution, to obtain sulfonamide AEM. This allows to maintain the same mechanical and chemical resistance of the pristine membrane, but, at the same time, it increases the thermal stability thanks to the formation of sulfonamide bonds. This functionalization is carried out in an aqueous media, which is clearly advantageous from the environmental point of view. The functionalized membrane achieves an ionic conductivity of 26 mS/cm at 80°C, 100% RH and shows excellent stability after 144 hours in 3M KOH solution at 80°C. The membrane has been tested as electrolyzer separator and for Fuel Cell applications.

Identification of Solid Oxide Cells Processes by Distribution of Relaxation Times: Model Creation and Validation

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Solid oxide cells (SOCs) represent one of the most efficient and promising electrochemical technologies for hydrogen energy conversion[1]. Understanding and monitoring degradation is essential for their full development and wide diffusion. Advanced processing of experimental data, such as Distribution of Relaxation Times (DRT) on Electrochemical Impedance Spectroscopy (EIS) measurements, is a powerful tool to investigate physicochemical processes occurring in SOCs and to analyses ageing mechanisms[2]. In the first part, a method is presented to identify the processes behind the polarization losses in order to build a proper equivalent circuit model (ECM) suitable for the operando diagnosis based on EIS. In the second part, a validation of the electrochemical model is done, by applying an a priori known stress agent to a SOC operated in laboratory conditions and analyzing the deconvolution of electrochemical impedance spectra. Finally, experimental evidence obtained from a fully operando approach was counterchecked through ex-post material characterization.

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Anode-supporting substrates with hierarchical porosity manufactured with freeze tape casting for reversible solid oxide cells

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A reversible Solid Oxide Cell (rSOC) is an electrochemical device able to operate both in power producing (Solid Oxide Fuel Cell, SOFC) and chemical energy producing (Solid Oxide Electrolysis Cell, SOEC) modes. It has the potential to become a key technology in a new energy scenario based on renewable sources, playing the role of grid-balancing solution [1,2], by its fast reaction kinetics, high fuel flexibility and conversion efficiency [3]. However, despite their estimated capabilities, durability is still a major factor for rSOC-based systems. The hydrogen electrode microstructure slowly degrades throughout the whole operation, whatever the current density; special attention must also be paid towards the degradation of the oxygen electrode, where delamination has been observed as one of the most severe causes of performance loss, with p(O_2) as a major standpoint [4].
Freeze tape casting has been regarded as a promising fabrication route with the purpose of producing robust ceramic materials featuring directional microstructures, improved tortuosity factor and tailored porosity [5]. The aim of this work is to employ freeze tape casting for the fabrication of YSZ (yttria-stabilized zirconia) and GDC (gadolinia-doped ceria) scaffolds, to be coupled with a YSZ electrolyte, in order to obtain a 3-layered anode/electrolyte/cathode backbone through the co-sintering process. The final purpose is to use this ion-conducting structure as support for the subsequent deposition of a high-performing electrocatalyst throughout the infiltration technique. Fig. 1 (a) and (b) show the YSZ scaffold highlighting its hierarchical porosity all along the thickness of the electrode and the morphology of the pores at the oxygen/electrode interface. The crucial parameters for the porosity optimization will be discussed in detail.

Fig. 1. Micro-images of the (a) cross-section and (b) top YSZ backbone after sintering at 1400 °C.

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Electrospun $MnCo_2O_4$/CNF as Oxygen Electrode for Alkaline Zn-Air Batteries

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Rechargeable aqueous (alkaline) Zn–air batteries are considered to be promising post-lithium energy storage technologies due to their environmental friendliness, safety, affordability and high theoretical energy density. However, they do not still offer adequate practical energy density and life cycle due to critical problems arising from the positive electrode, such as slow kinetics of the oxygen reduction (ORR) and oxygen evolution (OER) reactions. Spinel-type Cobalt-based catalysts, such as Co_3O_4, $NiCo_2O_4$, $FeCo_2O_4$, etc., present a suitable catalytic activity for the OER, but they are less performing for the ORR. A useful approach used in the literature to increase the activity towards the ORR was to combine these oxides with carbon nanostructures, in particular graphitic ones, doped with heteroatoms (N, S, etc.) [1-3]. Recently, our group investigated carbon nanofibers (CNF) loaded with $FeCo_2O_4$ or $NiCo_2O_4$ prepared by electrospinning.

This technique allows for the preparation of highly active metals or oxides supported on a graphitic carbon support, CNFs, also doped with N coming from the carbon precursor (Polyacrylonitrile). The as-prepared CNFs are characterized by a high interaction with the metal, porosity and good resistance to corrosion, due to their graphitic character. In the present work, $MnCo_2O_4$/CNF catalysts are synthesized and physico-chemically studied in terms of structure, morphology, and surface properties; these features have been correlated to the electro-chemical behavior for the ORR and OER in comparison with previously developed catalysts and state-of-the-art materials reported in the literature. A preliminary investigation in an alkaline Zn-air battery is presented.

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Disclosing the Electrocatalytic Behavior of Doped-MnO_2 for Lithium-Air Batteries

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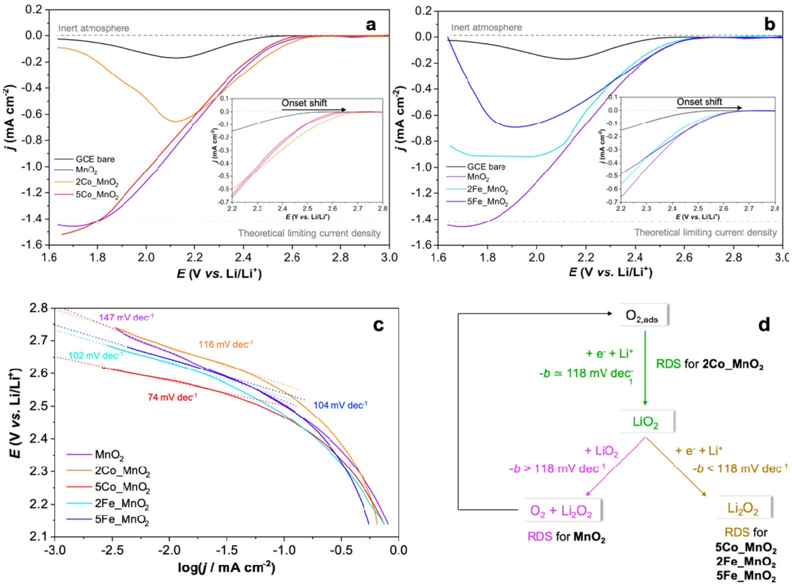
Due to the remarkably high theoretical energy and light weight, metal-air batteries represent one class of promising power sources for applications in next-generation electronics, electrified transportation and energy storage of smart grids [1]. The most prominent feature of a metal-air battery is the combination of a metal anode with high energy density and an air electrode with open structure to draw cathode active materials (*i.e.* oxygen) from air [1]. Gas Diffusion Electrodes (GDEs) are widely used as cathodes in metal-air devices [2]. However, one of the main drawbacks related to the cathodic reaction (ORR) is the overpotential loss (about 0.3-0.4 V) under operation conditions. Thus, lots of efforts were spent to inhibit the voltage loss requiring an effective ORR catalyst [1,3]. One of the most promising materials, in terms of both performances and costs, seems to be manganese dioxide. According to the recent literature, MnO_2 would ensure capacities comparable to those of platinum, letting higher capacity retention to be reached in non-aqueous electrolytes to prevent Li decomposition [1]. In the present work, the electrochemical performances of either bare or Fe/Co-doped (at both 2% and 5%) MnO_2 nano-electrocatalysts are evaluated by Linear Sweep Voltammetries (LSVs). The crystal structure and the surface properties of the present materials are examined by means of XRPD, BET-BJH, TEM, SEM/EDX and XPS analyses. Correlations between their physico-chemical features and the final electrocatalytic performances are drawn. Experimental results reveal that the as-synthesized powders have excellent electrochemical properties in organic electrolytes (0.15 M $LiNO_3$ in propylene carbonate, PC) showing a shift of the onset potential of about 150 mV with 2% Co-doped MnO_2 (Figure 1), thus resulting very promising candidates to be used in lithium-air batteries [4].



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Innovative Olivine Cathodes for High-Voltage Lithium Batteries

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Lithium batteries (LiBs) are among the most promising systems that could address today's strongly increasing needs for an efficient, compact and reversible electrochemical storage of energy [1]. Indeed, LiBs are characterized by a high specific capacity, a high efficiency, and a long lifespan [2]. Unfortunately, improvements in the working potential, in the specific energy, and in the rate capability properties of the cathodes are still needed to comply with the specifications required by practical applications.

This work describes the synthesis and the characterization of a new family of high-voltage and high-rate cathodes for LiBs. A high-performing olivine material of the type LiMPO4 (M = Fe, Ni, and Co) [3] has been modified by inserting into the structure high-valence transition metal ions (e.g., V(V), Nb(IV), and Ta(IV)) [4]. The effects of the insertion of the different ions on the structural, morphological, electrical and electrochemical properties of the materials have been thoroughly studied. The stoichiometry is evaluated by means of Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES); the morphology and size distribution of the grains are characterized by Scanning Electron Microscopy (SEM) and High-Resolution Transmission Electron Microscopy (HR-TEM); the structure is examined by powder X-Ray Diffraction (XRD) as well as a variety of IR spectroscopy techniques. The electrochemical characterization is carried out by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and charge/discharge tests at different current rates. Finally, the conductivity mechanism is studied by Broadband Electrical Spectroscopy (BES) and molecular dynamic. The cathode materials described in this report exhibit a high performance in terms of working potential (4.0 ÷ 5.0 V vs. Li/Li^+), specific capacity (149 $mAh \cdot g^{-1}$), and specific energy (656 $mWh \cdot g^{-1}$). Moreover, the insertion of high-valence transition metals results in an improvement of the rate capability of the cathodes, allowing for fast charge and discharge processes.

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Highly Versatile Gel Polymer Electrolytes for High Voltage Lithium Batteries

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Lithium-ion batteries (LIBs) have become a crucial device for energy storage in the recent years. However, they possess some drawbacks related to their limited safety, including a thermal runaway. Organic liquid electrolytes are flammable and form explosive vapors during a temperature rise. Consequently, there are strong requirements on the replacement of the liquid electrolyte with non-flammable ones. The use of ionic liquids and polymers as electrolyte components is an attractive approach to improve safety of the battery electrolyte and to allow efficient operations at high voltage [1,2].

In this work, safe and high-performance gel polymer electrolytes (GPEs) have been developed and combined with high-voltage spinel cathodes $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) in lithium metal cells. The GPEs are based on a poly(vinylidene fluoride-*co*-hexafluoropropylene) matrix and the electrolyte mixture of 1M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (LP30) and 1-butyl-1-methyl-pyrrolidinium hexafluorophosphate ($[Py_{14}]PF_6$). Non-flammable character and mechanical stability of the GPEs are demonstrated with flammability tests and rheological measurements, respectively. Lithium-ion conduction mechanism in the GPEs is evaluated by means of both impedance measurements and pulsed gradient spin-echo NMR technique. Galvanostatic charge and discharge cycles of lithium metal batteries with LNMO demonstrate improved electrochemical performance with coulombic efficiency above 99% and high specific capacity above 110 mAh g^{-1} at C/5 throughout 150 cycles, when the GPE with LP30/$[Py_{14}]PF_6$ 7/3 wt% mixture is used. In addition, its capacity retention is sufficiently high compared to GPE without $[Py_{14}]PF_6$, confirming that the ionic liquid is a highly promising additive for improving battery life.

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Protic ionic liquid electrolytes in lithium metal cells

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Lithium-ion batteries (LIBs) are dominating the portable electronic market and are currently being developped for the realization of hybrid-electric, plug-in and full electric vehicles, as well as for advanced delocalized energy storage units. For these applications, new improved electrolytes are highly desirable compared to the solutions based on flammable and volatile organic solvents currently in use, so as to increase the cycle life, safety, electrochemical permormance, and operative temperture range. Ionic liquids (ILs) are promising candidates in this respect, [1] due to their negligible vapour pressure at relatively high temperature, high chemical and thermal stability, good ionic conductivity and electrochemical stability. [2]

In this work, we investigate protic ionic liquids (PILs), which possess many attractive features of aprotic ionic liquid (AILs) and improved transport properties, while being also cheaper and easier to prepare. [3] The use of PILs as electrolytes in combination with Li metal anodes has not been considered before, due to the presence of acidic protons, which are highly reactive towards the Li metal electrode and limit the electrochemical stability.

Here we present for the first time the use of pyrrolidinium-based PILs with Li metal as anode in two different Li-metal cell configurations, using either LiFePO4 or LiNiMnCoO2 (NMC) as cathodes. The electrolytes consist of solutions of N-butylpyrrolidinium-bis(trifluoromethanesulfonyl)imide or N-butylpyrrolidinium-bis (fluorosulfonyl)imide in combination with lithium salts. The electrolyte solutions are combined with vinylene carbonate (VC), which has the fundamental purpose of promoting the formation of a stable protective layer on the Li metal anode, preventing detrimental reactions due to the protic Ils [5]. Stable ambient temperature cycling at different current regimes is demonstrated with >4 V class NMC composite cathodes. Notably, we could demostrate that PIL-based electrolytes can outperform their AIL counterparts under the same experimental condition.

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Long life lithium metal batteries employing dendrite-eating nanocomposite solid-state electrolytes based on hybrid fillers.

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The need for energy storage devices able to deliver higher amounts of specific capacity and energy densities has recently renewed the interest towards lithium metal batteries (LMBs), i.e. secondary batteries employing metallic lithium as anodic material. However, despite the incredible theoretical performances of lithium anode as an incredibly negative working potential and a specific capacity ten times higher than graphite, the implementation of these systems is currently hindered by many detrimental issues such as the uncontrolled growth of Li dendrites on the anodic surface [1]. Among all the possibilities that can be exploited to tackle this specific problem, the use of mechanically strong solid-state electrolytes (SSEs) is particularly showing its good effectiveness. Consequently, dispersing strengthening ceramic fillers into a soft polymeric matrix, otherwise prone to dendrite piercing, can hinder dendrite growth and enable stable cycling into LMBs [2]. Anyway, the addition of high amount of inorganic particles into a polymer usually results in strong aggregation and low homogeneity of the final product while reduced loading of ceramic are not able to effectively prevent dendrite penetration. Therefore, different strategies have to be tailored to improve the compatibility between these two phases.

Following an approach already successfully exploited for titania [3], we anchored short chains of poly ethyleneglycol (PEG) with different molecular weight on the surface of porous silica nanoparticles (NPs) exploiting (3-aminopropyl)triethoxysilane (APTES) as intermediate grafting agent. These hybrid fillers were then dispersed into high-M_w polyethylene oxide (PEO) in order to produce nanocomposite SSEs with ceramic loading up to 23% with a satisfying ionic conductivity and very high homogeneity endowed by the presence of the grafted PEG. Such electrolytes were able to sustain over 350 hours of continuous stripping-plating, tens of times more that pure polymeric membranes, in Li/Li symmetric cells both due to their increased mechanical toughness and to the ability of silica fillers to react with lithium dendrites, that also enabled some of these cells to autonomously restart their operation after short-circuit. Such dendrite-eating phenomenon of silica has been already reported for coated separators soaked in liquid electrolytes [4] but this is the first time that a similar behaviour is observed for all solid-state devices, also enabled by the high superficial area of our porous NPs. Additionally, implementing this electrolyte into Li/LFP full cells permitted the stable cycling at 70°C for over 50 cycles of lithium metal anodes and the delivery of discharge specific capacity values up to 156 mAh g^{-1}, with better results than liquid electrolyte analogue.

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Study of lithiated Nafion-based nanocomposites membranes as single lithium-ion conducting electrolytes for lithium batteries

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Solid-state polymer electrolytes (SPEs) have attracted great interest because of their propensity to improve lithium-battery technology by replacing the liquid electrolyte currently in use. SPEs are typically dual-ion conductor systems both cations and anions are mobile and cause a concentration polarization leading to poor performances of batteries. Recently, single lithium-ion conducting solid polymer electrolytes (SLIC-SPEs) have been proposed for polymer electrolytes, where anions are covalently bonded to the polymer, inorganic backbone, or immobilized by anion acceptors and only the Li^+ cation will contribute to a permanent flow of charge. They have advantages over conventional dual-ion conducting SPEs such as unity transference number, absence of harmful effect of anion polarization, extremely low rate of Li dendrite growth and immobilization of the lithium polysulfides in the lithium-sulfur (Li-S) batteries. In order to immobilize the polysulfide anions, the strategy adopted in this work is that of employing innovative SLIC-SPEs. For this purpose, lithiated Nafion-based nanocomposite membranes were synthesized by dispersion of nano-additives bearing suitable functional groups. Two nanostructures have been investigated: graphene oxide (GO) and Nanoscale Ionic Materials (NIM) functionalized. A thorough and systematic study of the lithium-ion transport was conducted by pulsed-field gradient nuclear magnetic resonance (PFG-NMR) and electrochemical impedance spectroscopy (EIS), while the mechanical properties of the film electrolytes have been tested by dynamic mechanical analysis (DMA) in a wide temperature range. Preliminary electrochemical studies have been conducted both in Li/Li symmetric cell and in secondary Li-S cells.

Li-ion Batteries with Innovative Silicon Anodes: Study of Electrolytes Based on Carbonates

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An innovative electrolyte for promising Si-based anode materials for Li-ion and post-Li-ion batteries is studied. Silicon features a tenfold theoretical specific capacity compared to graphite, although it presents the intrinsic disadvantage of a severe volume expansion during lithiation (about 300%), that undermines the lifetime of the device [1]. The combination of a newly formulated electrolyte with an active material consisting of silicon nanoparticles incorporated into β-cyclodextrins-based nanosponges matrix and reduced graphene oxide permits to overcome Si-related issues.

Starting from a mixture of ethers typical of Li-S cells, devised to obtain an electrolyte suitable for a future high energy and high capacity Si-S cell, FEC 5 wt% is used [2] and electrochemical tests show markedly improved performance with respect to VC-based standard electrolytes. XRD, EIS and CV studies highlight an increased activation of silicon and a less resistive SEI layer.

Overall, a favorable interaction of the newly formulated electrolyte with the nanosponges-based matrix leads to more durable and efficient cells.

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Novel methods for increasing energy and reducing environmental impact of lithium batteries.

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While lithium metal batteries are to be considered the next frontier and one of the most promising candidates for high energy density energy storage devices, the increased demand of electrochemical storage is leading the research towards new sustainable materials, to reduce their environmental and economic impact [1,2]. Lithium metal anode features a theoretical capacity of 3860mAh g^{-1} and the lowest negative electrochemical potential of -3.040 V (V vs standard hydrogen electrode). However, this material is still affected by unsolved problems that limits its industrial adoptions [3,4]. The use of ionic liquid as electrolytes can prevent and limit these problems forming a SEI with good characteristics. Moreover, ionic liquids have low vapor pressure and non-flammable properties that can enhance safety properties of li-metal batteries [5,6]. Metallic lithium can be combined with high potential cathodes to reach outstanding performances. Today, cathode electrodes are produced by exploiting F-based polymers binders, such as poly(vinylidene difluoride) (PVdF) which needs N-methyl-2-pyrrolidone (NMP) as solvent/dispersant, both very toxic for humans and environment. Transition to aqueous electrode processed in combination with natural polymers is expected to provide a great step forward towards an ideally sustainable and environmentally friendly technology for energy storage systems [7]. In this work we present a preliminary study on a high voltage cathodes prepared with water processable binders combined with lithium metal anode and ionic liquid electrolytes.

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Rheological properties of aqueous sodium alginate slurries

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Due to an ongoing decarbonisation of the economy and a raising demand of energy storage systems, intensive research on the optimization of lithium ion batteries is currently taking place. This is including not only active materials, but also conducting additives and binders. By now, the most widely used binder is polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone, which is not only flammable but also listed as a toxic substance. We are focussing on the replacement of standard binders by ones that can be dissolved in water and are therefore resulting in a reduced ecologic impact. Rheological properties like shear stress and sedimentation speed are crucial for electrode processing and its resulting performance properties. In order to gain a deeper understanding of these properties, we studied the flow parameters, oscillatory performance and contact angle characteristics of a promising bio-based polymer, sodium alginate (SA), as a suitable battery binder for lithium titanate (LTO) anodes. Several research groups have evaluated the rheological properties of sodium alginate [1-3], but none of them deals with SA in combination with LTO as anode material, which is a preferrable combination for the preparation of durable, safe and sustainable battery anodes.

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Enhanced Performance of a Sustainable Si/C Anode for High Energy Density Lithium-ion Batteries

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Since their development, rechargeable Li-ion batteries quickly became the most attractive energy storage devices for powering the emerging electric vehicles. However, with the advancement of technology, high-energy-density materials are required to satisfy the new energetic needs [1, 2]. Alternative materials which could ensure higher performance with respect of the state of the art, together with a lower environmental impact, have been studied for a long time, and Si-based composites have emerged as next-generation anode materials because of their peculiar characteristics [3, 4]. Taking into account sustainability, the present work proposes the study of a Si-C composite which combines the use of a green binder (Chitosan/Citric Acid) and a biomass-derived hard carbon as buffering components for volume expansion, together with a high Si content in the electrode (30%) for an improved specific capacity.

Structural and morphological characterizations are achieved through Raman spectroscopy and Scanning Electron Microscopy. Electrochemical characterization involves galvanostatic cycling, cyclic voltammetry at different scan rates, rate capability tests and electrochemical impedance spectroscopy, to study performance and stability of the material upon cycling, get a more detailed description of the limiting process in the composite and evaluate the interfacial stability upon cycling. The performance is compared to a Si/graphite composite fabricated as benchmark anode.

The material displays an average specific capacity close to 800 mAh/g over prolonged cycling at a high current density of 1A/g, with very good cycling stability and high coulombic efficiency.

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Carbon nitride based double layer approach for enhancing Li-S battery performances

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Lithium-sulphur (Li-S) technology presents high theoretical energy density (about 2600 Wh kg^{-1}) and low-cost (as sulphur is relatively inexpensive, highly available and non-toxic). Besides these well-known advantages, Li-S systems suffer from some issues, related to the multistep reaction process. In addition to low electronic conductivity of sulphur and Li_2S, and the volume expansion due to the solid-liquid transition during the conversion reaction with lithium, this system is deeply affected by the so-called "*shuttle phenomenon*"[1].

In this work, the use of a double-layer, based on carbon nitride, is proposed to limit the shuttle effect. Carbon nitride was chosen because it is a non-toxic, cheap and stable material, but in particular because, according to DFT calculation, it can directly interact with long chain polysulfides by electrostatic interaction. At the same time, the double-layer approach was chosen in order to avoid the direct mixing of carbon nitride inside the slurry composition of the cathode, so guaranteeing a good dispersion of carbon nitride on the electrode surface [2][3].

Starting from these considerations, a systematic study of carbon nitride was performed in order to study the influence of precursor, morphology, structure and surface chemistry with the aim of evaluating the polysulfides trapping ability in relation with the different properties of carbon nitride materials.

According to the observation carbon nitride obtained from urea at 550 °C resulted to be the best candidate as trapping agent in the double-layer sulphur cathode, showing long cycling performances, for more than 500 cycles, as well as better electrochemical performances at higher C-rates.

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Improvement of NMC layered cathode materials by combined doping/coating and evaluation of electronic-ionic transport properties by electrochemical impedance spectroscopy.

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To enhance Li-ion batteries (LIBs) in the continuous search for more well-organized and better electric energy storage systems, a good choice of cathode materials has considerable effect in terms of electrochemical performance, cost, safety, and sustainability [1]. $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC333) material is of substantial interest as cathode with high reversible capacity, low cost, and enhanced thermal stability [2]. Despite the enormous work invested so far in this cathode material, more attempt is still required to enhance NMC structural and interfacial stability [3].
Herein, two NMC (333) materials, pristine and modified by doping/coating, were successfully synthesized by a facile approach including a citric acid-assisted sol-gel method followed by heat treatment. The materials are studied by Inductively Coupled Plasma (ICP-MS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), X-ray Photoemission Spectroscopy (XPS). In order to assure a reliable evaluation, Rietveld refinement analyses of the data are carried out. The electrochemical properties of all electrodes are studied by cyclic voltammetry (CV) and charge/discharge cycles. To shed light on structural properties, electronic and ionic transport kinetics, and their effect on cycling performance, electrochemical impedance spectroscopy has been performed during the first two Li-extraction/insertion cycles for both pristine and modified NMC-based cathodes.

According to the results, the doped/coated NMC not only presents a better-organized layered structure but also enhances interfacial properties in comparison with the bare NMC. Electrochemical studies exhibit that doping and coating are beneficial regarding capacity retention, particularly at charge cut-off voltage of 4.2 V (capacity retention of around 95% after more than 200 cycles). Impedance spectra analyses show beneficial effects of doping with regard to better electronic properties and structural stability, and of coating regarding suppression of the electrolyte decomposition.

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Sodium-conducting, ionic liquid electrolytes for Na battery systems

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The sodium-ion battery (NIB) is a promising alternative technology to the common lithium-ions one, thanks to its lower cost, much larger word availability and similar redox potential (2.71 V vs. H^+/H_2) of Na with respect to Li [1,2]. Furthermore, the Na-system allows to use Al current collector, which is more lighter and cheaper than Cu.

Similarly to Li-ion devices, the use of volatile and flammables organic liquid electrolytes represent safety drawbacks [3]. A strategy for overcoming this issue is replacing the conventional organic electrolytes with ionic liquids (ILs), due to their particular properties, such as flame retarding, negligible vapor pressure, thermal-chemical-electrochemical stability and good ionic conductivity [4].

In this work, different ILs based on imidazolium (EMI) and tetra-alkyl-ammonium (N_{1114}) cations coupled with bis(fluorosulfonyl)imide (FSI) and bis(perfluroalkylsulfonyl)imide (TFSI) anions were studied as electrolyte materials in Na-ion batteries, in presence of sodium salts. These electrolyte mixtures were characterized in terms of ion transport properties, thermal, chemical and electrochemical stability. Also, preliminary battery test were run in half-Na cells.

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Aqueous sodium battery enabled by super-concentrated binary electrolyte.

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Super-concentrated aqueous electrolytes, also called water in salt electrolytes are attracting a growing attention among the scientific community owing to its enlarged electrochemical stability window. Conventional batteries operating with organic electrolytes have reached a good performance, but they suffer from the issue of flammability and cost [1]. To deal with these problems in state-of-the-art organic based battery storage applications, aqueous electrolytes could be viable alternatives. A serious concern in the use of aqueous electrolytes is the narrow electrochemical stability window of water which limits the output voltage and therefore the overall energy density. This extremely narrow potential window of water also narrows down the choice of electrode materials to a great extent. To tackle this problem the activity of water molecules must be reduced in such systems to enable a wider working window. The use of highly concentrated electrolytes has enabled a very wider potential window of up-to 3.0 V. Nevertheless, the use of fluorinated salts such as LiTFSI, LiFSI, NaFSI, NaOTF overcomes the benefits of concentrated aqueous electrolytes due to its fluorine content and high cost [2].

A smart approach to tackle the concerns in the use of aqueous electrolytes for battery applications is to use low cost and environmentally safe salts effective enough to offer a wider potential window. In our work we have explored a highly concentrated electrolyte based on binary salts of potassium and sodium acetate. This super concentrated binary electrolyte (20 m KAc + 7 m NaAc) enables a working window above 2.6 V. The electrolyte thermal behaviour is characterized via differential scanning calorimetry (DSC). The conductivity as well as the diffusion characteristics are analysed through impedance spectroscopy. Using a carbon coated NASICON as a negative electrode i.e., $LiTi_2(PO_4)_3/C$ (LTP/C) we have achieved a remarkable reversible intercalation performance of 85.1 $mAhg^{-1}$ for sodium with a retention of 92.6 % after 120 cycles in a potential range of (-0.6 -0.05 Vs SHE). We have also characterized LTP/C in organic electrolytes for sodium, lithium and potassium intercalation behaviour with promising results. Conclusively, the electrolyte based on safe and cost-effective acetate salts could lead to an effective step in the development of water-based energy storage devices.

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Improved zinc electrodeposition in mild-acidic aqueous Zn-ion batteries

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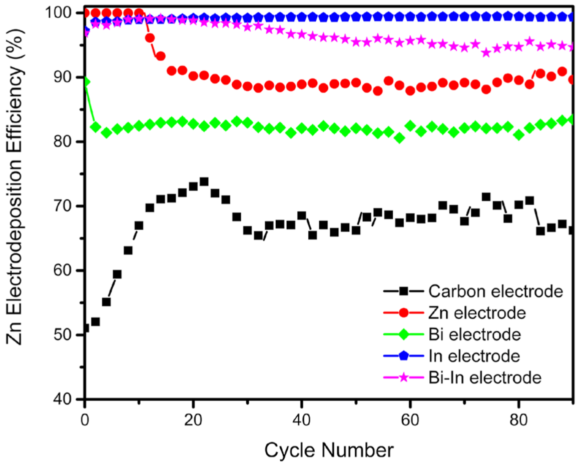
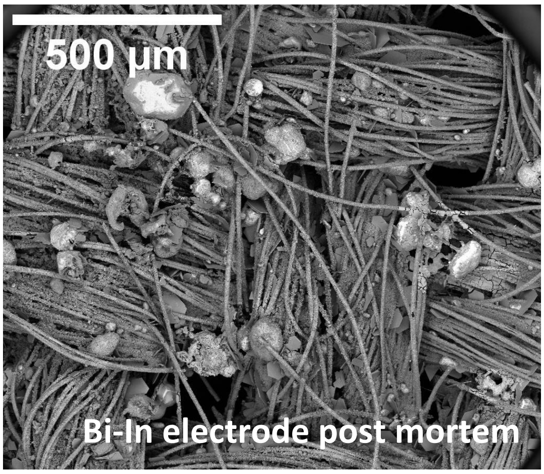
Mild aqueous zinc ion batteries (ZIBs) are considered one of the most promising aqueous-based post-Li ion technologies due to their high volumetric energy and power density, high environmental friendliness and low cost. However, the bottleneck for the commercialization of ZIBs is related to the inefficient electrodeposition of metallic zinc at the negative electrode because of: dendrites formation and hydrogen evolution [1]. Even though in literature various strategies to mitigate the dendrite formation can be found, very little attention is given to the problem of the gaseous H_2 formation concomitant to the Zn deposition step. Therefore, a negative electrode based on metallic bismuth and indium has been developed to improve the zinc electrodeposition/dissolution efficiency, thanks to the high overpotential of these two metals toward the hydrogen evolution [2].

Specifically, we studied the effect of several electrode formulations containing different amounts of bismuth and indium particles on the Zn electrodeposition/dissolution reaction from a 500 mM $ZnSO_4$ aqueous solution. The effect of the metallic substrates has been evaluated in terms of coulombic efficiency, deposition overpotential and electrode morphology pre- and post-mortem using SEM, quantitative EDS and XRD analyses. Moreover, the amount of gas resulting from the electrolyte's decomposition has been quantitatively defined during each Zn deposition-dissolution cycle through *in operando* differential electrochemical mass spectrometry (DEMS).

The best electrodes in terms of coulombic efficiency and morphology of the Zn deposits have been used as anodes in a Zn-ion full cell. To the best of our knowledge, our work is the first one addressing the Zn electrodeposition from mild aqueous electrolytes focusing on the quantitative determination of the amount of parasitic hydrogen evolution reaction.





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A lignin-based electrolyte for aqueous solar cells

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In the quest for sustainable materials for quasi-solid-state (QS) electrolytes in aqueous dye-sensitized solar cells (DSSCs), novel bioderived polymeric membranes were prepared in this work by reaction of pre-oxidized kraft lignin with poly(ethylene glycol)diglycidylether (PEGDGE).

The effect of PEGDGE/lignin relative proportions on the characteristics of the obtained membranes was thoroughly investigated, and clear structure-property correlations were highlighted. In particular, the glass transition temperature of the materials was found to decrease by increasing the amount of PEGDGE in the formulation, indicating that polyethylene glycol chains act as flexible segments that increase the molecular mobility of the three-dimensional polymeric network. Concurrently, their swelling ability in liquid electrolyte was found to increase with the concentration of PEGDGE, which was also shown to influence the ionic transport efficiency within the membrane.

The incorporation of these lignin-based crosslinked systems as QS electrolyte frameworks in aqueous DSSCs allowed to achieve devices with excellent long-term stability under UV-vis light, which was found to be superior to benchmark QS-DSSCs incorporating state-of-the-art carboxymethylcellulose membranes. This study provides the first demonstration of lignin-based QS electrolytes for stable aqueous DSSCs [1], establishing a straightforward strategy to exploit the potential of lignin as functional polymer precursor for the field of sustainable photovoltaic devices.

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Exceptional ORR catalytic activity of Pt_xY Nanoalloys prepared by Laser Ablation in Liquid

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Pt_xY alloy nanoparticles (NPs) were prepared by an innovative synthesis, i.e. Laser Ablation in liquid (LAL). The principal issues of LAL is the control of the composition and of NP size distribution, which are influenced by the experimental conditions, including the laser frequency, the beam wavelength or the different solvents. In particular, the employment of organic solvents leads to the formation of a thin carbon layer on the particle's surface, that limits the NP's growth but at the same time can suppress the NPs catalytic activity. In this work, LAL of PtY NPs was performed by focusing a Nd-YAG laser on a bimetallic Pt_3Y target. Pt_xY NPs were synthetized in three different solvents, ethanol (PtY-E), a mixture of EtOH and NaCl solution and acetone. PtY-E NPs solution was further irradiated in different conditions for resizing the NPs. TEM images of PtY-E NPs show three different size distribution picked at 4.08 nm, 18.37 nm and 47.76 nm. The alloyed component (21 % with respect to the Pt content) was evaluated by XPS analysis, which confirmed a Pt-Y ratio of *c.a.* 3, corresponding to the most active alloy [1]. The XRD analysis evidences the presence of a mixture of Pt_3Y and Pt_2Y phases and the absence of unalloyed Pt. The best performing catalysts is PtY-E_A_IRR1, which shows a half wave potential ($E_{1/2} = 0.943$ V vs RHE) 76 mV more positive than the commercial standard Pt/C TKK (Figure 1a) and a Mass Activity higher than 1000 A g^{-1}. The high electrochemical performance are connected to the good NPs distribution and dimension obtained with the irradiation treatment and to the removal of the carbon shell accomplished by acid washing [2,3]

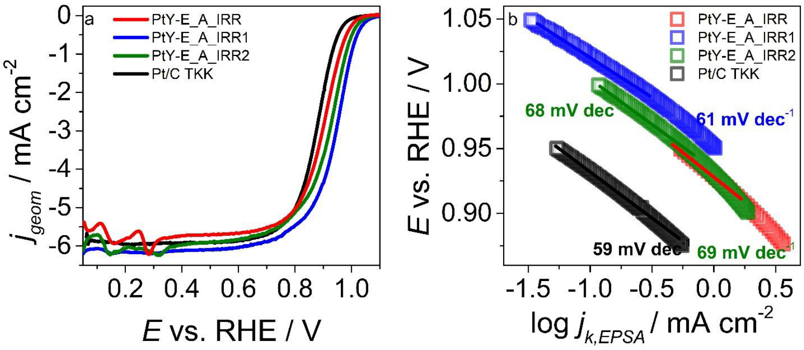

Figure 1 Electrochemical characterization for Pt and Pt_xY catalysts after the acid treatment a) LSV with RDE recorded at 20 mV s^{-1} and 1600 rpm in O_2 saturated $HClO_4$ solution. b) Tafel plots limited to the kinetic region, the current is normalized by the EPSA determined by CO stripping.

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Effect of synthesis on cathodes for sodium-ion batteries: correlation between morphology, structure and electrochemical performances

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Sodium-ion batteries (SIBs) have emerged as the most promising alternative to lithium-ion ones, due to their low cost and sustainability that makes them interesting candidates for application in many sectors, such as the automotive one.

Among all the cathodic materials tested in SIBs the most widely studied are layered sodium oxides, of general formula Na_xMO_2, where M is a transition metal, for their good performances and similarity with the lithium-ion cathodes.

An important issue to be considered during the development of cathode materials is their synthesis process, since its scalability is a key factor for industrial production. Moreover, different synthesis pathways can lead to different morphologies of the cathodic materials, affecting the electrochemical performances. Tuning the synthesis pathway and controlling important parameters such as particle size and density can in fact permit to obtain higher energy densities and stabilities of the cathode materials [1].

So far co-precipitation and sol-gel processes have been the most widely studied for industrial scaling up, due to their simplicity and versatility. Whereas many studies have been reported on how synthesis parameters can benefit on the morphology and performances of the cathodic materials for the lithium-ion based systems [2,3], the research for SIBs is still at the beginning. Important topics are related to the possibility of using complexing agents in the co-precipitation process, in order to obtain single crystal-like cathode particles. So far ammonia has been the most studied complexing agent for cobalt, nickel and manganese, but the introduction of other complexing agents could permit also the synthesis of iron-based cathodes with single crystal-like morphology, since the iron-ammonia complex is not stable in aqueous solutions [1].

Our preliminary studies have been aimed at synthetizing cathode materials with different methods: simple co-precipitation, sol-gel, co-precipitation with ammonia and different reaction times. The cathode materials so obtained have been analyzed, to determine the purity, the morphology, the particle size distribution and the tap-density of the powders.

Electrochemical measurements on the cathode materials so produced have shown important differences among the samples concerning capacity retention, sodiation and desodiation average voltage and mechanisms.

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Electrocatalyst materials for the iodide/iodine redox system

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Iodide/triiodide redox couple has been demonstrated as a high-efficient redox couple which is largely used in several applications, such as for dye-sensitized solar cells (DSSCs)[1], Redox-Flow Batteries (RFBs)[2], and Thermally Regenerable Redox-flow Batteries (TRBs)[3].

In the RFBs, this redox couple is used as active component of the catholyte, offering several advantages such as high solubility, faster kinetics, and being relatively cheap.

Unfortunately, there are some limitations associated with its application such as high volatility and the ability to corrode glass/TiO_2/platinum in DSSCs[4] as well as the most common electrodes. Although the electrochemical kinetics of the iodide/triiodide reactions is fast compared to other potential redox couples (cerium and chromium in RFBs, cobalt in DSSCs), improvements are required, and the development of noble metal free catalyst is desired.

The present contribute focusses on low-cost electrode materials, that contribute to reducing polarization and resulting in high reaction rates, that can be feasible for scaling up to grid energy storage size and for DSSCs.

Two different carbon-based substrates are used to support electrocatalyst materials, i.e. carbon clothes and hollow nanospheres produced by carbonization of PMMA. Carbon clothes substrates have been decorated with noble metal nanoparticles (Au) while the hollow nanosphere were wrapped with Ti_3C_2 nanosheets to produce a noble metal free catalyst. All these materials are characterized in terms of stability, charge-transfer resistance and electroactivity against different concentration of iodide/triiodide redox couple.

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Structural disorder and electrochemical stability in Ti3C2Tx MXene compound as negative electrode in Sodium Ion Batteries

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Sodium-ion batteries, SIB, represent the ideal candidate for the next generation large-scale energy storage devices due to the abundancy of Na, the theoretically high performance and the robustness of the working scheme, which is borrowed from the well-established lithium-ion batteries, LIB, technology [1]. SIB technology is not yet mature for the commercialization, and one of the main causes is the lack of high performing anode materials, able to combine high capacity, good mechanical stability, high cyclability and low cost. In the last years the new class of 2D materials of the MXenes has been profitably proposed as negative electrode material for SIB [2]. MXenes are a family of layered compounds with general formula $M_{n+1}X_nT_y$ where M can be a transition metal (Ti, Sc, Zr, Hf, Nb, V, Cr..), X is C and/or N, and T represent the terminations of the layers. The large interlayer spacing, the open morphology, the high electrical conductivity of such material are some of the key factors determining the good performances of MXene as anode for SIB [2]. At the same time some fundamental aspects still need to be defined. Beside the huge number al studies regarding the introduction of new compositions and doping the structural and compositional characterization is still missing. Indeed, the composition and stoichiometry of the terminations is not completely controllable neither with the synthesis and post-synthetic treatments and, at the same time, the actual composition is difficult to determine. Similarly, the overall structure of the MXene has not been described yet. A full understanding of these essential structural aspects is the missing step in the understanding of the peculiar functional properties and of the differences observed for MXene obtained with different synthetic routes and treatments [3]. Indeed, the available literature converges in pointing out the correlation among the termination's composition, structure, and morphology with the observed electrochemical behavior but no insight into these aspects have been reported yet. Moreover, the understanding of the specific structural features can be the starting point for the improvement of the properties through the control of the stoichiometry and structure. Aim of this contribution is the description of the results obtained in the structural characterization of the $Ti_3C_2T_2$ MXene compounds and the correlation with their electrochemical performances. The structural investigation is carried out with a multi techniques approach that allows to explore both the short- and long- range structure, combining the analysis of X ray and neutron diffraction data, XPS, and TEM images, while the electrochemical behaviour was characterized in half cells configuration vs. metallic sodium. In particular, the diffraction data have been analyzed with the approach embodied in the software Faults that accounts for the evaluation of extended defects allowing to fit, for the first time in our knowledge, the MXene diffraction patterns. The MXene structural model has been built up step by step based on the preliminary analysis of the parental compound, the MAX phase Ti_3AlC_2.

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$Ti_3C_2T_x$-SnO_2 nanocomposite for lithium ion battery

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MXene are promising lamellar materials that are extending their use in various applications day by day. The 2D structure, combined with their hydrophilicity and almost metallic conductivity, allows them to reach various fields, like electrochemical storage, electrocatalysis, sensors. The first MXene studied, as well as the main one still used today is $Ti_3C_2T_x$, where (T_x) identifies a functional group such as -O, -OH, -F. Each single lamella is made by a repeat of -$T_x(Ti_3C_2)T_x$- units that are oriented in the space in a hexagonal close-packed (HCP) crystal structure [1].

MXene based electrodes can be obtained as highly exfoliated sheets for supercaps or as bulk lamellar particles for batteries. The chemical properties of the surface, in particular the functional groups, keep the lamellae together giving a 3D morphology to the material. MXenes can also be act as platform for integrating or imprisoning ions, nanoclusters or nanoparticles [2].

Recently an important application of MXene is the use as a structural support to produce nanocomposites for high capacity sodium and lithium ion batteries. Very promising materials for lithium ion batteries such as conversion oxides or alloys cannot be used as such due to the pulverization of the particles during the delithiation/lithiation processes. As an example, MXene has already been used in many works to mitigate the effect of the pulverization of silicon in lithium ion battery [3].

In this contribute the application of nanocomposites obtained by mixing MXene and tin oxide for lithium ion batteries will be discussed. The insertion of nanoparticles into the MXene structure leads to obtain a capacity around 370 mAh g^{-1} in MXene-SnO_2 50:50 wt% composites when cycled with a current of 120 mA g^{-1}.

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Hydrogen production from photo-electrolysis based on anion exchange membranes

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Environmental emergencies that our planet is tackling, such as climatic changes and global warming, lie on thoughtless employment of fossil fuels over past decades to satisfy the increasing world energy demand for demographic, industrialization and urbanistic growths. Hydrogen fuel is characterized by high mass energy density (120-142 MJ/Kg) and recognised as the most attractive "green" alternative to running out fossil fuels, as gasoline (45 MJ/Kg), because its reaction, coupled with the oxygen reduction reaction in a polymer electrolyte membrane fuel cell, gives the spontaneous formation of water and electricity without any release of pollutant gases. However, hydrogen formation from water splitting is a process requiring an external bias, surplus of energy that could be provided by renewable and sustainable power sources, such as sunlight and wind.

In this field, the research on photo-electrochemical (PEC) water splitting (WS) relies on semiconductor electrodes that exhibit appreciable photogenerated charge separation at the solid/liquid interface when placed in a liquid electrolyte, generally metal-hydroxides, and illuminated by sunlight. In our recent works, tandem photoelectrochemical cells were constituted by a solid membrane as gas separator between a photoanode and a photocathode [1-2] to improve efficiency and durability of PEC cell. Particularly, anion exchange polymer electrolyte membrane, able to separate H_2 evolved at the photocathode from O_2 at the photoanode, was investigated in terms of ionic conductivity, corrosion mitigation, light transmission for a tandem photoelectrochemical configuration. The membrane was firstly investigated in alkaline solution, KOH or NaOH at different concentrations, to optimize the ion exchange process. Exchange in 1M KOH solution provided high conversion of the groups, a high ion exchange capacity (IEC) value of 1.59 meq/g and a hydroxide conductivity of 25 mS/cm at 60°C for anionic membrane. Another important characteristic, verified for hydroxide membrane, was its transparency above 600 nm, thus making it a good candidate for tandem cell applications in which the illuminated photoanode absorbs the highest energy photons (<600 nm), and photocathode absorbs the lowest energy photons. Furthermore, hydrogen crossover tests showed a permeation of H_2 through the membrane less than 0.1%. Finally, low-cost tandem photoelectrochemical cells, formed by titanium-doped hematite and ionomer at the photoanode and cupric oxide and ionomer at the photocathode, separated by a solid membrane in OH form, were assembled to optimize the influence of ionomer loading dispersion. Maximum enthalpy (1.7 %), throughput (2.9 %) and Gibbs energy efficiencies (1.3 %) were reached by using n-propanol/ethanol (1:1 wt) as solvent for ionomer dispersion and with a 25 $\mu L\ cm^{-2}$ ionomer loading for both the photoanode and the photocathode.

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Sustainable aqueous Na-ion batteries

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Energy storage systems will be crucial for the integration into the grid of renewable energy sources that, unlike fossil sources have a discontinuous energy production [1]. Amidst the possible technologies, the sodium ion storage systems emerged as a promising alternative to lithium-ion cells, featuring greater and more distributed availability of sodium and lower costs of materials used in production, despite the lower specific and volumetric energy performance [2,3].
This study focuses on the characterization of aqueous electrolyte media for sodium ion cells, taking into account sustainability, low risks for health and environment, and low costs.

Three different solutions were prepared: sodium sulfate 1.5 M, Mix 1 (sodium acetate 2 M and sodium sulfate 1.5 M, 1:1 v/v) and Mix 2 (sodium citrate 1.5 M and sodium sulfate 1.5 M, 1:1 v/v). Each solution has been physico-chemically and electrochemically characterized with self-standing cathodes, one based on sodium cobalt oxide ($Na_{0.71}CoO_2$) and one based on a Prussian blue analogue (PBA), coupled with an activated carbon anode. For the latter, the application of a more sustainable binder to substitute the usual fluorinated ones has been investigated. The binder, that can be processed in water and after drying become insoluble in aqueous electrolytes and guarantees the stability of the electrodes, has been tested and the results are here reported and discussed.

Acknowledgments
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Who Prevails Between Sulphur Doping and Hierarchical Pore Structure on the Fe-N-C Site Density, Activity and Selectivity in Oxygen Reduction Reaction Electrocatalysis?

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During past decades, various non-PGM catalysts were investigated: M-N-C based on M-N_x sites, non-precious metal oxide, chalcogenides and oxynitrides. The most studied are M-N-C, and among them, the most active metal center is Fe, where iron coordinate from 2 to 5 nitrogen functional groups, where Fe-N_4 site is considered the most important for the selectivity and activity in ORR. Different aspects need to be joint together to obtain good performances and among others, the site density, the carbon support hierarchical structure, the surface chemistry, the graphitization degree and other [1]. Choosing the right carbon matrix is fundamental to improve catalytic performance, in fact the increment of the density of active sites is not enough to enhance the activity, but it is necessary to rationally design the textural and porous properties to facilitate the mass transport between micropores and the bulk solution. In addition to that, the incorporation of heteroatoms is another strategy; the idea is to modulate the electronic structure of the carbon plane via the delocalization of the π-electrons by addition of atom like S, P and B into N-doped carbon structure generating a synergistic effects between the dopants. Considering the S doping, the high electron spin density of doped S atoms enhances the electrocatalytic activity, in particular the asymmetric charge density distribution creates oxygen adsorption sites to an enhanced performance for ORR. However, it is uncharted how the S dopants, interacts with both Fe-based active sites and N species. Oxidized S functionality (-SO_x) and thiophene-like structure (C-S-C) could be beneficial [2,3]. Herein, we investigate the effect of sulphur doping of the carbon support, on the Fe-N_x site formation and on the textural properties (micro- and mesopore surface area and volume) in the resulting Fe-N-C catalysts. The Fe-N-C catalysts were prepared from mesoporous carbon with tunable sulphur doping. The carbon with the highest sulphur content was also activated through steam treatment at 800 °C of different duration, which allowed to modulate the carbon pore volume and surface area. The resulting catalysts were tested in O_2 saturated 0.5 M H_2SO_4 electrolyte, and the site density (SD) was determined using the NO-stripping technique. Here we demonstrate that sulphur doping has a porogenic effect increasing the microporosity on the carbon support and it also facilitates the nitrogen fixation on the carbon support as well as the formation of Fe-N_x sites. It was found that the Fe-N-C catalytic activity not directly depend on sulphur content, but rather on the microporous surface and therefore any electronic effect appears to be not determinant. Comparing Fe-N_x SD versus the sulphur content gives a volcano like shape, where the maximum value is obtained for sulphur/iron ratio close to 1.8, i.e. a too high sulphur doping has a detrimental effect of Fe-N_x formation. However, it was highlighted that the increasing of Fe-N_x SD is a necessary but not sufficient condition for increasing the catalytic activity of the material, unless the textural properties are also optimized, i.e. there must be an optimized hierarchical porosity that allows better use of the active sites.

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Poly(vinylidenefluoride)-based Janus separators for lithium batteries

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The next step towards the development of new-generation the lithium-ion batteries (LIBs) is to replace the traditional graphite anode with lithium metal to improve the energy density of the battery [1]. The problem of using lithium metal is the generation of dendrite, conductive filaments of lithium, which eventually penetrate the separator and short the cell causing thermal runaway and degradation [2].

In the last few years, functionalized "Janus" separators for LIBs able to mitigate dendrite formation and growth have been proposed [3]. In this work we report on a nano-composite Janus separator made by an insulating side, in contact with the anode, based on PVDF-HFP and Al_2O_3 and a semiconducting side including multi-walled nanotubes (CNT's). The ionic conductivity at room temperature of the separator exceeds $2.4*10^{-3}$S cm^{-1}. The blocking effect of the separator vs. lithium dendrites has been investigated by galvanostatic cycling on symmetric Li/Janus/Li cells with the help of post-mortem SEM analysis (Figure 1.).

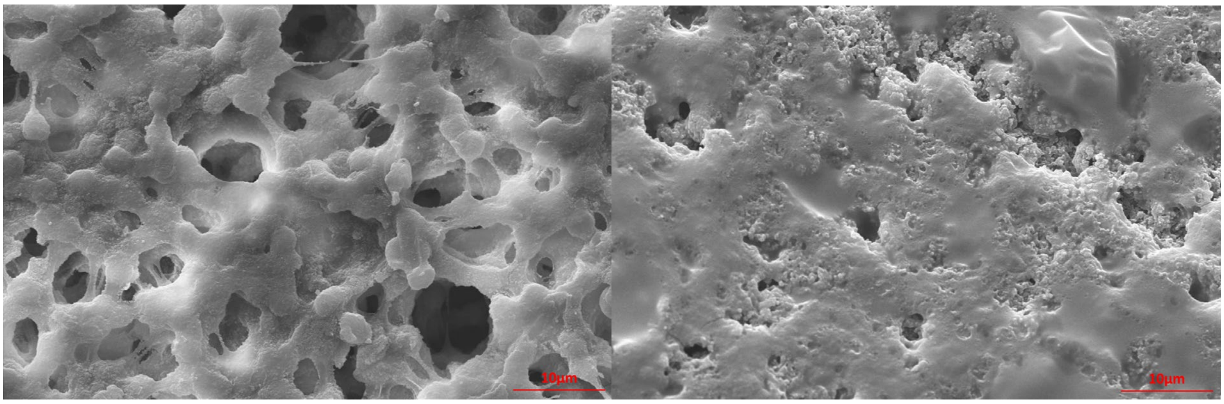

Figure 1. SEM images of the Janus separator before (left) and after (right) the activation with LP30

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Expansion of the scope of cyclic voltammetry with the thin-film rotating (ring) disk electrode in the study of oxygen reduction reaction electrocatalysts

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In electrochemical energy conversion and storage (EECS) devices, performance is modulated by a cascade of phenomena including: (i) the redox processes at the electrodes; (ii) the transport of charge, especially of ions through the electrolyte; and (iii) the transport of mass (*e.g.*, for the provision of reactants/removal of products to/from the electrodes). Thus, it is often very complex to unravel the different contributions to the overall system performance. A purely *"trial-and-error"* approach to fabricate and test full-fledged EECS prototypes is thus impractical, as this would entail too massive an investment in terms of both resources and time. Hence, it is crucial to implement experimental approaches for the elucidation of the details of specific electrochemical features (*e.g.*, reaction kinetics) of the various functional materials used in EECS devices. The resulting information is critical in the development of advanced functional materials bestowing to the EECS device a performance and durability beyond the state of the art.

Cyclic voltammetry carried out with a thin-film rotating disk electrode or ring-disk electrode (CV-TF-R(R)DE) is one of the most successfully and widely adopted methods to achieve this goal [1]. CV-TF-R(R)DE is typically used to screen quickly the performance and reaction mechanism of electrocatalysts (ECs) for the oxygen reduction reaction (ORR). The latter process is widely exploited in a broad variety of EECS devices (*e.g.*, fuel cells, FCs, and metal-air batteries). The ORR is particularly critical since it often bottlenecks the operation of the entire system. Even though the CV-TF-R(R)DE method is very popular, the full scope of its remarkable capabilities is often not explored.

This work reports how to implement both innovative and more traditional (but half-forgotten) approaches to exploit CV-TF-R(R)DE to its full potential, with the purpose to study the most relevant electrochemical features of ORR ECs and quickly identify the most promising candidates for application in FCs or other electrochemical devices [2]. An approach to compare the ORR kinetic features of vastly different ECs is discussed, allowing for quantitative performance comparisons at the same high level of accuracy. It is also shown how to adopt CV-TF-R(R)DE to understand quantitatively whether an ORR EC exhibits improved morphology/mass transport features in comparison with a Pt/C benchmark. In conclusion, herein it is elucidated how to expand significantly the scope of CV-TF-R(R)DE studies with respect to the level typically achieved in the state of the art, taking into consideration both kinetic and morphology/mass transport features by means of a simple morphokinetic (MK) correlation map.

Acknowledgements
The research leading to the results reported in this work has received funding from: (a) the European Union's Horizon 2020 research and innovation programme under grant agreement 881603; (b) the project *"Advanced Low-Platinum hierarchical Electrocatalysts for low-T fuel cells"* funded by EIT Raw Materials; and (c) the project *"Hierarchical electrocatalysts with a low platinum loading for low-temperature fuel cells e HELPER"* funded by the University of Padova.

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Cobalt-Copper mixed oxides by simple electrodeposition route for supercapacitor electrodes

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Cobalt based mixed metal oxides are being extensively proposed as promising material to increase energy density of modern supercapacitors. Among the various structures of cobalt based mixed oxide, cobalt-copper (Co-Cu) spinel arises due to its superior performance in terms of high specific capacitance, rate capability, and capacitance retention. It has been demonstrated that performance of electrodes based on this spinel strongly depends on surface morphology and porosity. Many attempts have been done to prepare such materials, all of which are based on the thermal annealing of coatings at high temperatures to obtain a spinel structure [1- 4].
Here we report about the synthesis, chemical-physical and electrochemical characterization of supercapacitor electrodes based on cobalt-copper mixed oxides prepared by a simple electrochemical route assisted by H_2 evolution and pH variation at the electrode/electrolyte interface.

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1mol% Ru and Pt-doped perovskite oxides for IT-SOFCs

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Solid oxide fuel cells (SOFCs) have a great potential among the emerging energy conversion technologies because they can efficiently convert various types of fuel (hydrogen, methane, CO, biogas) into electrical energy in the temperature range 650-850 °C. The choice of electrodes remains a challenge because most metal oxides suffer from low chemical stability and conductivity in reducing atmosphere and low electrocatalytic activity toward oxygen reduction reaction (ORR) in the intermediate temperature range [1].

In this view, perovskite oxides (ABO_3) have shown excellent properties in terms of thermal stability, compatibility with other cell components, low production cost and, most importantly, great flexibility [1]. $La_{0.6}Sr_{0.4}FeO_{3-\delta}$, (LSF) perovskite oxide has been widely investigated for the high electrical conductivity and good electrochemical properties [2]. However, the main drawback is the poor activity towards ORR in the intermediate temperature range (500-700 °C) as in the case of most iron-based perovskites [3]. The B-site doping with a small amount of platinum group metals (PGM) can be a strategy to sensitively improve the electrocatalytic properties [4,5].

In our work, we investigate the physico-chemical and electrochemical properties of 1mol% Ru and Pt-doped LSF compounds (LSFRu and LSFPt). The powders are synthesized using solution combustion synthesis (SCS). To maximize the surface area, the powders are calcinated at quite low temperature (750 °C) for 6h. The structural analysis showed that both Ru and Pt-doping causes a progressive shift of the XRD peaks toward lower 2θ angles indicating an expansion of the unit cell volume due to the substitution of Fe^{4+}/ Fe^{3+} sites with larger Ru and Pt cations. Thermogravimetric analyses reveal that oxygen non-stoichiometry of perovskite structures is affected by the oxidation state of dopants. Ru shows a stable 4+ oxidation state retaining a larger oxygen amount than Pt into the lattice. The electrical properties of LSFRu and LSFPt sintered pellets are measured by four-probes technique and area specific resistance (ASR) values of LSFM/$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)/LSFM with M=Ru, Pt symmetric cells are assessed in the temperature range 550-800 °C using electrochemical impedance spectroscopy (EIS). The results are discussed and related to the structural and microstructural properties. Preliminary fuel cell tests on LSFM/LSGM/LSFM cells show promising results in terms of power output and polarization resistance at 750°C.

Our investigation shows that the low 1mol% doping largely improves the electrocatalytic properties making the LSFM with M=Ru and Pt perovskite compounds valuable for electrodes application in the intermediate temperature range, moreover, it keeps their cost comparable to widely used and largely substituted compounds such as $La_{0.6}Sr_{042}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFCo).

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Hard carbons derived from pyrolysis of tires as electrodes for electrochemical storage systems

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Carbonaceous materials are widely used in industrial production and materials fabrication, thanks to their high abundance and versatility. Tires, for example, are composed by a series of natural rubbers, polymers, and carbons, which are able to deal with the hard conditions needed (mechanical stress, heat, etc.). Since about 1.5 billion waste tires are produced each year[1], recycle can be considered a resource other than a necessity. With pyrolysis, for example, rubbers and polymers can be converted into carbon black, which can be used for many purposes, such as energy storage.

Even though graphite cannot be used as anodic material for sodium-ion batteries (due to exfoliation), other carbonaceous materials, such as hard carbons, have proven to be able to reversibly store sodium ions. Chars derived from pyrolyzed tires can be directly used as anodic material in NIBs. Results of chars derived from pyrolysis of tires' wastes carried out at high temperature (≥1100°C) in inert environment have been already reported in literature[2], however milder methods, such as Microwave Assisted Pyrolysis (MAP), can be used.

In our work, hard carbons derived from disposed tires were obtained by MAP in nitrogen atmosphere at four different gravimetric powers (24, 32, 40 and 48 kW kg^{-1}). Aside from the compositional (CHNS and elemental), morphological (SEM) and structural (XRD) analysis, electrochemical tests were performed in coin cells vs metallic sodium using carbonate-based electrolytes (1M solution of $NaPF_6$ in carbonate solvents). Each carbon showed very good performances in terms of capacity and coulombic efficiency. Changing from EC/DEC to EC/PC as solvent for the electrolyte made the capacity increase of about 46%. The gravimetric surface of the carbons (< 100 m^2 g^{-1}) makes them suitable for batteries' purpose, but the surface can be enhanced by chemical activation to make them useful for supercapacitors, both aqueous and nonaqueous ones.

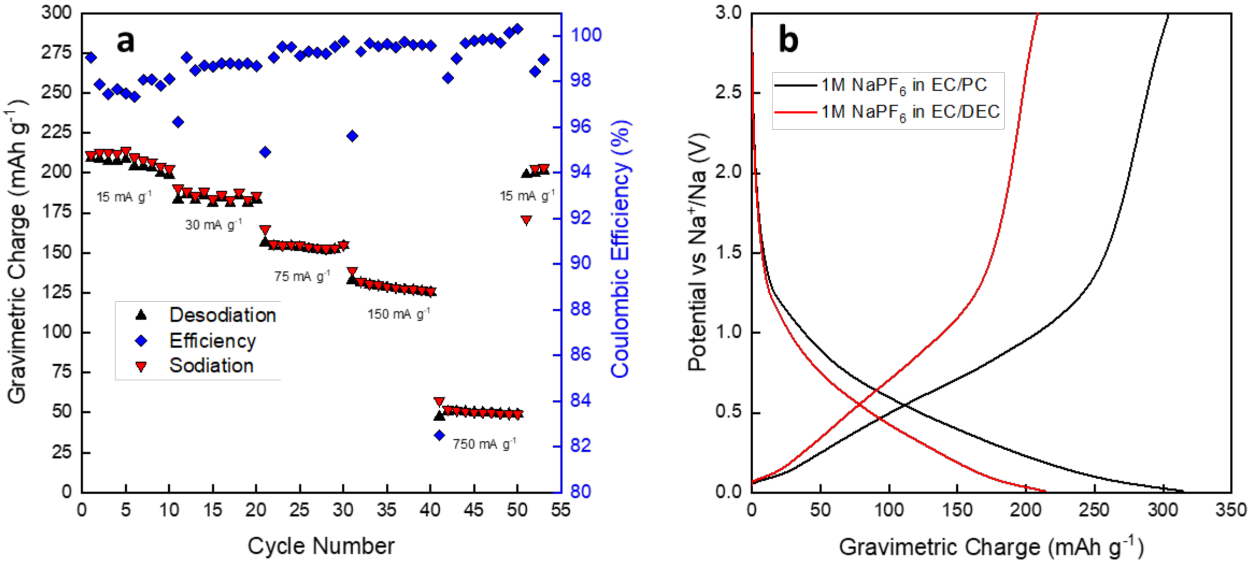

Figure 1: Electrochemical performances of tire-derived hard carbons. (a) Cycling properties of a hard carbon in a 1M $NaPF_6$ in EC/DEC. (b) Voltage - charge profile of the hard carbon with different electrolytes

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Lighting up the Electrochemiluminescence of Carbon Dots through Pre- and Post-Synthetic Design

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Electrochemiluminescence is a luminescent phenomenon induced by an electrochemical stimulus. In the last decades, ECL became a very promising analytical technique for clinical applications, mainly thanks to high signal-to-noise ratio. In order to generate electrochemically the excited state, two different precursors, i.e. luminophore and co-reactant, are required. In the quest for ever-increasing sensitivities, ECL can ideally be coupled to nanotechnology to develop new systems and strategies for analyte determination even in very complex matrices.[1] Nanotechnologies, as dye-doped nanoparticles and Bodipy Carbon Nanodots (BCDs), can improve the sensitivity and sensibility of ECL technique thanks to their advantageous and tuneable properties.[2] They exploit different strategies for increasing the ECL signal intensity. Dye-doped silica nanoparticles concentrate a huge number of dyes, protected by the external environment, in a single nanoparticle. Moreover, they are easily synthesized, hydrophilic and prone to bioconjugation thanks to silica chemistry.[3]

BCDs are Carbon Nanodots functionalized with boron-dipyrromethene (Bodipy). Carbon Dots are a class of photoluminescent and electrochemiluminescent nanomaterials, specifically carbon-based nanoparticles, with ECL elusive properties. Here we focus our attention on ECL proprieties of BCDs and how pre- and post-synthetic design strategies improve the ECL emission properties, opening new opportunities for exploring CDs in biosensing applications. BCDs are excellent candidates as an alternative to $Ru(bpy)_3^{2+}$ luminophores thanks to their features, such as nontoxicity, chemical inertness, high resistance to photobleaching and unique ECL properties.[4]

The final goal is the development of an efficient ECL nanomaterial with high ECL intensity and simple bioconjugation. The study conducted will open new opportunities for exploring CDs in biosensing applications.

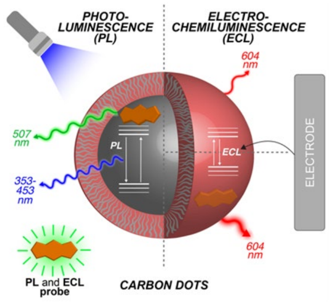

Figure 1. Schematic representation of the ECL and PL mechanism of Bodipy Carbon Nanodots

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Redox behaviour of dibenzopyrene derivatives and their electrochemical generation of conductive film

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Planar and curved polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic molecules with an extended and delocalized π-system that provides interesting properties for optoelectronic [1] and energy storage applications [2]. In the framework of our recent work on corannulene polymerization [3], we investigated a series of rationally designed dibenzo[a,i]pyrene (DBP) derivatives which, in principle, could lead to an extension of the aromatic π-system through an anodic oligomerization on the electrode followed by an electrochemically induced cyclodehydrogenation reaction.

In this study, we report the electrochemical characterization by cyclic voltammetry of a family of pristine and mesitylen-substituted mono- and dimeric DBP. The presence of bulky and non-linear side groups, as mesitylene (Mes), provides a more stable electrochemical behavior, as well as prevents the π-π stacking in solid state films, which is generally deleterious for light emitting devices (OLED) [4]. Furthermore, the interesting optical properties of DBP and derivatives have preliminary been investigated by electrochemiluminescence (ECL) in solution.

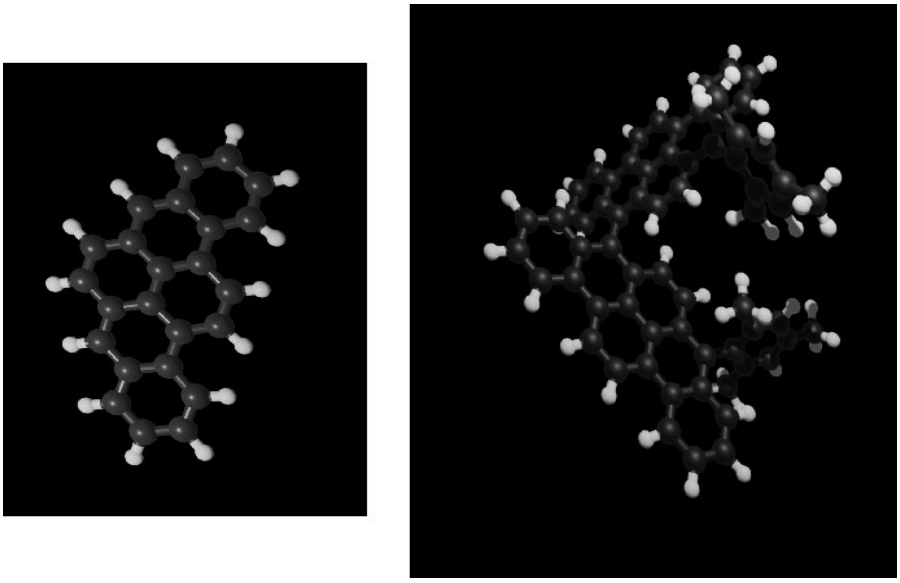

Figure 1 Molecular structures of DBP and mesitylen-substituted dimer

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Towards solid-state Na-ion batteries via easily processable electrodes and electrolytes

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In recent years, large-scale energy storage systems are becoming fundamental to realize the load levelling of intermittent renewable energy sources, such as wind and solar, into the grid. Secondary (rechargeable) sodium-based batteries may represent the key enabling technology in this respect, because of high-energy density, low-cost, simple design, and easiness in maintenance. However, currently studied materials and processes are not in line with a truly sustainable point of view.

Here we offer an overview of our recent developments on innovative polymer electrolytes for Na-ion batteries. In our labs, we develop different kind of polymer electrolytes by means of different techniques, including simple solvent casting [1] and UV-induced photopolymerization (UV-curing) [2], being simple, low-cost and easily scalable to an industrial level. Besides, our research focuses on new sustainable polymers, also including ionic liquids to enhance safety and oxidation stability. All samples were thoroughly characterized from the physico-chemical and electrochemical viewpoints. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation even at ambient conditions. Electrochemical performances in lab-scale devices were evaluated by means of cyclic voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials.

Our developed polymer-based electrolytes, when assembled in lab-scale sodium cells with different electrolyte materials prepared by sustainable approaches, such as high-voltage cathodes, like vanadium phosphates [3], and carbonaceous or 2D structured anodes, delivered stable specific capacity values even exceeding 200 mAh g^{-1} at ambient temperature upon constant current cycling at 0.1 mA cm^{-2}. Their intrinsic stability was also confirmed by very long-term cycling test that exceeded thousands of hours of continuous operation, which is definitely remarkable for truly quasi-solid-state systems.

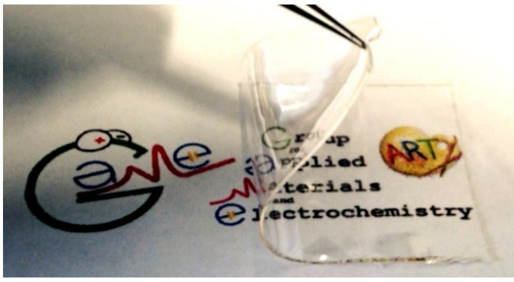

Figure 1: Digital photograph of a UV-crosslinked polymer electrolyte membrane.

Acknowledgements

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MoS_2/PANI composite as suitable functional interlayer for Li-S batteries

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Lithium-sulfur (Li-S) battery technology promises much higher energy storage capacity compared to common Li-ion commercial batteries. Li-S batteries have high theoretical capacity of 1672 mAh g^{-1}, thanks to conversion reaction from solid sulfur (S_8) to lithium polysulfides (LiPS) [1].

At the same time, sulfur allows for a wide range of operation temperature, being non-toxic abundant and low-cost element.

Instead of mentioned advantages, few issues are still hindering the commercialization of Li-S battery. The main problem afflicting lithium sulfur batteries is the shuttle phenomenon, due to soluble long chain LiPSs generated at the cathode, which are soluble and able to migrate to the anode were they directly react with lithium, by a parasitic passivation reaction [2].

In the last years most interlayer separators are based on materials showing a great physical blocking of PS, like graphene. Unfortunately, many of these materials are still not effective enough in preserving long life performance. Recently was demonstrated that metal sulfides and conductive polymers can directly interact with lithium polysulfides through electrostatic or chemical bonds, inhibiting the dissolution of LiPSs. In particular, MoS_2 and PANI separately showed strong adsorption capability, preventing polysulfides dissolution and accelerating the redox reaction kinetics of polysulfides conversion [3][4].

In the present work we rationally designed some binary materials based on PANI and MoS_2 at different ratio, with the aim to evaluate the different role of the two components and their synergy as PS blocking agent.

By the implementation of a second layer containing the MoS_2/PANI composite directly on the top of the standard S/KjB electrode.

The systematic study confirms that double-layer containing the composite remarkably improves the performance of the sulfur cathode, showing a final specific capacity close to 600 mAh g^{-1}, 25% higher than the standard sulfur cathode, after 500 cycles.

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Graphene quantum dots@Benzoquinone@β-cyclodextrin systems for a dual mode sensing

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Host-Guest inclusion systems have aroused widespread interest, since they play important roles in molecular recognition, particularly in sensor devices. A class of host molecules that has often been used in sensing applications is that of the cyclodextrins, cyclic oligosaccharides that consist of six (α-cyclodextrin), seven (β-cyclodextrin, β-CD), or eight (γ-cyclodextrin) glucose moieties [1]. Depending on the cavity size, cyclodextrins have shown a selective affinity to a wide variety of molecules. For instance, in a previous work we succeeded to demonstrate the affinity of cyclodextrins for o-toluidine, a toxic water pollutant [2].

Various functional composites based on β-CD have been developed in the Literature. Particularly, Organic-Metal oxides nanocomposites have emerged as an outstanding surface modifier for sensors construction. However, the composite concept can even go beyond this approach by combining electroactive and fluorescent nanomaterials for the creation of a dual-mode sensing device.

Based on this, a novel system based on Graphene Quantum Dots GQDs@Benzoquinone@β-cyclodextrin as a host guest capturing probe was proposed. In this approach, EDC/NHS chemistry was used to covalently immobilize benzoquinone, the electroactive probe, via a cysteamine spacer on graphene quantum dots. Finally, β-cyclodextrin was added via a reductive amination. The optical properties of the synthesized GQDs were studied using UV-vis and PL spectroscopy. Structural and morphological characterizations were examined by the Transmission Electron Microscopy and Fourier-Transform InfraRed spectroscopy. Cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy were performed to investigate the surface modification at each step.

The system was firstly immobilized directly on glassy carbon electrode, then on fluorine tin oxide glass, bare or covered with a thin layer of titania film, to test the possibility of a dual mode sensing. In fact, the capturing of the target molecule will be accompanied by a simultaneous substantial variation in the benzoquinone electrochemical signal and an evident fluorescence quenching of GQDs.

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SPETTROMETRIA DI MASSA (MAS)

- Orals
- Posters

Non-targeted authentication of food products: the synergic combination of ambient mass spectrometry, data fusion and machine learning

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Mass spectrometry-based methods are being developed in the last decades to monitor food authenticity and detect food frauds.

The majority of them are targeted methods, which search for pre-selected adulterant markers, thus being focused on the detection of known analytes capable of reveling the adulteration. Note that food fraud encompasses a wide range of intentional and accidental fraudulent actions, from adding low-value substances to removing or replacing the authentic products. Besides, new types of adulterantions appear every day.

Therefore, non-targeted methods, based on the analysis of the chemical signatures of food products have been recently developed. These methods do not look for what should not be there (the markers of the adulteration), but define very carefully the chemical fingerprint of the authentic food. Through the precise determination of the molecular features that codify the genuine food items, non-targeted methods reveal anomalous fingerprints that deviates significantly from that of the authentic food. For this reason, non-targeted approaches are advantageous when new unknown adulterants are added. Ambient mass spectrometry is a sensitive and simple analytic platform that can authenticate food from their chemical fingerprinting in a non-targeted manner. In particular, high resolution mass spectrometry analysis with direct analysis in real time (DART-MS) has shown its utility in the authentication of various food products[1]. DART does not require extensive sample preparation, and the data collection and analysis can be done within a few seconds. In this oral presentation, we show the synergic combination of DART-HRMS, data fusion and machine learning for the authentication of food products. While data fusion methods allow the combination of multi-blocks of data, classification models allow the prediction of food authenticity of unknown samples. In this keynote, we will first present the application of this approach to the authentication of spices. Spices are considered high value commodities due to the high demand and the complex supply chain. For these reasons, spices are frequently frauded to increase profits and meet consumers' demand. Multiple extractions (with polar and non-polar solvents) and multi-modalities DART-(+/-) HRMS acquisitions were performed on the spice samples. The complementary multi-blocks of data were merged by means of mid-level data fusion. Supervised statistical analysis on the merged unique fingerprint suggested a clear statistical discrimination between adulterated and pure spices. The most informative *m/z* values, capable of codifying genuine and adulterated samples, were used to build the classifiers and predict unknown samples. They were validated on independent sets of samples and are now routinely used in our laboratory as screening methods. The joint application of ambient mass spectrometry, data fusion and machine learning for spice authentication is only one example of the powerful performances of this approach. Our laboratory is being developing non-targeted methods for the authentication of fish, flours and other food commodities that will be also described during this oral presentation

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Future challenges in MS based technologies applied to the safety of foods

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The lecture will provide an overview about Mass Spectrometry methods applied to assure safety of foods. Bottlenecks and advantages of this technique will be extensively described along with some case studies illustrating the use of mass spectrometry to detect and quantify undesidered and banned contaminants in foodstuffs. As a whole, despite the multitude of coupling with Mass Spectrometry so far available and the diverse analytical tools for final data mining, Mass Spectrometry has proved to be a versatile and valid tool also for ascertaining the safety and authenticity of foods. The need for harmonization of MS based methods still remains a major challenge in the future and will be discussed in the present note.

Mass spectrometry for the monitoring and protection of the environment

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The description of the quality of the environment needs information as more accurate and reliable as possible. There is an unavoidable time gap between gaining this information and policy actions for environmental protection.

The cutting-edge technology mainly based on high-resolution mass spectrometry (HR-MS) coupled to gas or liquid chromatography (GC or LC) seems to fit with both aims and approaches used for environmental risk management.

Anyway, some analytical protocols pertain to the "big data affair", and also the time of response remains a limitation for implementing mitigation actions, mainly if the chemical description is not supported by a biochemical and toxicological evaluation.

Several case studies are here presented to show the ability of mass spectrometry to cope with environmental monitoring and protection, and the necessity of new tools and strategies to empower the “green deal” purposes is discussed.

Integrated lipidomics and proteomics reveal cardiolipin remodelling, upregulation of HADHA and long chain fatty acids in pancreatic cancer stem cells

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Pancreatic cancer stem cells (PCSCs) play a key role in the aggressiveness of pancreatic ductal adenocarcinomas (PDAC) [1]; however, little is known about their signaling and metabolic pathways. Therefore, in the current study LC-MS/MS proteomic and lipidomic analyses were integrated to investigate the signaling and metabolic dysfunctions implicated in the pathophysiology of PCSCs obtained from parental PaCa3, PaCa44, MiaPaCa2, and PC1J PDAC cell lines.

For proteomics analysis cells were collected (three biological replicates for each cell type) and tryptic peptides were subjected to SWATH acquisition label-free MS, by using a micro-LC interfaced with a 5600^+ TripleTOF MS (AB Sciex). For lipidomics, untargeted analysis was performed by a UPLC system with a C4 column and an Orbitrap Elite MS (Thermo Fisher Scientific); whilst targeted analysis of lysolipids, ceramides and dihydroceramides was performed using a QTRAP 6500 MS (AB Sciex) operating in MRM mode.

The obtained results showed that PCSCs have specific and common proteome and lipidome modulations. In particular, PCSCs displayed upregulation of trifunctional enzyme subunit alpha (HADHA) involved in cardiolipin remodelling [2]. We also found that the upregulated proteins of PCSCs are mainly involved in fatty acid (FA) elongation and biosynthesis of unsaturated FAs. Accordingly, lipidomics revealed an increase in long and very long-chain unsaturated FAs. Moreover, in accordance with HADHA upregulation, lipidomics showed the induction in PCSCs of molecular species of cardiolipin with mixed incorporation of 16:0, 18:1, and 18:2 acyl chains.

To our knowledge, the current work presents the first proteome and lipidome investigation of PCSCs. The results shown here support the potential of a MS-based multiomic approach and contribute to the understanding of PDAC biology, revealing mitochondrial cardiolipin remodelling and enhanced fatty acid elongation as promising targets in PDAC.

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Metabolomic approaches to investigate the role of the mitochondrial regulatorZc3h10 in adipocytes

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Introduction

We characterized the protein zinc finger CCCH-type containing 10 (Zc3h10) as a new mitochondrial regulator and we validated its role during adipocytes differentiation [1]. Mitochondria play a crucial role in many cellular processes, including cellular metabolism, and they are essential organelles for the health of the cell. Beyond their contribution to energy production, they are key regulators of tissue development and cell differentiation. The aim of this study is to use metabolomic approaches to understand the role of Zc3h10 on energy metabolism during adipocyte differentiation by using a targeted metabolomic approach.

Materials and Methods

C3H/10T1/2 cell line (mesenchymal stem cells) can be differentiated into white adipocytes using a specific adipogenic cocktail. Quantification of different metabolites was performed with a liquid chromatography/tandem mass spectrometry (LC-MS/MS) on an API-4000 triple quadrupole mass spectrometer coupled with an HPLC system using a C18 column for amino acids, Pursuit XRs Ultra 2.8 Diphenyl for acyl-carnitine and cyano-phase LUNA column for energy metabolites.

Results

Zc3h10 depletion significantly reduces adipocyte differentiation and mitochondrial activity. To demonstrate that Zc3h10 impacts mitochondrial function and metabolism, we performed a metabolomic analysis at two different stages of adipocytes differentiation, early and terminal phase. We evaluated the intracellular levels of by-products belonging to the main metabolic pathways: glycolysis, tricarboxylic acid (TCA) cycle, pentose phosphate pathway (PPP), amino acids, and acyl-carnitines using LC-MS/MS. Steady-state metabolomics indicated that Zc3h10 depleted pre-adipocytes showed decreased levels of PPP intermediates and several TCA cycle metabolites, while various amino acids and acyl-carnitines were increased compared to the control group. Zc3h10 silenced mature adipocytes showed a more altered metabolic profile characterized by decreased $NAD^+/NADH$ ratio, reduced levels of acetyl-CoA, malate, citrate, and fumarate, and increased levels of several acyl-carnitines. We also used metabolic tracers ([U-$^{13}C_6$]-glucose, [U-$^{13}C_{16}$]-palmitate, or [U-$^{13}C_5$]-glutamine) to confirm that the flow of energy substrates into the TCA cycle is affected by Zc3h10 silencing at both considered time points.

Discussion/Conclusions

Zc3h10 silencing in white pre-adipocytes and adipocytes deeply impaired mitochondrial function, decreased adipogenic potential and altered metabolic profile.

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Spatial proteomics to map tissue alterations during the progression of fibrosis in an IPF and Nintedanib-treated mouse model

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Idiopathic pulmonary fibrosis (IPF) is a rare chronic lung disease, characterized by the aberrant accumulation of fibrotic tissue in the lungs. Whilst nintedanib has been used to slow its progression [1], little is known about the proteomic changes that occur in the lung after its administration. In this preliminary study we aim to explore the feasibility of MALDI-mass spectrometry imaging (MSI) to investigate changes in the proteomic profile related with the progression of fibrosis as well as with the anti-fibrotic effect after nintedanib administration.

FFPE lung tissues from 16 mice (n=4 saline-controls; n=9 bleomycin-induced (administration at days 0 and 4) lung fibrosis and sacrificed after 7, 14, 21, and 28 days; n=3 treated with bleomycin (at day 0 and 4) followed by nintedanib administration from day 7 to day 21) were assembled on a tissue microarray (TMA) of a total of 32 cores (two cores from each FFPE block). TMA tissue sections were digested (trypsin and collagenase type III) and analysed by MALDI-MSI. After the analysis, CHCA matrix was removed and digested peptides were identified by nLC-ESI-MS/MS.

Principal component analysis of fibrotic regions of bleomicyn-induced samples, highlighted four clusters which were associated with each time point, respectively, with the samples at 21 days being most separated from the starting point.

ROC analysis of 21 days bleomycin-induced and saline samples identified 53 peaks with AUC≥0.70, including proteins associated with fibroblast mobility and collagen deposition. Among these, *m/z* 1105 (COL1A1) had a lower intensity in nintedanib-treated samples compared to 21 days bleomycin-induced samples as a molecular indicator of fibrosis slowdown.

This pilot study highlights the proteomic profile of fibrosis progression in bleomycin-treated samples and the proteomic signature of fibrosis slowdown after nintedanib treatment.

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Quantitative analysis of resolvins in biological matrices by means LLE-µSPE-HPLC-MS/MS

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Resolution of inflammation is a finely controlled and different active processes are based on highly coordinated actions of various immune and non-immune cells [1]. The key players in the resolution of inflammation are cross-talking lipids and proteins; a novel group of pro-resolving lipid mediators such as lipoxins, resolvins, protectins and maresins, which are defined "specialized pro-resolving mediators (SPM)". To date, resolvins have been characterized by using different approaches, including enzyme linked immunoassays and nuclear magnetic resonance (NMR), or reversed phase liquid chromatography (RP-LC) and tandem mass spectrometric (MS/MS) [2]. To date, only a few methods have been developed and validated for the analysis of resolvins, and even fewer techniques have been validated to analyze many resolvins in different matrices [3]. Resolvins are active in the picogram to nanogram dose range, whereby they can directly modulate a plethora of anti-inflammatory responses.

The presented method proposes an analytical protocol for the extraction and to quantification of 6 different resolvins from 3 different matrices (plasma, cells and exudates); it was validated according to the EMA guideline for bioanalysis, showing good precision (between 1% and 20%) and accuracy (between 3% and 20%). In particular, the combination of two different sample preparation techniques, Liquid-Liquid Extraction (LLE) and micro-Solid Phase Extraction (µSPE), applied for the first on this class of molecules, used for the extraction and clean-up respectively, led to high enrichment factor and consequently a high sensitivity (LOQ between 1 and 38 pg mL^{-1}); moreover the validation data proved the versatility of µSPE as clean-up tool as it was capable to manage huge enrichment factor without negatively affect accuracy and precision of analysis. Here, the combination of two extraction techniques, LLE for extraction of the analytes and µSPE for the clean-up, providing a 20 fold enrichment factor, allowed the detection of the target compounds at very low levels, even by using an average level LC-MS/MS instrumentation, reaching comparable levels with reference methods that are developed for top level instrument. The method performances showed high level performances in the analysis of Rvs in different matrices [4]. To the best of our knowledge the use of µSPE is unprecedented for this class of molecules and presents a good clean-up procedure providing very low ion suppression and maintaining good performance in term of accuracy and precision. Finally, the suitability of the present method to quantify resolvins in authentic biological matrices was ascertained in plasma samples of healthy patients, where indeed RvD1 could be detected at a very low level.

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A Combined GCxGC-MS and GC-MS Approach to Discovery and Validate New Potential Biomarkers for Prostate Cancer Diagnosis

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Although prostate cancer is one of the most diagnosed tumors in males, to date, a non-invasive test that able to diagnose the disease is still missing. Digital rectal exploration, ultrasound imaging, quantification of PSA (prostate specific antigen) and a final biopsy to confirm the results are the main tests used for the diagnosis. The biopsy involves the sampling of several areas of the prostatic gland in order to obtain an accurate and clear diagnosis. It is therefore necessary to develop new non-invasive methods for the reliable and rapid diagnosis of prostate cancer and to avoid invasive analyses such as biopsies.

The aim of this research was to identify new potential serum biomarkers for the diagnosis of prostate cancer through the use of two-dimensional gas chromatography mass spectrometry (GCxGC-MS). GCxGC-MS allows a higher resolution of chromatographic peaks and consequently a greater number of identified compounds.

Serum from patients with elevated PSA and Gleason score of seven, and therefore with a probable diagnosis of the tumor, were analyzed using GCxGC-MS. Half of the patients had the prostate cancer while the other half had a prostatic chronic inflammation. The metabolomics analysis allowed the identification of more than 2000 metabolites, while their relative quantification was used to compare the two groups of patients. The fold change was used to identify potential biomarkers and the bioinformatic analysis of modulated metabolites was used to highlight the pathways associated to the disease. Multivariate analysis was able to clearly separates the two group of patients and to identify a specific metabolomics signature of prostate cancer biomarkers in serum. A validation analysis performed on an external cohort of patients (120) using a GC-MS confirmed the biomarkers identified in the discovery phase.

In conclusion, GCxGC-MS, thanks to the high-resolution power and sensitivity, resulted a powerful tool for the discovery of new potential biomarkers.

Influence of mixed starter cultures of *Hanseniaspora osmophila* and *Saccharomyces cerevisiae* on wine flavor profile explored through HS-SPME/GC-MS

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Wine is a complex beverage matrix which contains over 800 identified volatile compounds contributing to its overall aroma, many of them being formed during the fermentation process [1]. The widespread use of inoculated fermentation with commercial *Saccharomyces cerevisiae* strains has determined a uniformity in wine organoleptic properties. Thus, the need to select new starter cultures to satisfy winemakers requests for product differentiation has recently emerged [2]. In this context, non-*Saccharomyces* yeasts have obtained special attention. Among all the available non-*Saccharomyces* strains, in this study a wild *Hanseniaspora osmophila* strain was tested in microvinification trials as mixed starter cultures in combination with a commercial S. *cerevisiae* starter during microfermentations trials in Aglianico grape must. The selected *H. osmophila* strain was tested in mixed culture as free and microencapsulated cells in comparison to single fermentation with the S. *cerevisiae* commercial starter. The fermentative process was monitored by evaluating the sugar consumption during the time. A method based on headspace solid phase microextraction (HS-SPME) followed by gas chromatography coupled to mass spectrometry (GC-MS) was optimized to obtain a comprehensive profile of the aroma and flavor compounds of wines understudy through the design of experiments (DoE), since the classical univariate approach (one-at-a-time, OVAT) for the optimization of all the parameters influencing SPME remains still hindered due to the high number of experiments needed to establish the best conditions for samples analysis [3,4]. The non-targeted HS-SPME/GC-MS analyses of wine revealed the effectiveness of mixed starter culture on enhancing and defining the complexity of the final wine aroma. Moreover, the obtained results confirmed the influence of cells formulation on wine characteristic.

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Lipidomic approach to evaluate the effect of X-ray irradiation treatment on the lipid profile of Camembert cheese

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Camembert is a surface mould-ripened soft cheese, characterized by the presence of a felt-like coating of white mycelia due to the growth of *Penicillium camemberti* on the surface. The raw milk cheeses as the Camembert, typically are subjected to spoilage bacteria and for thus they have a short shelf-life. Among the non-thermal technologies to inactivate and destroy pathogenic and spoilage microorganisms, there is the ionizing radiation [1-2]. This technology is able to preserve organoleptic characteristics and health benefits of treated foodstuffs, if it carried out in the range established by the legislation from a dose level of 1 up to 10 kGy [3-4]. In this study, X-rays irradiation was applied to Camembert cheese and a lipidomic approach was used to evaluate the possible modifications on lipid composition, induced by this treatment. The Camembert samples were irradiated with increased doses of 1.0, 2.0 and 3.0 kGy at a dose rate of approximately 2 kGy h^{-1}. The lipid extraction procedure was based on slightly modified Folch method. Ultra-High liquid chromatography coupled to Q-Exactive Orbitrap mass spectrometry (UHPLC-ESI-Orbitrap-MS) equipped with a heated electrospray ionization (HESI) probe was employed to analyse the lipidomic profiles. Lipids are identified by both accurate precursor ion mass and fragmentation features and quantified using LipidSearch^{TM} software. Furthermore, chemometric analyses were used to establish possible differences among irradiated and non-irradiated samples.

A total of 8 classes of lipids, including ceramides (Cer), monoacylglycerol (MG), diacylglycerols (DG), triacylglycerols (TG), phosphatidylcholines (PC), phosphatidylethanols (PEt), cholesterol ester (ChE) and zymosteryl ester (ZyE) were identified. In particular, in cheese irradiated samples, MG and PEt increased, while TG and DG decreased. This behavior has already been observed at a dose level of 1.0 kGy. These results confirm that the lipidomic approach is a powerful means to provide more information on the changes induced by X-ray radiation treatment.

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Metabolomic approaches to investigate the role of the mitochondrial regulatorZc3h10 in adipocytes

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Introduction

We characterized the protein zinc finger CCCH-type containing 10 (Zc3h10) as a new mitochondrial regulator and we validated its role during adipocytes differentiation [1]. Mitochondria play a crucial role in many cellular processes, including cellular metabolism, and they are essential organelles for the health of the cell. Beyond their contribution to energy production, they are key regulators of tissue development and cell differentiation. The aim of this study is to use metabolomic approaches to understand the role of Zc3h10 on energy metabolism during adipocyte differentiation by using a targeted metabolomic approach.

Materials and Methods

C3H/10T1/2 cell line (mesenchymal stem cells) can be differentiated into white adipocytes using a specific adipogenic cocktail. Quantification of different metabolites was performed with a liquid chromatography/tandem mass spectrometry (LC-MS/MS) on an API-4000 triple quadrupole mass spectrometer coupled with an HPLC system using a C18 column for amino acids, Pursuit XRs Ultra 2.8 Diphenyl for acyl-carnitine and cyano-phase LUNA column for energy metabolites.

Results

Zc3h10 depletion significantly reduces adipocyte differentiation and mitochondrial activity. To demonstrate that Zc3h10 impacts mitochondrial function and metabolism, we performed a metabolomic analysis at two different stages of adipocytes differentiation, early and terminal phase. We evaluated the intracellular levels of by-products belonging to the main metabolic pathways: glycolysis, tricarboxylic acid (TCA) cycle, pentose phosphate pathway (PPP), amino acids, and acyl-carnitines using LC-MS/MS. Steady-state metabolomics indicated that Zc3h10 depleted pre-adipocytes showed decreased levels of PPP intermediates and several TCA cycle metabolites, while various amino acids and acyl-carnitines were increased compared to the control group. Zc3h10 silenced mature adipocytes showed a more altered metabolic profile characterized by decreased NAD^+/NADH ratio, reduced levels of acetyl-CoA, malate, citrate, and fumarate, and increased levels of several acyl-carnitines. We also used metabolic tracers ([U-$^{13}C_6$]-glucose, [U-$^{13}C_{16}$]-palmitate, or [U-$^{13}C_5$]-glutamine) to confirm that the flow of energy substrates into the TCA cycle is affected by Zc3h10 silencing at both considered time points.

Discussion/Conclusions

Zc3h10 silencing in white pre-adipocytes and adipocytes deeply impaired mitochondrial function, decreased adipogenic potential and altered metabolic profile.

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High-resolution mass spectrometry approaches finalized to identification of new glycoside compounds in grape

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Grape polyphenols determine the biological and organoleptic properties of wines. For example, berry skin anthocyanins are characterized by antioxidant activity, and flavan-3-ols and proanthocyanidins protect human low-density lipoprotein (LDL) against oxidation, act as cardio-protective agents, and prevent oxidative damage by reduction of the lipid oxidation and inhibition of free radical production.[1-4] Stilbenes (e.g., *trans*-resveratrol, piceatannol, piceids, and viniferins) are constitutive compounds in vine tissues and are phytoalexins produced as active defense of the cell. These compounds are characterized by anticancer, antioxidant, anti-inflammatory, platelet aggregation inhibition, and cardio-protective activity, and contribute to the nutraceutical properties of wines.[5] Many glycoside flavonols and flavanones were identified in grapes.[6,7] In general, they are bioactive and antioxidant compounds: e.g., quercetin showed to inhibit platelet aggregation and cancer cell growth in human tumors.[8] Flavonols, along with anthocyanins, are also involved in the phenomenon of copigmentation, which induces a bathochromic shift to purplish hues in red wines, and are studied as chemotaxonomic markers and for industrial purposes.[9-11]

Previously, a database (DB) containing high-resolution mass spectrometry (HR-MS) data of overall grape and wine compounds (*GrapeMetabolomics*) was constructed to study grape metabolomics by performing UHPLC/QTOF analysis coupled to *targeted* data analysis, MS/MS, and in-silico fragmentation.[12,13] Because of their relevant importance in grape, a DB specific for identification of flavonols and flavanones (*GrapeFlavMet*) was constructed by including the possible formulas calculated using the molecular moieties of compounds identified in other natural extracts and reported in the literature. By coupling UHPLC/QTOF, targeted data analysis using this DB and HR-MS/MS, several new pentoside and acetyl-hexoside derivatives were characterized in grape extracts.

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Paper Spray tandem mass spectrometry: an innovative approach to assess flavonoid content in citrus drinks

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Herein, a novel methodology for quantifying the most abundant flavonoids in citrus beverages is presented. Citrus fruits are rich in flavanone glycosides, especially rutinosides and neohesperidosides of eridictyol, naringenin and hesperetin. These compounds confer a value-added to the juice, due to their nutraceutical properties [1,2]. In this framework, the development of a rapid, accurate and sensitive approach for their determination assumes great significance since it enables to better highlight the quality of these food products.

The methodology is based on the use of paper spray ionization coupled with tandem mass spectrometry [3,4]; Multiple Reaction Monitoring scan mode has been applied, in order to obtain the best specificity and sensitivity. This method has allowed to obtain the total amount of each flavanone glycoside in few minutes, by analyzing the samples without pre-treatment and recording MS data in 2 minutes (figure 1).

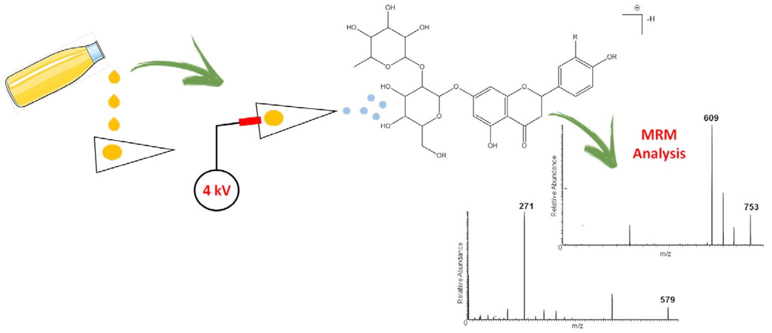

Figure 1 Workflow of the proposed methodology

The analytical parameters were all satisfactory; for each analyte a good linearity was observed in the selected calibration range (2mg/L – 20mg/L), LOD values ranged from 0.21 to 0.88 mg/L, LOQs were below the lowest calibration level, the accuracy ranged from 95% to 114%, and the method precision (repeatability and reproducibility) was always lower than 15%. The results coming from the PS-MRM analysis of real samples were compared to those obtained by the traditional HPLC-UV assay, proving the robustness of the proposed approach.

Lastly, an innovative MRM-based approach has been also developed to discriminate the flavanone glycosides isomers (rutinosides and neohesperidosides), based on the different fragmentation pattern of structural isomers, only meant as intensity of product ions.

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Temporal trend of per- and polyfluoroalkyl substances in air samples collected at the rural site of Monte Martano (Central Italy)

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Thirty-thee per- and polyfluoroalkyl substances (PFASs) were determined in filters collected at the rural regional background site of Monte Martano (MM, Central Italy, 42°48′19″N, 12°33′55″E, 1100 m asl) during a thirty-month period (January 2018-July 2020). The site experiences low background concentrations and is therefore well suited to study long-range transport of pollutants [1]. After spiking with a mixture of labelled internal standards, 96 filter samples collected at MM were extracted adding water, acetonitrile and then acidified acetonitrile. The reunited extracts were evaporated and purified as described by Barola et al. [2]. Finally, the redissolved samples were injected in a liquid-chromatography coupled to high resolution mass spectrometry platform (LC-Q-Orbitrap). Analytes were quantified applying isotopic dilution methodology. The most frequently found and abundant was perfluorooctane sulfonate (PFOS). In Figure the temporal trend of the measured airborne concentration of this PFAS is shown.

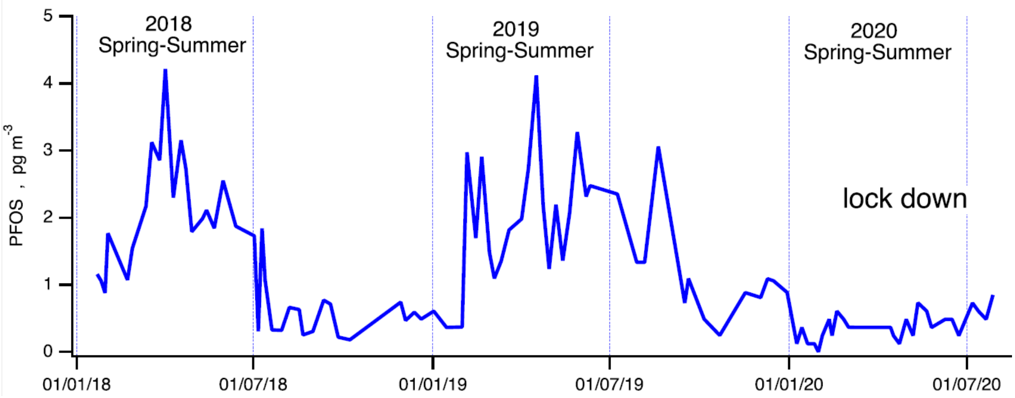

Figure – Temporal trend (01.2018-07.2020) of airborne PFOS concentration

In the years 2018 and 2019 a trend with the increase of PFOS concentrations during the spring-summer period is evident and correlated with the evolution of the atmospheric mixing layer that brought pollutants at the altitude of the MM site. In 2020, this trend was suddenly interrupted in correspondence of the severe restrictions imposed by the pandemic emergency from SARS-CoV-2 (lockdown). These results demonstrated that *(i)* PFAS are dispersed in the atmosphere with a clear seasonal pattern which may influence the air quality, at least at a regional scale, and *(ii)* the emissions have been drastically reduced due to the pandemic restrictions in the spring-summer 2020.

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Fabric Phase Sorptive Membrane Array: A Novel Approach for Non-Invasive *In Vivo* Sampling

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In recent years, increasing attention has been paid to the development of new technologies and innovative devices able to monitor, through non-invasive sampling, the levels of human exposure to different compounds present in the environment, as well as the evaluation of compound(s) that could be related to a specific disease. Exhaled breath aerosol (EBA) containing water molecules, volatile and non-volatile compounds, micro-drops and particles of biological origin that are extremely interesting from analytical/clinical point of view. EBA could be enriched with numerous metabolites/biomarker compounds, easily exploitable for diagnostic purposes. These compounds actually represent chemicals to which the subject is exposed, as well as the biomarker(s) pertaining to any specific disease condition [1]. The development of innovative technologies, like Fabric Phase Sorptive Membrane (FPSM) array, able to perform the sampling step through a non-invasive procedure, is utterly needed in order to increase the knowledge of the exposure to different chemicals. In this work, this novel approach for non-invasive *in vivo* sampling was presented for the first time and compared with other technologies currently in use. During the presentation, the advantages, disadvantages and limitations of all the procedures for this type of analysis will be highlighted. Moreover, the different approaches will also be critically assessed based on the "green" profile characteristics of the procedures [2], both relating to sampling and subsequent instrumental analysis.

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An interplay between FT-ICR MS and LC-LTQ MS/MS for Metabolic Profiling of Peperoni di Senise PGI Bell Peppers

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Peperoni di Senise PGI bell peppers (*Capsicum Annuum L.*) are a typical food product, cultivated in Basilicata (Southern Italy), protected with a protected geographical indication (PGI) quality mark and known for their unique taste. Over the past decade, there has been an increasing number of studies focused on metabolite profiling of bell peppers [1]. Here, for the first time, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to obtain the "metabolomic fingerprint" of Peperoni di Senise bell peppers. To increase the performance of the FT-ICR MS method, we processed the recorded time-domain ion signals (transients) into the absorption mode FT-ICR mass spectra (aFT) [2], thus profiling, in a few seconds, a higher number of metabolite classes of the methanolic extract of sample understudy. In detail, bell peppers resulted an excellent source of health-related compounds, such as ascorbic acid (vitamin C), carotenoids (provitamin A), tocopherols (vitamin E), polyphenols and capsaicinoids. These compounds are known for their biological activities, including antioxidant, anti-inflammatory and anticarcinogenic properties [2]. In addition to untargeted FT-ICR MS analysis, a targeted liquid chromatography (LC) coupled with linear ion-trap mass spectrometry (LTQ MS) was applied for screening quercetin glycoconjugates, one of the most widely distributed polyphenolics in plants, which distribution could be considered a potential quality/geographical marker. A correlation between experimental RP chromatographic retention time and those predicted by partition coefficients (log P), along with MS/MS data and an in-house developed database (named QUEdb), provided deep coverage for sixteen quercetin glycoconjugates. Among them, eleven quercetin glycoconjugates were already described in the literature and five were reported for the first time. These last acyl glycosidic quercetin derivatives were tentatively identified as quercetin-(galloyl-rhamnoside)-hexoside, $[C_{34}H_{33}O_{20}]^-$ at *m/z* 761.1; quercetin-(sinapoyl-hexoside)-rhamnoside, $[C_{38}H_{39}O_{20}]^-$ at *m/z* 815.4; quercetin-(galloylcaffeoyl-hexoside)-rhamnoside, $[C_{43}H_{39}O_{23}]^-$ at *m/z* 923.0; quercetin-(feruloyl-hexoside)-rhamnoside, $[C_{37}H_{37}O_{19}]^-$ at *m/z* 785.1; and quercetin-(succinyl-rhamnoside)-rhamnoside, $[C_{31}H_{33}O_{18}]^-$ at *m/z* 693.1 [4]. Therefore, FT-ICR MS and LC-LTQ MS/MS represented a powerful diagnostic tool, useful to identify potential metabolic markers, occurring in complex food matrices.

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Volatile organic compounds in Gorgonzola cheese and their relationship with sensory descriptors and consumers' liking

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Gorgonzola is an Italian popular veined blue cheese. Since 1996 is recognized and listed by the European Economic Community as PDO. There are two varieties of Gorgonzola, the sweet and the piquant. Sweet Gorgonzola is characterized by a delicate flavour that comes from a maturation of at least 50 days while the Piquant version has a stronger and piquant taste due to a longer maturation period of at least 80 days. During the ripening period, the growth of moulds contributes to shape the smell and flavor of Gorgonzola by proteolysis and lipolysis and the consequent development of volatile compounds. Among the latter, 23 odour impact compounds were detected in Gorgonzola by Moio and co-workers [1]. The aims of this study were: i) to characterize the volatile organic compounds in Gorgonzola cheese, both sweet and piquant, by SPME/GC-MS [2]; ii) identify the role of measured volatile compounds on sensory perception; iii) identify possible relationship of volatile compounds with consumers' liking.

Six Gorgonzola cheeses from one of the main producer in the PDO production area were used in the study. Fifty-four volatile organic compounds were identified in the headspace of cheeses by SPME/GC-MS. The volatile organic compounds data were then analyzed together with the sensory data obtained from a liking and a rate-all-that-apply (RATA) tests performed by 358 subjects (46% males, 18-77 years) [3].

Regression models were implemented in order to identify the most contributing volatile compounds to the flavours perceived by the consumers.

The highest associations of volatile compounds were found for "ammonia", "pungent", "soapy" and "mould" flavors. A good association was also found with consumers' liking.

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New Synthetic Opioids: Development of Analytical Methods for Their Characterization and Determination by Means of HPLC-HRMS/MS

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In recent years, the synthesis and introduction into the illicit market of New Psychoactive Substances (NPS) has reached alarming levels. More than 790 compounds have been identified by the European Monitoring Center for Drugs and Drug Addiction [1]. Among the newest NPS, synthetic opioids deserve special attention, in particular fentanyls, which covered more than 70% of the opioid's world demand [2]. In this context it is essential to have the right tools to identify these recent NPS and verify their consumption.

The aim of the project involves the characterization of new fentanyls, the identification of their main metabolites and the development of innovative, fast and simple analytical methods, for the determination of these compounds in different biological matrices. Thanks to its high versatility and performances, UHPLC-HRMS/MS was used to characterize, identify and quantify the target analytes. Thanks to the collaboration with National Police Forces, two new fentanyls, found in seizures, were characterized, by means of the application of different analytical techniques [3]. Furthermore, metabolic pathway of these new opioids was ascertained by means of in silico, in vitro, in vivo and ex vivo studies [4].

Analytical methods for the identification of these analytes in different biological matrices were also developed and validated. Miniaturized preparation technique, such as micro extraction by packed sorbent (MEPS), parallel artificial liquid membrane extraction (PALME), dispersive liquid-liquid micro-extraction (dLLME) were optimized for the analyses of tissues, whole blood, plasma, oral fluid and urine. All methods involve the use of a small amount of biological sample (100 µL of biological fluids or 1 mg of tissues). Thanks to the application of different analytical techniques, and to the development of new analytical methods, we have broadened the knowledge about this class of NPS, enabling the identification of fentanyls consumption and providing an effective contribution to the estimation of their real propagation in Italy.

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The Role of Mass Spectrometry in the – omics Era

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In the past 30 years, mass spectrometry (MS) has undergone a spectacular development, moving from the analysis and identification of single molecules and/or peptides by dedicated researchers to the analysis of complex mixtures of small molecules (metabolomics) or proteins (proteomics) run in core facilities. Advances in MS technologies in combination with liquid chromatography (LC-MS) and user-friendly software for MS instruments have allowed scientists to reach high productivity in data acquisition. Nowadays, LC-MS analyses of highly complex samples from different species are routinely performed in medical and biology research labs. MS-based proteomics methods have been shown to be a powerful approach for biomarker discovery. Therefore, the demand of MS analysis for protein and metabolite identification, characterization and quantification has dramatically increased, so that MS core facilities are established to offer expertise and state-of-the-art methodological approaches.

Along these lines, at Max Planck Institute of Psychiatry the Proteomics core facility works in close interaction with the researches to help in gaining knowledge about and understanding the causes of stress-related disorders such as major depression and anxiety diseases. In this presentation we will discuss examples of MS-based proteomics applications, including protein sequence characterization and modification localization, interactome identification as well as strategies for neddylation identification.

High-dimensional molecular phenomics in systems, synthetic, and chemical biology

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One of the predominant challenges in systems-wide analyses and molecular phenomics is the broad-scale characterization of the molecular inventory in cells, tissues, and biological fluids. Advances in computational systems biology rely heavily on the experimental capacity to make omics measurements, i.e. integrated metabolomics, proteomics, lipidomics, glycomics, etc., accompanied with fast minimal sample preparation, fast measurements, high concentration dynamic range, low limits of detection, and high selectivity. This confluence of figures-of-merit place demanding challenges on analytical platforms for such analyses. Ion mobility-mass spectrometry (IM-MS) provides rapid (ms) gas-phase electrophoretic separations on the basis of molecular structure and is well suited for integration with rapid (us) mass spectrometry detection techniques. This report will describe recent advances in IM-MS integrated omics measurement strategies in the analyses of complex biological samples of interest in systems, synthetic, and chemical biology. New advances in bioinformatics and biostatistics will also be described to approach biological queries from an unbiased and untargeted perspective and to quickly mine the massive datasets gathered to provide targeted and actionable information.

Mass spectrometry in coffee science: From bean to drink to human?

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The chemical composition of the coffee beverage and its associated health benefits are in large parts related to their main phenolic constituents named chlorogenic acids (CGAs). CGAs are by definition esters between quinic acid and hydroxycinnamic acids. Due to the four non-equivalent hydroxyl groups CGAs exist as groups of multiple regio-isomers. In a first part of the lecture we will review our work on the unambiguous identification of regio-isomeric CGAs using tandem mass spectrometry, energy resolved mass spectrometry and ion mobility mass spectrometry.

Following coffee roasting the around 90 different CGAs in a green coffee bean are transformed into further derivatives. Again we show how tandem mass spectrometry allows identification of isomeric CGAs, in the case of roasting mainly diastereoisomers of quinic acid.

We furthermore report on data comparing different coffee varieties and coffee grown under different agricultural regimes using multivariate statistical methods of LC-MS data. Finally, we report on the application of multivariate statistical methods and tandem MS networking approaches that allows identification of CGA derived human metabolites in human urine.

Mass spectrometry for the environmental analysis of halogenated organic pollutants

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Halogenated organic pollutants, including both potential and legislated persistent organic pollutants and their precursors, represent a significant environmental concern as they show hazardous effects in humans and wildlife, have a tendency to bioaccumulation through the food chain, exhibit a high resistance to environmental degradation, and a long-range atmospheric transport potential. Monitoring of these compounds in the environment at ultra-trace concentration levels requires highly selective and sensitive analytical methodologies. The lack of systematic reference methods resulted in a large number of reliable determination methodologies depending on analytes, sample complexity, and available instrumentation.

Thus, this presentation shows some of the main advances in analytical methodologies based on mass spectrometry for the determination of halogenated organic pollutants and highlights the future perspectives to improve the analytical determination of halogenated organic pollutants and the throughput of environmental control laboratories.

How can energetics in CID MS/MS help the analytical chemists?

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High-throughput structural and quantitative analysis is now routinely performed with mass spectrometry hyphenated to chromatographic separation techniques. However, with the goal of gaining more knowledge on increasingly complex samples, the resolution of iso-baric/meric impurities becomes even more critical. This indeed remains a challenge to perform by mass spectrometry. Nevertheless, among the proposed strategies, by using tandem mass spectrometry one takes advantage of differences in the fragmentation patterns (fingerprinting for structure elucidation or SRM/MRM for quantification) but also in the fragmentation energetics. If the former approach is extensively used, the latter is much less used. This is the focus of the results presented here.

Survival Yield (SY) curves are obtained from energy-resolved tandem mass spectrometric experiments by monitoring the portion of parent ions surviving the excitation process as a function of the excitation amplitude. Such curves are typically of sigmoid type. In the context of Collision Induced Dissociation experiments, it has been observed that, in some cases, Survival Yield curves may exhibit a plateau in place of the smooth and monotonous expected decrease.[1] We have shown this plateau can be used to obtain both relative[1-3] and absolute[4] quantitative information on model but also "real-life" mixtures of isomers and isobars. Moreover, by using MS3[2] and pseudo-MS3[5], we have demonstrated the extraction of structural information is also feasible as if the analyte were free from any impurities: a strategy called *"gas-phase collisional purification"*.

For the last few years, the behavior of SY curves has been studied and used in the case of various iso-baric/meric mixtures both for structural analysis and quantification purposes with small organics[7,8], synthetic polymers[1-3], peptides[4-6] or in the context of host-guest chemistry.[9] The coupling with ion mobility mass spectrometry also lead to a 4D on-line analysis of isomeric carbohydrates.[10] More recently, up to 3 isobaric compounds were revealed in a model mixture after optimal MS2 only experimental conditions were determined[11] paving the way for extracting even more information on endlessly increasing complex samples.

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LIPIC: An Automated Workflow to Account for Isotopologue-Related Interferences in Electrospray Ionization High-Resolution Mass Spectra of Phospholipids

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In the past two decades, advances in Mass Spectrometry (MS) have greatly contributed to the rapid expansion of *lipidomics* [1], with key steps represented by the coupling with liquid chromatography (LC) through ElectroSpray Ionization (ESI) [2], and, more recently, by the use of High-Resolution Mass Spectrometry (HRMS) [3]. Among the LC-MS approaches, those based on Hydrophilic Interaction Liquid Chromatography (HILIC) have proved to be very powerful for profiling amphiphilic lipid species in complex biological samples, thanks to a lipid class-selective separation. Accordingly, mass spectra averaged under HILIC bands can be considered a "snapshot" of a lipid class [4] and the intensities of the monoisotopic (M+0) peaks can be used for quantitative purposes. However, for a more accurate quantification, intrinsic differences in the contribution of the M+0 peak to the isotopic pattern of a lipid ("Type I" isotopic effect) have to be considered [5]. Furthermore, the overlap of isotopic patterns for lipids differing only by the number of C=C bonds in their structure has to be taken into account. Indeed, the M+0 peak intensity for a lipid can be artificially enhanced by the contribution of M+2 and M+4 isotopologues of lipids with one or two additional double bonds, respectively ("Type II" effect) [5, 6]. The correction of Type II effect is particularly complicated in high-resolution mass spectra, due to the misalignment between the M+0 and the interfering isotopologue peaks, resulting from slight differences in the corresponding exact *m/z* ratios.

We have recently addressed the problem of Type I and Type II isotope corrections in lipid class-related high resolution mass spectra by designing a novel algorithm based on the experimentally verified assumption of HRMS signals to have a gaussian shape [7]. Starting from the *m/z* and intensity coordinates of the experimental M+0 peak maximum, we managed to remove the contribution of M+2 and M+4 isotopologue peaks of interfering lipids, thus retrieving a more reliable value of M+0 peak intensity, prior to performing Type I correction. A series of computational tools in the R operating language, recently enclosed in a dedicated R package named "*LIPIC*" (*Lipid Isotopic Pattern Interference Corrector*), hosted on the Github platform, was developed. In this communication, the reliability of the isotopologue interference correction performed by the *LIPIC* package will be demonstrated by considering both simulated and real ESI-FTMS mass spectra of phosphatidylcholines (PC) and cardiolipins (CL), obtained upon HILIC separation of lipid extracts from chia microgreen and yeast mitochondria, respectively.

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Molecular portraits of diffuse large B-cell lymphoma: towards the discovery of novel phenotypes

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Diffuse large B-cell lymphoma (DLBCL) is the most common lymphoid malignancy and can be considered a sort of “Pandora’s box”, with the disease encompassing a range of neoplasms which cannot be further classified using traditional histopathology. Currently, DLBCL are classified in two subgroups, activated B cells (ABC) and germinal centre B cells (GCB), depending on their cell of origin (COO) [1]. However, work is ongoing to discover further subgroups that can explain the heterogeneous outcomes in terms of patient outcome and sensitivity to R-CHOP therapy [2].

MALDI mass spectrometry imaging was performed on FFPE tissue microarray cores from patients with DLBCL (n= 37). All mass spectra were acquired in reflectron positive mode, within the *m/z* 700 to 3000 range, using a rapifleX MALDI Tissuetyper™ (Bruker Daltonik GmbH, Bremen, Germany) MALDI-TOF/TOF MS equipped with a Smartbeam 3D laser operating at 2.5 kHz frequency. MALDI-MS images were acquired with a beam scan setting of 6 µm and a raster sampling of 10 µm in both *x* and *y* dimensions. COO was determined by gene expression profiling using the NanoString Counter® Analysis System.

Each core was histologically annotated in order to define the neoplastic cells and the tumour microenvironment (TME). While proteomic alterations were present in the neoplastic regions of the DLBCL tissue, a greater degree of proteomic heterogeneity was observed in the TME of the GCB DLBCL subtype with respect to that of the ABC subtype. In particular, those proteins up-represented in the TME of GCB DLBCL co-localised to tissue regions which showed an accumulation of extracellular matrix (ECM), both with clear-cut and minor histological evidence. This included proteins associated with ECM deposition such as various fragments of collagen (CO1A2; *m/z* 840.45, CO3A1; *m/z* 1105.80, and CO6A3; *m/z* 1530.77) and fibrinogen (*m/z* 1117.56). Moreover, when stratifying the patient cohort by R-CHOP response status, the up-representation of these protein signals was observed in the group which responded more favorably to the immuno-chemotherapy and had an extended progression-free survival time.

This work highlights the utility of performing spatially resolved molecular imaging in the search for novel molecular subtypes of DLBCL and indicates specific protein signatures of the TME that may be associated with more favourable outcomes. Our final goal will be to integrate this proteomics data with that obtained using gene expression profiling to refine personalised medicine strategies in the treatment of DLBCL.

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Biofluid sampler: A new gateway for mail-in-analysis of whole blood samples

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The current study describe a novel biofluid sampler (BFS) which is able to simplify the sampling and sample preparation of whole blood without converting it into plasma or serum. The sampler can retain a whole blood sample from 10 to 1000 μL. Although the device shares the same working principle of dried blood spot (DBS) cards, it eliminates most of the technological shortcomings of DBS cards such as low maximum sample volume (~50 μL), sample inhomogeneity due to haematocrit, and poor physical adsorption driven analyte retention by incorporating sol–gel derived high efficiency, multi-functional sorbents on cellulose fabric substrate.

The performance of BFS was tested via "Mail-in-Analysis" using three non-steroidal anti-inflammatory drugs (NSAIDs, ketoprofen, carprofen and diclofenac) as the test compounds. Human whole blood samples were fortified with the test compounds and sampled on conventional DBS cards and biofluid samplers (BFSs) in the University of Florida (USA). After drying at room temperature, the samples were shipped to Italy for chromatographic analysis. The analytes were back-extracted from the DBS cards and BFSs using methanol and subsequently analyzed. The chromatographic analysis was carried out using a short Symmetry C18 (75 × 4.6 mm, 3.5 μm) column and Acetonitrile (ACN) and PBS (30 mM; pH = 2.5) as the mobile phases (isocratic conditions). Compared to the classical dried blood spot cards (DBS), BFSs offer better performance in retaining the selected NSAIDs under conventional postal shipment. By substantially expanding the sampling capacity, eliminating most of the shortcomings of classical DBS cards and exploiting the better materials properties of sol–gel based functional sorbents, BFSs could represent a new and profoundly simplified approach for whole blood sampling and analysis and is expected to change the current practice of blood analysis, allowing accurate quantitative analyses either in a local laboratory (*on site*) or using mail-in-analysis (*off site*) without compromising the quality of bioanalytical data.

Phytochemical composition and in -vitro pharmacological evaluation of Emex australis Steinh: A natural source of enzyme inhibitors

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The current research investigated the chemical profiling and biological activities of *Emex australis* Steinh. aerial and fruit parts (methanol and dichloromethane-DCM extracts). Chemical composition was established by determining the amounts of phenolic and flavonoid contents, HPLC-PDA polyphenolic quantification, and UHPLC-MS secondary metabolites profiling to understand the observed biological activities. Antioxidant evaluation was performed utilizing six different assays (DPPH, ABTS, FRAP, CUPRAC, phosphomolybdenum, and metal chelation). Moreover, enzyme inhibition abilities against cholinesterases, α-amylase, α-glucosidase, and tyrosinase were also determined. The fruit methanol extract contained the highest phenolic (157.96 mg GAE/g extract) and flavonoid contents (41.43 mg QE/g extract), which could justify the observed significant antioxidant (except metal chelating), α-amylase, α-glucosidase, and tyrosinase inhibitory potentials. The other extracts were active against cholinesterases and tyrosinase. The HPLC-PDA polyphenolic analysis quantified a number of 11 phenolic secondary metabolites. The fruit-MeOH extract was found to quantify the maximum phenolics with catechin (4.27 mg/g extract) and gallic acid (4.84 mg/g extract) in higher amounts. Similarly, rutin was found in maximum quantity in the aerial-MeOH extract (2.93 mg/g extract). Furthermore, the UHPLC-MS study of aerial and fruit methanol extracts reveals the existence of 22 secondary metabolites, most of which were flavonoid derivatives. Besides that, Pearson coefficient analysis (PCA) was also carried to determine a possible correlation between bioactive contents and observed biological assays. These results have shown that *E. australis* extracts contain important classes of secondary metabolites and also exhibited considerable antioxidant and inhibition potential against clinically relevant enzymes.

Double bond positional assignment in unsaturated fatty acids by *m*-CPBA epoxidation and RPLC-ESI tandem mass spectrometry

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Painting is the ritual of applying paint, pigment, or color to a solid flat surface; to ensure the grip of the colored paint onto the surface of an artwork, a material in which the pigments are suspended as *medium* or binder is required. For instance, drying oils (e.g., linseed, poppyseed, walnut, and safflower oils) are oil-based media that can undergo chemical reactions leading to the formation of transparent films after exposure to air [1].

Drying oils, which are mixtures of triacylglycerols, are often affected by a degradation phenomenon triggered by pigments, named metal soaps, whose main appearances are efflorescence and patinas. The final effect is the structural integrity loss of the paint [2]. The lipid composition of the drying oil has been found to play an active role in the development of metal-soap-induced alteration; the identification of the binders employed in a work of art has always received particular attention because it can not only provide key information about the artistic technique and the historical period of the artist but is also crucial for preserving and restoring the artwork itself [3].

Although spectroscopic techniques are extensively employed in the field of cultural heritage [4], preliminary results are often provided, and additional investigations are required for the unambiguous identification of lipidic binders [5]. Hereby, we discuss the detailed characterization of free and bound fatty acids (FA) in drying oils; in particular, our study was devoted to the identification of free fatty acids by reversed-phase liquid chromatography coupled with high-resolution/accuracy mass spectrometry using and electrospray ionization source (RPLC-ESI-FTMS). The lipid fraction was firstly extracted from specimens, then unsaturated lipids were subjected to epoxidation reaction by *meta*-chloroperoxybenzoic acid (*m*-CPBA) [6]. Finally, the positional assignment of DBs in FA epoxides was attempted by reversed-phase liquid chromatography (RPLC) via electrospray ionization (ESI) coupled to an Orbitrap-based mass spectrometer (FTMS) and MS/MS by high-energy collisional dissociation (HCD) of deprotonated epoxide species $[\text{epoM-H}]^-$. While the DB geometry (i.e., *cis* or *trans*) was assigned by the FA retention time, the epoxide ring fragmentation cleaved yielding diagnostic ion pair for C=C double bond position [7]. In this communication, the most important experimental data are reported and discussed.

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Quantitative analysis of Neurohormones in biological fluids

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Neurohormones regulate several biochemical paths involved in different type of cellular responses both in normal and pathological states. They are a part of chemical connections between central nervous system (CNS) and the rest of the organism: in mammalians and other species these molecules regulate endocrine and reproductive systems, metabolism and adapt biological settings in response of different environmental stimuli. The characterization and quantification of neurohormones in biological fluids allow to expand both clinical knowledge of different diseases and social behaviour (cit). Nowadays the main tools to measure neurohormones levels in biological matrices are immunochemical assays and mass spectrometer-based approaches. Several studies [1] have reported dissimilar basal or pathological levels of neuropeptides in different matrices depending on performances and limitations of methods used. The challenge in the peptidomic field is the development of standardized method(s) capable to detect analytes at very low concentrations (pg/mL) which allow to monitor neurohormones versus time and biological conditions [2]. Therefore, research on basal levels of neuropeptides requires elevated assays sensitivity, accuracy and precision that are pre-eminent HR/HA MS (High Resolution/High Accuracy Mass Spectrometer) features. This work deals about nanoHPLC-HRMS methods to quantify GnRH (Gonadotropin Releasing Hormone) and Oxytocin levels in Human plasma and Pan Paniscus urine respectively. In particular: i) GnRH is a neuronal decapeptide, playing a crucial role as regulator in reproductive systems' maintenance. Its increased concentration level both in CNS and plasma may to be one of the causes of reproductive disorders such as infertility and PCOS (Polycystic Ovary Syndrome) [3]; ii) Oxytocin is a neuro nonapeptide that presents hormone activity especially in social relations and during childbirths' labor. It is possible its physiological trend can control social bonding correlate dynamics [4]. Both methods developments have required sample pre-treatment steps in order to obtain a purified extracts and to concentrate analytes due to their low biological abundance. After applying a protein precipitation step where needed, a SPE (Solid Phase Extraction) was found to be an efficient and suitable clean-up step for HPLC-HRMS technique. After SPE, the dried extract was reconstituted to increase concentration and 6 ⌠L of final extract were injected into nanoHPLC instrument. An online pre-concentration step employing online C18-SPE was performed to load the sample on the analytical column. The nano HPLC system with C18 Easy Spray column and integrated nano ESI source was coupled to an Orbitrap Fusion HRMS. Different ratios of acidified water/acetonitrile were used as loading solution and eluents. Full mass and MS/MS spectra of peptide fragments by CID (Collision Induced Dissociation) activation modes was used for analytes characterization: double charged ions were chosen as precursor ions. Finally, a calibration curves with a proper ISs (Internal Standards) were used to quantify analytes. These methods guaranteed an appropriate cleaning steps and the resolving power necessary to identify distinctly both analytes in analysed matrices.

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Understanding the interaction between amyloid-β-peptide (1–42) and its aggregation inhibitors: application of ESI and MALDI mass spectrometry

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Neurodegenerative disorders (NDs) such as Alzheimer's disease (AD), Parkinson's disease (PD) and prion diseases are some of the most common forms of age-related diseases. Even if pathogenesis of these neurodegenerative diseases remains unclear, increasing evidences point out a common critical molecular process involving the assembly of various aggregated protein with a β-sheet conformation, termed amyloids.[1] The inhibition of this process could be a viable therapeutic strategy for the treatment of neurodegenerative diseases. Peptide based inhibitors of β-amyloid fibrillation are emerging as safe drug candidates as well as interesting compounds for early diagnosis of AD.[2] Some papers in the past reported that the KLVFF peptide, by binding the homologous sequence in full-length Aβ, can prevent at aggregation into fibrils[2] and this ability is maintained after conjugation to different scaffold.[3-6]

One of the main hindrances in amyloid protein investigation concerns the low peptide solubility. In this contest, the high sensitivity of mass spectrometry may overcome this limit. Besides measuring the m/z, mass spectrometry enables the identification of adducts formation and it can be used to obtain direct evidence of the interaction between Aβ(1–42) and its aggregation inhibitors. Despite these informations were deduced from the gas-phase system, the results observed support what can be observed in solution by limited proteolysis experiments.[5] In particular, the identification of proteolysis resistant peptides fragments by mass spectrometry can reveal the binding regions of Aβ(1-42) to specific molecules in solution.

Here we report two different mass spectrometry approaches to investigate the interaction of Aβ(1-42) monomer with aggregation inhibitors that we recently studied.[5, 6] In particular, high resolution mass spectrometry (HR-MS) was employed to point out direct interaction of the p-amino-calix[4]arene-GPGKLVFF conjugate with the Aβ(1-42) monomer.[5] We resorted to limited proteolysis experiments to investigate, by means of MALDI-TOF, the interaction of Aβ(1−42) with chimera peptides τ9−16-KL and τ26−33-KL and KLVFF.[6]

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Investigation of Gut Microbiome in a Mouse Model of Alzheimer Disease Using a Metabologenomics Approach

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The role of the gut microbiota in neurodegenerative diseases is an emerging research field. Parkinson disease patients showed a different gut microbiota than healthy controls, and increasing evidence are also indicating that a gut microbiota dysbiosis in patients affected by Alzheimer could influence the disease progression and development. Characterizing the bacterial populations and the metabolites involved in the dysbiosis, is therefore important as this might be helpful to understanding the complex microbial ecosystem in Alzheimer disease.

In the present research we used a metabologenomic approach to analyze the gut microbiome in a deterministic mouse model (3xTg) of familiar AD.

Stools from wild type (WT) and AD mice were collected at weaning (T0), 2 months (T1) and 6 months (T2). DNA and small molecules from each sample were extracted analyzed. Untargeted metabolomics analysis of fecal samples was performed using a bi-dimensional gas chromatography coupled to mass spectrometry (GCxGC-TOFMS, Pegasus BT 4D, LECO), while short chain fatty acids (SCFAs) analysis was carried out using a mono-dimensional GC-MS.

We found increasing level of SCFAs (acetic, butanoic, and propanoic acid) in AD mice over the time, but a drastic longitudinal decrease of these molecules in AD mice compared to WT. Our analysis also evidenced a significant decreased concentration of a group of amino acids in samples from AD mice at 6 months compared to WT matched controls, some of which have been reported to be potentially linked to gut inflammation. Finally, an integrated analysis of both metagenomic (16S) and metabolomic data allowed the correlation of small molecules abundances with the intestinal ecosystem.

In conclusion, metabologenomics revealed new insights related to the complex microbial ecosystem in an Alzheimer disease mouse model.

CoA biosynthetic pathway quantification by LC-MS/MS in COASY-depleted mice brain

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Acetylcoenzyme A (AcCoA) and its precursor Coenzyme A (CoA) are crucial regulators of diverse cellular pathways, including cell signaling, energy metabolism, and post-translational protein modifications[1–3]. To explicate their moonlight functions, the acetyl moiety (CH_3CO-) of AcCoA, linked to the CoA backbone through a thioester bond, is enzymatically transferred to other metabolites, proteins and lipids, thus starting a continuous AcCoA/CoA recycling[1]. Being central regulators of metabolic transformations and therefore involved in various metabolic affections[4,5], great interest arouses for the analytical quantification of AcCoA and CoA[6–8]. Nevertheless, due to their chemical instability, these metabolites remain challenging to detect and quantify. Recent studies provide elegant extraction and quantification methods, yet they require high-resolution spectrometers and turn out to be cost-limiting and time consuming[9]. Moreover, the total levels of AcCoA and CoA could be unchanged due to the recycling of these metabolites throughout the cytoplasm and the mitochondria. For this reason, the quantification of the upstream metabolites in the CoA biosynthetic pathway, as pantothenic acid (Pan) and dephosphocoenzyme A (dpCoA), could offer a more complete picture of CoA metabolism. In this context, we measured the levels of Pan, dpCoA, CoA and AcCoA in a conditional neuronal-specific-COASY-deleted mouse model, characterized by the deletion of the key enzyme that catalyzes the last step of CoA biosynthesis. While the quantification of free CoA, dpCoA and AcCoA was unchanged, we observed a significant increment of Pan levels, thus confirming its upstream accumulation.

Here is presented an easy-going LC-MS/MS method, using a reversed phase chromatography coupled to ESI triple quadrupole. As a starting point, we tried several chromatographic conditions and eventually chose isocratic run with 95% MeOH and 5% H2O with 5mM ammonium formiate (NH_4HCOO) pH 7.5, with Luna CN at room temperature, at 0.8 ml/min, positive ion mode. Attempts switching MeOH with acetonitrile (ACN) revealed a strong ion suppression and were therefore called off. Afterward, different extraction procedures were tested. First, a generic metabolite extraction consisting in a mixture of MeOH ACN in 1:1 ratio showed a poor extraction yield. Folch method analyzing both aqueous and organic fractions failed too. Finally, we used a polar extraction mixture of MeOH and H2O in 8:2 ratio with or without 0.1% of formic acid (HCOOH) to prevent base-catalyzed hydrolysis. However, the presence of other ions affected the ionization of the metabolites of interest.

Our future perspective will focus on quantifying of the whole CoA biosynthetic pathway and the flux analysis of ^{13}C ^{15}N pantothenic acid.

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A molecular imaging approach to individuate tumour infiltrating lymphocytes

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Among the different components of the microenvironment, tumour infiltrating lymphocytes (TIL) may play an important role in predicting treatment efficacy, being a key player in anti-tumoural immune response and therefore have implications in patient outcome. Nevertheless, recent studies revealed that a subtype of T CD4+ cells, named T regulatory CD4+CD25+ (Treg), can supress the response against the tumour. However, individuating these using classical methods still remains challenging. Therefore, this project aims to use MALDI-MS imaging to directly pinpoint in situ the different TILs cell subpopulations in tumoural tissue depending on their molecular signatures.

Initially, in order to obtain their lipidomic and proteomic profiles, peripheral blood obtained from six patients was collected and isolated using FACS (Fluorescence-activated cell sorting) to obtain three different samples containing CD4+, CD8+, or Treg cells, respectively. Moreover, an additional sample containing CD14+ isolated macrophages was used as a negative control. The distinct lipidomics and proteomics signatures were obtained and used to define the presence of lymphocytes subpopulations in colon cancer tissue, rich of TILs, using MALDI-MSI.

Distinct signatures were observed among the lipidomic profiles obtained from the subset of different lymphocyte subpopulations. In particular, the macrophages revealed a vastly higher presence of sphingomyelins compared to the other cells type. Additionally, the proteomics analysis revealed a distinct signature for each lymphocytes subtype. These findings were then exploited to characterise the TILs present in colon cancer tissue samples.

Concluding, these findings indicate that the specific molecular profiles of different lymphocytes can be used to individuate the presence of TILs using MALDI-MSI. Following on from this proof-of-concept, we aim to exploit these molecular signatures to aid in predicting the efficacy of new generation anti-tumoural treatments, such as mABs that specifically target infiltrating T regs.

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An insight into *Olea Europaea* bioactive phenolic compounds: assessment of effective analytical approaches for secoiridoids and related enzymes in olive-based matrices

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Secoiridoids belong to a class of compounds known as *iridoids*, characterized by a coumarin-based structure, produced via the secondary metabolism of monoterpenes as precursors of indole alkaloids, and widely spread in nature, being identified in many plant families [1,2]. Secoiridoids are unique of *Oleaceae* plants, including *Olea europaea* L., whose drupes and leaves are rich in *oleuropein* and *ligstroside*, arising from an ester linkage between the glucosidic form of the iridoid known as *elenolic acid* and phenolic compounds known as *hydroxytyrosol* and *tyrosol*, respectively [1,2]. Upon olive drupe crushing during extra virgin olive oil (EVOO) production, transformations catalyzed by endogenous β-glucosidase and methylesterase enzymes lead to the aglycones of the two compounds and then to two further secoiridoids, *oleac(e)ine* and *oleocanthal* [3], representing some of the most valuable compounds among bioactive phenolics of EVOO, due to several beneficial effects for human health and organoleptic features [4,5]. Interestingly, thanks to their strong ability to denature proteins, the same compounds are also directly involved in the olive plant defense system as *phytoalexins*, which are antimicrobial/antifungal low-molecular-weight compounds synthesized *de novo* following a pathogenic attack [6]. Due to the described bioactivity, the cited secoiridoids have been the object of a deep structural investigation recently performed in our laboratories on EVOO and olive leaves, based on reversed-phase liquid chromatography coupled to electrospray ionization Fourier-transform high resolution/accuracy mass spectrometry (RPLC-ESI-FTMS), emphasizing their structural complexity, related to the presence of several isomeric forms [7]. In a parallel development, enzymes involved in the secoiridoids biosynthesis, whose activity is usually cultivar-dependent and may be influenced by biotic and abiotic stimuli [3,6,8], have been targeted, using a *bottom-up* proteomic approach for their identification.

In the present communication, the main results obtained using both mentioned analytical approaches for the identification of bioactive secoiridoids and related enzymes in olive-related matrices, with a special focus on leaves, will be shown as an example of a comprehensive analytical approach to investigate the involvement of secoiridoids in the olive plant diseases.

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LC-MS/MS method for the determination of tetracyclines in swine manure

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Antibiotics are essential compounds commonly used to treat bacterial infections and to promote growth in zootechnical animals; the risk associated with their misuse is the loss of their effectiveness at an increasing rate. The absorption of antimicrobials takes place during digestion and a significant fraction of these molecules and their metabolites can be excreted with feces and urines [1]. Therefore, the presence and the accumulation of antibiotics and their metabolites residues could occur in livestock manure. This phenomenon could lead to the development and spread of antibiotic resistance in various environmental compartments, as soil [2]. Thanks to its potential benefits livestock manure could be used as agricultural fertilize, promoting recycle and eco-efficiency, as requested by circular economy model. Over the last few years, many papers have documented that exposure to low levels of antimicrobials may increase the selection of zoonotic resistant bacteria which can adapt and survive the effects of antibiotics [3]. This represents a potential hazard in the environmental and a relevant health concern. Therefore, monitoring antibiotics concentration in manure could be a relevant issue.

The aim of this project is the development of a sensitive and reliable liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) method to detect tetracyclines in swine manure (n = 76). The investigated samples were collected in six selected intensive pig farms with a closed system. Tetracyclines are mainly excreted by feces, and as they are scarcely degradable can persist for a long time in this matrix [4].

Analytical *in-house* method was developed to determine oxytetracycline (OTC), tetracycline (TCL), chlortetracycline (CTC) and doxycycline (DOC). A modified QuEChERS (quick, easy, cheap, effective, rugged, and safe) approach for the rapid and simultaneous extraction of tetracyclines was used. The Exion LC system from AB SCIEX (Milan, Italy) coupled to the triple quadrupole mass spectrometer QTRAP 5500 from AB SCIEX (Milan, Italy) was used for LC-MS/MS analyses. Chromatographic separation was performed on reversed-phase 150 x 3 mm, 100 Å, Luna Omega 1.6 μm Polar C18 Column (Phenomenex, Milan, Italy), using as mobile phases HCOOH 0.1 % in ultrapure water (mobile phase A) and HCOOH 0.1 % in acetonitrile (mobile phase B).

20 out of the 76 analysed samples resulted < LOQ (0.5 mg /kg) while 56 showed the presence of at least one tetracycline: 28% CTC, 24% OTC, 14% DOC and 8% TCL. CTC concentration ranged from 0,641 to 78,7 mg/kg, OTC from 0,754 to 20,4 mg/kg, DOC from 1,26 to 16,6 mg/kg and TCL from 1,48 to 4,28 mg/kg. The high levels of tetracyclines found in most of the analysed samples highlight the widespread of these antibiotics, and reveal an increasing hazard associated on this matrix. These kind of data could be a useful tool to evaluate the risk associated to the use of manure as agricultural fertilizer. In conclusion further investigations should be carry out to ensure a safe use of manure as fertilizer.

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Determination of hidden milk allergens in meat-based foodstuffs by liquid chromatography coupled to electrospray ionization and high-resolution tandem mass spectrometry

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In recent years, food allergy has become an increasing health issue being considered a disease with different effects depending on the suffering subject[1]. Food allergens are proteins capable to develop an adverse immune mediated reaction in sensitized people. Currently, the most allergenic foods are listed by European Commission and comprise egg, milk, gluten cereals, crustaceans, fish, peanuts, soy, nuts, celery, mustard, sesame, lupine, sulphites and clams[2]. To safeguard vulnerable persons the European Commission established that food allergenic ingredients must be indicated on the label using different size, font, or colour labels. However, this regulation does not provide any guidelines for allergen cross contamination. With the aim of protecting the consumer health, the search of allergenic ingredients not reported on the food labels has significantly increased using several analytical techniques. In this study we investigated various meat-based products labelled as "milk free" to verify the absence of hidden milk allergens. Low-cost vegetable, e.g. soybean and lupin, or animal, such as milk and egg white, proteins are usually added during the production of meat foodstuffs to improve water absorption, gelation, emulsion of fat droplets and to enhance organoleptic properties such as flavour, texture, and colour[3]. A method based on reversed-phase liquid chromatography coupled to electrospray ionization and hybrid orbitrap high-resolution/accuracy mass spectrometry (RPLC-ESI-HRMS) in conjunction with tandem MS was exploited to identify and quantify bovine milk allergens in meat-based products. In detail, α-S1-casein and β-lactoglobulin were used as representative of casein and whey fraction of bovine milk, respectively. Stable qualifier and quantifier marker peptides is demanded to identify and quantify milk allergenic proteins. In the present work, the following peptides were chosen: YLGYLEQLLR (m/z 634.355^{2+}) and FFVAPFPEVFGK (m/z 692.868^{2+}) as qualifier and quantifier, respectively, of α-S1-casein and VLVLDTDYK (m/z 533.294^{2+}) and TPEVDDEALEK (m/z 623.295^{2+}) of β-lactoglobulin[4]. Once optimized the extraction, digestion, and purification steps of protein samples, the method's validation including recovery, matrix effect, precision, linearity, method variation, limit of detection, and limit of quantification was carried out. The occurrence of hidden milk proteins in chicken/turkey and swine sausages in milk-free labelled samples was verified, with milk protein contents up to 50 times the action level.

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Characterization and quantification of arsenic species in foodstuffs of plant origin: optimization and validation of a High-Pressure Ion Chromatography and Inductively Coupled Plasma - Mass Spectrometry (HPIC/ICP-MS) method.

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Arsenic is a persistent, bioccumulative and carcinogenic pollutant, however it is well established that its toxicity hinges on the chemical forms. Particularly, inorganic arsenic (iAs) species, both as arsenite (As^{III}) and arsenate (As^{V}), are more harmful than organo-arsenic compounds (oAsC), with LD_{50} values from 100 to 500 times higher for the latter. Drinking water and food products contribute most to the total exposure to arsenic, posing a severe health hazard [1,2].

Recently, the European Food Safety Authority – EFSA, following on European Commission request, published a report on chronic dietary exposure to iAs and recommended the development and validation of analytical methods with adequate sensitivity and refined extraction procedures for this determination. Moreover, the authority called upon new arsenic speciation data for complex food matrices such as seaweeds, mushrooms, grains and grain-based products [3]. The same concern was previously reported by World Health Organization – WHO, which expressed a pressing need for "*validated methods for selective extraction and determination of inorganic arsenic in food matrices*" and "*improved data on occurrence of different species of arsenic in, and their bioavailability from, different foods as consumed*" [4].

Looking at this context, an optimized, sensitive and fast analytical method using high pressure ion chromatography followed by inductively coupled plasma - mass spectrometry (HPIC/ICP-MS) was developed, starting from the European standard method EN-16802 [5]. The extraction of iAs and the most abundant oAsC, monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and arsenobetaine (AB), was performed comparing two techniques (shaking water bath and ultrasonic bath) at 90°C with a nitric acid/hydrogen peroxide solution. The PSDVB/Trimethylammonium anion exchange column and alkaline elution conditions (42.5 mM $(NH_4)HCO_3$ in 3% methanol at pH 10.3) ensured the best separation of analytes in seven minutes. One minute of washing with nitric acid 4% was added in order to minimize phenomena of matrix and carbonate deposition on sample introduction system. The method was validated with good results in terms of linearity ($R^2 > 0.999$), recovery values (ranging from 81.3% to 117.8%), limits of quantification (0.075 for iAs, 0.241 for MMA, 0.235 for DMA, 0.321 ng g^{-1} for AB), and precision (CV% lower than 7.3). A rice flour certified reference material, NIST-1568b, was used for quality assessment. The method was successfully applied to several matrices, i.e. processed and unprocessed cereal and cereal products, fruits and vegetables (including mushrooms, roots and tubers, pulses and legumes), seaweeds, nuts and seeds.

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Investigation of natural hormones profiles in bovine blood serum by LC-MS/MS: multi-year survey in northern Italy

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Among forbidden substances included in the EU legislation, steroid compounds and, particularly, endogenous steroids (androgens, estrogens and progestins) constitute a challenge in the framework of veterinary official monitoring plans. Natural and synthetic hormones have been widely illegally used in animal husbandry for several decades as growth promoters especially in bovine farming. Their use in animal fattening has been prohibited because of their toxic effects on public health [1]. Controls are regulated under Directive 96/23/EC [2]. In Italy, maximum physiological levels have been established in 1996 for 17β-estradiol, progesterone and testosterone in bovine serum [3]. These levels allowed to discriminate between treated or untreated animals. In order to monitor possible illicit use of these three steroids in bovine, very sensitive analytical methods are required since these molecules are naturally present at low and variable serum concentrations depending on the animal race, sex and age. Currently, chromatographic techniques associated with mass spectrometric detection play a major role in this kind of analysis, due to their high sensitivity and selectivity. However, 17β-estradiol physiological concentrations in blood serum are much lower than that of testosterone and progesterone, so two different sample preparation protocols are generally applied to analyze the three steroids. A method to overcome this issue and improve the selectivity can be obtained using molecularly imprinting polymers (MIPs) cartridges as solid-phase extraction [4]. This kind of sorbent is made by a polymerisation process to create a three-dimensional network that recognizes the shape and the functional group positions of a template molecule.

The aim of this study was the development of a multiresidue, rapid and effective analytical procedure for the quantitative determination of progesterone, testosterone and 17β-estradiol in bovine blood serum.

The analytes were detected by LC-MS/MS in ESI positive and negative mode; chromatographic separation was performed on a Waters XSelect HSS T3 XP column, using gradient elution. The method was successfully validated both for screening and quantification purposes according to Commission Decision 2002/657/EC at the following concentration range: 0.020-0.080 μg/L for 17β-estradiol, 0.25-10 μg/L for testosterone and 0.5-20 μg/L for progesterone.

Finally, the results of two-years of controls carried out analyzing 203 bovine serum samples were discussed.

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The methods for official control of heavy metals in food by ICP-MS: applications and perspectives

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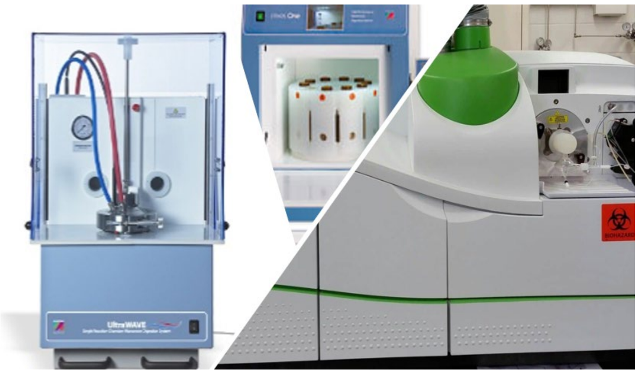
Food safety is one of the most relevant policy of the European Union, to ensure public health, the protection of consumers, legal trade practices, animal welfare and plant production. The official control of contaminants from the environment and from production processes is one of the main tasks for ensuring public health [1]. The Istituto Zooprofilattico Sperimentale del Mezzogiorno (IZSME) is a public organization belonging to the Italian National Health System, providing control laboratories and appointed for monitoring activities in the area of food safety, regarding both local productions and commodities imported from EU Member States and third countries. The IZSME is part of a national network providing also technical and scientific support to the competent authorities for official control. The control about environmental inorganic contaminants in food, feed and animal productions is a very important task for the Department of Chemistry. Trace elements naturally occur into the environment, are present in soil, water, air, can enter the food chain, and can bio-accumulate in food. This way, many heavy metals represent a risk for consumers, and are subject of official control monitoring programs. In the last years, at the Department of Chemistry of the IZSME, several methods based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were introduced, to analyze trace elements in food and feed. For the need of national and local monitoring plans, we developed ICP-MS methods for the simultaneous determination of As, Cd, Co, Cr, Cu, Ni, Pb in seafood and milk. The methods were in-house validated according to the requirements of EU regulation [2], then accredited in compliance with the ISO/IEC 17025:2017 standard. Regular quality assurance controls, the use of certified reference materials, the participation to proficiency test rounds account for reliability of the methods. Method performance were evaluated in terms of specificity, trueness, precision, ruggedness, linearity. The validation studies showed high specificity and accuracy; trueness, in terms of mean recoveries, was in the range 91.0%-114.00%, and repeatability, calculated as relative standard deviations (RSDs), were between 5.74% and 6.0%. The linearity of detector response for each element showed linear correlation coefficients r2 ³ 0.998. For the 7 elements, the detection limits (LODs) were calculated and the limits of quantification (LOQs), in the range between 0.020 and 0.100 mg/kg, were experimentally measured.The introduction of these methods improved the official control activity of the laboratory regarding Cd and Pb. More rapid analysis were introduced; at the same time, it was possible to get data for the monitoring of Ni and As in some food, required by the European Commission. Moreover, the ICP-MS methods allows to get information about some oligoelements such as Co and Cu.ICP-MS is a current and versatile analytical technique [3]. Work is in progress to extend the method to different matrices, such as feed and vegetables, and to other elements (Be, Ga, Sr, In, Cs, Tl, Bi, U, Mn, Se, V), and to expand the panel of both contaminants and oligoelements monitored.



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Efficient lipid profile characterization of mozzarella cheese by optimizing accelerated solvent extraction combined with liquid chromatography-Orbitrap mass spectrometry

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Lipidomics is known as the large-scale and comprehensive study of lipid molecules in different systems, such as biological tissue or food, and for different purposes [1]. The recent progress in high-resolution MS techniques [2] has significantly influenced the research of Lipidomics, improving the confidence of molecular species assignment and accuracy of their quantification, in particular low-abundance lipid species [3]. Lipid extraction is the first step in Lipidomics to isolate a subset of components and remove possible interferences. It constitutes a step of fundamental importance for high quality and exhaustive lipidomic approach [4]. In this study, a novel accelerated solvent extraction (ASE) procedure combined with Ultra High liquid chromatography-electrospray ionization Orbitrap mass spectrometry (UHPLC-ESI-Orbitrap-MS) was developed for the detailed untargeted lipidomic profile of mozzarella cheese. Response surface methodology (RSM), obtained from a central composite design (CCD), was used to define the best extraction conditions. Lipid identification from raw data was performed using LipidSearch^{TM} software, allowing chromatographic peak detection, peak extraction, peak alignment and quantitative processing. A total of 14 classes of lipids, including ceramides (Cer), diacylglycerols (DG), triacylglycerols (TG), lysophosphatidylcholines (LPC), lysophosphatidylethanolamines (LPE), phosphatidylcholines (PC), phosphatidylethanolamines (PE), phosphatidylinositols (PI), sphingomyelins (SM), bismethyl phosphatidic acids (BisMePA), cholesterol ester (ChE), zymosterol (ZyE), hexosyl ceramides (Hex1Cer, Hex2Cer) were measured, confirming that ASE technique associated to high resolution mass spectrometry detection is an efficient tool for Lipidomics in food science.

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Multiclass Determination of Antibiotic Residues in Honey by LC-Q-TOF

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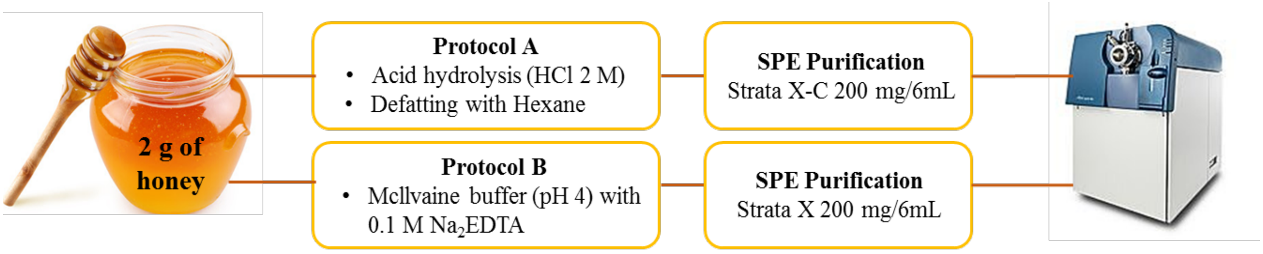
The use of antimicrobial substances for the treatment of honey bees diseases is banned in European Union and also in the third countries few substances are regulated. However, unauthorized administrations of a plethora of antibiotic substances are well documented worldwide [1]. Among these, aminoglycosides, macrolides, nitrofurans, nitroimidazoles, quinolones, sulfonamides, tetracyclines, chloramphenicol, fumagillin and lincomycin. In the last ten years multiclass analytical approaches have been more and more developed to determine antibiotic residues in food. Unfortunately, this approach can be only partially adopted for honey, not only because of the very particular properties of some classes of interest (e.g. aminoglycosides and nitrofurans), but also because acid hydrolysis is needed to extract sulfonamides [2], hampering the recovery of acid-sensitive antimicrobials (macrolides and tetracyclines). Therefore, more than one procedure must be applied to control the presence of the most used antimicrobials in honey bees farming.
In this work two confirmatory methods were developed in parallel: protocol A for sulfonamides, nitroimidazoles and quinolones and protocol B for acid quinolones, amphenicols, macrolides, tetracyclines, fumagillin and lincomycin. The two sample preparations are summarized in Figure.



Protocol A
- Acid hydrolysis (HCl 2 M)
- Defatting with Hexane

SPE Purification
Strata X-C 200 mg/6mL

Protocol B
- McIlvaine buffer (pH 4) with 0.1 M Na_2EDTA

SPE Purification
Strata X 200 mg/6mL

Figure - Sample preparation scheme

The analytical determination was carried out by a LC-Q-TOF system (SCIEX TripleTOF® 6600+) operating in positive ionization mode (ESI+), except for chloramphenicol. The data were acquired in MRM^{HR} mode. Chromatographic separation was achieved on a Poroshell 120 EC-C18 column. Both procedures were validated according to Commission Decision 2002/657/EC [3] in the range 0.2-50 µg/kg with satisfactory recoveries (80 - 90 %) and precisions (RSD% < 15%) for 64 antibiotic substances. The limits of detection were from 0.2 µg/kg to 5 µg/kg. An investigation is in progress to assess residue prevalence in honey samples collected from local markets.

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A general analytical platform and strategy for the screening and determination of pyrrolizidine alkaloids in food matrices with high risk of contamination using high-resolution mass spectrometry (Q-Orbitrap)

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Pyrrolizidine alkaloids (PAs) are a large group of naturally occurring phytotoxins recently regarded as undesirable substances in plant-derived food products due to their genotoxic and carcinogenic activities [1-2]. A high-throughput screening and confirmatory method combining salting-out assisted liquid-liquid extraction (SALLE) with ultra-high performance liquid chromatography coupled with high resolution tandem mass spectrometry (UHPLC-MS/MS) for the detection of pyrrolizidine alkaloids in food matrices with high risk of contamination (beehive products, herbal infusions and plant-based dietary supplements) was developed in this study [3-4]. Firstly, an in-house diagnostic product ion filtering strategy was developed and applied to naturally PAs-producing plants in order to build a spectral library to be used for the screening of a huge amount real samples. A total number of 73 pyrrolizidine alkaloids were analyzed, including 9 reference standards, 38 PAs identified and characterized in four PAs-producing plants from two different families: Asteraceae (Petasites spp., Tussilago spp.) and Boraginaceae (Symphytum spp., Borago spp.), based on their exact mass and fragmentation pattern and confirmed with well-known chemotaxonomic data and online databases, and 26 tentatively identified using the diagnostic product ion filtering strategy and literature information. The mass spectrometer operated in positive ion mode and full-HRMS-data-dependent-MS^2 (full-HRMS-dd-MS^2) acquisition mode at a resolution of 70 000 (full-HRMS) and 17 500 (dd-MS^2). The screening method was applied and then validated in food matrices with high risk of contamination (beehive products, herbal infusions, and plant-based dietary supplements), which differ in the nature of co-extractants and may cause a variable matrix effect [5]. The method proved to be linear up to a concentration of 50 µg L^{-1} ($R^2 > 0.99$). The limits of quantification (LOQs) of the reference standards were lower than 1 µg kg^{-1} for all the tested matrices. Recoveries were in the range of 70-120% and repeatabilities, expressed as relative standard deviations (RDSs) lied in the range of 1-11%.

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Animal poisoning: untargeted analysis by GC-EI/MS to identify toxic substances.

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The practice of animal poisoning is widespread, and represents a serious problem of public hygiene, because of the consequences for domestic and wild animals, including endangered species, but even for the risks to the environment and humans [1]. To face these illegal practices, in 2008 the Italian Ministry of Health issued a decree, revised in 2020 for new computerized communication procedures, that prohibits the preparation and dissemination of baits and bites containing toxic substances. The decree identified also the requirements and tasks for all the people involved (the owner of the animal deceased or poisoned, freelance veterinarians, the mayors, the veterinary services of the local health authority, the Istituti Zooprofilattici Sperimentali), in order to implement all the measures [2-3].

In this framework, the suspect poisoning case (both in presence of bait/bite and dead animal) is subjected to an inspection by a vet, that can ask for a chemical analysis to confirm his diagnosis. In the IZSM Department of Chemistry, usually targeted analyses are carried out to identify the presence of pesticides, rodenticides and other chemicals, that are presumed to be responsible for poisoning. The method we developed and validated involves a solid-liquid extraction followed by a purification step, then the analysis is performed by a gas chromatograph coupled to a mass spectrometer [4]. Anyway, the diagnosis by the vet often indicates only a presumed cause of poisoning, because too many toxic substances could be used; but, more important, often the clinical records are insufficient to correlate the poison to the animal symptoms, or to the evidences from the autopsy, or the characteristics of bait/bite to. For these reasons, the classical targeted analysis is unsuccessful. To improve the activity for identifying and confirming the poisoning substances we recently introduced a new detection approach, namely the untargeted analysis. To this aim, the sample is prepared like previously described, and the GC separation performed. After GC separation, we acquire a full scan mass spectrum, in the mass range 50-650*m/z*. If a chemical is present and ionized, we get a characteristic mass spectrum. The untargeted analysis allows for the identification of a wide range of substances of toxicological interest by comparing the mass spectrum of the unknown substance with those reported in the National Institute for Standard and Technology library. The unknown substance identified this way, can be confirmed by direct comparison with its respective standard. A poison is present in relatively high concentration to be effective; then, it is decomposed only partially. For this reason, good full scan mass spectrum is recorded. This approach needs to focus the analysis on the tissues where poison can accumulate.

The introduction of the untargeted analysis allowed us to broaden the panel of chemicals detected and identified, to confirm the cause of a poisoning case, both in baits/bites, and in animal tissues. This way, the effectiveness of our controls increased, even if the vet is not able to address the chemical confirmation during his diagnosis, for limited information about the poison.

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Intracluster sulfur dioxide oxidation in $NaClO_2$ cluster anions: a mass spectrometric study

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Sulfur dioxide is an air pollutant mainly emitted from anthropogenic sources that has important effects on human health and on climate changes. [1] For this reason, the European Union ratified the 2016/2284/UE Regulation, which defines new and more severe reduction targets for a progressive reduction of SO_2 emissions. The removal of sulfur dioxide from combustion flue gases can be accomplished by water-based desulfurization technologies which exploit the capacity of freshwater or seawater to solubilize and remove acid gases. SO_2 removal is enhanced by adding an oxidant such as $NaClO_2$ that converts the sulfurous (S(IV)) ions to the sulfuric (S(VI)) ions. Although the wet oxidation scrubbing of SO_2 is a popular method for the removal of this poisonous gas, the oxidation mechanism occurring in such complex systems has not yet been elucidated. [2, 3]
Accordingly, gas-phase studies performed by mass spectrometric techniques allow the molecular-level investigation of the elementary steps of complex chemical processes, without the interference of the solution effects. Electrospray ionization mass spectrometry (ESI-MS) has also been long-time devoted to the study of salt speciation occurring in solution, showing its capability in controlling size and charge of the cluster ions. [4, 5] Considering the promising information that gas-phase studies can provide, here we investigate the reactions of $[NaClO_2{\cdot}X]^-$ cluster anions (X = halide ion; ClO_x^- with x = 1-4) with SO_2 by ion-molecule reaction experiments performed in an Ion Trap mass spectrometer, in-house modified to perform kinetic measurement. Intracluster oxidation of SO_2 occurs by oxygen-atom, oxygen-ion and double oxygen transfer reactions, which may be a useful parallel to the pathways underlying the oxidation mechanism occurring in solution.

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Application of LC-MS/MS for Ultra Pure Water (UPW) quality control in superconductive cavities production

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One of the main challenge in the production of superconductive cavities (SC) is the quality control of the inner surface of the cavities which may strongly influence cavities performances (field emission, multypacking). High Pressure Rinsing (HPR) is procedure of two hours that consists in washing the cavity surface with high pressure jets (100 bar) of Ultra Pure Water (UPW) capable to assure both the full removal of chemicals residuals and the cleanliness of the cavity itself. The quality of UPWused for the treament is normally checked by measuring resistivity, Total Organic Carbon (TOC) and particles accordingly to the common standard adopted in superconductor industry. However this methods cannot assure the absence of some recalcitrant organic compound that may be presence in the water pipeline, such as the plasticizer leached from the plastic material after long use and/or stress condition

For this reason we developed a new LC-MS/MS method to monitor the UPW quality from control point in ISO 6 clean room production facility. Since the most important required features of the methods were control of the background contamination and the easy handling, we applied solid phase micro extraction (SPME) as sample preparation method, by using C18 tips for 15 min contact time.

LC-MS/MS analyses were carried out by using a TSQ Quantum Access Max (ThermoScientific) equipped with a UHPLC/HPLC chromatographic system, an ESI interface, and a triple quadrupole mass analyzer. Mass spectrometric detection was obtained by applying time segmented selected reaction monitoring (tSRM). MS/MS transition were optimized by using certified reference standard. One qualifier and one quantifier were used for each analyte. A Thermo Scientific Accucore C-18 aQ column (100 mm x 2.1 mm, I.D. 2.6 μm) was used for the chromatographic separation. Elution was carried out at 0.6 mL/min with methanol and water and by eluting from 80% to 9% of methanol in 12 min. Linearity and limit of quantification were evaluated by using matrix-matched calibration curves and following the IUPAC recommendations, R2 values ranged between 0.995 and 0.998 and MDLs from 0.5 to 2.8 ng/ml respectively. Low but consistent absolute recoveries, back-calculated through estimated concentration values, were also obtained (from 91% to 103%). Analysis of blanks showed that the method provided precise control of the background contamination determining reliable quantitation limits (LOD's). The method was therefore efficiently applied on XXX production line

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Paralytic Shellfish Poisoning Toxins (PSP) in bivalve molluscs: a new method based on liquid chromatography coupled to high resolution tandem mass spectrometry (UHPLC-HRMS^2).

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Saxitoxin and its analogues are potent neurotoxins that can contaminate bivalve molluscs, causing an acute human neurological syndrome known as paralytic shellfish poisoning (PSP) [1]. Reliable test methods are necessary to monitor the presence of these toxins in seafood and prevent consumers' health and economic loss to manufacturers.

We developed, validated and accredited a new test method for simultaneous determination and confirmation of 13 PSP toxins in fresh and canned bivalve molluscs by liquid chromatography coupled to high resolution mass spectrometry (UHPLC-HRMS). The quantitative analysis of saxitoxin (STX), neosaxitoxin (NEO), decarbamoyl saxitoxin (dcSTX), decarbamoyl neosaxitoxin (dcNEO), gonyautoxin 1 (GTX1), gonyautoxin 2 (GTX2), gonyautoxin 3 (GTX3), gonyautoxin 4 (GTX4), gonyautoxin 5 (GTX5), gonyautoxin 6 (GTX6), N-Sulfocarbamoylgoniautoxin 1,2 (C1&C2), decarbayl gonyautoxin 2 (dcGTX2) and decarbayl gonyautoxin 3 (dcGTX3), was performed by homogenation of molluscs, hot extraction with 1% v/v aqueous acetic acid and centrifugation. Then, the toxins were separated by reversed phase ultra-high performance liquid chromatography (UHPLC), coupled to a hybrid quadrupole-Orbitrap Q-Exactive mass spectrometer (Thermo Fisher), working in tandem mass spectrometry (HRMS^2). Determination was carried out in positive ion mode for STX, NEO, dcSTX, dcNEO and in negative ion mode for the remaining toxins; the resolution was set at 70,000 (m/z 200, FWHM). Chromatography was run on a TSK-Gel Amide-80 column (5 µm particle, 2.0 × 150 mm, Tosoh Corporation) by gradient elution using ammonium formate aqueous solution and acetonitrile as mobile phases.

For each toxin, the molecular precursor ion and 1 or 2 product ions were monitored, with a mass accuracy better than 5 ppm. The method was in-house validated, considering the concentration range for each analyte: Stx (4.1÷164); Dc-Stx (3.6÷143); Gtx1 (3.9÷157); Gtx2 (3.4÷135); Gtx3 (1.4÷57); Gtx4 (1.2÷49); Gtx5 (3.5÷141); Gtx6 (3.5÷139); Dc-Gtx2 (2.9÷117); Dc-Gtx3 (0.9÷34); Neo (3.3÷133); Dc-Neo (3.4÷135); C1,2 (4.7÷187). The detector linearity was satisfactory ($r^2 > 0.98$). The limits of quantification (LOQs) measured were: Stx (21 µg/kg), Dc-Stx (9 µg/kg), Gtx1 (32 µg/kg), Gtx2 (84 µg/kg), Gtx3 (36 µg/kg), Gtx4 (10 µg/kg), Gtx5 (29 µg/kg), Gtx6 (30 µg/kg), Dc-Gtx2 (29 µg/kg), Dc-Gtx3 (9 µg/kg), Neo (43 µg/kg), Dc-Neo (44 µg/kg), C1,2 (97 µg/kg).

The method was accredited according to the standard ISO/IEC 17025:2017, and used for routine determination of PSP toxins in bivalve molluscs within the regional monitoring plans for the control of local production, as well as of products from extra-European Union countries. This method showed sensitivity and precision higher than the AOAC Official Method 2005.06 [2], fitting for the purposes of official control. Moreover, the UHPLC-HRMS^2 method allowed us to introduce new toxins such as gonyautoxin 6, decarbamoyl neosaxitoxin, decarbayl gonyautoxin 2, decarbayl gonyautoxin 3 increasing the panel of the PSP detectable simultaneously, to reduce the time and cost of the analysis.

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Quantitative evaluation of bioactive compounds in different parts of *F. vulgare* waste by liquid chromatography coupled with high-sensitivity ESI-Qtrap MS/MS

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Introduction

Nowadays the fruit and vegetable waste are considered as a great source of bioactive compounds with ant-inflammatory, antioxidant, immunomodulatory and apoptotic proprieties, which can be used as fertilizers, livestock feed and biogas production, but also to produce cosmetics and nutraceuticals and enriched functional foods [1]. The cultivation of *F. vulgare* (Apiaceae/Umbelliferae) produces large quantities of waste, rich of bioactive compounds such as flavonoid glycosides, phenolic acids and iridoid derivatives [2].

Material and methods

With the aim of select the specific part of fennel waste to be the better source of bioactive compounds, in the present experimental study a targeted quantitative analysis of the selected known metabolites of four different parts of *F. vulgare* (FVBU, *Foeniculum Vulgare* BUlb; FVST, *Foeniculum Vulgare* STeam; FVLS, *Foeniculum Vulgare* Little Steam; FVLE, *Foeniculum Vulgare* Little Steam) was set up by using Tandem Mass Spectrometry.

The hydroalcoholic extracts of the Tiziano Fennel variety were analyzed using a Shimadzu Nexera LC system in line with a Sciex 6500 QTrap MS equipped with a Luna Omega C18 1.7 µm column (*Phenomenex*) (100 x 2.1 mm). The mass spectrometer operated in negative ion mode and the metabolites were detected using *Multiple Reaction Monitoring* (MRM), with the selection and fragmentation of ions with a defined molecular mass and monitored at least two products of fragmentation.

UPLC-ESI-QTrap-MS/MS method was validated evaluating the precision at six concentration levels for eleven compounds. Their calibration curves were linear in the concentration range from 0.125 µg/mL to 1 µg/mL. The limit of quantitation (LOQ) was determined by injecting a series of increasingly dilute standard solutions until the signal-to-noise ratio was reduced to 10

To deepen the results obtained, preliminary analyses were carried out on the little steam and leaf of the Pegaso variety (FVLS-P, FVLE-P). Spectrophotometric assays were carried out for evaluating the antioxidant properties and the phenolic content of the various extracts.

Results and conclusions

A high content of feruloyl quinic acid was revealed in each part of Tiziano variety of *F. vulgare*, even if the steam and the bulb are the parts with the most intense content. The interesting data that emerged from this study is that only the leaves of both varieties are rich of flavonoid glucuronides, such as quercetin glucuronide, kaempferol glucuronide and isorhamnetin glucuronide. In addition of these data also the spectrophotometric assays confirmed that the leaf is the part of *F. vulgare* waste with the highest antioxidant activity and with a higher phenolic content. In conclusion, the present study showed that fennel waste is an excellent source of bioactive compounds useful to produce nutraceuticals or even functional products, but especially the leaf is the most promising part.

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- Orals
- Posters

Computations for investigating anticancer activity of metal-based compounds beyond cisplatin

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The study of the mechanism of action (MOA) of anticancer drugs plays a key role in drug discovery and development.[1,2] If targets are identified and the ways of interaction of drugs with targets along with subsequent cellular responses are disclosed, strategies to design new drugs and modify existing drugs against diseases can be proposed. However, ascertaining the MOAs of anticancer drugs is a very challenging task because many kinds of biomolecules can be the targets as well as many modes of interaction are conceivable.

The most famous and investigated anticancer agent cisplatin is the best example of how the knowledge of the MOA can be useful for designing new more efficacious and less dangerous drugs. However, in spite of the huge number of synthesized metal-containing compounds proposed for fighting cancer, only a few of them have entered clinical trials due to their not significant therapeutic enhancements. The increasing availability of mechanistic information about the modes of action of established inorganic drugs, however, should drive the examination of various approaches for developing effective inorganic chemotherapeutic agents.

Here some of the outcomes that we have obtained exploring the MOA and properties of “classical” and “non classical” metal-containing anticancer drugs using computational tools are reported. For some of the reported examples open questions still remain. The aim of the research we carry out in this field is to contribute to the optimization of the design and, in general, the development process of the family of metal-based anticancer compounds.

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Exploiting Machine Learning Methods in Atomistic Simulations of Oxide Glasses

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In the last years, machine learning (ML) approaches have been widely used in computational chemistry since they allow to narrow the gap between the accuracy of *ab initio* methods and the efficiency of classical and/or phenomenological approaches to compute and simulate structure, properties and behaviour of molecules and materials.[1,2]

Although, the literature is flourishing of ML applications on molecules and one-component crystalline materials poor advances have been accomplished for oxide glasses.[3] This is due to the multicomponent and amorphous nature of such systems that pose several issues and limitations on the generation of large and reliable reference quantum mechanical datasets and on the definition and efficient management of descriptors used to map structure-properties relationships.

In this presentation, we will review the foundations of the most employed supervised ML methods, especially the Kernel Ridge Regression (KRR) and artificial Neural Network (NN) techiques and their applications on the prediction of NMR properties and Force-Fields of oxides glasses.[4]

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Modelling extended-core π systems and their aggregates: charge transport and optoelectronic properties

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Understanding relationships between structure and opto-electronic properties is an important goal for the science of organic semiconductors and is motivated by the desire to improve materials performance. In this perspective, one major objective is to achieve a deep understanding of the interplay between intramolecular properties and intermolecular interactions governing, among others, charge conduction mechanisms, energy transfer, optical properties of molecules and aggregates.[1] Organic semiconductors with extended-core π systems may display, in some cases, di-radical / multi-radical character. Organic molecules with unpaired electrons are intriguing for advanced applications in molecular electronics, spintronics and organic batteries, as well as other possible applications.[2] In this contribution I will summarize some results of recent computational investigations in my group, covering the following subjects: a) the impact of intra- and inter-molecular parameters on the charge transport of several organic semiconductors among which cycloparaphenylene (CPP) carbon based nanohoops [3]; b) the assessment of different computational strategies to capture the distinctive character of conjugated diradicals, namely the appearance of a low lying excited state dominated by the doubly excited HOMO,HOMO→LUMO,LUMO configuration [4,5]; c) the hole/electron delocalization in mixed valence systems [6] and, d) the interplay of Frenkel and charge transfer character in the low lying electronic excited states of molecular aggregates [7].

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Predictive optical photoabsorption of metal clusters via efficient TDDFT simulations

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We report a computational study via time-dependent density-functional theory (TDDFT) methods of the photo-absorption spectrum of an atomically precise monolayer-protected cluster (MPC), the $Ag_{24}Au(DMBT)_{18}$ single negative anion, where DMBT is the 2,4-dimethylbenzenethiolate ligand. The use of efficient simulation algorithms, the complex polarizability polTDDFT approach [1] and the Hybrid-Diagonal Approximation (HDA) [2], allows us to employ a variety of exchange-correlation (xc) functionals at an affordable computational cost. We are thus able to show, first, how the optical response of this prototypical compound, especially but not exclusively in the absorption threshold (low-energy) region, is sensitive: (1) from a methodological point of view, to the choice of the xc-functionals employed in the Kohn-Sham equations and the TDDFT kernel, and (2) from a chemical-physical point of view, to the choice of the MPC geometry. By comparing simulated spectra with experimental data, we then demonstrate how a hybrid xc-functional employed in both the Kohn-Sham equations and the diagonal TDDFT kernel at the crystallographically-determined experimental geometry is able to provide a consistent agreement between simulated and measured spectra across the entire optical region. Single-particle decomposition analysis tools finally allow us to understand the physical reason of the failure of non-hybrid approaches.

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Improving empirical force fields for molecular dynamics simulations of oxide glasses.
The importance of three-body interactions in rigid-ion models

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Multicomponent oxide glasses play a key role in addressing major global challenges in energy, medicine, and advanced communications systems[1,2]. Unfortunately, the development of new glass compositions with tailored properties is hampered by the lack of a complete understanding of their structure. Among the physics-based methods, classical Molecular Dynamics simulations based on empirical interatomic potentials have emerged as a powerful and efficient tool to gain insight into the composition-structure-properties relationship of a wide range of amorphous and glassy materials[3,4]. The accuracy and reliability of classical MD results strongly depend on the interatomic potential used and thus it is of great importance to develop new, accurate, and transferable force-fields. In this contribution we will show the great improvement of the prediction of glass structure and properties when three-body potentials acting between T-O-T bridges (T = Si, P), coupled with T-T repulsive interactions (T = Si, Al, P) between network-former elements are included in the PMMCS force field, a wide used potential based on cation-oxygen and oxygen-oxygen two body interactions computed with Morse functions[5]. This new force-field, named BMP[6], has also been parametrized to include boron, that was absent in the original potential. We will show that our new FF better reproduces the bond angle distributions and distances between atoms, leading to a better description of the structure. This is confirmed by a comparison with experimental Q^n speciation (Q stands for quaternary specie and n is the number of bridging oxygens around it), density, bond preferences in glasses with multiple former oxides, and neutron total diffraction spectra. We will show the great correlation between a better description of the structure, and in particular of the angles, and the reproduction of NMR spectra of spin active nuclei (^{11}B, ^{17}O, ^{27}Al, ^{29}Si, ^{31}P), which has been extremely improved. In addition to the improvement of the structure, the new FF has revealed to reproduce fairly well also the ionic conductivity in mixed alkali aluminosilicate glasses and the elastic properties.

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First-principles study of Oxygen redox activity in P2-type $Na_xNi_{0.25}Mn_{0.68}O_2$ high energy cathode for Na-ion batteries

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Na-ion batteries (NIBs) are rapidly emerging as convenient alternative to state-of-the-art Li-ion battery for large-scale applications, thanks to wide availability and consequent low cost of raw materials [1]. Layered transition metal oxides (Na_xTMO_2) have been proposed as promising active components at the cathode side of NIB cells, where design and optimization seem to rely on enhanced energy density and stability. Higher operating voltage in P2-type polymorphs of Na_xTMO_2 can be achieved by enabling anionic reactions, but the irreversibility of $O^{2-}/O_2^{n-}/O_2$ evolution leads to large capacity loss at first charge cycle [2, 3]. Here we propose a first-principles investigation of P2-type $Na_xNi_{0.25}Mn_{0.68}O_2$ as a case study. Computational strategies are employed to dissect the structural and electronic features of the redox-active elements in this material at different sodiation stages [4]. In particular, we address the oxygen redox processes by investigating the formation of oxygen vacancies and dioxygen-metal complexes at low Na loads (high voltage range). Our PBE+U-(D3BJ) calculations show that low-energy superoxide moieties can be formed at x Na = 0.25 in the Mn-deficient site, while the x Na = 0.125 content enables the release of molecular O_2 via preferential breaking of Ni-O bonds. Mechanistic insights show that dioxygen formation is driven by the M-O covalency and unveil that O_2 loss can be effectively suppressed by Fe doping [5]. Our findings pave the route for the rational design of high-energy Na_xTMO_2 cathodes that feature enhanced reversible capacity and thus boost the development of efficient NIB devices.

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An atomistic insight on the hot-electron injection mechanism

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The study of the opto-electronic properties of metallic nanoparticles (NP) is a lively field in nanoscience. The presence of Surface Plasmon Resonance (SPR) and its fine control through the manipulation of the NP sizes and geometries, make them suitable for a broad variety of applications in biomedicine, catalysis, electronics, optics and more. [1,2] It was recently discovered that as the SPR start to dephase, there is the generation of hot-carriers (HC), which are energetic, out of equilibrium electrons and holes. Such HC can be exploited to activate chemical reactions on molecules adsorbed on the NP surfaces. [3,4] Although many theoretical advances have been made to determine the mechanism of this phenomenon [5,6], there is still an open debate on the mechanism of interaction of HC with the adsorbate and it is not yet understood how the HC energy can be transferred to the reactive degrees of freedom. [7] Our work aims to investigate one of the suggested HC injection routes which involves the transient tunneling to the adsorbate and further energy release to the molecular vibrations. To do that, we explored the interaction between a hot-electron (HE) and a small molecule at the real-time Time Dependent Density Functional Theory (rt-TDDFT) level. To simplify the system, we represented the NP structure as a linear metal (Ag or Au) chain and the adsorbate as a small molecule (CO or H_2O) adsorbed on the edge. By simulating the real-time dynamics of an HE on the metal chain and approaching the molecule, we observed that they can interact with the adsorbate by releasing part of their kinetic energy on some specific molecular normal modes, which are the ones involved in bonds dissociation. The magnitude of such interaction strongly depends on the HE energies. Even if a single HE can release a small amount of energy this effect would become significant when the collective contribution of all produced HE is taken into account. As such, all the generated HE can compete to the activation of the motion involved in the photocatalyzed reaction Furthermore, we applied our methods to study the HE-catalyzed CO_2 reduction on the Rh (100) surface. To do that we investigated the dynamics of this reaction starting from the characterization of the ground state mechanism through Nudge Elastic Bands (NEB) calculations. This allowed us to carefully characterize the dynamics and the energetics of the process and to obtain a reliable starting point for further investigation on the photocatalyzed reaction. [4]

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Computational characterization of single-atom species on metal-supported oxide thin films

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Metal-supported oxide two-dimensional films represent an interesting class of materials, whose properties depend on the low dimensionality of the film, as well as the interplay with the metal substrate, with relevant implications in many fields. Indeed, the metal-supported oxide thin films display the peculiar property to trigger the electron transfer from the metal substrate to a reactive adsorbate (or vice versa) via tunnelling through the film. This has consequences on the adsorption of single metal adatoms, acting as active species in heterogeneous catalysis or atomic-scale magnets. Aiming at a systematic investigation, we report a comparative DFT study of single (K, Au, and Pt) atoms adsorption over a wide range of metal-supported oxide ultrathin films (MgO on Ag and Mo, ZnO on Cu, Ag, and Au, SiO_2 on Pt and Ru, TiO_2 on Ag and Pt, ZrO_2 on Pt and ZrPt). These films include experimentally studied reducible and non-reducible oxides, showing very unusual and interesting behaviour towards metal atoms adsorption. The interaction of K and Au with the metal/oxide substrates is dominated by charge-transfer aspects, where K tends to assume positive charge and Au negative charge. This fact reflects into a general trend where metal-supported oxide films displaying large work function (i.e. deep empty states) tend to bind K cations strongly, while supports with small work function (i.e. shallow donor states) strongly stabilize Au in anionic form. The correlation between adsorption energy and work function is not strong enough to neglect several other aspects related to chemical and morphological properties of the specific oxide/metal interface. The case of Pt is completely different: here, covalent contributions to the bonding prevail, and the bond strength depends on factors such as the surface morphology and local atomic coordination, rather than the support's work function.[1]

In a subsequent work, we then focus on a wider series of transition-metal adatoms (Cu, Ag, Au, Ni, Pd, and Pt) adsorbed on SiO_2/Pt, SiO_2/Ru and on a model of a silicon slab coated by an SiO_2 film. Here, we characterize from a thermodynamic and kinetic point of view also the penetration of the adatom through the porous silica film and its bonding at the interface with the substrate. An interesting interplay between the support's work function and the chemical nature of the adatom emerges, determining its bond strength, its charge state, and its tendency toward diffusion to the metal/oxide interface.[2]

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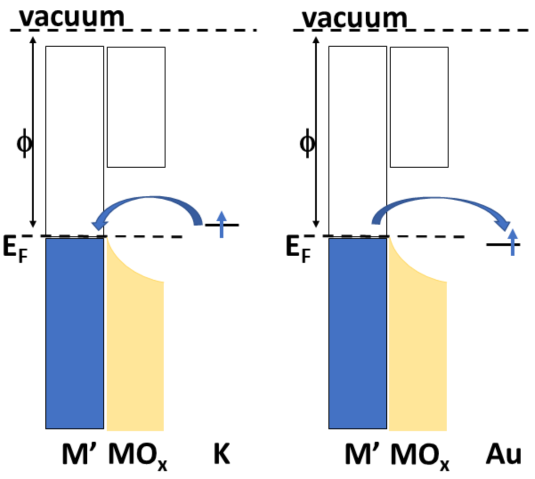

Spontaneous Production of Ultrastable Reactive Oxygen Species on Titanium Oxide Surfaces Modified with Organic Ligands

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The spontaneous formation and long-term surface stabilization of superoxide radicals is observed on specific TiO_2 hybrid materials, in which titanium is coordinated to an organic ligand. Here the rationale for this uncommon phenomenon is investigated by a synergistic theoretical and experimental approach involving DFT calculations and spectroscopic techniques. Stoichiometric and reduced anatase (101) surfaces modified with acetylacetone, dibenzoylmethane and catechol are comparatively examined. Our results reveal that the interaction between organic ligands and adsorbed O_2 molecules improves when O vacancies are present on the external layer of the surface, promoting O_2 reduction. The electronic features of the ligand play a pivotal role for both an effective electronic interaction with the surface and the stabilization of the generated reactive oxygen species. These results agree with experimental data [1], showing that sol-gel-derived Ti-diketonate hybrid oxides spontaneously produce very persistent superoxide radicals in ambient conditions, thus holding a high intrinsic oxidative activity.

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Development and application of a ReaxFF Reactive Force Field for Cerium Oxide/Water Interfaces

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Ceria (CeO_2) is a well-known catalytic oxide with many environmental, energy production and industrial applications, most of them involving water as reactant, byproduct, solvent, or simple spectator. [1]

So far, most of the theoretical studies have dealt with studying the adsorption and dissociation of a monomer or small oligomers of H_2O on periodic surfaces models of the oxide surfaces, using static DFT calculations, with only an ab-initio molecular dynamics investigation of a thin liquid-water/ceria interface.[2]

To facilitate large-scale reactive MDs of the water-ceria systems we have developed a reactive force field ReaxFF for the Ce-O-H species.

In this contribution, we present the re-parameterization of the ReaxFF Ce/O of Broqvist *et al* [3], first developed for the study of ceria, and its extension to the hydrogen to make it suitable for the accurate study of ceria/water interfaces. [4]

The parameters were fitted to an *ab-initio* training set obtained at the DFT/PBE0 level, including the structures, cohesive energies and elastic properties of the crystalline phases Ce, CeO_2 and Ce_2O_3; the O-defective structures and energies of vacancy formation on CeO_2 bulk and CeO_2 (111) surface, as well as the absorption and reaction energies of H_2 and H_2O molecules on CeO_2 (111).

The new potential reproduced reasonably well all the fitted properties as well as the relative stabilities of the different ceria surfaces, the oxygen vacancies formation and the energies and structures of associative and dissociative water molecules on them. Molecular Dynamics simulations of the liquid water on the CeO_2 (111) and CeO_2 (100) surfaces were performed. The results showed that about 35% of surface sites of CeO_2 (111) are hydroxylated whereas 15% of them are saturated with molecular water associatively adsorbed. As for the CeO_2 (100) surface, we observed that water preferentially dissociates covering 90% of the available surface sites in excellent agreement with recent experimental findings.

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Computational study on the structural stability of mutated Affitins

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Affitins are a class of small proteins derived from the DNA binding protein Sac7d [1], found in the microorganism *Sulfolobus acidocaldarius*. They are highly resistant to heat and low pH. Their tertiary structure is characterized by a five-stranded incomplete β-barrel and a three-turn C-terminal α-helix (*Figure 1*).

The aim of our study is the identification of affitins that can be exploited as diagnostic or therapeutic probes, by recognizing selected receptors overexpressed in tumor cells, which are already used in targeted therapies.

Here we report on our preliminary results concerning the structural characteristics of affitins obtained by mutating *in silico* 14 residues involved in the interaction with DNA, for a total of five structural mutant models of Sac7d. Two affitins were built by substituting all residues with alanines or isoleucines; two affitins were built with glutamates in the place of positive charged residues and one with arginines as substitutes for negative ones, to check the structural role of electrostatic interactions.

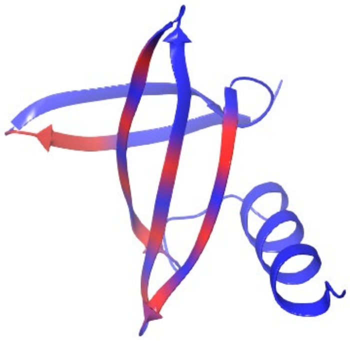

Figure 1-Affitin Sac7d. Residues interacting with DNA shown in red

Molecular Dynamics simulations of these models of mutants were performed in aqueous solution at standard ambient temperature and pressure by using the Gromos 53A6 force field [2] implemented in the GROMACS (release 2016.1) program. Trajectories analysis included calculations of the root-mean-square deviations (RMSD) along the simulation time and the root-mean-square fluctuations (RMSF) of each residue for the positions of backbone atoms; the calculation of the fraction of secondary structure by means of the DSSP algorithm; clustering of sampled conformations; essential dynamics performed on C_α coordinates. Results show that RMSF have similar trends for all mutants, with higher fluctuations on terminals, α-helix and inter-strand residues. All mutants show a percentage of secondary structure slightly lower with respect to the wild-type, however no considerable difference in the tertiary structure of centrotypes of the three main clusters of each mutant have been observed. These results suggest that mutations of the DNA-interacting residues do not significantly affect the structural stability of Sac7d, therefore mutations could be designed for targeting a receptor of interest in a specific way, without impacting the overall 3D structure.

Future work consists in drawing up a reliable protocol for molecular docking for determining models of complexes for selected affitins and receptors relevant in targeted therapies. Benchmarking of different protein-protein docking approaches will be performed using as a reference experimental complexes involving Sac7d homologues. Moreover, the calculation of the matrix of local coupling energies [3] will be helpful to guide the docking towards proteins areas with a lower energetic coupling with rest of the structure, as they are supposed to be the recognition sites of possible partners.

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Molecular Simulations of $CO_2/N_2/H_2O$ Gaseous Mixture Separation in Graphtriyne Membrane

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Graphynes are porous derivatives of graphene that can be considered as ideal 2D nanofilters. Here, we investigate by theoretical methods graphtriyne single/double and three layer, proposing them as membranes featuring pores of subnanometer size suitable for $CO_2/N_2/H_2O$ separation and CO_2 uptake. The potential energy surfaces, representing the intermolecular interactions within the $CO_2//N_2/H_2O$ gaseous mixtures and between the graphtriyne layers and the molecules, have been formulated in an internally consistent way, by adopting potential models far more accurate than the traditional Lennard-Jones functions, routinely used to predict static and dynamical properties of matter. In this work, we have exploited the Improved-Lennard Jone formulation[1].

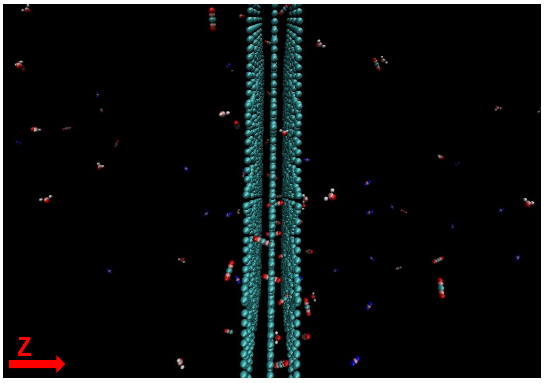

Fig. 1 Snapshot of configurations for the trilayer system at 4.62 atm and 353 K

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Electrode-electrolyte interface in solid-state lithium batteries: new insights from density functional embedding theory

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Solid-state lithium batteries represent the most promising among the next generation of energy storage technologies [l]. The use of metallic lithium as anode in these new devices poses several challenges related to the long-term stability and performance of the battery. A strategy to achieve durable and effective electrode of this kind is by engineering the solid-electrolyte interphase (SEI) with purposely designed electrolyte molecules. For example, such artificial SEI formation can be very effective if the lithium metal is covered with polymer layer, and it is better if the polymerization occurs in situ at the electrode surface [2]. To this end, some recent studies have focused the structure and reactivity of electrode molecule on the lithium metal: for example, the interaction of ethylene carbonate (EC) with lithium has been addressed with DFT-based approaches [3]. Starting from these results we here propose a theoretical study on the similar electrolyte vinyl carbonate (VC) that contrary to EC can undergo a polymerization ontop of lithium metal in presence of a radica initiator [4, 5]. Our results will show the many possible interaction modes between the metal and VC, plus we characterize all the possible VC dissociation pathways once it interacts with the Li surface. Moreover, we provide a high-level description of these processes going beyond the local and semi-local DFT by application of the Density Functional Embedding Theory [6]. Such approach is well suited for modeling the local interaction of molecules on metal surfaces and in this case it will be applied for decoupling the complex electronic structure of the reacting electrolyte molecule from that of the metallic background. We will discuss our results also in perspective of further applications of this method in other electrocatalytic context.

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Multi-replica biased sampling for photoswitchable π-conjugated polymers

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In recent years, π-conjugated polymers are attracting considerable interest in view of their light-dependent torsional reorganization around the π-conjugated backbone, which determines peculiar light-emitting properties.[1-3] More specifically, polyfluorene derivatives are of wide interest in the field of organic electronics, because their peculiar photo-induced twisted-coplanar transition, enabling a specific molecular response after light-irradiation.

Motivated by the interest in designing conjugated polymers with tunable photoswitchable pathways,[4] we devised a computational framework able to enhance the sampling of the torsional conformational space and, at the same time, to estimate ground to excited-state free energy differences. This scheme is based on a combination of Hamiltonian Replica Exchange Method (REM),[5] parallel bias metadynamics[6] and free-energy perturbation theory[7,8] and it has been applied on a pentamer of 9,9-dioctylfluorene by biasing multiple torsions. The Parallel Bias metadynamics approach combined with Hamiltonian Replica Exchange (REM) are used to increase the efficiency of our scheme and, in combination with FEP, to characterize the free-energy landscapes of the singlet ground state (S_0) and the lowest singlet excited states (S_1 and S_2), as well as the transitions between these states. Moreover, we predicted that, upon irradiation, the investigated system can undergo a dihedral inversion from -155° to 155°, crossing a barrier that decrease from 0.1 eV in S_0 to 0.05 and 0.04 eV in S_1 and S_2, respectively. Furthermore, S_1 and even more S_2 were predicted to stabilize coplanar dihedrals. The simulation results were compared with the experimental emission spectrum, showing a quantitative agreement with the predictions provided by our framework.[9]

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A computational view of ionic liquid crystals

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Ionic Liquid Crystals (ILCs) are materials composed of the same types of cations and anions as typically found in ionic liquids (ILs), but exhibiting mesomorphism as in liquid crystals (LCs) compounds. The prototypes of such systems are 1-alkyl-3-methylimidazolium salts with various inorganic anions and alkyl chains of at least 12-14 carbon atoms [1]. In this presentation, I will highlight the results of molecular dynamics simulations of ILCs using three types of force fields: fully atomistic systems, coarse-grained models and highly coarse-grained models based on single-site soft ellipsoidal potentials.

Fully atomistic models have been used to investigate the orientational and positional order of smectic ionic liquid crystal phases. Results of the simulations have been compared with experimental NMR data revealing microscopic details of the ILCs structural features [2]. Together with atomistic models, slightly coarse-grained models, keeping the general topology, flexibility and charge distribution of the atomistic version, have been used to investigate the molecular features that affect the stability and phase behavior of ILCs, with a focus on the charge density and relative size of cations and anions [3]. In agreement with the experimental observations, the stability of the ionic smectic phase has been found to depend on the relative trends of the anion charge density and cation alkyl chain length. Finally, highly coarse-grained models based on charged spherical Lennard-Jones particles and anisotropic Gay-Berne ellipsoids have been used as models of ILCs. Phase separation is usually observed for generic rod-sphere mixtures of non-charged particles; however, once the charge is switched on, a completely different behavior is observed: we have found a rich polymorphism with ionic nematic and ionic smectic phases. The structural and dynamic parameters of the various phases have been evaluated and their analysis has enabled us to investigate the key features that can stabilize the ionic LC phases compared to the high temperature isotropic (IL) phase and low temperature crystal phase [4,5].

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Electronic attosecond dynamics: Ab initio treatment of photo-induced excitonic states

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Time-dependent electronic structure theories can model the subpicosecond evolution in time of excited electronic states from first principles. Among non-perturbative approaches to mean-field quantum electronic dynamics, real-time time-dependent density functional theory combined with ab initio molecular dynamics have shown to be very powerful, providing a molecular interpretation of a plethora of transient photo induced phenomena, such as the interplay between initial photoexcited states, exciton and polaron formations. [1-3]

Real-time propagation and ab initio molecular dynamics combined with an innovative time-resolved electronic and vibrational analysis protocol are presented to disentangle the most relevant features underlying both linear and non-linear effects, capturing the resulting spectroscopic fingerprints of charge transfer, exciton formation, and long-lived charge species.

In this context, photo-induced metal-to-ligand charge-transfer excited states in the attosecond time domain are presented in this contribution, since their paramount importance for light harvesting and photocatalysis.[4-8] Lately, their range of applications have expanded in the field of circular economy and green chemistry, given their importance as alternative approaches to solar activation of nanostructured systems widely employed in the biomass conversion to solar fuels and the selective production of fine chemicals from agricultural residues and food processing waste.

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Quantum Chemistry using Quantum Computers

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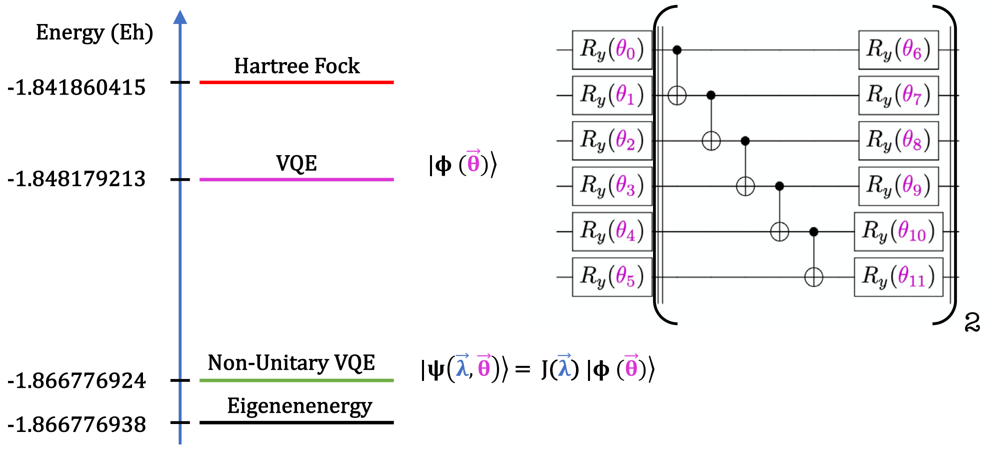
Among the important problems that quantum computers promise to solve in the future, Computational Quantum Chemistry will probably be one of the firsts in which quantum computers might show advantage over classical computers [1,2]. This perspective goes beyond the computational aspects, since the different computing paradigm offered by such devices is promising an exponential increase of computing power which is compatible with the principles of a sustainable development.

The near-term gate-model quantum computers will still have limitations due to a reduced number of qubits, a high level of noise and a short coherence time. New theoretical techniques and algorithms must be designed by theoretical and computational chemists to take advantage of such new devices. The present contribution will review in an introductive and pedagogical way the basic concepts of quantum computation and the main algorithms that are currently used in imperfects but currently available quantum computers to solve small Quantum Chemistry problems. Recently, we have proposed a non-unitary version of the Variational Quantum Eigensolver algorithm that can be used to effectively improve the variational space of wavefunction ansatzes. [3-4] Using the proposed strategies it is possible to recover a large amount of electron correlation energy using shallow-depth quantum circuits.



$$E_{nu-VQE}=\frac{\langle\psi(\vec{\lambda},\vec{\theta})|H|\psi(\vec{\lambda},\vec{\theta})\rangle}{\langle\psi(\vec{\lambda},\vec{\theta})|\psi(\vec{\lambda},\vec{\theta})\rangle}=\frac{\langle\phi(\vec{\theta})|J(\vec{\lambda})HJ(\vec{\lambda})|\phi(\vec{\theta})\rangle}{\langle\phi(\vec{\theta})|J(\vec{\lambda})J(\vec{\lambda})|\phi(\vec{\theta})\rangle}$$

$$J(\vec{\lambda})=\mathbf{1}-\sum_i \lambda_i Z_i-\sum_{i<j}\lambda_{ij} Z_i Z_j$$

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Molecular view on crystals nucleation and growth on different PVDF polymorphs

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Membrane assisted crystallization (MCr) is a hybrid membrane separation crystallization process where a solution (at retentate side) becomes first saturated, then supersaturated and finally, the crystals are obtained [1,2]. MCr can promote crystals nucleation and growth in a well-controlled pathway, thus modulating the final properties of the crystals produced both in terms of structure (polymorphism) and morphology (habit, shape, size, and size distribution).
It is generally difficult to monitor the growth mechanisms of crystals formation however, molecular modelling helps to investigate the mechanism of nucleation and crystals growth [3,4]. This work aimed at analyzing the crystal nucleation and growth of sodium chloride in contact with hydrophobic polyvinylidene fluoride (PVDF) surfaces (amorphous together with alpha and beta phases) at a supersaturated concentration of salt. The results show that salt nucleation is faster with amorphous PVDF model then α and β PVDF. Molecular models confirm the highly efficient packing of the alfa and beta polymer chains, in comparison to the amorphous one resulting in greater diffusion of water molecules

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Multi-Scale Charge-Transfer Modeling in Enzyme Catalysis

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An Electron Donor Acceptor Complex (EDAC) is a transient species formed by two molecules, one electron donor and the other electron acceptor. Under visible light excitation the EDAC reaches an excited state characterized by charge transfer. Excitation of an EDAC can be used to catalyze. In recent years, the renewed interest on EDA complexes allowed chemical functionalization also on *non-activated substrates* [1].

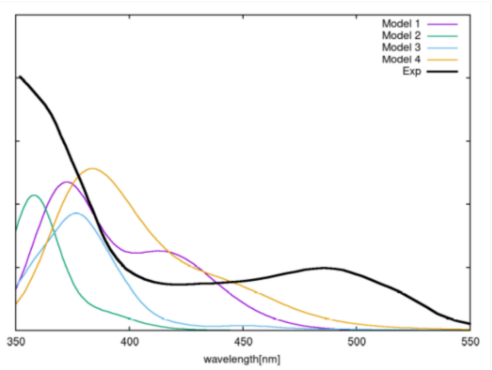
A protein-based EDAC is an ideal kind of catalyst due to the intrinsic regio- and stereo-selectivity. Additionally, in the excited state the protein-based EDA complexes can fulfill reactions that are precluded to the ground state of the protein, as for example in Flavin mononucleotide (FMN) enereductases [2]. In addition to the transient nature of an EDAC, the protein anisotropic contribution of the environment increases the complexity of its characterization.

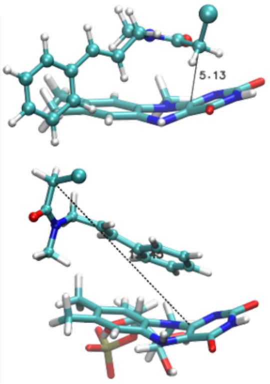
Canonical multiscale QM/MM molecular dynamics (MD) would be suitable for the description of the excitation properties of an EDAC in isotropic environments, such as in solvent, but the characterization of a large number substrate-FMN conformations in complex environments, such a protein, would be precluded.

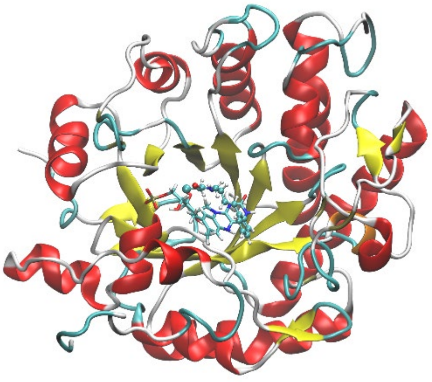
Herein we employ a methodology based on the Perturbed Matrix Method that allows to extend the analysis to a larger number of conformations and to include the dynamics of the protein in the EDA complex characterization [3,4].

With this approach, we were able to identify several EDAC configurations of the substrate α-chloroacetamide-(1) [2] in a FMN enereductase that give rise to charge-transfer excited states which could in principle then trigger the catalytic reaction.

The final aim of the study is to characterize the EDAC electronic structure and catalytic mechanism, that are still poorly understood in order to predict which substrates and which reactions can be expected in specific conditions.







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Computational study of dicationic ionic liquids based on imidazole

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Ionic liquids (ILs) gain a high relevance in the last decades and have been extensively studied as alternatives solvents due to their properties such as negligible vapor tension, thermal and chemical stability, and the possibility to recycle [1]–[4]; A promising application of ILs is for CO_2 capture [5]–[7]. In this context, we use the molecular dynamics technic to determine the stability of the IL-based on the two imidazolium rings connected by a xylene spacer with ortho (**Figure1a**), meta (**Figure1b**), and para (**Figure1c**) isomers with bromide, tungstate (**Figure1d**), and tungstate combined with the CO_2 anions. The program XTB [8] was used for the simulation, a total of 2ns of production was made with a 1fs step and the coordinate was saved every 100fs, with a total of 2000 points.

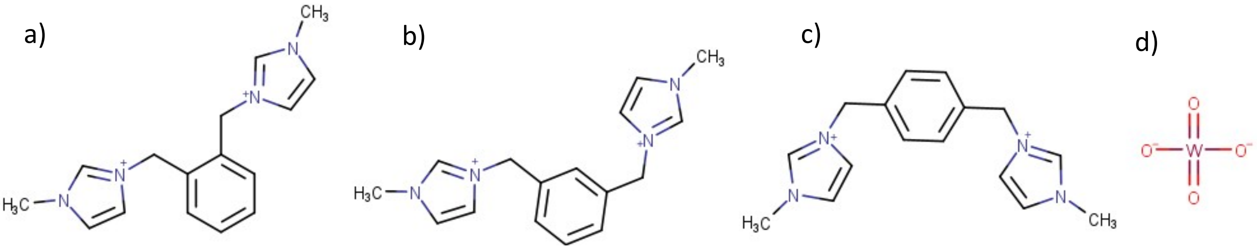

Figure 1: Structure a) orto; b) meta, c) para and d) tungstate anion.

Using molecular dynamics is found that the system based on WO_4^{2-} anion are more stable than those with the Br^- anion. These calculations demonstrate that the presence of the WO_4^{2-} anion creates strong ionic bonds between the cation and the anion leading to stable ionic pairs. Is also observed that the system with the CO_2 is stable, meanly on the meta system, the CO_2. For this system, is also observed the interaction between the WO_4^{2-} and the cation, however, is also observed that the CO_2 interacts with the tungstate and oxygen atom, this interaction creates a structure with lower energy. This result demonstrates that the system with tungstate presents a stable IL and present interesting interaction with CO_2, which can be a good clue to the functionality of this compound.

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An experimental and theoretical investigation on the electronic structure of indole, 2,3-dihydro-7-azaindole, and 3-formylindole in the gas phase by synchrotron-based spectroscopic techniques

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Heterocycles, such as indoles, represent a very important class of compounds that play fundamental roles in biology, chemistry and medicine [1] [2]. The present study is focused on the indole molecule and its 2,3-dihydro-7-azaindole (7-AI) and 3-formylindole (3-FI) derivatives. These three heterocycles are of major importance in bacterial physiology, ecological balance, and human health [1], and also find useful applications in chemistry as coating materials, selective electrodes and biosensors [3] [4]. The present study intends to provide a detailed characterization of the electronic structure of these three molecules to elucidate the mechanisms underlying their potential applications, which have been not so far in-depth investigated in literature. This aim has been achieved by combining experimental measurements and theoretical simulations on valence band (VB) spectra as well as C, and N 1s X-ray Photoelectron (XP) and Near Edge X-ray Absorption Fine Structure (NEXAFS, [5]) spectra of the three heterocycles in gas phase. The measured XP and NEXAFS spectra have been interpreted by means of theoretical calculations based on Density Functional Theory (DFT, [6]) within the Transition Potential scheme (TP, [7]) as well as on Time-Dependent Density Functional Theory (TDDFT) in the linear response regime [8] within the relativistic two-component Zeroth-Order Regular Approximation (ZORA, [9]). VB spectroscopy has allowed the experimental determination of the ionization energies that can be correlated to the energies of occupied molecular orbitals (MOs) [10]. The calculated XP spectra have shown a good agreement with the binding energies (BEs) of the core level features observed in the experimental spectra [10]. A similar good agreement has been achieved in the case of NEXAFS spectra; in particular, the DFT-TP scheme has revealed to be accurate enough for a general reproduction of the measured C 1s NEXAFS spectra, while the ZORA-TDDFT formalism has proven to be better suited for the N 1s ones [11]. This discrepancy has been ascribed to the many-body effects associated with the core electron excitation. The C, and N 1s NEXAFS spectra of all three heterocycles are characterized by a low-lying intense peak associated to transitions toward virtual antibonding π* MOs as well as by several weak transitions to mixed valence/Rydberg or pure Rydberg MOs occurring in the higher-energy range [11].

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Addressing the Frenkel and charge transfer character of exciton states with a model Hamiltonian based on dimer calculations: application to large aggregates of perylene bisimide

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The interchromophoric arrangements influence the intermolecular interactions inside an aggregate, which in turn, determine the optical properties and photo-induced processes of the aggregate. The nature of the exciton states can generally be classified as Frenkel (FE)-dominated, charge-transfer (CT)-dominated or mixed CT/FE. CT states have a crucial role in the photo-induced processes of an aggregate. [1–6] It is fundamental to assess their contributions to exciton states. Generally, from a quantum-chemical (QC) calculation, exciton states are expressed in terms of delocalized excitations (DEs). In order to extract the CT/FE character, we performed a diabatization procedure with diabatic states chosen to coincide with local excitations within a restricted orbital space. On the other hand, a QC calculation will soon become unfeasible when going to large aggregate. In this regard, we propose a model Hamiltonian (mH) approach built on the basis of QC calculations carried out only on dimers composing the aggregate [7]. Perylene bisimide (PBI) is chosen as model system. Excitation energy profiles and CT/FE character modulations as function of the interchromophore rearrangement are studied for aggregates of PBI up to tetramer. The dimer-based approach closely reproduces the results of full-aggregate calculations and we showed that CT/FE interactions modulate the interchange of the H-/J- type aggregate for small longitudinal shifts of the chromophores.

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Study of ligand binding to HIF-2α through Path-Metadynamics

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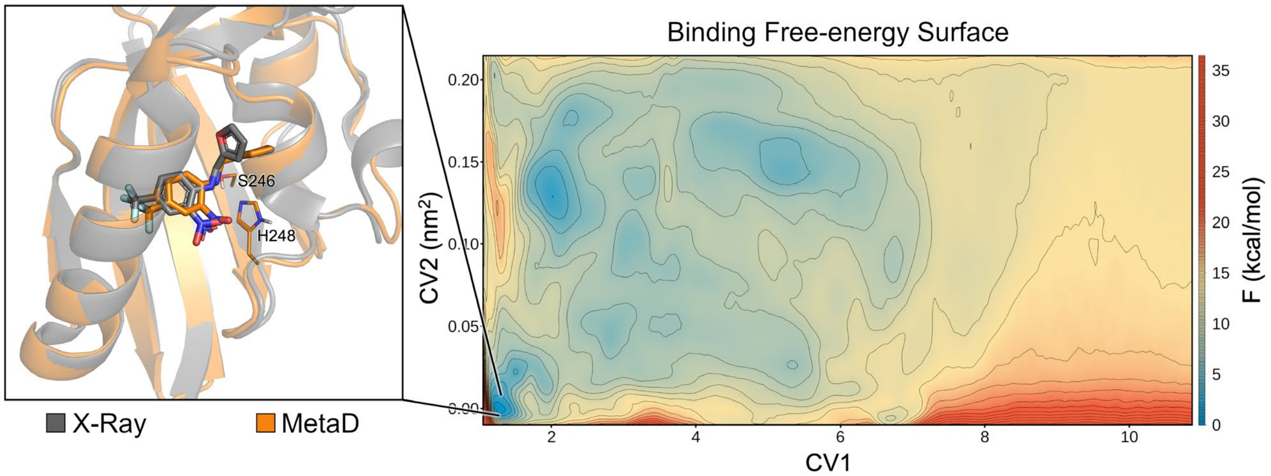
Several methods based on enhanced-sampling molecular dynamics have been proposed for studying ligand binding processes[1]. Herein we developed a protocol that combines the advantages of steered Molecular Dynamics[2] (SMD) and Metadynamics[3]. In SMD a moving restraint bias is applied to the system to pull it along a selected variable. [2]. In Metadynamics simulations, a history-dependent bias potential is applied to a small number of suitably-chosen collective variables (CVs) to discourage the system from revisiting already sampled configurations. Since the choice of CVs is a crucial aspect to obtain an accurate free-energy calculation, Branduardi et al.[4] developed the Path Collective Variable (PCVs) method, which allows exploration of complex multidimensional processes along a predefined pathway described by a single CV.

In this work we propose a combined use of SMD and Metadynamics for the investigation of ligand binding processes. SMD was used to compare the forces required to achieve ligand unbinding through different pathways and identify the preferred one. The employment of Metadynamics with PCVs was used to explore the binding processes along the pathway defined on the basis of SMD. We applied our approach to study the binding of two known inhibitors of the Hypoxia Inducible Factor 2α (HIF-2α), a pharmaceutically relevant system widely recognized as a target for cancer therapy[5].The buried nature of the binding cavity of this protein makes simulation of the process a challenging task. Our approach allowed identification of the preferred entrance pathway for each ligand, highlighted the features of the bound- and the intermediate- states in the free-energy surface, and provided a binding-affinity scale in agreement with experimental data.[6] Therefore, it seems to be a suitable tool for elucidating ligand binding processes of similar complex systems.



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The multifaceted roles of copper ion in human body explored by computational tools

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Copper is an essential metal ion, very important for the survival of all living organisms. Small amounts are required for normal metabolic processes such as brain development, synthesis of neurotransmitters, maintenance of healthy skin and connective tissue as well as immune response, angiogenesis and in the mitochondrial apparatus for energy production [1]. This is possible since it is combined with enzymes as cofactor in cellular reactions.

Unbalanced conditions can lead to a dangerous copper deficiency or excess. In this scenario, several unhealthy effects are detected. At high concentrations, Cu(II) is known to produce oxidative damage to biological systems, including macromolecules and it is considered a contributing cause for the progression of neurological illnesses, like Alzheimer's Disease (AD), where the metal ion increases the growth of Aβ aggregates in the brain and produces oxidative stress that kills neurons. Copper toxicity can be reduced by using copper chelators as drugs [4]. Such ligands must be selective towards Cu(II) and must also work in AD as antioxidants and inhibitors of amyloid fibrils formation. Natural compounds and derivatives represent a good example of such multiple target drugs and the design of new molecules in the pharmacological research, nowadays, also considers boron-containing compounds as promising alternative [6].

Moreover, copper complexes have demonstrated also good antitumor activity and compared to conventional chemotherapeutics like cisplatin and its derivatives, minor toxic with fewer side effects, being the ion among the most abundant essential transition metals in human body [7]. Recently, copper complexes have been used also to improve the selectivity and efficacy against cancer in Photodynamic Therapy (PDT) [8] and as dual-action chemotherapeutics in combination with ligands like thiosemicarbazones, which work as antitumor agents [9]. So, several of the both beneficial and unhealthy roles of copper have been explored by using different computational approaches, QM, TD-QM, QM/MM, MD, with the aim to elucidate the involved mechanisms in treatment of several diseases for providing, also, inspiration and suggestions in drug design and synthesis.

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Unravelling the reaction mechanism of Mo/Cu CO dehydrogenase using QM/MM calculations

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Aerobic CO-oxidising bacteria play a central role in the regulation of tropospheric chemistry by consuming about 10% of annual CO emissions [1]. Among these, the soil bacteria *Oligotropha carboxidovorans* exploit the redox activity of the Mo/Cu-dependent CO dehydrogenase enzyme (MoCu-CODH) [2] to convert atmospheric carbon monoxide, according to the following reaction:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

The active site architecture of MoCu-CODH is peculiar. It is constituted of a unique $MoO_2(\mu S)Cu$ bimetallic centre in the oxidised active form of the enzyme. The molybdenum ion shows a distorted square pyramidal geometry, with one axial oxo ligand and four equatorial ligands: a dithiolene ligand from a molybdopterin cytosine dinucleotide (MCD) cofactor, one oxo (O^{2-}) ligand and a μ-sulfido ligand. The latter links the Mo-centre to the Cu-centre, which is also coordinated by the sulphur atom of Cys388 and by a weakly coordinated water molecule [2, 3, 4]. The CO molecule binds to the Cu(I) centre and its oxidation takes place at the same site, thanks to the high degree of delocalisation within the Mo(μ-S)Cu unit [5]. Such delocalisation allows for facile electron transfers, during catalysis, toward the redox-active Mo ion, which switches between Mo(VI) and Mo(IV) redox states.

Despite the fact that several theoretical and experimental studies have been carried out concerning this enzyme over the last two decades, no consensus about the catalytic mechanisms of MoCu-CODH has been reached so far [6]. In particular, a rather controversial aspect concerns the plausible formation of a thiocarbonate intermediate, first suggested by Dobbek [2]; subsequent theoretical studies suggested that its formation would prevent an easy progress along CO oxidation catalysis. However, in a recent study based on a hierarchy of QM and QM/MM models we actually showed that the thiocarbonate intermediate does not represent an energy sink on the catalytic energy profile [7]. Ongoing work in our laboratory − which is the main objective of the present conference communication − regards the theoretical study of the overall catalytic cycle of the enzyme. Apart from evaluating the energetics associated with a mechanism in which the equatorial Mo-bound oxo group behaves as a nucleophile, we also considered a recently proposed alternative hypothesis [6] implicating that an activated water molecule, within the active site, would play such key role along the catalytic cycle of CO oxidation.

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How water density responds to the presence of a crowding agent

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Crowded environments are able to affect the behavior of molecules in solution [1].
This, for instance, is believed to explain part of the inconsistency between *in vivo* biochemical processes and corresponding dilute solutions experiments, given the highly concentrated intracellular environment[2]. From a technological perspective, the effects of molecular crowding are exploited when tuning chemical processes in aqueous solutions to prevent water-related side reactions [3]. Nevertheless, many aspects of the interplay between water, the crowding agent and the solute are still not fully unveiled. A fundamental question is: how is water affected by the presence of a crowding agent? As a matter of fact, whether bulk-like water may be found within crowded environments is still a matter of debate. It has been posited [4] that even for highly concentrated solutions of macromolecular crowders, water arranges in such a way to create "pools" where two types of water molecules are identified: those mainly interacting among themselves, and the others interacting with the crowding agent. In fact, two types of water dynamics are detected, that is, bulk like from one side and a slowed down dynamics from the other side.
Along this line, our work aims at investigating the response of water to the presence of a macromolecular crowder by analyzing the corresponding hydration pattern, especially in terms of density deviations from the bulk condition. We chose Poly(Ethylene Glycol), or PEG, as crowding agent, since it is one of the macromolecules most widely used for this scope[5] and we studied the hydration pattern of PEG aqueous solutions of increasing fractions of the polymer (see Figure 1). By means of Molecular Dynamics simulations and previously developed analysis tools we characterize the water density within the crowded aqueous solutions by focusing on the density properties of the hydration shells and water clusters. We compare and complement the computational results with experimental data of diffusion, measured by means of NMR techniques for the differently crowded solutions. Taken together, these data provide an additional perspective through which assess the nature of water in crowded conditions.

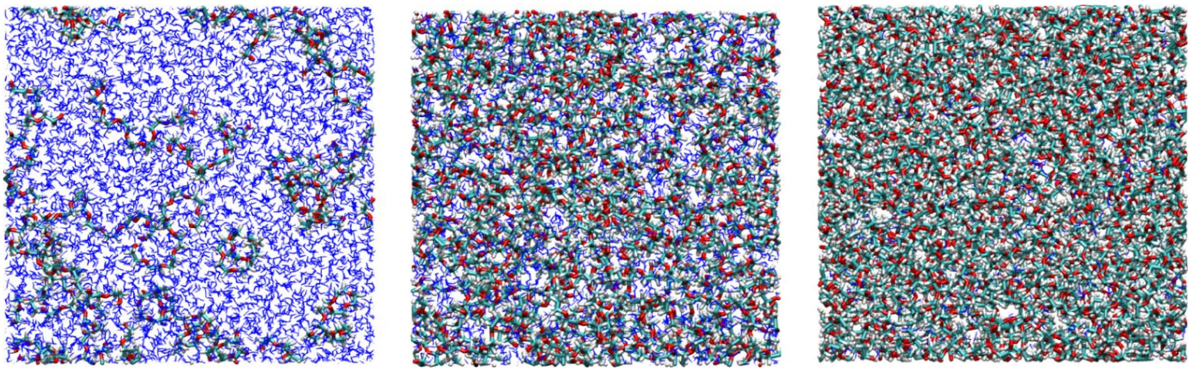

Figure 1. From left to right, snapshots from the MD simulations of PEG and water (colored in blue) at weight fractions of 0.1, 0.5 and 0.9, respectively.

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SYSMOIC: A Program Package for the Calculation of Origin-Independent Electron Current Density and Derived Magnetic Properties in Molecular Systems

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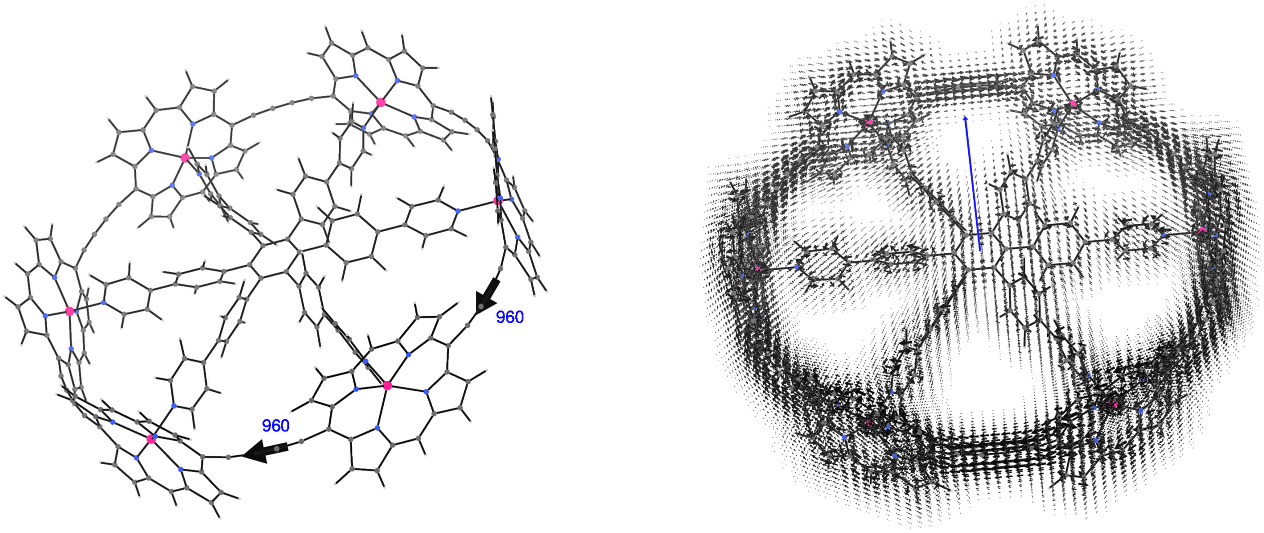
We present SYSMOIC, a program package for the calculation of the origin-independent current density induced at first order by an external magnetic field in planar and nonplanar molecular systems. Origin independence is obtained adopting the continuous transformation of the origin of the current density method,[1][2] implemented at both density functional theory (DFT) and Hartree−Fock (HF) levels. A number of different functionalities that are connected to the induced current, such as current density maps for any orientation of the inducing magnetic field, net bond current strengths, stagnation graphs, magnetic shielding densities, vorticities, and anisotropies, are now made available all together in a single multiplatform package installation[3] which allows the study and design of new materials. The package can be interfaced with the Gaussian suite of programs (G03, G09, and G16) from which it takes the expansion coefficients for unperturbed and perturbed molecular orbitals over the basis set containing up to m-type Gaussian basis functions. Analytic geometrical derivatives of the current density tensor can also be determined, which permits the topological analysis of the induced current density field. To assess the program performance, we present the current density induced in the challenging c-P6[b6] hexacation introduced by Anderson group.[4]



Net C-C bond current strength respect (left, as percentage over the benzene value) and current density vector (right) for a magnetic field parallel to the main symmetry axes, calculated using the CSGT-BS[5] method at the LC-whPBE/6-31G* level of theory for the c-P6[b6] hexacation.[4]

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Quantum nuclear densities from semiclassical on-the-fly molecular dynamics

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Semiclassical molecular dynamics is a rigorous approximation to quantum dynamics obtained from the exact quantum propagator expressed as Feynman's path integral.[1] Recently, our group has introduced the Multiple Coherent Semiclassical Initial Value Representation (MC SCIVR) technique to reduce the number of classical trajectories required to converge vibrational spectra calculations from thousands to just a handful.[2-4] MC SCIVR has been applied successfully to several medium- and large-size molecular systems,[4-10] including fluxional and condensed phase ones.[11-13] In addition to the accurate anharmonic vibrational eigenvalue calculations, MC SCIVR yields vibrational eigenfunctions for both the ground and excited vibrational states.[14] In this talk, I will survey how we obtain the quantum anharmonic vibrational eigenfunctions from ab-initio on-the-fly trajectory simulations and how we extract the quantum nuclear densities and the geometry parameters probability distributions.[15,16] This information allows us to assign each peak in vibrational spectra, going beyond the usual harmonic normal-mode analysis. Our technique quantitatively determines how normal modes involving different functional groups cooperate to originate the spectroscopic signal. Furthermore, it allows for the visualization of the nuclear vibrations in a purely quantum picture, letting us both directly observe and quantify the effects of the full potential energy surface anharmonicity on the molecular structure. In particular, I will illustrate applications to the protonated glycine to reveal quantum mechanical and anharmonic vibrational features. The method will allow for a better rationalization of experimental spectroscopy.

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An easy and efficient strategy to compute an accurate SCF guess for ab-initio molecular dynamics simulations

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Born-Oppenheimer ab-initio molecular dynamics (BOMD) simulations are a powerful tool to study complex molecular systems and phenomena. However, they are also computationally very demanding, as the require the solution to the quantum mechanical (usually, density functional theory, DFT) equations at each step of the trajectory propagation. It is therefore paramount to reduce as much as possible the cost of each energy calculation, which can be achieved by providing an accurate guess to the self-consistent field (SCF) solver. This is, however, not straightforward, as the density matrix must satisfy non-linear constraints to ensure its idempotency. As a consequence, a linear combination of idempotent density matrices is not idempotent, which makes interpolating and extrapolating densities a complex and cumbersome task. Recently[1], we have used tools from differential geometry to map the manifold to which the density belongs onto its tangent space, which is indeed a vector space, and viceversa: this allows us to perform an extrapolation in a vector space and then map the extrapolated density back to the manifold, ensuring that it satisfies the correct physical requirements. Using these tools, we propose a strategy to compute an idempotent guess density for the SCF procedure starting from few densities available from the previous steps of MD. The extrapolation coefficients are computed on-the-fly by solving a least square problem. The proposed strategy is compared to Niklasson's extended Lagrangian Born-Oppenheimer (XLBO) scheme[2] on several multiscale BOMD simulation, showing very good performances especially if a tight SCF convergence is required.

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Accuracy and Reliability in the Simulation of Vibrational Spectra: A Comprehensive Benchmark of Generalized Vibrational Perturbation Theory to the Second Order (GVPT2)

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Vibrational spectroscopy represents a powerful tool for the investigation of the physical-chemical processes of molecular systems, providing detailed information related to the structure and dynamics. Furthermore, it is routinely used for pharmaceutical and technological applications, and an active frontier for astrochemistry, thanks to the incoming data over broader ranges and at higher resolution. Computations play an increasing role in providing extensive characterizations of the recorded band-shapes, while also being able to match extreme conditions found in the interstellar medium (ISM) or some planetary atmospheres[1]. The challenge remains the accuracy, which must be sufficient to match state-of-the-art spectroscopic techniques in laboratories or to provide unequivocal identifications of astrochemical species for instance.

The best compromise between reliability, feasibility and ease of interpretation is still a matter of concern due to the interplay of several factors in determining the final spectral outcome. The dichotomy between accuracy and computational cost is further exacerbated with larger molecular systems and non-covalent complexes. In this context, second-order vibrational perturbation theory (VPT2)[2,3] coupled with density functional theory (DFT) has become particularly appealing. The well-known problem of the reliability of exchange-correlation functionals, and the treatment of resonances in VPT2, represents a challenge for the determination of standardized or “black-box” protocols, despite successful examples in the literature.

With the aim of getting a clear picture of the achievable accuracy and reliability of DFT-based VPT2 calculations, a multi-step study[4] will be presented. Beyond the definition of the functional, the impact of the basis set and the influence of the resonance treatment in VPT2 will be analyzed. For a better understanding of the computational aspects and the results, a short summary of vibrational perturbation theory and the overall treatment of resonances for both energies and intensities will be given. The first part of the benchmark will focus on small molecules, for which very accurate experimental and theoretical data are available, to investigate electronic structure calculation methods. Beyond the reliability of energies, widely used for such systems, the issue of intensities will be investigated in detail. Applications of the best performing electronic structure calculation methods to larger molecular systems will be presented, with more complex topologies and resonance patterns. Further extensions to large and flexible molecular systems will be discussed.

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Improving accuracy and efficiency of ADMP Extended Lagrangian Molecular Dynamics

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Ab initio molecular dynamics techniques are widely employed to simulate equilibrium and non-equilibrium properties of molecular systems. [1] In particular, the so-called extended Lagrangian methods are a good compromise between accuracy and computational cost. In the Atom-centered Density Matrix Propagation (ADMP) approach, the one-electron density matrix is treated as a (classical) dynamical variable and propagated along with the nuclei. [2-5] Therefore, a fictitious electronic mass has to be introduced. This parameter has a fundamental role in governing the degree of adiabaticity between the (fictitious) electronic and (real) nuclear degrees of freedom.

A rational way to non-uniformly attribute masses to the density matrix elements in an orthonormal atomic basis is here proposed. To this end, density matrix harmonic normal modes are defined and a common frequency is set. The corresponding mass-matrix is then derived. Both light and heavy atoms (treated as all-electron as well as with pseudopotentials) can be modelled with consistent accuracy. A detailed analysis of improvements and limits of the method performances is then carried out through test simulations of model and real-world systems. This approach can enhance adiabaticity between the electronic and nuclear degrees of freedom and allows for the employment of a wide range of time steps, without loss in accuracy. [6]

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Probing the electronic structure of gold dihydride with state-of-the-art relativistic approaches

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Gold dihydride is among gold's simplest $ML_2^{-/0}$ complexes, yet it represents a compound of interest for the purposes of hydrogen storage[1]. Indeed, the neutral dihydride is unstable with respect to atomic gold and dihydrogen, thus making, in principle, the decomposition to H_2 accessible at low temperatures.[1]

The electronic structure of neutral gold dihydride is, however, rather complex, as demonstrated by photoelectron spectroscopy (PES) experiments, which upon photodetachment lead to the six lowest-lying electronic states of neutral AuH_2, with the ground state undergoing bending upon photodetachment.[2] From the experiment, Vertical Detachment Energies (VDEs) were extracted for all the states, whereas Adiabatic Detachment Energies (ADEs) were only determined for the ground state, due to limitations of the experiment. The complexity of the experiment and therefore the interpretation of the experimental photoelectron spectra often requires relativistic quantum chemical approaches that accurately account for scalar relativistic (SR) effects and inclusion of spin-orbit coupling (SOC) is mandatory.

For this reason, we decided to test some approaches for the prediction of VDEs for the states of neutral AuH_2 by accounting for the role of relativistic effects, orbital relaxation and electron correlation. Our results[3] clearly suggest that both the energy order of the experimental bands and the experimental VDE values are correctly reproduced only when SOC and electron correlation are included in the calculations with a high degree of accuracy. By applying the IP-EOM-CCSD approach in its relativistic formulation[4], we are able to gain complementary results with respect to the experiments, such as the optimized geometries of all the states and the corresponding ADE values that could not be determined experimentally.

Our approach confirms that the ground and first excited state lie very close in energy and for this reason vibronic coupling effects may take place which can be evaluated through the scan the Potential Energy Surface not only in the direction of the bending, but also in the direction of the asymmetric stretching. Eventually, we find the ground state to be also affected by a symmetry breaking in the asymmetric stretching direction due to the Pseudo-Jahn-Teller Effect (PJTE). This last finding makes the intriguing gold dihydride, to the best of our knowledge, the first reported heavy-metal-containing molecule to be affected by PJTE.

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Theoretical Approaches to Quantum Molecular Dynamics in Out of Equilibrium Environments

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The description of quantum molecular dynamics as influenced by a polarizable and dynamically evolving environment is critical to understand the nature of various physical processes, from solvation phenomena to photobiological processes in protein environments, and transport of charge carriers and excitons in nanostructures. Indeed, experimental molecular systems, S, are not closed systems due to the interaction with the surrounding environment, generically denoted the bath, B. Large effects on S dynamics can be expected depending on the nature of the environment as well as on the SB interaction strength. The typically used dielectric continuum picture for B is likely to fail when dealing with nonequilibrium solvation effects. On the other hand, fully atomistic first principles quantum calculations are hardly feasible due to the large number of environmental degrees of freedom.

Against this background, we present the effect of a dynamic environment on a time-evolving molecular system, using the Quantum-Classical Reduced Hydrodynamic (QCRH) approach [1]. In particular, the hydrodynamic formalism naturally describes density, current and heat transport phenomena. Accordingly, the QCRH theory can describe molecular relaxation in condensed dynamic phases, complementing typically used dielectric continuum models for the environment. At present, we have extended the QCRH approach in order to deal with orientational solvation processes in charge-transfer phenomena, using a DDFT (Dynamical Density Functional Theory) closure for the hydrodynamic hierarchy.

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Extending and assessing composite electronic structure methods to the solid state

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A hierarchy of simplified Hartree-Fock (HF) and density functional theory (DFT) methods have been recently proposed for the fast electronic structure computation of large systems [1]. The covered methods are a minimal basis set Hartree–Fock (HF-3c), a small basis set hybrid functional (PBEh-3c), and its screened exchange variant (HSE-3c), all augmented with semi-classical correction potentials [1]. Here, we extend their applicability to inorganic covalent and ionic solids, layered materials as well as porous materials. The new methods have been dubbed HFsol-3c, PBEsol0-3c and HSEsol-3c, respectively, to indicate their parent functional as well as the correction potentials. They have been implemented in the CRYSTAL code [2] to enable routine application for molecular as well as solid materials. We validate the new methods on diverse sets of solid state benchmarks that cover more than 90 solids ranging from covalent, ionic, semi-ionic, layered, and molecular crystals. While we focus on structural and energetic properties, we also test band gaps, vibrational frequencies, elastic constants, and dielectric and piezoelectric tensors. Finally, we apply revised composite methods to study porous materials such as metal-organic frameworks. Overall, results not only show that the revised methods perform equally well as the original ones but also that the range of applicability is significantly extended and improved. Hybrid composite methods appear to be most promising and show accuracy competitive to converged basis set dispersion corrected DFT with substantial increase in computational efficiency.

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An in-depth look into the mechanism of crystallization of lithium disilicate: a metadynamics study

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Glass ceramics are well-known and performing materials in many different fields, and they are made up of one or more crystalline and glassy phases mixed up. Since the properties depends strongly on how the crystalline phase is formed, a lot of effort has been devoted to study this phenomenon experimentally [1].

Lithium disilicate is a prime example of glass-ceramic which has attracted a lot of scientific interest [2] because of the controversies about its crystallization mechanism which is still an open question. The predominance of a homogeneous nucleation instead of a heterogeneous mechanism aided by the formation of intermediate metastable phases remains uncertain [3].

Molecular dynamics allows to follow processes from an atomistic viewpoint, and it is therefore a fundamental tool to analyze the crystallization mechanism. However, it is not able to overcome the long time needed to the crystallization of this highly viscous materials to occur.

Enhanced sampling techniques have proved to be essential to simulate this kind of phenomena, in particular metadynamics [4,5] allows to overcome energy barriers and simulate events overcoming time limitation according to the choice of a collective variable.

In this communication, I will show that metadynamics makes the crystallization of lithium disilicate accessible and the sampling of the phase space gives access to insights of the mechanism of nucleation. It is thus possible to estimate the free energy surface [6] which allows to identify a two-step mechanism, moving from the melt to a layered disordered structure and finally reaching the stable crystal.

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Molecular spectroscopy in condensed phases: an antiadiabatic approach to the medium polarizability

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Understanding how the local environment affects the photophysics of molecular materials is a theoretical challenge with enormous practical implications: medium effects can negatively affect the performances of devices such as OLEDs and solar cells, but, if properly understood they can be exploited towards optimized materials in a smart matrix approach.

When addressing the dielectric properties of the medium, two different timescales enter into play, related to polar and electronic solvation. In the first case, the orientational degrees of freedom (DoF) of polar molecules are of interest, whose dynamics, slow dynamics if compared to the solute DoF, can be treated in the adiabatic approximation (i.e. freezing the relevant coordinates in their equilibrium configuration for the reference state during the transition). On the other hand, electronic DoF have faster dynamics and cannot be treated adiabatically.

We introduce an antiadiabatic approach to fast solvation,[1] leading to the definition of a single effective molecular Hamiltonian, where the solvent polarizability enters as a two-electron term, that, in the dipolar approximation, is simply proportional to the squared molecular dipole moment. We then focus on charge transfer dyes[2] and thermally-activated delayed fluorescence (TADF) emitters.[3]

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Tunneling splitting and the stochastic description of activated processes

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Whenever two equivalent potential wells are kept apart by a finite energy barrier, degeneracy is excluded and all the energy levels, below the barrier top, are organized in doublets separated by a small energy gap usually referred to as tunneling splitting.

The aim of the presentation is to show how the isomorphic relation between the Born-Oppenheimer quantum Hamiltonian and the Fokker-Planck-Smoluchowski operator opens a direct correspondence between the estimation of tunneling splitting and the calculation of transition rates for activated processes. Making use of this similarity an alternative calculation procedure will be outlined and some early results will be presented in order to quantify the accuracy of the method in simple model systems.

This formal connection creates, in our opinion, a new and interesting link between topics otherwise not related and paves the way to a new, asymptotically justified, approach to the computation of tunneling splitting in molecules.

Exploring Chemistry through Multiple Time and Size Scales

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Chemical processes cover a wide range of time and size scales and each phenomenon needs specific experimental and theoretical-computational treatment. In this context, both the theory level in terms of quantum mechanics (QM), molecular mechanics (MM) or coarse-grained treatment and the employed simulation technique such as ab-initio molecular dynamics (either in the adiabatic or non-adiabatic approximation), or classic molecular dynamics can give an idea of the large heterogeneity of the available computational strategies.

The study of complex solute-solvent interactions, treated at mixed QM/MM theory level and simulated through ab-initio molecular dynamics, can give precious insights on the vibrational spectroscopic behavior of biological systems. In this context, amides in aqueous solution are used as prototype to represent the skeleton part of proteins and peptides. In this work, we present the development of a recent theoretical-computational technique based on the wavelet transform, allowing to investigate vibrational band shifts and anharmonic couplings among amide bands during the time.[1] The versatility of this approach was employed to investigate also non-equilibrium phenomena such as the dynamics of the Stokes-shift of a solvatochromic dye in water solution, unveiling the importance of collective water motions in determining the kinetics of the fluorescence signal.[2] The Green Fluorescent Protein photo-induced proton transfer was explored next, by combining non-equilibrium ab-initio exited state molecular dynamics, wavelet analysis through a mixed QM/MM approach allowing to simulate the entire protein. The obtained results were successfully compared with femtosecond stimulated Raman spectroscopy and both the concerted nature of the mechanism and the presence of photo-induced motions driving the reaction were investigated.[3] The described phenomena belong to a time and size scale ranging from femtosecond to picosecond and from Angstrom to nanometers, respectively.

In this contribution, we face also phenomena such as polaron and plasmon excitations. The quenching of these excitations represents a limit for their applications, and understanding the molecular reasons behind them, is a precious help in improving their design. Techniques capable to retain the electrons-nuclei interaction dynamics are needed in these cases.[4] Here, attosecond to femtoseconds and few Angstroms are the investigated time and size scales.

A completely different scenario in terms of simulation and description techniques, is represented by the intriguing world of composite materials with smart features. CNTs give unique thermal and electrical properties to polymer matrices, and the knowledge of their organization at nanoscale level is crucial to improve their performances. Joule effect and piezoresistivity are additional features coming from the presence of CNTs and give self-sensing properties to the material. In the last part of the presentation, our recent protocol to simulate Joule effect and piezoresistivity at the nanoscale is presented. The influence of different morphologies, applied voltage, heat diffusion coefficient, filler concentration, is investigated and modeled through the proposed approach. Our data, successfully compared with experiments, can help designing more performing devices.[5] Finally, here a time scale of millisecond and size scale of hundreds of nanometers is reached.

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The Role of Fock Exchange in Relativistic Density Functional Theory

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The spin-current density functional theory (SCDFT), when formulated in a basis of Pauli spinors, provides a proper theoretical framework for the study of materials in an arbitrarily oriented external magnetic field [1-2] and/or upon inclusion of spin-dependent relativistic effects, such as spin-orbit coupling [3]. The SCDFT is formulated in terms of the particle-number density n, the Cartesian components of the magnetization m_x, m_y, m_z, the orbital-current density $\boldsymbol{j}$ and the three spin-current densities $\boldsymbol{J}^x$, $\boldsymbol{J}^y$ and $\boldsymbol{J}^z$, where each of these eight density variables depends on specific blocks of the density matrix. Exchange-correlation (xc) functionals within the SCDFT should therefore depend on all of these eight fundamental density variables: $F_{xc}[n,m_x,m_y,m_z,\boldsymbol{j},\boldsymbol{J}^x,\boldsymbol{J}^y,\boldsymbol{J}^z]$, which makes their parametrization a formidable task.

In this contribution, I discuss the adiabatic connection of the SCDFT for a treatment of exact Fock exchange in the theory, that we have recently formulated [4]. It is shown how the inclusion of a fraction of Fock exchange in standard functionals of the (spin) DFT (either in their collinear or non-collinear versions: $F_{xc}[n]$, $F_{xc}[n,m_z]$, $F_{xc}[n,m_x,m_y,m_z]$) allows for the two-electron potential to depend on all those blocks of the density matrix that correspond to the eight density variables of the SCDFT, in a sensible and yet practical way [4-5].

Formal aspects are complemented with numerical calculations to highlight the fundamental role of Fock exchange in the DFT, as in hybrid xc functionals, upon inclusion of a spin-orbit coupling operator [6].

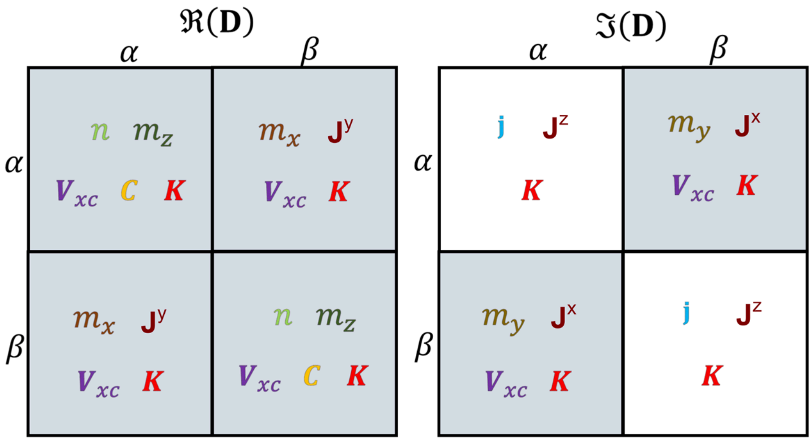

Figure: *Schematic diagram of the spin-block structure of the complex density matrix* **D** *in the framework of two-component relativistic DFT in the LDA or GGA. In each block, the first line reports the density variables which make use of the corresponding spin-block in their definition. The second line indicates bi-electronic operators (Coulomb C, exchange-correlation Vxc and Fock exchange K), which make use of the corresponding spin-block in the definition of the electron-electron potential.*

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Rational Design of Semiconductor Interfaces for Photocatalysis

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Composite materials made by two units in intimate contact are widespread in materials science applications, such as photo-catalysis, solar cells, and sensors [1]. Their major advantage is represented by the possibility to hinder the charge carriers' recombination process, provided that their alignment of the band edges is favorable [2]. Among all, oxide-oxide interfaces have been widely applied in photo-catalysis experiments, including water splitting and pollutants degradation [1,2].

The nature of an interface at the atomistic level may be hard to be accessed by experimental techniques, while computational studies may provide insightful information at the atomist level on the nature, structure, and electronic properties of interfaces.

Here, we present a computational overview of our recent studies on interfaces, focusing on virtues and criticalities of the approach based on Density Functional Theory (DFT) at the level of hybrid functionals. We will discuss the different amount of information that one can access from first principles, such as the structure of an interface, its stability and energetics, and important electronic properties as band edges alignment, charge separation and interface polarization. We will show that the combination of all of these aspects is responsible of the overall properties of devices. We will focus on recently established *i)* TiO_2 [3,4] and *ii)* $BiOIO_3$ [5,6] surface junctions showing that *i)* the interface promotes the charge separation, and *ii)* its formation can be explained in the light of energetically favorable matching of surfaces' terminations. Last, we discuss the crucial role of the interface polarization in the g-C_3N_4/TiO_2 interface, driving the favorable path for carriers' separation [1,7].

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First Principles Approaches for Heterogeneous Functional Materials

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The increasingly fast technological growth that characterized the last few decades of human history is strongly connected to the progress of scientific knowledge. In particular, advancements in the field of materials science are what make the development of new, cutting-edge devices a reality. One notable example is the revolution in portable electronic devices, made possible by the development of Li-ion batteries, for which a Nobel Prize was awarded two years ago[1].

As the ever-growing global population approaches 8 billion, the effective and environment-friendly production and storage of energy remains one of the most pressing problems of the century. Many devices that have been under the spotlight in recent years, as possible solutions to such problems, involve rather complex materials and interfaces.

The tools of computational chemistry can help dissect such complexities and give insight on the electronic structure properties and how these are affected by different components. This allows us to move towards a rational design of new systems, that are engineered to have the desired structural and electronic properties.

A strong interplay between theoretical analyses and experimental measurements is in fact the only way to design and develop new, efficient materials for the desired purposes. However, complex interfaces (e.g. organic-inorganic interfaces, stacked 2D materials, supramolecular assemblies) are also challenging for state-of the art computational methods. The need for high accuracy, which would require computationally expensive methods, clashes with the need to describe extended systems, for which such methods are not affordable. Sometimes a trade-off can be found, in other cases multi-level embedding approaches can be used to overcome the problem.

In this contribution, we will illustrate different examples of first principles analysis of complex materials and interfaces for photo-electrochemical applications. These can range from electrodes for p-type dye-sensitized solar cells[2–4] to two dimensional materials[5,6]. We will show how the theoretical analysis of these materials can give us important insights that will help us in developing more efficient devices.

Lastly, we will show a high-level ab initio analysis of the interaction between pnictogen compounds and π-systems that play very important roles in molecular solids and supramolecular assemblies [7]. This will provide an illustration of how the theoretical analysis can shed light on what kind of interactions are at play and how they determine the formation of particular structures.

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Multiscale investigation of chlorophyll fluorescence quenching in plant light-harvesting complexes

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Photosynthetic organisms such as plants and algae need light to thrive, but their photosynthetic apparatus can be damaged by an excess of light. Plants and algae can dissipate excess energy in their light-harvesting complexes (LHCs) through a multifaceted mechanism known as nonphotochemical quenching [1]. LHCs themselves can exert a dual function of light-harvesting and quenching, mediated by conformational changes [2-4]. The electronic mechanism of quenching and the identity of the quenching species are still fiercely debated, but arguably this mechanism must be controllable by the protein when it changes conformation in response to external conditions.

Here we present a combination of microsecond molecular dynamics simulations, multiscale quantum chemical calculations, and kinetic modelling, applied to the major antenna complex of plants, LHCII [5]. We show that a charge transfer state involving Lutein can quench chlorophyll excitation, reducing the excitation lifetime of the complex to the levels measured in deeply quenched aggregates. This mechanism can be finely tuned by the protein, by regulating the energy of the charge transfer state through a limited protein conformational change, which acts as a molecular switch.

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Computational Strategies for Environmental Chemistry

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Composition changes of the Earth's atmosphere, mainly due to various anthropogenic factors, are considered responsible for several adverse climate and environmental impacts. Climate change studies need the temporal trend of hazardous pollutants and, for the purpose, remote sensing spectroscopic techniques are widely used to retrieve the concentration profiles of a number of species. Besides, the fate of the compounds released into the atmosphere needs to be precisely characterized in order to understand how rapidly these substances degrade, when and where they are destroyed, and whether the degradation products can lead to more climate forcing than the parent species. A complete mapping of the degradation pathways of the chemicals released in the atmosphere and their detailed spectroscopic characterization represent a daunting task from the purely experimental point of view. Quantum mechanical (QM) approaches, on the other hand, can be exploited to systematically investigate reactivity and spectroscopy thus contributing to a better understanding of several important atmospheric processes, provided that they attain suitable accuracy.

In the present contribution, purposely tailored computational strategies capable of satisfying the accuracy requirements, yet at an affordable computational cost, for the investigation of the structural, spectroscopic and thermochemical properties of atmospheric species are presented and applied to selected case studies. The proposed approach relies on using hybrid QM/QM' methods mixing, to a various extent, and depending on the target property, CCSD(T)-based composite schemes [1] and last generation density functionals, namely PW6B95 and rev-DSDPBEP86 [2]. Then, second-order vibrational perturbation theory is employed to account for anharmonic effects in both spectroscopic and thermochemical properties [3]. The proposed strategy is applied to investigate the atmospheric degradation and vibrational spectra of halogenated organics, with particular emphasis on hydro-fluoro-olefines, which have been recently proposed as zero-climate forcing replacements of hydro-fluoro-carbons. Next, attention is given to the study of processes occurring at the gas-solid interface, which are of relevance, on one side, in ice-mediated multiphase atmospheric chemistry, on the other in the heterogeneous degradation of environmental pollutants. Here the size of the systems prevents the use of computationally demanding coupled-cluster approaches and density functional theory represents the working option. While periodic computations can properly model the solid morphology [4], the cluster approach allows for the use of the more advanced methods developed for finite-size molecular systems. Within this framework, a QM/QM' method for the simulation of ice-mediated reactivity is presented, based on the use of last-generation double-hybrid- and hybrid-density functionals for the description of the reaction center and the surrounding medium, respectively. As to the vibrational signature of molecules adsorbed at surfaces, a hybrid periodic/cluster approach, supplemented by reduced-dimensionality schemes [1], has been devised in order to mix harmonic frequencies obtained from the periodic approach to the main anharmonic corrections. Preliminary results are discussed and directions of further development outlined.

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Multimode Redfield-Smoluchowski approach for quantum-classical dynamics of polar dyes

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Modeling the relaxation of excited states is a crucial issue in spectroscopy to address dynamical processes in time-resolved spectroscopies as well as spectral bandshapes in steady-state spectra. As typically done in the field of open quantum systems, we describe the relevant systems in terms of a quantum-mechanical Hamiltonian that interacts with the macroscopic environment, the bath. The bath and its interaction with the systems are described in a phenomenological approach, to be validated against experiment. In this work we refine the model proposed in ref[1] and ref[2], where a quantum-classical Redfield-Smoluchowski approach is exploited to describe the relaxation of a single charge-transfer D-π-A dye in solution. The dye is described in terms of few essential electronic states and a small number of non-adiabatic vibrational coordinates. We account for polar solvation and its dynamics and introduce a coupling between vibrational coordinates and a dissipative Redfield bath to account for relaxation. The coupling between the system and the dissipative bath is discussed in detail: we compare results obtained with linear and bilinear coupling and with different choices for the spectral density. Finally we underline that when more than a single vibrational mode is considered, each mode must be independently coupled to a different Redfield bath. Finally, we stress the importance of an accurate preparation of the initial conditions for a reliable solvation dynamics.

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A computational scheme based on DFT-TP method for time-resolved NEXAFS spectra: Application to Perylene-3,4,9,10-tetracarboxylic diimide

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Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is a useful tool to analyse the electronic structure of molecules in a site-specific way [1]. In particular, this technique can be used to probe the K-edge of light atoms by exciting an electron from a localized atomic 1s orbital into an empty valence orbital. Combining this spectroscopy with transient, or pump-probe (PP), absorption techniques, it is possible to probe out not only empty valence orbitals but also occupied valence orbitals [2]. Therefore, time-resolved NEXAFS (TR-NEXAFS) spectroscopy can provide additional information on the electronic structure of the system, which would be inaccessible with standard NEXAFS experiments.

Recently, two computational approaches have been proposed in the literature to calculate TR-NEXAFS spectra: the first one at the ab-initio level [3], while the second one [4] at DFT level combined with the Transition Potential (TP) scheme [5]. The latter method affords a significant reduction of the computational cost, but without losing in accuracy. It is therefore promising for application to more complex systems, such as molecules adsorbed on metallic surfaces, which are the focus of recent experimental studies [3].

In this work we present the setup of a computational scheme, also based on the DFT-TP approach, for the calculations of TR-NEXAFS spectra. The proposed protocol has been validated on four systems (gas-phase thymine, trans/cis-azobenzene and pentacene), by comparing our results with the experimental and theoretical data available in the literature [3, 4, 6]. Afterwards, the method has been employed to investigate the TR-NEXAFS spectra of Perylene-3,4,9,10-tetracarboxylic diimide (PTCDI). This study would aim to guide the experimental measurements which will be performed for the molecule adsorbed on the Ag(111) surface, within an existing collaboration with researches of the Elettra Synchrotron Laboratory in Trieste.

A preliminary analysis of the valence excited states of PTCDI molecule has been conducted at the Time-Dependent DFT (TDDFT) level. The calculations suggest that PTCDI can be pre-excited in a triplet state (TS) located 1.32 eV above the ground state (GS). We then calculated both the GS NEXAFS spectra and the NEXAFS spectra for the molecule in the TS, from which the TR-NEXAFS spectrum can be obtained. Three different K-edges (C, O and N edges) of PTCDI have been investigated. The study suggests that for both C and O K-edges the lowest energy transition observed in the spectra of the pre-excited molecules (i.e., C, O 1s → HOMO) is well separated from the first absorption band of the GS spectra, at variance with what observed at the N K-edge. These information will be used to guide the planned PP NEXAFS experiments on PTDCI adsorbed on Ag(111).

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An enhanced sampling QM/AMOEBA approach: 3-hydroxyflavone excited state intramolecular proton transfer

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We present the extension of the polarizable embedding QM/AMOEBA approach to enhanced sampling techniques. This is achieved through the integration of the PLUMED library [1] with the machinery based on the interface of Gaussian and Tinker to perform QM/AMOEBA molecular dynamics [2].

As an application, we study the excited state intramolecular proton transfer of 3-hydroxyflavone [3,4] in two solvents: methanol and methylcyclohexane. By using a combination of plain molecular dynamics and umbrella sampling, we find an ultrafast component of the transfer, which is common to the two solvents, and a much slower component, which is active in the protic solvent only. The mechanisms of the two components are explained in terms of intramolecular vibrational redistribution and intermolecular hydrogen-bonding, respectively. Ground and excited state free energies along an effective reaction coordinate are finally obtained allowing for a detailed analysis of the solvent mediated mechanism.

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The superoxide disproportionation and its relevance for degradation pathways in metal-O_2 batteries investigated by means of ab-initio calculations

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The development of aprotic metal-oxygen batteries represents one of the most intriguing challenges for the future of sustainable technologies, including areas such as electric automotive industry and renewable energy storage. However, up to the present their appealing potential is still largely offset by practical limitations, such as a low energetic efficiency, low cyclability and a high degree of parasitic reactivity [1]. In this computational study we tackle the topic of the superoxide anion disproportionation, which plays a fundamental role in the chemistry of aprotic metal-O_2 batteries both for the mechanism of the charge/discharge processes [2] and for the occurrence of parasitic reactions which promote the electrolyte degradation [3]. In our approach we make use of advanced multireference quantum mechanical calculations on a model bimolecular reaction, which enable us to treat complex excited-state patterns and diradical systems with a high degree of accuracy. Here we present the results arising from two main research topics: i) the role of different cations in promoting the disproportionation reaction, covering alkali and alkali-earth metals up to potassium and calcium, and the likelihood of the formation of singlet oxygen ($^1\Delta$ O_2) among the reaction products, which is actually believed to be the species responsible for the major part of the parasitic reactivity in the Li-O_2 and Na-O_2 cells [4], and which we show to be dramatically boosted by the presence of proton contaminations [5]; ii) the existence of accessible excited electronic states in the disproportionation products leading to the formation of $M^{(0)}$-containing species (M = Li, Na, K) in solution, which may provide alternative chemical routes for the degradation reactive pathways.

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Structural and energetic validation of new AMOEBA parameters for biocompatible ionic liquids.

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The parametrization [1] and validation of AMOEBA (multipolar and polarizable force field) for ionic liquids is presented in this work. These liquids are based on a combination of choline cations and deprotonated amino acid. The procedure of gaussian distributed multipole analysis (GDMA) [2] has been used for obtaining the multipoles distribution; this approach allows to proper simulate the electrostatic potential and the polarization between molecules is provided by the force field with explicit induced dipoles. The choice of the force field has been critical since the bulk properties of ionic liquids strongly depends on accurate modeling of polarization [3]. First step of validation consists in checking that the new force field parameters can reproduce the correct structural properties of isolated ionic couples in vacuum. The binding energies obtained with the force field are quantitative consistent with ab-initio calculations [4], yielding relative errors under 5%; this is a result that cannot be achieved by classical force fields which do not consider polarization. After valued the single ionic couple binding energy it has been seen how the force field perform with cluster of ions compared to DFT calculations when many body effects start to manifest.

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Società Chimica Italiana SCI2021

CHIMICA PER LE TECNOLOGIE (TEC)

- Orals
- Posters

Nanogels as smart drug delivery systems

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Drug nano-encapsulation holds promise as an effective tool to augment payload delivery and target specificity in a wide range of therapeutic treatments. In this scenario, nanogels (NGs) present the distinctive feature to swell while maintaining their structural integrity, thus reproducing the characteristics of macroscopic hydrogel systems at the nanoscale [1]. Moreover, their small size (from a few nm to several hundred nm) results in a large surface area, enhancing the encapsulation stability and bioavailability of the loaded drugs, which are retained in the nanogel meshes, until the drug release mechanism is activated. In addition, it makes them profoundly less susceptible to reticuloendothelial system clearance and ensures the crossing of the biological barriers for a better cellular uptake.

Our group has developed a synthetic route to formulated nanogels based on the emulsion-solvent evaporation method, which can be fine-tuned to specific clinical applications by adjusting NG composition, decoration with specific ligands and/or conjugation with contrast agents.

For the screening and biological validation of the developed NGs, our group has established a number of in vitro disease models exploiting advanced biofabrication techniques, including bioprinting and organ-on-a-chip [2,3].

As a salient example, NG formulation and decoration with specific ligands has been pursued for cancer therapy, targeting EGF-R and CD44 as candidate cancer cell markers for the enhanced delivery of antiblastic drugs. At the same time, NGs have been demonstrated to enhance the efficiency of antioxidants in lowering intracellular triglyceride deposition in an *in vitro* model of non-alcoholic fatty liver disease (NAFLD) [4].

With an eye on scalability, our recent activity has been focused on the translation of NG synthesis from batch to continuous flow, also leveraging microfluidics for improved control over process parameters.

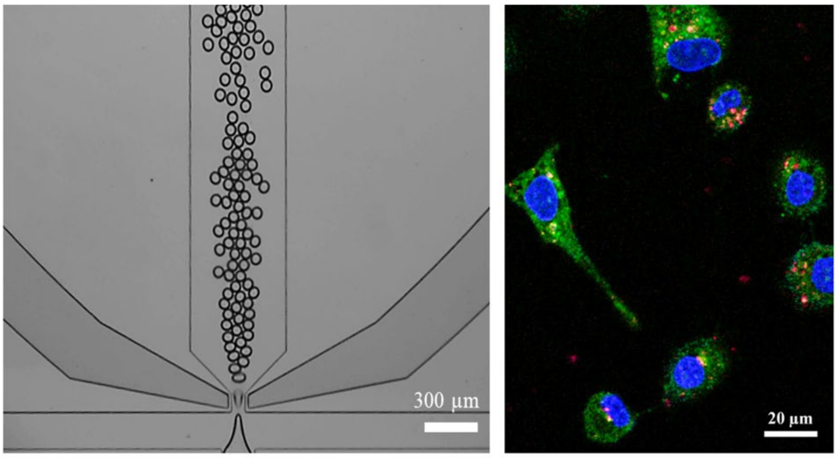

Figure 1. Left: microfluidic flow-focusing device for the flow synthesis of NGs. Right: uptake of NGs (in red) by OVCA433 cancer cells.

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Recent advances in potentiometric sensors for environmental purposes: from single ion-selective electrodes to multisensor analysis

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Chemical sensors are the effective, easy-to-handle and non-expensive analytical devices especially promising for the environmental monitoring purposes [1]. Among the chemical sensors, the class of electrochemical, and in particular, of potentiometric polymeric membrane-based sensors are of particular interest, due to the possibility to tune the sensing properties of such devices through the accurate selection of the membrane active components (such as ionophores, neutral and charged carriers, ion-exchangers and membrane matrix material) [2]. In addition, potentiometric sensors do not require expensive equipment, do not damage the analyzed sample (no irreversible chemical reactions occur in tested media during the potentiometric analysis), are portable and can be easily used for on-site and on-line analysis, requiring only a portable measuring device and often limited to a few drops of the sample to be analyzed.

The synthesis of novel compounds with predictable properties, for instance, porphyrin ligands, has made it possible to develop highly selective sensors, ion-selective electrodes (ISEs), for the detection of many substances [3]. However, for a number of vital analytes (for example, pollutants, drugs, various metabolic products, etc.), existing sensors are ineffective or completely absent. The problem of the insufficient sensitivity of potentiometric sensors for determination of individual components in complex media can be compensated for by using a chemometric approach, which consists in the use of mathematical methods for processing experimental data to obtain qualitative and quantitative information on the sample [4]. In fact, sensors with cross-sensitivity (not having a pronounced selectivity) to a certain group of analytes are successfully used as part of multisensor system for the fast and non-invasive multicomponent analysis of liquids, called "electronic tongue" (or E-tongue), and employing the working principle, similar to the "chemical" senses (olfaction and taste) of mammalians [5].

In this contribution the working principle, main benefits and drawbacks of single potentiometric ISEs in comparison to the multisensor approach will be discussed, and the selected application of potentiometric chemical sensors for the environmental analysis from our team will be presented [6-8]. Moreover, the examples of hybrid and multi-transduction multisensory systems, combining several transduction principles to the same sensing layer, will be illustrated in order to demonstrate the effectiveness of such systems for concrete analytical applications [9].

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Liquid biopsy at the crossroads of chemistry and technology: the extracellular vesicles case study

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Extracellular vesicles (EV) are membranous micro- and nano-sized biological particles released by cells that play a major role in inter-cellular communication. EV shuttle an impressive amount of molecular information, including proteins and non-coding RNAs, thus representing a phenomenal source of circulating biomarkers [1]. As such, EV are arising unparalleled expectations as the next generation theranostic tools. However, several challenges are yet to be overcome to translate EV promise into daily clinical reality [2]. Here, our most recent contribution in EV research will be highlighted, with a particular focus on the interplay of chemistry and technology towards the full exploitation of EV potential. In particular, a custom EV microarray platform for the integrated isolation and analysis of EV will be presented [3]. Key features of this platform are clickable polymers for microchip coatings, the use of membrane-sensing peptides as molecular baits for small EV, an interferometric, label-free single particle counting and sizing of EV, and a fluorescence digital co-localization of surface protein markers for EV phenotyping.

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Hydrothermal Carbonization as a sustainable approach for the single-step upgrading of industrial citrus processing waste into platform chemicals and biocarbon

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Citrus fruits are among the most worldwide cultivated fruits. Their annual production is about 88 million tons and the citrus processing industry yearly generates huge amounts of agricultural waste, in the form of peel, pulp, and segment membranes, from the extraction of citrus juice in industrial plants, and citrus peel waste alone accounts for almost 50% of the wet fruit mass. Orange peel is the primary waste fraction of the juice extraction industry, which is derived from the huge global orange production estimated at over 50 million metric tons for 2020 (FAS-USDA, 2020). The considerable volume characterizes the exhausted citrus peel as well as the high biodegradability involving high rates of fermentation processes. Therefore, the direct disposal of this secondary product, without previous proper processing, causes serious environmental issues and economic loss for the citrus industry since the traditional fruit waste disposal strategies, such as incineration or landfilling, are insufficient in terms of environmental impacts and energy efficiency. Hydrothermal carbonization (HTC), a thermochemical conversion process, in a water medium under autogenous pressure at a quite low temperature (180−300 °C), could represent a promising treatment technique for wet lignocellulosic biomass waste overcoming the drawbacks of conventional thermochemical processes, since the moisture is not an impediment, and is even used as the reaction medium for hydrothermal reactions [1]. During hydrothermal carbonization, usually performed at mild processing temperatures (150–300°C), and under autogenous pressures, biomass is dehydrated and processed into solid, liquid, and non - condensable gaseous products. The carbonaceous residue obtained by the HTC of citrus processing waste, named hydrochar, is rich in oxygenated functional groups, making it a promising material that has huge potential to be used in a wide range of applications, such as pollutants adsorbent and soil amendment, as fuel in energy application, and as low-cost material for electrochemical applications [2-3]. Moreover, the light bio-oil extracted from the aqueous phase, resulting from the hydrothermal carbonization of citrus wastes, consists mainly of aldehydes, phenols, ketones, acids, and some small molecules and heterocyclic compounds of potential interest as feedstocks for the synthesis of chemicals and liquid bio-fuels.

In this contribution, the potential of the hydrothermal carbonization (HTC) of industrial citrus processing waste, for the production of both bio-carbon and bio-oil, along with the identification of the key issues for the optimization and scale-up of the process, will be highlighted. Furthermore, some advanced sensing applications of the obtained bio-carbon, i. e. the conductometric detection of NO_2 in the air at ppb (part per billion) levels, and the electrochemical determination of dopamine at nanomolar concentration will be discussed. The exploration of this single-step hydrothermal process represents a promising example of wet organic waste valorization to produce value-added products with high yields, and at the same time, to avoid potential and serious environmental issues arising from the citrus processing waste management and disposal.

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Chemistry of materials for energy technologies

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Chemistry enables technological advancements in our everyday lives and chemistry of materials contribute to overcome many cross-cutting challenges (availability, chemical robustness, service life efficiency and duration of component materials) that concern technologies for the Clean Energy Transition.

In agreement with many others EU and international documents, the Italian Recovery and Resilience Plan points to reach the objective of environmental sustainability. In particular, in the chapter "Green Revolution and Ecological Transition" Hydrogen and offshore renewables have been taken into account for achieving the decarbonisation targets included in the National Energy and Climates Plans and in the strategies announced at EU level.

The most recent international documents outline the importance of the entire value chain from materials to suitable technologies. With this in mind this communication will illustrate two researches that are ongoing in our laboratory.

The first will concern the synthesis and set-up of different materials for the selective hydrogen separation by dense membranes. In fact, ssustainable extraction of H_2 from a gas mixture can be considered as an enabling technology for using H_2 as energy carrier or chemical reagent. With dense membranes the separation of hydrogen occurs selectively thanks to the chemical-physical properties of the active materials that have to be durable, tolerant to pollutants, easily to synthesise.

In the second example an ongoing investigation is focusing the fabrication of ceramic and metal coatings for the protection of large wind blades. Indeed, as wind turbines grow in size, so do their blades, from about 8 m long in 1980 to more than 100 m for current offshore applications. Materials blades primarily based on composites are used for reducing the load-carrying requirements, but innovative solution for blade protection are necessary in order to limit the erosion on the leading edge of wind blades that can dramatically limit the turbine output.

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Fourier transform IR micro-spectroscopy of biological tissues: a promising tool for diagnostic and assessment of tissue functionality.

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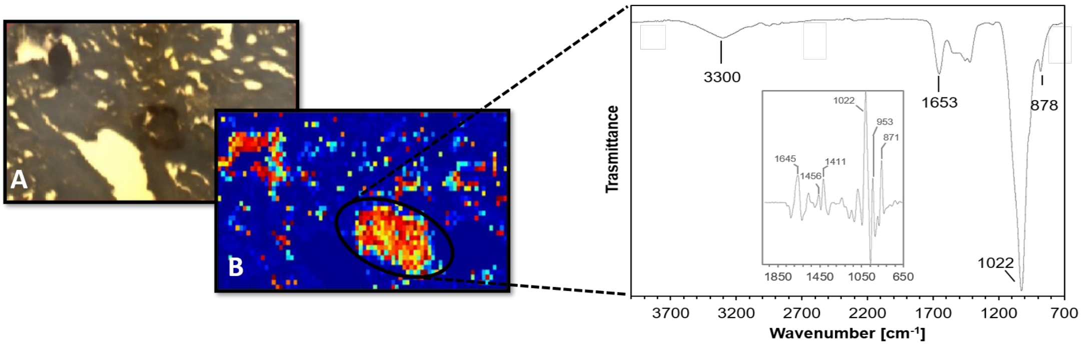
Fourier transformed infrared spectroscopy (FTIR) is a robust analytical technique for detecting and characterizing the molecular components of materials with many applications in the non-destructive studying of biological samples. The key point prompting the development of this label-free tool for objective, automated cytological and histological diagnosis relies on the fact that chemical changes precede or accompany any morphological variation symptomatic of disease. The coupling of FTIR with microspectroscopy (micro-FTIR) allowed for the generation of information-rich maps and images based on the extraction of spatially resolved chemical composition information from cells and tissues. Applying multivariate analysis to micro-FTIR data it is possible to examine the structure and conformation of lipids, proteins, and nucleic acids to recognize chemical clues underlying pathological conditions, to identify reliable biomarkers for tissue classification (normal versus diseased), and to grade diseases.

Here I report on micro-FTIR applied to two of the most diagnosed neoplasms in humans, colorectal carcinoma (CRT) and papillary thyroid carcinoma (PTC). The presence of calcinations known as psammoma bodies (PBs) is considered a relevant diagnostic feature of PTC and has been associated with high-stage cancer. By applying, fuzzy c-means clustering (FCM) and Principal component analysis (PCA) to spectral maps obtained by IR analysis of tissue samples, the automated blind detection on unstained thyroid tissue samples was demonstrated [1]. A deeper insight into spectral data allowed for the recognition of carbapatite as the main component of PBs [2]. Stroma, the complex microenvironment cells are immersed in, has recently been found to be actively involved in the growth and progression of tumors. Spectra relative to this specific region were selected from FITR maps obtained from patients diagnosed of CRT of different grades. The main chemical changes in the stroma and the possibility of employing them as biomarkers for early diagnoses were assessed.

The promising findings discussed strongly indicate that micro-FTIR spectroscopy could successfully support the conventional histopathological analyses. FTIR studies also contribute to deepening the understanding of the physiological processes taking place in tumor tissues, thus significantly contributing to the development of effective anti-cancer protocols.



Micro-FTIR identification of the features of interest in a tissue: black spots in the microscope image (A), yellow to red pixels in the chemical map(B). The mean spectrum associated with the cluster allows for precise signal assignation.

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Diclofenac adsorption on carbon-based nanomaterials: a molecular dynamics study

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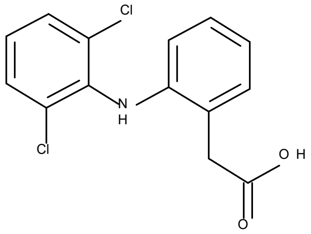
Pharmaceutical compounds received a great deal of attention in the last two decades as their appearance in the water cycle was detected at relatively high concentrations[1]. Consequently, the long-term exposure of living organisms to low levels of such compounds or their metabolites has generated an increasing concern. Numerous specific water treatment methods have been proposed, but they are not completely efficient and the treatment of large volumes of liquid is required. Adsorption of drugs on a suitable material, has the advantage of a low operation cost, low energy demand and easy implementation [2]. After use, the adsorbent materials can be regenerated, and the concentrated pollutant efficiently degraded *in situ* by other methods.

Diclofenac (DCF, Scheme 1) is a non-steroidal anti-inflammatory drug which is commonly detected in surface waters and soil at relatively high concentrations [1,3]. To date, carbon-based adsorbent materials resulted to be the attractive in water treatment due to their high affinity for drugs, high loading capacity and ability to be regenerated. Some examples include: activated carbons, graphite, carbon nanotubes (CNT), graphene (G), graphene oxide(GO) and G/CNT composites.

The understanding of molecular mechanisms at the basis of adsorption of such compounds stimulated also several theoretical studies to support the design of materials able to adsorb pharmaceuticals efficiently. As far as DCF is concerned, several experimental works on adsorption by carbon-based nanomaterials are available, while only few computational studies, essentially based on quantum mechanical approaches [3], have been carried out.

In this contribution, the adsorption of DCF by different carbon nanomaterials is investigated by molecular dynamics (MD) simulations and the first results reported. Graphene (G) and two graphene oxide models surfaces presenting regular distributions of hydroxyl (GOH) and epoxy (GOE) groups have been considered. At neutral pH DCF is present in the deprotonated form only, therefore in our study only this species was considered. MD simulations of the adsorbed drug showed that it remains adsorbed on the surface and depending on the material displays a different mobility. Free energy calculations based on umbrella sampling technique allowed to determine the ΔG of adsorption which results negative and close to the values obtained from experiments.



Scheme 1. Diclofenac

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Biowaste as valuable resource: humic acids valorization into multifunctional materials

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Humic acids (HA) are the alkali-soluble fraction of natural organic matter, consisting in a multitude of heterogeneous organic molecules surviving the biological and chemical degradation of both vegetal and animal biomasses. The great availability and chemical richness of these residues make their valorization one of the most promising challenge in the context of a circular economy.
In fact, their functional groups (i.e. quinones, phenols and carboxylic and hydroxyl moieties) confer them multifunctional behavior including the adsorbing capacity of metals and organic pollutants as well as a relevant red-ox activity accounting for antioxidant, antibacterial and anti-inflammatory behavior. However, their fast conformational dynamics and, hence, poor stability and rapid reactivity in water environments make humic substances not useful for several applications in aqueous media. A suitable solution may rely on the combination of HA onto an organic or inorganic matrix, providing for mechanical and physico-chemical stability and preserving their intrinsic properties.
This study demonstrates that wet chemistry strategy can be a powerful tool to obtain robust bio-hybrid materials with a wide range of shapes and morphology, as well as enhanced chemical stability and tunability. Following this approach, hybrid nanomaterials were obtained by combining HA with an inorganic oxide (i.e. TiO_2 or SiO_2), which is a biocompatible matrix able to control HA supramolecular structure and boosting their multifunctional properties [1,2]. At same time, HA-based 3D porous architectures (hydrogel, aerogel) were obtained by gelification strategy with aldehydes or bioavailable organic polymers (chitosan or gelatin) acting as reticulating agents.
Obtained structures exhibit promising antimicrobial and antioxidant features, as well as great efficacy towards water and soil micropollutants removal (Figure 1).

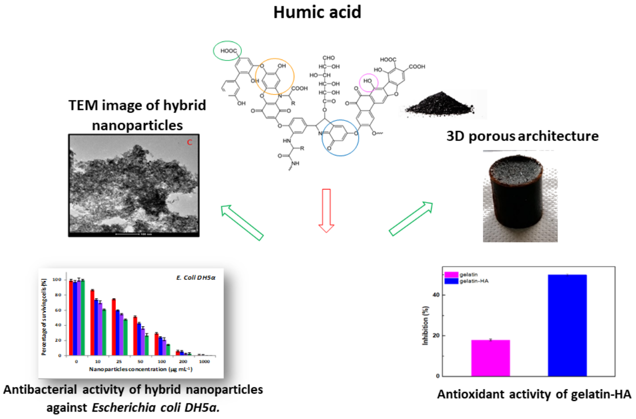

Figure 1. Hybrid multifunctional materials based on HA

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Sustainable Valorization of Anchovy Leftovers into Value Added Chemicals, Products and Energy

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Anchovies are among the largest fish catch worldwide. The anchovy fillet industry generates a huge amount of biowaste (e.g., fish heads, bones, tails) that can be used for the extraction of several potentially valuable bioproducts including omega-3 lipids.

In this contribution, a complete valorization of anchovy processing waste for the sustainable production of fish oil, biogas and fertilizer is presented.

The green process for the recovery of the fish oil - rich in omega-3, eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA), vitamin D3 and zeaxantin - employs citrus-derived d-limonene as a non-toxic and edible extraction solvent in a closed-loop process in which the solvent is fully recovered and recycled after the extraction [1, 2].

The residual product (anchovy sludge) was used as starting substrate for the production of biogas by anaerobic digestion. A good methane yield (about 280 $\mathrm{mL_{CH4}\cdot g_{VS}^{-1}}$) was obtained despite the unbalanced carbon to nitrogen (C/N) ratio, proving to be an ideal substrate for co-digestion along with other carbon rich wastes and residues. Furthermore, it was demonstrated that the presence of residual limonene did not affect the microbial methanogenesis [3].

At the same time, the use of the anchovy sludge and of the anaerobic digestion residue as readily available fertilizers was also assessed.

Finally, a simplified LCA analysis to verify the overall sustainability of the overall process is also presented. Preliminary results show that, due to the huge amount of biowaste generated every year from the landing of small pelagics in the EU, a new "blue-biorefinery" scenario can be imagined at a large- scale in the next years for Mediterranean nations.

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Utilization of biosourced materials in chemical nanotechnologies developing controlled release systems for human and plants health

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Sustained release of bioactive compounds is still a current topic, especially when considering natural ingredients, which have a strong activity, but their low bioavailability and poor solubility have seriously restricted their usage. Many materials and encapsulation techniques are exploited developing microparticles, microsponges and nanoparticles with tunable properties. Considerable progress towards materials for drug delivery derived from the combination of chemical nanotechnology and bio-resources. Our work concerns smart nano-systems exploiting the biomineral $CaCO_3$, biopolymers and biosourced active ingredients. We have demonstrated $CaCO_3$ nanocrystals biocompatibility and capacity to interact both with human cells and bacteria [1,2]. Furthermore, $CaCO_3$ nanocrystals have already shown a good affinity for different compounds [3]. So, these nanocarriers are investigated to improve bioactivity of aqueous pomegranate peel extract, that is rich of interesting anti-microbial, antioxidant and anticancer metabolites [4]. Adsorption on $CaCO_3$ has been widely characterized and release valuations have been supported by NMR analysis. The new extract formulation has been studied towards two human cell lines for antiproliferative and antioxidant activities, demonstrated nanocrystals key role. Antimicrobial effect has been investigated for *Fusarium oxysporum* and *Botrytis cinerea* providing a valid alternative to conventional chemical treatments for phytopathologies managing and post-harvest fruit diseases. Biopolymers-based systems show different structures such as hydrogel, nanofibers and sponges for applications as enzymes immobilization, drug delivery and bioimaging. We investigated nanocellulose from agricultural biomass wastes for fabrication of new delivery systems in different applications. The current PON project NEMESI is focused on nanocellulose-based carriers for loading of essentials oils, as antimicrobial agents in crops protection. The next outlook is nanocellulose utilization and smart modification, encapsulating bioactive ingredients for a new theranostic platform in cancer therapy.

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CNSL components as green building-blocks for bio-based nanovesicles

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The attention towards the use of renewable resources in scientific research is increasing; so, the Cashew Nut Shell Liquid (CNSL), extracted from the cashew nuts, is among the most investigated bioresource, thanks to the chemical versatility and biological activities of its components [1-3].
In this context, CNSL components such as anacardic acid (AA), cardanol (CA) and its derivatives, have been used as molecular building blocks for the practical and environmentally friendly preparation new classes of nanovesicles, as summarized in figure.

CA, as the main component of CNSL, and cholesterol mixtures have used to embed minor amounts of functional molecules inside the nanometric sized vesicles [4,5]. Particular attention has been devoted to investigate these vesicular nanosystems in terms of stability, antioxidant and cytotoxic activity [6], ability to stabilize the encapsulated molecules [7] and *in vitro* uptake process in human cells [8].
More recently, CA-based benzoxazines [9] or AA [10] have been used as molecular mono-block components with the scope to improve the sustainability of production of structurally innovative vesicular nanosystems, in view their potential applications in cancer treatment, drug delivery, bioimaging and so on.

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N-Hydroxyphthalimide role in Aerobic Oxidations: Homogeneous *versus* Heterogeneous Catalysis

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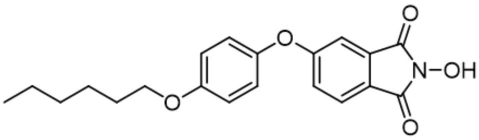
N-hydroxyphthalimide (NHPI) has emerged as a "green" alternative to the use of transition metal complexes to promote the selective aerobic oxidation of hydrocarbons.[1] Nevertheless, three main interconnected problems still prevent its final implementation for large-scale processes. They are: i) its poor solubility in apolar media at room temperature; ii) its autodecomposition at high temperatures and iii) the difficult catalyst recovery process.[2] As a consequence, NHPI-promoted liquid phase aerobic oxidations have always been performed in the presence of polar co-solvents, thereby introducing further economical and ecological drawbacks.[3]

To overcome these limitations, we have investigated the development of solvent-free processes, and both homogeneous and heterogeneous conditions have been considered.

As far as homogeneous systems are concerned, on the one hand, we designed a novel lipophilic NHPI derivative (**1**) showing high solubility in aromatic hydrocarbons with unprecedented catalytic efficiency.[4] On the other hand, we developed a novel NHPI/ionic liquid combined system (**2**) operating under effective homogeneous solvent-free conditions.[5]

As to heterogeneous systems, we synthesized an NHPI-tagged ligand (**3**) suitable for the construction of metal-organic frameworks (MOFs), an innovative class of crystalline, intrinsically porous, non-inert supporting materials.

Finally, we designed a novel multipurpose NHPI derivative with tunable reactivity to be used both under homogeneous and heterogeneous conditions. Its derivatization to lipophilic (**4**), ionic liquid-like (**5**), and zeolitic-imidazolate framework (ZIF) ligand (**6**) analogs is reported.



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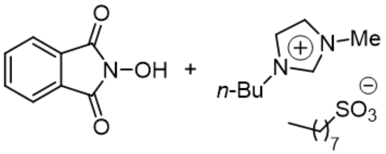

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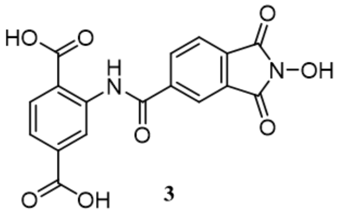

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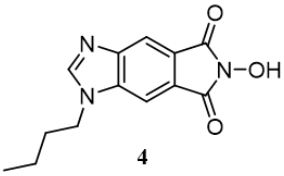

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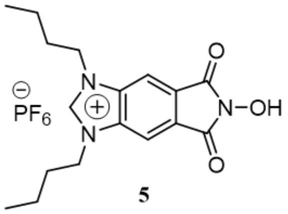

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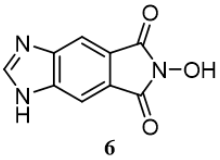

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Co-Polymeric Nanosponges from Cellulose Biomass as Heterogeneous Catalysts for Organic Reactions

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Heterogeneous catalysts prepared from biopolymers and biomass waste sources are attracting increasing interest, as reported in the recent literature [1–3]. The reasons can be related to the possibility of combining the virtuous approach of circular economy with the consolidated advantages of heterogeneous catalysis, namely the recycling of the system and the possibility to drive selectivity towards desired products.

Herein we present a highly porous cellulose-based nanosponge (CNS) used as heterogeneous and recoverable catalyst for organic reactions. The material is obtained by a thermal cross-linking between TEMPO-oxidized cellulose nanofibers (TOCNF) and branched polyethyleneimine 25 kDa (bPEI) in the presence of citric acid [4,5].

Given the alkaline properties of CNSs, Henry and Knoevenagel reactions, known amino-catalyzed reactions, were chosen as the model of study [6]. By considering also the high sorption capacity of these materials towards a wide range of transition metal ions, previously exploited in the field of water remediation [7,8], we were able to extend the scope of CNS by preparing new classes of catalysts, loaded with different metals, for promoting other organic reaction for the formation of aromatic acetals from carbonyl compounds using Cu (II) and Zn (II) and the cross-coupling Suzuki reaction using Pd (II) as catalytic metal.

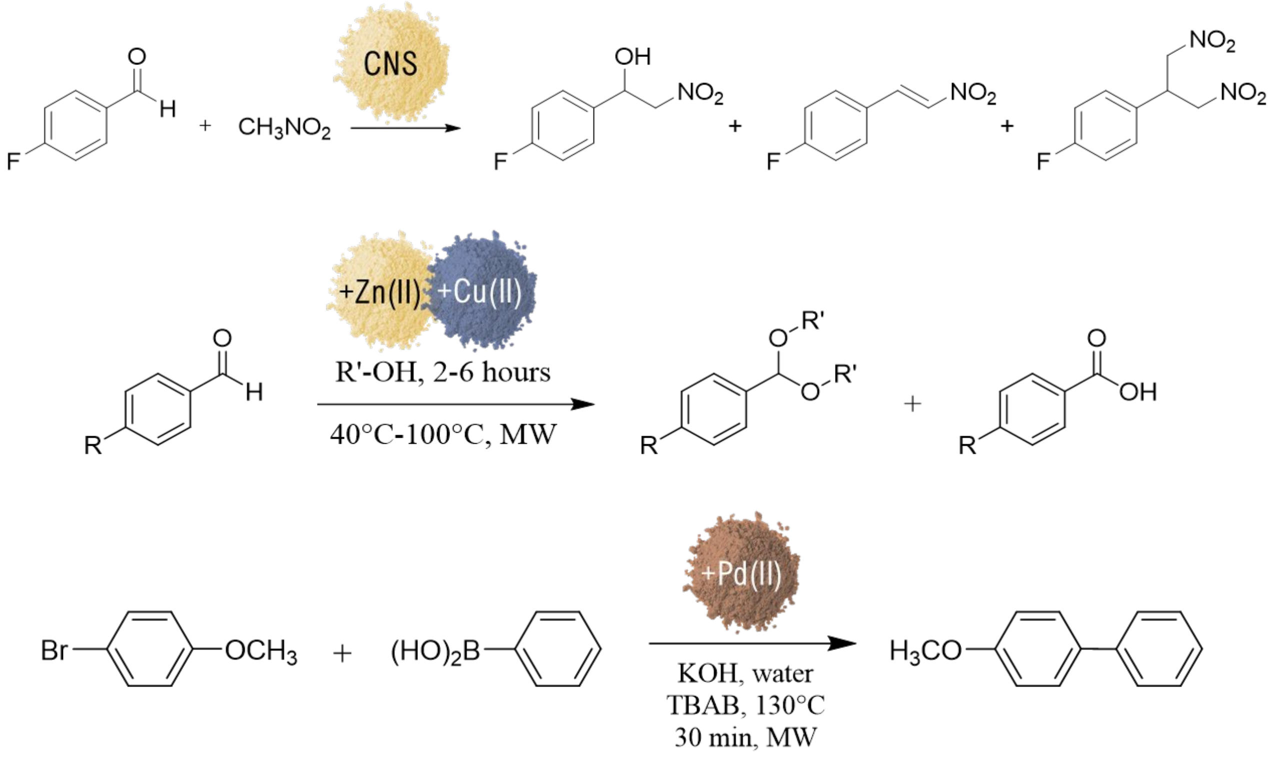

Figure 1. Schemes for the reactions chosen as model of study for heterogeneous catalysis tests with CNS.

For Henry reaction, by modulating reaction conditions (catalyst loading, temperature, solvent, microwave *versus* conventional heating, relative ratio of reagents) it was possible to drive selectivity towards different desired products, while maintaining high efficiency in terms of conversion. In most cases the products' distribution results quite different from homogeneous conditions, this much more emphasizing the importance of this heterogeneous solution [6].

Another important aspect was the reusability of the system. For all the analyzed reactions, the catalyst could be re-used several times without losing its catalytic efficiency, demonstrating once again the advantages of heterogeneous catalysis over homogeneous once.

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Use of a bio-derived polymer as crosslinking agent for stable-polyvinyl alcohol membrane development

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In a society that aims to preserve the environment, tuning of new green chemical-based methods for technological product development is still a great challenge. In membrane science, the use of synthetic and natural biopolymers is increasingly emerging to produce membrane based on more sustainable materials and processes.

Polyvinyl alcohol (PVA) is one of the best-known water soluble synthetic polymers with numerous properties such as biocompatibility, non-toxicity, and good film forming ability.

As greater strength is required, especially for applications in water, in recent years the interest in studying modification of PVA to produce water insoluble and stable membranes has increased. The hydroxyl groups distributed along backbone of PVA are suitable for chemical crosslinking reactions. The most used crosslinkers are aldehyde ones, and recently also di(tri)-carboxylic acids (e.g., malic acid, citric acid) have been applied [1].

The aim of this work was to test new environmentally friendly crosslinker. Exploiting its carboxyl functions, pectin (PEC) was used as crosslinking agent to form covalent bonds with PVA.

Membranes were prepared by evaporation-induced phase separation. A screening study on water stability of membranes prepared with casting solution made of different PVA/PEC mass ratio permitted to observe that PVA/PEC 1:1 membrane was the most stable in water also at high temperature (tested up to 100 °C). 86% of crosslinking degree, calculated by titration measurements, was obtained in PVA/PEC 1:1 membrane prepared from casting solution previously crosslinked for 5h.

Antiradical and antibacterial membranes were obtained: these new functionalities are due to the presence of PEC. The new covalent ester bonds between PVA and PEC, confirmed also by FTIR and TGA profile, increased the tensile strength (from 29±4 N/mm^2 to 88±4 N/mm^2) and the chemical stability (in solutions at different pH) of the crosslinked membrane compared to bare PVA membrane. The water vapor permeance results obtained for bare and crosslinked membranes will be also illustrated.

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Thermal-Oxidative Stability of PHBV/LDH Nanocomposites

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A growing research interest is currently directed to a greater use of bio-based resources especially for the application in food packaging [1, 2]. Poly(hydroxy butyrate-*co*-valerate) (PHBV) copolymers have attracted great attention for their high versatility, discrete production rate, as well as high biodegradability [3]. PHBV copolymers have high melting temperature and relatively high tensile strength, but their use is limited by their inherent brittleness and narrow heat processing window [4]. To improve the mechanical properties and thermal stability of a commercial PHBV copolymer (2 mol% of HV units), new organic-inorganic hybrid nanocomposites have been prepared. The filler employed is a layered double hydroxides (LDH) compound with a natural antioxidant, ferulic acid (FA), as intercalating agent, and acetyl tributyl citrate (ATBC) is exploited as bio-based plasticizer. PHBV samples were adversely affected by the presence of the additives (incorporated at different concentrations) at the processing conditions. In addition, infrared spectroscopy (IR) and electron paramagnetic resonance (EPR) showed that the rate and extent of their oxidative degradation varied significantly among formulations (Fig. 1). Further investigations with EPR have highlighted the presence of a "hidden" antioxidant added by the supplier of the polymer (belonging to the family of butylated hydroxytoluene), which in the presence of FA is suspected to cause a combinatorial pro-oxidant effect on PHBV when processed at high temperature.

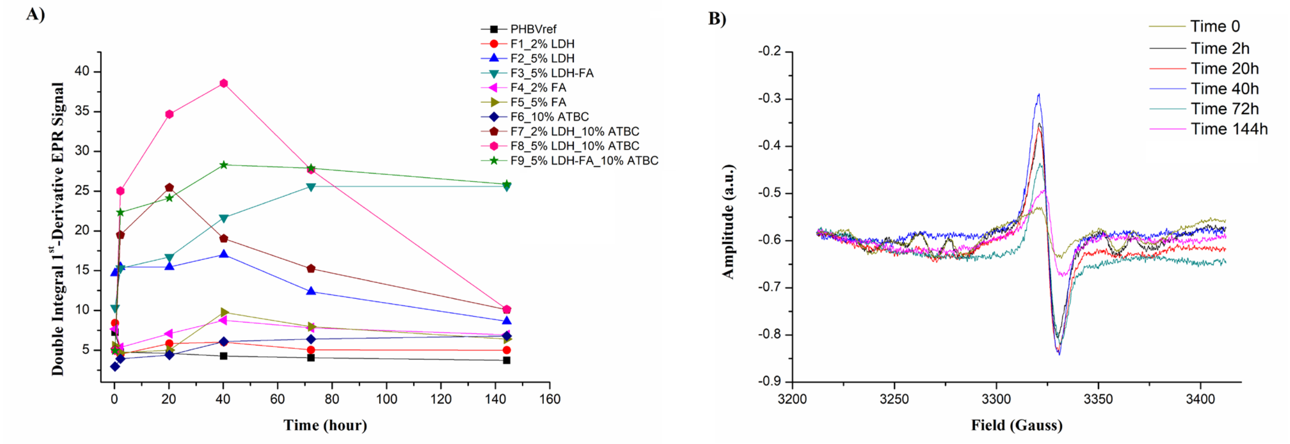

Fig.1. A) Double integral of EPR signal of all formulations versus time; B) example of EPR signal variation of F9 formulation.

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USABLE PACKAGING
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Furan as platform molecule in the production of greener epoxy-resins

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The increasing environmental as well as economic concerns about the availability of the finite petrochemical resources is boosting the necessity to find more sustainable resources. Under this perspective, the European Union policies are even more oriented on strategies for sustainability towards a toxic-free environment [1]. Also consumers and manufacturers are more conscious about the need to provide goods that affect less the already limited resources and, at the same time, preserve the environment and human health.

Epoxy resins represent a class of materials widely employed in a broad range of applications due to their excellent properties, from electronics to protective coatings. In the latter application, one of the major issues is the use of Bisphenol A (BPA), which is the most used precursor for their synthesis. BPA leads endocrine disrupting activity, causing severe pathologies in humans and their offspring. Nowadays, the necessity to find non-toxic building blocks to replace BPA in the production of epoxy resins results mandatory and sustainable molecules can answer also to the global necessity to move towards a greener chemistry.

New thermosetting polymers proposed as BPA substitute should possess a rigid structure, which guarantees high-performances and comparable chemical-physical properties. In this framework, furans, produced from cellulose and hemicellulose, are feasible building blocks for sustainable epoxy resins. They may replicate BPA behavior, due to their aromatic structure, without being harmful to human health and the environment.

The diepoxy derivatives 2,5 furan dicarboxylic acid (FDCA) and 2,5-furan dimethanol (FDM), in particular, were shown to be highly promising as starting compounds for the synthesis of sustainable epoxy resins with good mechanical properties. [2,3] The same furan-based epoxy resins exhibited promising performances characterized by properties such as good corrosion resistance when used in coating application, and intrinsic flame-retardancy properties, assisted by the addition of proper fillers. [4,5]

On the basis of the optimal properties exhibited by these furan-based resins, further efforts are now being made to develop fully bio-based resins by selecting, among the variety of bio-derived molecules, proper curing agents, leading to resins with tailorable properties.

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Insights on Ionic Liquids structure and dynamics:
NMR methods and recent advances

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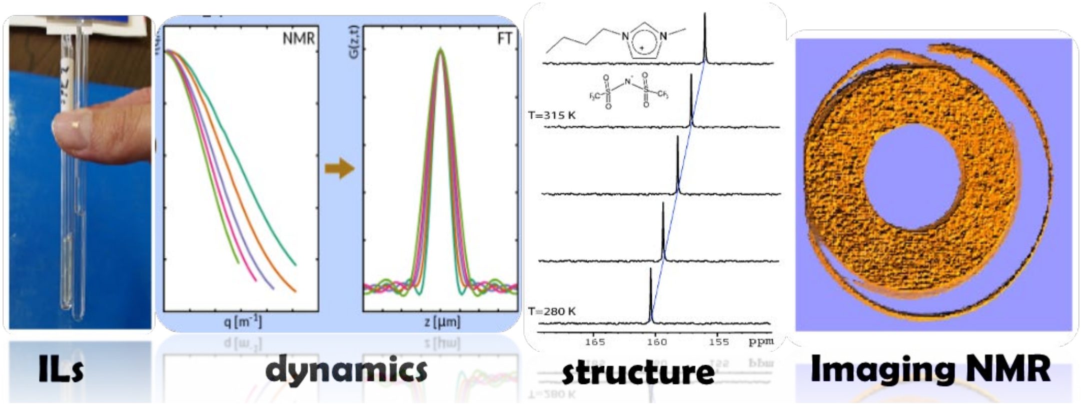
Ionic Liquids (ILs) represent an important and broad class of materials, characterized by low melting temperature (below 100 °C) composed entirely of ions, usually a large and asymmetric organic cation and an inorganic/organic anion. Their unique properties, such as low vapor pressure, high electrochemical/thermal stability, and high ionic conductivity favour their applications [1] in diverse fields, as biocatalysis, electrochemistry, gas adsorption/separation, purification technology including biomass processing and as materials for energy production. Besides this, ILs mixtures with lithium salts are used as an electrolytic media for lithium battery and solar cells.
A molecular-based understanding of ILs nano-structure [2] and ions dynamics, is relevant for all the applications, yet it is a great challenge because the charge and the peculiar chemical structure of the ions give rise to a complex interplay of molecular interactions leading to the formation of polar/apolar nano-domains. Among all the experimental techniques, Nuclear Magnetic Resonance (NMR) spectroscopy plays a key role in the characterisation of structure, ions interactions and dynamics in neat ILs, mixture of different ILs and/or with the addition of lithium salts.
Here we present the results, on several ILs and their blends, obtained with common NMR methods as multinuclear chemical shift, relaxation and pulsed field gradient techniques for the study of ions transport properties over a wide range of time scale [3], and multidimensional/multinuclear correlation methods like (^{19}F-^{1}H) (^{7}Li-^{1}H) HOESY for structure investigation. In parallel, some recent advances based on magnetic resonance imaging, capable of obtaining spatially resolved information, and ^{129}Xe chemical shift/dynamics, sensitive to the chemical environment and local cage, will be presented [4]. Molecular dynamics simulations have also been performed to rationalize the experimental results on the molecular scale.



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Ionic conductivity and thermal characterization of DBU-based protic ionic liquids

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Lithium-ion batteries (LIBs) are considered the most promising energy storage devices. However, serious safety issues of the LIBs are related to the flammability of the organic carbonates used as electrolyte components. Hence, developing nonflammable solvents as alternative electrolyte components is one of the most important targets to solve the above-mentioned safety problems of the LIBs. Protic ionic liquids (PILs) are a unique class of solvents due to their characteristics such as low flammability, negligible vapor pressure, and high ionic conductivity. Besides, PILs are easy to synthesize when compared to conventional aprotic ionic liquids. All these advantages make PILs promising alternative electrolyte components, enabling an improved safety of LIBs. However, a challenging task when working with PILs is to tune their properties according to the target application. Currently it is still unclear if the difference between aqueous pKa values of the protonated base and the acid (ΔpKa) or the chemical structure are governing the features of the PILs. Therefore, understanding the key factors controlling the characteristics of PILs is an ongoing research subject. The present work characterizes a series of promising PILs based on the 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) cation and anions from acids with a widely varying strength (bis(trifluoromethanesulfonyl)imide ($TFSI^-$), (trifluoromethanesulfonyl-nonafluorobutylsulfonyl)imide ($IM14^-$) bis(pentafluoroethanesulfonyl)imide ($BETI^-$), trifluoromethanesulfonate (TFO^-), methanesulfonate (MS^-) and trifluoroacetate (TFA^-). From the thermal characterization, DBUH-TFO, DBUH-TFA, DBUH-MS form glasses at very low temperatures rather than exhibiting crystallization or melting transitions. Besides, the latter two PILs exhibit an ionic conductivity far below room temperature. In contrast, the DBUH-IM14 DBUH-TFSI, DBUH-BETI that have a well-defined melting point show a significant increase in the ionic conductivity profile after the melting process. DBUH-TFO also shows similar behavior in respect to its ionic conductivity. Finally, the investigated physicochemical properties were correlated to the change in ΔpKa and the structure of the anion.

Deep Eutectics: what is inside the solvents for the 21st century?

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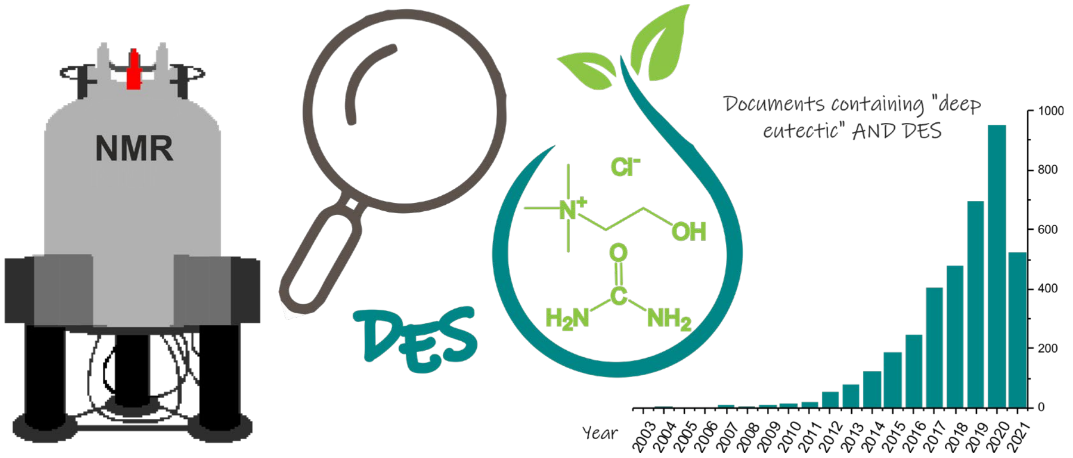
Deep Eutectic Solvents (DESs) are an emerging class of sustainable materials of great interest in green chemistry and with enormous potential in several technological and industrial applications [1]. These low transition temperature mixtures, foreseen as the next generation solvents, consist of a hydrogen bond donor salt and a hydrogen bond acceptor, which self-associate to form a eutectic phase characterized by a marked depression in melting point compared to both the constituents and the ideal mixture. Next to the desirable physicochemical properties (good thermal and chemical stability, low flammability, exceptional dissolution capabilities, among others) and the environmental and economic advantages (ease of preparation from mostly largely available and environmentally-friendly and safe raw materials, leading to low cost and high sustainability), an added value of DESs is their potential as tunable solvents. Not only the constituents can be mixed in a very high number of combinations, but the mixtures are also compatible with the addition of a third component (solute or cosolvent), opening up many new opportunities in terms of applications.

In view of their potential applications, a proper fundamental understanding of DESs basics at the molecular level is imperative. Although strong hydrogen bonding between the species of the mixture is postulated as the root cause of DESs' unusual physicochemical properties [1], more efforts are needed to elucidate the intermolecular network of the mixtures and how they are affected by the replacement of one or more species or by the presence of additives.

Here we illustrate the potential of multiple NMR techniques to get unique insights into structure and dynamics of choline-based type III DESs and their mixtures with water at different dilution and/or cyclodextrins [2]. We demonstrate that the results obtained by chemical shift analysis, correlation experiments, and relaxation and diffusion measurements, acquired on different nuclei, all converge to a detailed and consistent picture of the systems. Noteworthy is also the multifaceted and all-embracing description that can be achieved when NMR spectroscopy is used jointly with other techniques (X-ray, UV Resonance Raman, MD and Monte Carlo simulations).



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Mesoporous Silica Nanoparticles: a powerful platform for biocatalysis

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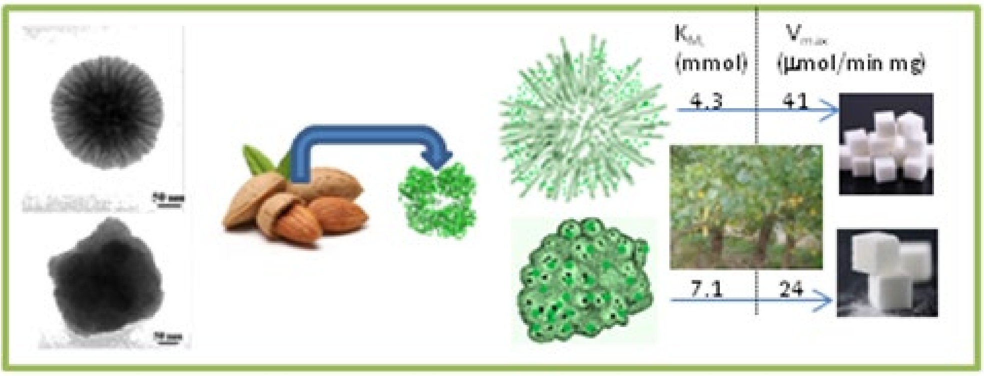
Enzymatic catalysis offers many advantages over chemical catalysis, including sustainability, selectivity towards the products and milder operational conditions (lower energy expense and non-corrosive environment). Fossil fuel depletion and environmental degradation have led researchers towards more sustainable energy sources. Lignocellulosic biomass, such as forestry and agricultural waste, has been considered as a strategic fuel source. The main component of lignocellulosic biomass is cellulose, a polymer composed by glucose units that can be hydrolyzed to glucose. Glucose is easily fermented into biofuels such as ethanol and butanol.

In the last decade, a great interest was devolved to nanostructured materials for biocatalytic applications. In this contest, mesoporous silica nanoparticles (MPSN) attracted a particular attention, proposing as large and promising platform thanks to their endogenous properties. Among a variety of organic and inorganic available materials, MPSN are excellent candidates for enzyme immobilization, since they present high porosity and large surface area useful for a high enzyme loading and a homogeneous distribution. Moreover, their surface can be easily functionalized to improve the enzyme immobilization. MPSN can enhance the enzyme stability, thanks to a limited exposure to environmental factors and to the constrains of polypeptide conformational freedom due to the interactions with the pore walls.

β-Glucosidase (BG) is a key enzyme for the degradation of cellulose into fermentable sugars. To exploit their catalytic ability, we have developed different strategies to alternatively immobilize β-glucosidase on wrinkled silica nanoparticles (WSNs) and tannic acid-templated silica nanoparticles by both physical adsorption and covalent linking. We have focused on their physico-chemical properties and catalytic performance in the cellobiose hydrolysis by kinetic studies, demonstrating they are the efficient, active and reusable biocatalysts with potential industrial applications.



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Tandem Catalytic Upgrading of Limonene and Methyl Levulinate promoted by Pd-based Catalysts

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Limonene, a cyclic monoterpene easily obtainable from citrus peel waste (OPW), can be used for the preparation of several building block chemicals, including p-cymene that is an important intermediate in several industrial processes [1]. The catalytic dehydrogenation of limonene is a promising alternative to the current preparation of p-cymene *via* the Friedel-Crafts alkylation of benzene with methyl and isopropyl halides that implies large quantities of hazardous acid catalysts and generates a large amount of byproducts (the overall p-cymene yield usually does not exceed 50%). Noteworthy, the dehydrogenation process of limonene into p-cymene leads to hydrogen as a co-product that can be used as an indirect H-source in Catalytic Transfer Hydrogenation/Hydrogenolysis (CTH) reactions that received a great deal of attention since, with respect to traditional high-pressure-hydrogen processes, offer better efficiency and atom economy thus improving the sustainability of industrial processes [2].

Accordingly, alkyl levulinates are promising platform compounds derived from cellulosic biomasses (including OPW) representing a renewable starting substrate for the CTH synthesis of γ-valerolactone (GVL) which is commonly adopted as a flavoring agent in the food industry, as a green solvent, as an intermediate in the bio-based chemical industry [3, 4].

In this context, this contribution is focused on the production of p-cymene from limonene by using heterogeneous Pd-based catalysts (Pd/C e Pd/ZrO_2) in the presence of simple aliphatic alcohols (MeOH, EtOH and 2-PrOH) as the reaction medium under both batch and gas-flow conditions. Under batch conditions, the experimental evidence shows that the conversion of limonene into p-cymene was found to be dependent on the reaction temperature adopted with the best results obtained in ethanol. On the other hand, under continuous gas-flow conditions, a complete limonene conversion into GVL is observed with all investigated solvents for at least 6 h of time-on-stream.

Finally, the one-pot tandem catalytic upgrading of limonene and methyl levulinate for the simultaneous production of p-cymene and γ-valerolactone is also presented.

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Synthesis, characterization, and photocatalytic activity of Eu doped ZnO prepared by supercritical antisolvent precipitation route

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Europium (Eu) doped ZnO has attracted attention as a red emitting nanophosphor [1] and as a promising photocatalytic material [2]. While the higher photocatalytic activity of Eu-doped ZnO compared to bare ZnO is generally ascertained, contrasting hypotheses on the underlying reasons have been reported. Moreover, currently used preparation methods, variously affecting the properties of the resulting material, generally use organic solvents or toxic and expensive reagents, as well as long production times. The supercritical antisolvent precipitation route overcomes these drawbacks, and allows achieving regular nanoparticles with narrow particle size distributions and low tendency to aggregation [3]. In this work bare and Eu^{3+} doped ZnO samples have been prepared through precipitation by using supercritical carbon dioxide as the antisolvent. The powders were tested as photocatalysts for two well investigated model reactions, i.e. the degradation and mineralization of crystal violet [4] and the partial oxidation of ferulic acid to vanillin [5] under UV light irradiation. Europium doped samples showed superior ability to degrade the organic substrates, while slightly higher selectivity values towards vanillin have been obtained in the presence of bare ZnO. A thorough characterization of the samples allowed justifying this behaviour. In particular, doping with europium does not change the potential of the photogenerated charges and slightly widens the band gap of the doped materials with respect to the bare sample. On the other hand, Raman and EPR spectroscopy highlight the introduction of novel defects in the Eu doped samples, which confer higher hydrophilicity to the Eu doped samples. Moreover, the presence of Europium totally quenches the visible light emission of ZnO resulting from recombination of photogenerated holes at defective sites. The resulting stabilization of photogenerated holes, coupled with the higher hydrophilicity has been related to the higher photocatalytic activity of the Eu doped samples.

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Microwave-assisted synthesis and isopropanol extraction in the preparation of TiO_2 nanoparticle suspensions

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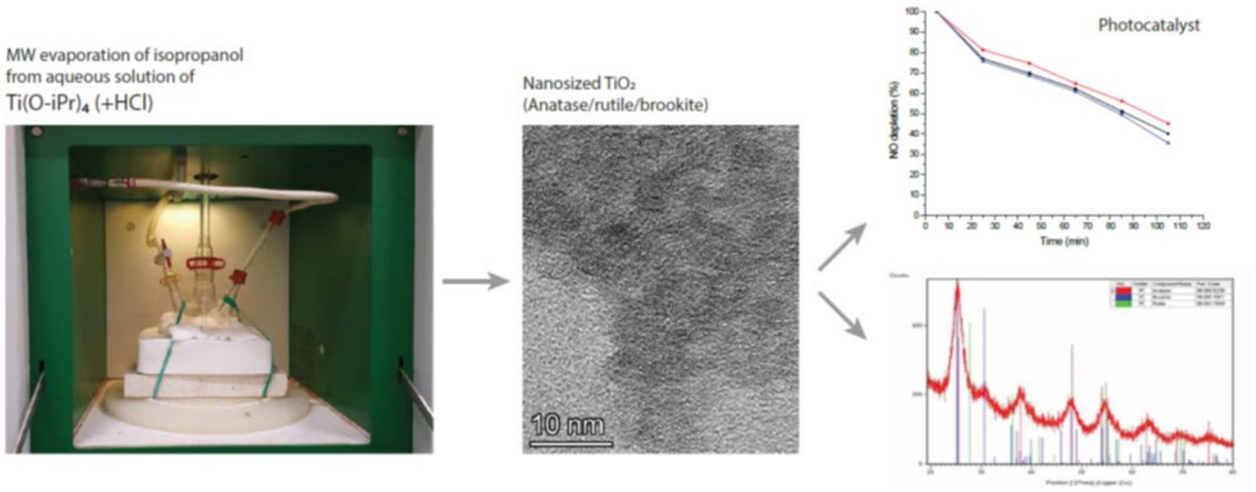
In this paper we evaluate the effect of isopropanol arising from the reagent $Ti(O\text{-}iPr)_4$ on the long-term stability of nanoparticle size of TiO_2 produced during a microwave assisted sol-gel synthesis [1]. Different configurations of microwave apparatus have been considered: the synthesis was carried out both in vessel or flask, and both performing or not isopropanol distillation through a modified microwave apparatus. Results revealed that isopropanol distillation after a short reaction time provided suspensions with slightly smaller particle size, that also show longer stability over time, especially for syntheses carried out at certain temperatures. Reactions performed distilling isopropanol from vessel and flasks showed comparable results, superior to the corresponding suspensions obtained without distilling isopropanol. The nanosized TiO_2 obtained in this way is a mixture of its three main polymorphs with anatase being the most abundant phase. The material is photocatalytic under UV light: the suspensions obtained from reactions can directly be applied on marble slabs and their photocatalytic performance is comparable with a commercial product.
One of the most interesting aspects of the approach followed in this work is the idea of producing the ready to use suspension in a one pot synthesis and alcohol distillation procedure. This approach can potentially be adopted in a continuous flow microwave reaction and could be valuable for further industrial implementation.



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Hybrid Strategies for the Improvement of the Flame Retardancy of in-situ Silica-Epoxy Nanocomposites cured with Aliphatic Hardener

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The flexibility of epoxy chemistry allows the development of a wide variety of materials with different mechanical, thermal, fire, electrical and chemical properties. The use of aliphatic amines for manufacturing of epoxy resin is preferable over the toxic aromatic amines, however with a compromise in mechanical, thermal and fire behavior. It is very challenging to flame retard an epoxy resin cured with an aliphatic hardener [1-3]. Herein, a hybrid flame retardant (FR) strategy was used for the synthesis of a self-extinguishing modified bisphenol A diglycidyl ether (DGEBA) resin cured with isophorone diamine (i.e. cycloaliphatic amine).

The FR epoxy nanocomposites were prepared by DGEBA modification with silica nanoparticles via an in situ sol-gel process followed by incorporation of DA (i.e. 3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl) propenamide) flame retardant together with melamine and subsequent curing with amine hardener [3]. DA has been previously shown to be a non-toxic FR additive. A non-dripping V0 classification in UL 94 vertical flame spread tests was obtained for epoxy nanocomposites with 2 wt.% phosphorus (P). Epoxy resin containing DA alone could achieve V0 rating in UL 94 test at 2 wt.% P, albeit with dripping. The presence of silica nanoparticles is important to achieve a V0 non-dripping rating in UL 94 test [3]. The pristine resin and silica-epoxy nanocomposites without DA could not be classified in the UL 94 tests.

In cone calorimetry experiments a strong reduction (up to 70%) in peak heat release rate and delay of the ignition time (up to 50%), and thus an increase (up to 75%) in the time to flashover, were observed for silica-epoxy nanocomposites when both DA and melamine were used. Increased CO/CO_2 ratio was observed for epoxy samples containing the phosphorous-based FR, indicating its gas phase flame inhibition behavior [4]. In addition to this gas phase flame inhibition, a higher char formation and intumescence were observed, which indicates a simultaneous condensed phase activity. Based on the various thermal and fire studies, the FR mechanism of DA in the epoxy degradation was postulated.

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Chemical stabilization in a single step process: geopolymerization of tannery wastewater pollutants

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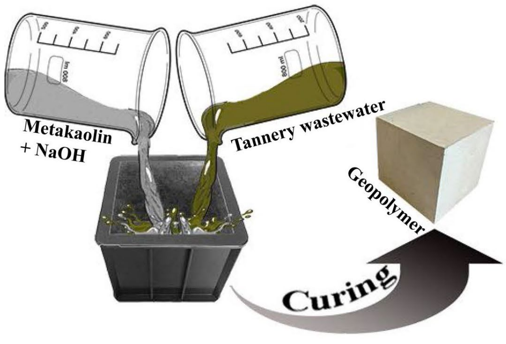
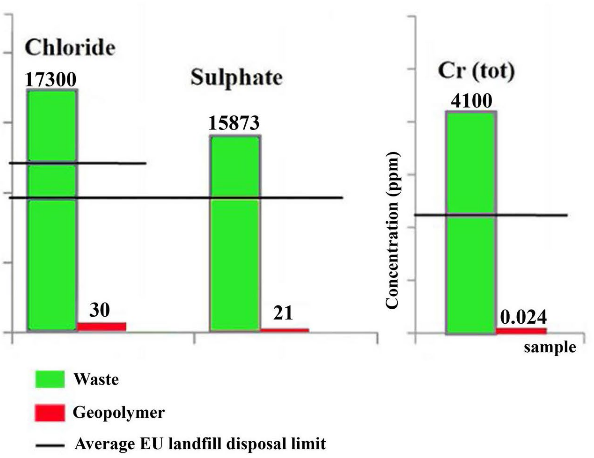
Geopolymers are a class of inorganic binders obtained by alkali activation of aluminosilicate powders at room temperature. Such activation process leads to a cement like matrix that drastically decreases mobility of several components. In this work we use a metakaolin based geopolymer to tackle the problem directly in an actual industrial environment, the stabilization of tannery wastewaters. Such waste is a mixture of several pollutants, both anionic and cationic as well as organic macromolecules which are very hard to treat for disposal all together. To obtain a solid stabilized and dense material, the metakaolin was mixed with 10wt% of wastewater added with sodium hydroxide and sodium silicate as activating solutions. This process allowed a rapid consolidation at room temperature of the waste that showed a high immobilization efficiency of anion and cations. We focused on the release of Cr which was proved to be well below law limit for reuse or dispose in landfill as nonhazardous material. The leaching tests performed at different aging times proved an increased efficiency in Cr and anions entrapment in the geopolymeric matrix that resulted an amorphous aluminosilicate network [1].



10% Cr-bearing wastewater
400 mg of Cr per kg of solid geopolymer

Leaching test results (ppm) UNI EN 12457-2-2004



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Hematite nanoparticles as promising catalyst

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The past decade has witnessed a great deal of research into the catalytic reactivity of nanoparticles controlled by size [1], shape [2] and composition. In these contests, the idea of more economic and eco-friendly catalysts is one of the primary concerns for sustainable chemistry. In the last years, several efforts were done to replace noble metals-based catalysts (Pd, Pt, etc.) with non-noble metals, such as Co, Ni, and Fe. These materials drawn wide attention due to their abundant earth storage, economic price, and low toxicity. Unfortunately, to recover good catalytic results strong reaction conditions are required, such as high temperature (≥100 °C), high H_2 pressure (≥1 MPa) and additives (acid, base and metal salts) [3]. It is worth mentioning that the combination of controlled nanoparticles synthesis and inexpensive metals, is one of the most ambitious goals of recent years. Here we report the results of an investigation of iron oxide nanoparticles obtained by controlled thermal treatment of polymer supported iron (III) complex [4] (Fe-pol). The Fe-pol was observed by field emission scanning electron microscopy and heated up to 400 °C, monitored every 25 °C by powder X-ray diffraction (PXRD) and thermogravimetric analyses. PXRD patterns showed the hematite (α-Fe_2O_3) formation after 300 °C with relevant diffraction effects at 400 °C, which is the limit temperature for polymer decomposition. Therefore, three iron catalysts were synthesized at different temperature (300/400 °C) and reaction conditions (air/N_2), comparing their properties, activity, and selectivity. Results demonstrated that the catalyst synthesized at 400 °C under air conditions (α-Fe_2O_3-400A) is magnetic and catalyzed in an excellent way the hydrogenation of nitroarenes in ethanol at 80 °C, by using hydrazine as reducing agent. Complete conversion of the substrate was obtained after 3 h, and the catalyst could be recycled on nitroarenes and halonitroarenes at least 7 times, with no drop of catalytic activity and selectivity. The magnetic properties of α-Fe_2O_3-400A makes the catalyst an interesting material for its easy recyclability.

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Functionalization of graphene related materials with biosourced C-3 and C-6 building blocks. From synthesis to applications

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The functionalization of sp^2 carbon allotropes is one of the hot research topics in advanced research on materials. Nowadays, carbon nanotubes and graphene related materials are extensively studied due to their exceptional mechanical and electrical properties. They are capable of substantially improving the properties of polymeric materials. Their functionalization is a crucial step, for allowing an even dispersion in the matrix.

In this research, the functionalization of graphene related materials was performed with biosourced C-3 [1, 2] and C-6 molecules [3]. They were glycerol and galactaric acid derivatives: pyrrole compounds (PyC) and 2-pyrones (Figure 1a). The reactions for their synthesis and for the carbon allotrope functionalization were green and characterized by high atom efficiency, with a yield up to 96%. Indeed, the reactions were carried out in the absence of solvents and catalysts and adducts were obtained by simply mixing, with the help of either thermal or mechanical energy. The developed functionalization methods were successful for: carbon black, carbon nanotubes, few layers graphene. The bulk structure of the carbon substrate was left substantially unaltered: functionalization occurred in peripheral positions, at the edges of the graphene layers. Functional groups of defined chemical structure were covalently bound to the carbon material and stable adducts, up to very high temperature, were formed. Reliable hypotheses for the functionalization mechanisms were elaborated. In Figure 1b the supposed domino reaction based on the pyrrole compound, with the Diels Alder cycloaddition as the last step is represented [1].

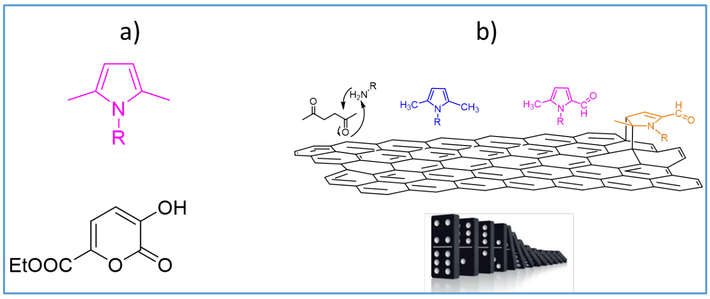

Figure 1

Such functionalization technique was developed as a pervasive technology, which allowed to pursue a variety of applications: (i) decoration with metals to obtain catalysts for the selective deuteration of pharmaceutical molecules [4] as well as antibacterial ingredients [5] (ii) rubber compounds for dynamic-mechanical applications (tires) [1] (iii) conductive inks.

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Polymer/rubber nanofibrous interleaves for the enhancement of delamination resistance of CFRP laminates

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In the field of nanotechnology, electrospinning is a very effective processing technique to obtain polymer micro/nano-fibers through the use of an electric field applied to a polymer blend or melt. The rising interest to this technique is due to the high versatility and potential for a wide range of applications, including tissue engineering, (bio)sensors, filtration and as reinforcement of advanced polymer composites [1-2] . In particular, for carbon fiber reinforced polymers (CFRPs) the huge specific surface area of electrospun nanofibers results in very large interfacial area between the nanofibers and the polymer matrix and, in turn, into a substantial increase of fiber-matrix interactions, with a consequent improvement of the fracture toughness of the laminates. [3] Rubbers are among the type of materials used to solve or mitigate the inherent brittleness of the highly crosslinked resins used in combination with carbon fibres for the production of high-performance composites. They are also particularly useful when noise or vibration damping is required. Unfortunately, the rubber fraction necessary to attain significant effects in terms of toughening or vibration damping detrimentally impact on other important mechanical properties of the laminates and weight. Using rubbery nanofibers would allow to confine the rubber where it can be most effective. Rubber electrospinning is quite challenging, due to the low glass transition temperature (Tg) of these materials, that causes the nanofibre to coalesce into films minutes after the spinning [5]. The use of a second, higher Tg, polymer can help stabilising the fibrous morphology [6].

In this work, electrospun nanofibers mats were prepared by solutions of a terpolymer of butadiene, acrylonitrile, acrylic acid mixed with different polymers, such as Nylon 6,6 or poly acrylonitrile (PAN). The blend composition and processing parameters (voltage, tip to collector distance, flow rate) were tuned and optimized in order to get uniform nanofibrous mats with reduced defects. The morphology of the produced mats was characterized with scanning electron microscopy (SEM), and their thermal behaviour was characterized with both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Selected mats were also used to produce mat/epoxy monolayers. The effect of the mat presence on the resin cure reactions, the nanocomposite monolayer fracture surface morphology, and signs of the activation of fracture energy dissipation mechanisms were then assessed.

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Silica Hairy Nanoparticles in Rubber Nanocomposites

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The addition of silica nanoparticles (SiO_2 NPs) to polymer matrices is known to be a promising strategy to produce nanocomposite materials with improved mechanical and functional properties [1]. These properties are largely determined by the distribution of SiO_2 NPs within the nanocomposite, which in turn is influenced by SiO_2 NPs morphology and surface chemistry. Recently, SiO_2 NPs functionalized with polymer brushes, i.e. SiO_2 Hairy Nanoparticles (SiO_2 HNPs, a in Fig.), have raised much interest due to the improved filler/matrix compatibilization and their ability to self-organize in ordered superstructures. [2][3] Nonetheless, the study of the relationship between self-assembly and the functional properties of the nanocomposite materials remains an open challenge.
In this context, we propose a versatile three-step colloidal synthesis of core-shell SiO_2 HNPs based on the Stober method, which provides accurate control of both morphology and surface chemistry. Size-controlled spherical SiO_2 NPs were first functionalized with an aminosilane and subsequently grafted with polymer brushes of different density and chemical structure. The obtained HNPs were fully characterized by a variety of analytical techniques which confirmed that self-assembly occurs.
SiO_2 HNPs were employed in the preparation of rubber nanocomposites to study the fillers self-organization within the matrix and their effect on the mechanical properties. Tensile and oscillatory shear tests were performed on both the uncured and vulcanized composites, showing that SiO_2 HNPs produce improved reinforcement (b in Fig.) compared to the bare and aminosilane-functionalized SiO_2 NPs. TEM analysis of the composites reveals that SiO_2 HNPs tend to self-organize in anisotropic domains (c in Fig.) where the filler-filler interaction is mediated by the grafted polymer layer, thus creating a reinforcing filler network.

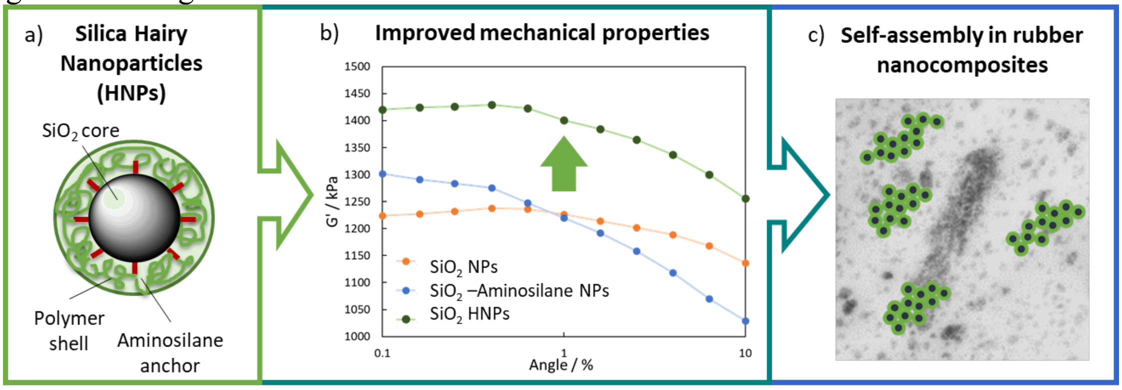

Figure. a) Schematic representation of HNPs, b) reinforcement effect and c) self-assembly of HNPs.

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Titanosilicalite as Nickel Support for Methanation Reaction

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The Power to Gas technology currently represents a promising approach to solve the energy storage problems and to reduce greenhouse gas emissions. The Power-to-Methane or P2M system, in particularly, offers a pathway to convert the renewable electric energy or surplus electrical energy into chemical energy in form of methane, using hydrogen produced by water electrolysis and carbon dioxide sourced from biogas or natural gas. The methane gas produced in this way represents a more appropriate medium for the storage applications than hydrogen gas because it is much easier to handle and it could be directly transported through the already existent pipeline networks or storage infrastructures [1]. The effectiveness and efficiency of power-to-gas plants strongly depend on the catalytic hydrogenation of CO_2 to methane also called CO_2 methanation [2].
Carbon dioxide methanation is an exothermic reaction typically operating at temperatures between 200°C and 550°C and at pressures ranging from 1 to 100 bar. Due to competing reactions including the reverse water-gas shift reaction, the conversion of CO_2 into CH_4 requires an active catalyst at relatively low temperatures and selective towards methane. Nickel, among the transition metals, is the most commonly used catalyst in CO_2 methanation, due to its high activity and selectivity in combination with its relatively low price. In this work, a nickel catalyst supported onto an innovative support, Engelhard Titanium Silicates ETS-10 [3] was proposed and its catalytic performance was investigated towards the CO_2 methanation reaction in the temperature range 200-500°C at a GHSV of 30000 hour^{-1}. The catalyst reaches the highest value of CO_2 conversion (68%) and selectivity towards CH_4 (98%) at T=400°C. The present study confirms the affinity between the surface of the ETS and CO_2 molecules.

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Phenolic compounds in alcoholic and low-alcoholic beer by fast HPLC-PDA-MS/MS analysis: impact of malt composition, hops and dealcoholization process.

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Beer is one of the most consumed beverages worldwide, whose market is constantly increasing. In addiction a side-market of alcohol-free and low-alcohol beer is fast growing, with a consequent strong demand of technologies with a minimum impact on organoleptic and nutritional properties. Polyphenols from malts and hops are the main antioxidants in beer, that affect flavor, color and stability, besides being considered responsible for health benefits. Our recent research aimed to provide a method for the fast analysis of phenolic profile and content, and to investigate the suitability of membrane-based dealcoholization processes. So, we developed a method to fill the need for analysis without samples pretreatments, based on HPLC-PDA-MS/MS in SIR mode [1]. The method, as also assays for total phenolic content, antioxidant activity or NMR investigation, was applied to craft beers differing in the recipe (India Pale Ale, Amber Ale and American Pale Ale, IPA, ALE and APA, respectively) [1] and in malt compositions (Pale Ale with increasing percentage of dark malt, PA100 and PA85, respectively) [2]. The last ones were dealcoholized by osmotic distillation and analyzed (LA100 and LA85, respectively) [2]. A commercial alcoholic beer (AB) was used to investigate a new cascade process: the first diafiltration step was first studied by using two different membranes (cellulose, LAB1, and polyacrylonitrile, LAB2), and the phenolic content was analyzed [3]. Some results of phenolic content (mg/L) are resumed in the Table.

STD	**IPA**	**ALE**	**APA**	**PA100**	**LA100**	**PA85**	**LA85**	**AB**	**LAB1**	**LAB2**
GA	nd	nd	nd	0.1±0.0	0.1±0.0	0.1±0.0	0.1±0.0	0.3±0.1	0.2±0.0	0.2±0.0
PCA	nd	nd	nd	0.1±0.0	nd	0.3±0.0	nd	0.1±0.0	0.1±0.0	0.1±0.0
5CQA	0.4±0.1	nd	nd	< 0.24	< 0.24	< 0.24	< 0.24	< 0.24	< 0.24	< 0.24
pHBA	5.5±1.0	1.9±0.1	2.3±0.2	0.4±0.0	0.4±0.0	6.0±0.1	2.5±0.3	1.3±0.1	1.2±0.1	0.9±0.1
VA	2.4±0.1	2.5±0.5	0.7±0.1	1.0±0.1	1.1±0.1	0.8±0.0	0.8±0.0	0.8±0.0	0.8±0.0	0.8±0.0
mHBA	1.0±0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd
CA	nd	nd	nd	nd	nd	0.1±0.0	0.2±0.0	nd	nd	nd
SyA	nd	nd	nd	nq	nq	nq	nq	nq	nq	nq
pCuA	1.5±0.0	0.6±0.1	<0.06	0.3±0.0	0.3±0.0	0.2±0.0	0.4±0.0	0.8±0.0	0.7±0.0	0.6±0.0
SA	nd	nd	nd	0.8±0.0	0.6±0.0	1.6±0.0	0.5±0.0	0.6±0.1	0.4±0.0	0.4±0.1
FA	3.2±0.1	1.9±0.0	0.5±0.1	1.2±0.1	1.3±0.0	0.8±0.0	1.3±0.1	2.1±0.1	1.8±0.1	1.7±0.1
Ru	4.9±0.3	<0.09	0.2±0.0	0.7±0.1	0.5±0.1	0.7±0.1	<0.29	< 0.29	< 0.29	< 0.29
Q	2.2±0.2	<0.07	<0.07	< 0.23	< 0.23	< 0.23	<0.23	< 0.23	< 0.23	< 0.23
K	2.6±0.2	<0.06	<0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06	< 0.06

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Early-Detection of *Xylella fastidiosa* in Olive Trees by Hyperspectral Reflectance and Non-targeted Metabolomics

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In recent years and hitherto, the olive quick decline syndrome (OQDS), caused by *Xylella fastidiosa* (*Xf*) subsp. *pauca* De Donno strain (ST53),[1] is the most serious disease of olive trees in the Mediterranean area. More than 11 million plants were infected in the Apulia region, Southern Italy, covering an area of about 50,000 ha. The main control strategy is based on the rapid identification and elimination of *Xf*-infected plants.[2] For the next 50 years, the economic damages were projected to be up to 5.2 billion euros.[3] Therefore, the early detection of *Xf*-infected olive trees would offer a competitive advantage against the spread of the infection by enabling preventive actions to be taken before the onset of the disease. The phenotypic and metabolic changes that occur during the period from tree infection to symptoms manifestation also depend on the different susceptibility of the cultivar to infection. Therefore, the goal of the present study is to develop an analytical method able to detect variations in the metabolome of olive leaves at the early stage of *Xf* infection. Inoculated olive plants were subjected simultaneously to a non-targeted metabolomics (NMR and HRMS) and hyperspectral reflectance (HSR) analyses. Young healthy olive plants of the susceptible cultivar 'Cellina di Nardò' were artificially infected with *Xf* De Donno strain and co-inoculated with some isolates of xylem-inhabiting fungi, often detected in OQDS trees.[4] Inoculated olive plants were grown in a thermo-conditioned greenhouse. Leaves were subjected to HSR acquisition while their extracts were analysed by NMR and HRMS. The data collected through these three analytical methods were further subjected to chemometrics analysis. As a result, covariance matrices were obtained providing useful insights into the optimal associations between the HSR spectral features and the diagnostic NMR and HRMS signals. The results obtained are promising for the future development of new sensors for the early detection of *Xf* infection in olive plants.

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Hydrophobin coated superfluorinated nanoparticles for ^{19}F-MRI cell tracking

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^{19}F-MRI has emerged as a promising diagnostic tool providing hot spot imaging along with ^{1}H-MRI. We previously reported a superfluorinated imaging agent, PERFECTA, bearing 36 equivalent ^{19}F atoms and therefore showing a single, intense resonance peak.[1] As most of the superfluorinated contrast agents, PERFECTA is highly hydrophobic, which makes it difficult to be used in biological environment systems. In this work, an amphiphilic protein, hydrophobin (HFBII), which is a natural biosurfactant with filming properties, was used to disperse PERFECTA in aqueous solutions[2]. We optimized a protocol to obtain colloidally stable formulations of PERFECTA. The obtained formulations were characterized by NMR, DLS, microDSC, TEM, ^{19}F-MRI and FTIR. The results showed that these nanoformulations were composed of monodispersed PERFECTA nanoparticles coated by a HFBII shell that also have good NMR relaxation times to be used as ^{19}F-MRI tracking contrast agents [Figure 1]. Cytotoxicity and cellular uptake studies also demonstrated nanoparticle biocompatibility and their ability to label cells. Moreover, hydrophobin protein has been shown to possess stealth properties, thereby reducing the attachment of serum proteins on to the nanoparticles. Thus, the obtained nanoformulation represents a versatile labeling agent that can also be used as delivery vector.

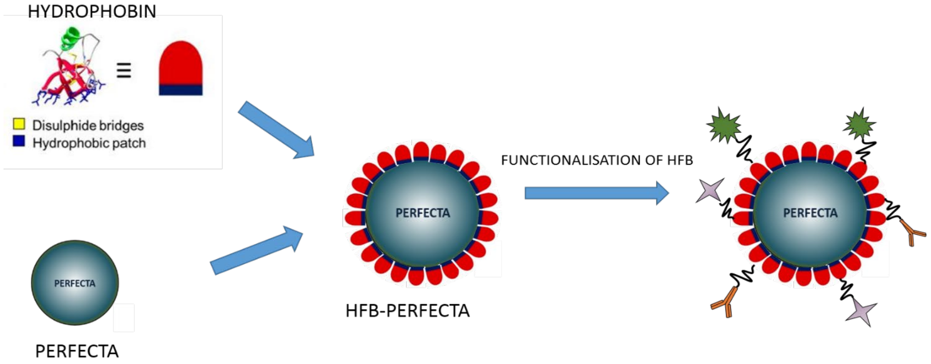

Figure 1: Schematic drawing of the hydrophobin coated superfluorinated nanoparticle.

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S-PEEK membranes optimized for Vanadium Redox Flow Battery: the effects of sulphonation degree and filler content on operative conditions and set-up configurations

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Vanadium redox flow battery (VRFB) has attracted extensive attention as one of the most promising large-scale electrical energy storage system, thanks to the advantages of decoupled energy storage and power output, the high-energy efficiency, the fast response and ambient temperature operations, the flexible design and safety, the long cycling stabilities [1, 2]. Specifically, VRFB has an additional advantage in that it does not suffer from permanent self-discharge thanks to the use of the same element in both cell compartments. Therefore, VRFB possesses the proper technology maturity for market uptake in the next years and several VRFB systems have been already demonstrated all over the world [3-6]. Nevertheless, the commercialization of the VRFB is still hindered by the low stability and the high costs of some components such as vanadium precursors, electrolyte temperature management system in order to prevent precipitation of vanadium compounds, and mainly the membrane which is the key component to separate the catholyte and anolyte and to transport protons [7]. Therefore, to replace the widely used but expensive perfluorinated Nafion membranes, great efforts have been made to search alternative ones; among all candidates, sulfonated poly(ether ether ketone) (SPEEK)-based membrane seems to be the most suitable to replace Nafion membrane because of its lower cost, high proton to vanadium ion selectivity, if only the poor stability be solved [8].

In this contribution, S-PEEK membranes with different sulphonation degrees and $SiO-NH_2$ filler contents were prepared and, after chemical and morphological characterizations [9], tested in lab-scale VRFB system by means of several consecutive charge-discharge cycles, and of Electrochemical Impedance Spectroscopy (EIS) measurements The performances of those prepared membranes were evaluated in terms of effectiveness, feasibility and sustainability, and the results were compared to those of commercial Nafion membrane, used as reference.

The interplay between the chemical-physic, structural and electrochemical properties of S-PEEK membranes with different sulphonation degree and of the filler content grade was evaluated.

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Selective photocatalytic partial oxidation of aromatic alcohols to aldehydes in aqueous suspensions of C_3N_4 obtained by polycondensation of melamine and cyanuric/barbituric acids

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Carbon nitride has been successfully used for partial photo-oxidation reactions of alcohols in aqueous suspensions achieving high yields of aldehydes [1]. In the present research, some materials based on the organic semiconductor polymer C_3N_4 have been prepared from melamine along with cyanuric and barbituric acids to be used as photocatalysts under UV and visible light irradiation [2]. The obtained semiconductors were physico-chemically characterized and they have been used as photocatalysts for the selective partial photo-oxidation of aromatic alcohols in water suspension at room conditions. The photocatalytic activity of these materials was compared with that of commercial TiO_2 Evonik P25. Aromatic alcohols, i.e. benzyl alcohol and derivatives possessing substituent in para- position were photocatalytically oxidized to the corresponding aldehydes. Noteworthy, the aldehydes obtained from the partial photo-oxidation of these alcohols are important intermediates for the synthesis of fine chemicals and, moreover, they bear different substituent groups influencing conversion and selectivity [3].

The materials were subjected to physico-chemical characterization including XRD, SEM, specific surface area measurements, FTIR, DRS and photoelectrochemical insights.

The presence of cyanuric acid slightly modified the C_3N_4 structure obtained by polycondensation of melamine. By increasing the amount of barbituric acid in the preparation, both a decreasing of the order of the structure and the ability of light to activate the material was observed, and consequently the photocatalysts showed to be less active. Also, the type of the substituents in the –para position of the aromatic alcohol substrate strongly influenced conversion and selectivity of the reaction, being the presence of the electron-releasing group ($–OCH_3$) the most beneficial for the reactivity. The most active material was prepared in the presence of melamine and cyanuric acid, showing a complete conversion of 4-methoxybenzyl alcohol with a 100% selectivity towards the aldehyde even under visible irradiation, so opening the possibility to use this material for selective oxidations under solar conditions.

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Crystalline Molecular Rotors Assembled through Halogen Bonding

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Amphidynamic crystals are materials designed to possess rapidly moving components (rotators) in the solid state.[1] Typically, molecular design in this field has taken inspiration from structures akin to those of macroscopic compasses and gyroscopes to explore and control rotation in the solid state. Rotation in solids has been studied in molecular crystals, inclusion compounds, metal organic frameworks (MOFs), porous molecularly ordered (PMO) silicates, and amorphous solids.[2]

In this communication, we report a crystal engineering approach where stators and rotators are assembled in cocrystals resulting in the high-yield synthesis of active supramolecular rotor arrays. Specifically the supramolecular rotors, discussed here, have been assembled through halogen bond (XB).[3]

We studied molecular motions of a series of halogen-bonded cocrystals involving 1,4-diazabicylo[2.2.2]-octane (DABCO) and several differently functionalized halobenzenes. Crystal structures, dynamic performances and thermodynamic parameters of the halogen bonded supramolecular rotors will be discussed highlighting similarities and differences between halogen bonded rotors. [4,5] For example in one system the fast rotation of DABCO follows a six-fold potential energy surface with three lowest energy minima showing a very low activation energy, the lowest reported in the field of amphidynamic crystals (Figure 1).

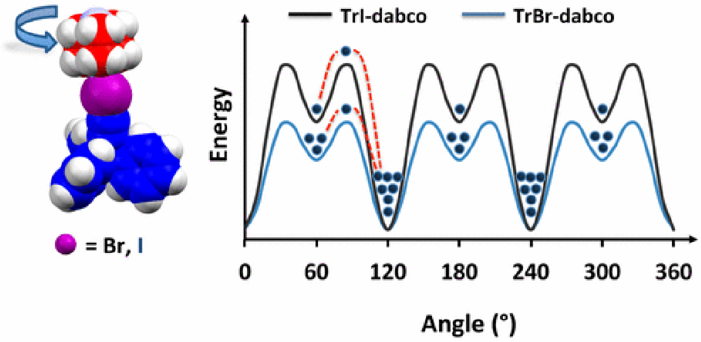

Figure 1. Crystal structure and potential energy surface for the rotation of DABCO in the XB rotors.

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Multi-branched perfluoro-*tert*-butoxyl scaffolds for the functionalization of surfaces and nanomaterials

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Fluorinated materials play a constantly increasing role in materials science, medicine, industry and technology. Among them, per- and poly-fluoroalkyl compounds with chains longer than six carbon atoms have been banned, because of their environmental impact and bioaccumulative potential.[1] In the search of more sustainable alternatives, we focused on a multi-branched fluorinated scaffold with several short-chain perfluoroalkyl groups (27 F atoms per molecule) surrounding a hydrocarbon polar core (Figure 1). The presence of ether bonds in the core may hasten degradation in the environment and in physiological conditions, thus overcoming bioaccumulation issues.

This moiety can be linked to different functional groups, including thiols, alcohols, carboxylic acids or esters, azido- or amino- functionalities, leading to a variety of possible applications. For example, a derivative containing a thiol unit (X = $(CH_2)_2SH$ in Fig. 1) was effectively used as stabilizing ligand of fluorous NIR-luminescent gold nanoclusters.[2] More recently, its self-assembled monolayers on gold and copper surfaces afforded stable (super)hydrophobic coatings, with an even better frictional behavior if compared to commonly used long-chain perfluoroalkylthiols.[3]

Finally, the carboxylic derivative of this fluorinated scaffold (X = CH_2CO_2H) has been successfully esterified with cellulose. The resulting innovative materials showed tunable mechanical and wettability properties, and appeared extremely promising for their potential use as waterproof-breathable films or coatings in textiles.[4]

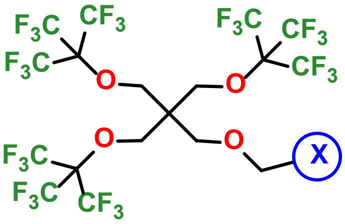

Figure 1. Chemical structure of the selected multi-branched highly fluorinated scaffold.

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A dinuclear Zn(II) Schiff-base complex as molecular tweezer: binding properties and sensing towards biogenic diamines

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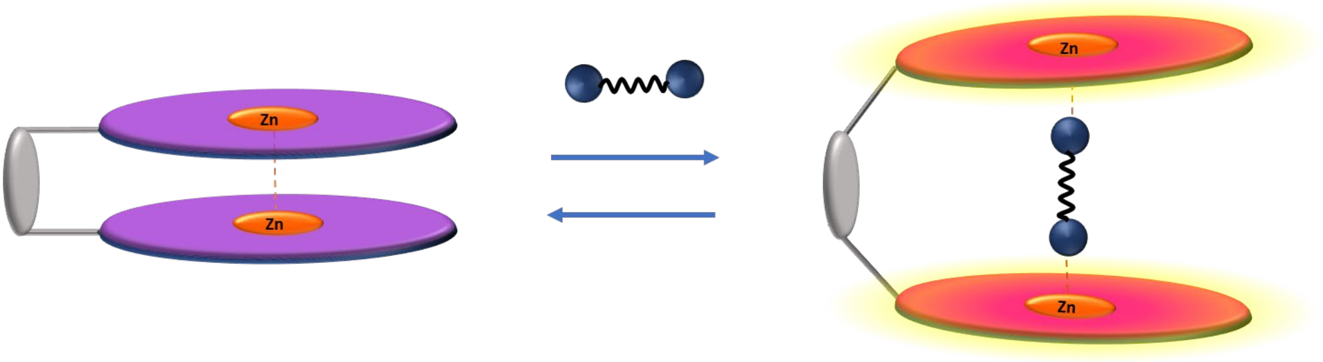
Recently, Zn(II) salen-type complexes have been studied for their aggregation and sensing properties, mostly related to their Lewis acidic characteristics. These complexes interact with Lewis bases to form stable adducts.[1]

A dinuclear Zn(II) salen-type Schiff base complex with a flexible spacer, derivative from the 2,3-diaminomaleonitrile, has been synthesized and characterized. It has been demonstrated that it behaves as a molecular tweezer towards ditopic amines.[2] In fact, in non-coordinating solvents the complex is stabilized as a monomeric aggregate by Zn···O intramolecular interactions, which in the presence of strong ditopic Lewis bases, deaggregates with formation of stable, intramolecular cyclic 1:1 adducts:



The deaggregation leads to remarkable variations in the optical absorption and fluorescence spectra. Thus, the binding properties towards a series of ditopic diamines of different lengths and flexibility have been studied. For α,ω-aliphatic diamines, binding constants progressively increase with the increasing length of the alkyl chain, thanks to the flexible nature of the spacer. Stable adducts are also found even for the short, rigid diamines.

Given its unique characteristics, this molecular tweezer can be exploited for the colorimetric and fluorometric detection of biogenic diamines. Biogenic diamines are the product of the degradation of various aminoacids and have various physiologic roles. In particular histamine is responsible for allergic response and high levels of this biogenic amine are indicators of food spoilage.[3] The sensing properties of the complex towards different biogenic diamines have been studied, and the ability as chemodosimeter for histamine, cadaverine, putrescine, spermidine and spermine has been demonstrated. Competitive experiments for the selective detection of histamine have been performed and the practical application for quantification of histamine in a fish matrix has been demonstrated.[4]

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Dynamic 1D Bispidine-based Coordination Polymers for Adsorption Applications

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Research on Coordination Polymers (CPs) has increasingly advanced in recent years. The self-assembly between specifically designed organic ligands and carefully selected metal salts has produced functional materials with wide applications in areas such as storage, separation and catalysis.[1] In particular, dynamic CPs are especially interesting due to their ability to structurally adapt in response to an external chemical or physical stimulus.[2] This can be of real advantage in adsorption applications, especially for 1D CPs, whose specific architecture does not frequently warrant for a porous structure, usually required for this purpose. However, there are several examples of 1D CPs able to adsorb gas and larger molecules mainly due to their intrinsic flexibility.[3]

In this work, we report on a new family of dynamic 1D CPs with tunable adsorption properties. Novel bispidine ligands having different chemical substitutions at position 7 (Figure 1a) were designed and synthesized to explore whether a structural modification in the ligand could control the final dynamic attitude of the materials. 1D Mn-based CPs were produced in the form of single crystals (SCs); their detailed structural characterization showed the formation of non-interpenetrated 1D ribbon-chains (Figure 1b) assembled *via* weak inter-ribbon interactions, which define different packing orientations in each system.[4,5,6]

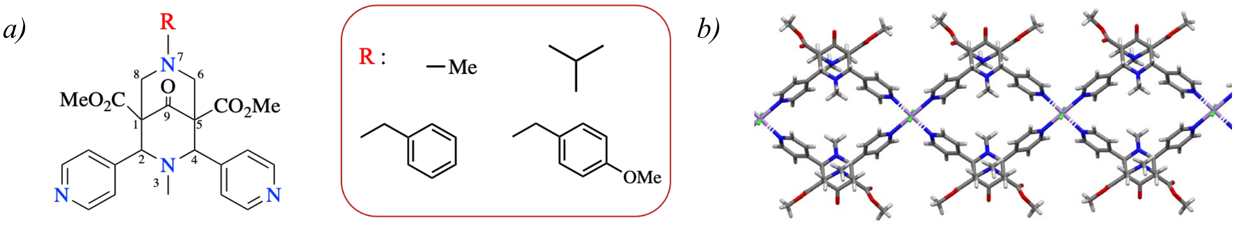

Figure 1. a) Schematic representation of different functionalization on aliphatic aminic group of bispidine. b) 1D ribbons of repeating 2:1 ligand:metal complexes.

Reproduced also in form of microcrystalline powders and characterized by PXRD, NMR, TGA and *ab initio* PXRD[5], these novel 1D CPs feature a highly dynamic attitude in terms of adsorption capability and selectivity as demonstrated by heterogeneous solid/liquid and solid/vapor guest exchange and selective adsorption reactions.[6] Additionally, we proposed a way to predict the dynamic behavior of a given CP by evaluating the packing efficiency of the ligand alone in the solid state *via* DFT calculations based on SCXRD data of the corresponding ligands.[7]

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Mechanism of oxygen evolution and Mn_4Ca cluster restoration in the natural water-oxidizing catalyst

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Water oxidation reaction occurring in the first steps of the natural oxygenic photosynthesis is catalyzed by the pigment/protein complex Photosystem II. This process takes place on the Mn_4Ca cluster located in the core of Photosystem II and proceeds along the five steps (S_0-S_4) of the so called Kok-Joliot cycle until the molecular oxygen release. The catalytic cycle can therefore be started afresh through insertion of a new water molecule. Understanding the molecular mechanisms behind this photoreaction will unravel the secrets of solar energy conversion in biochemistry and may inspire the design of artificial bio-mimetic materials for green energy production. Starting from available experimental data [1,2], in the last years we contributed by means of theoretical calculations to refine the structures of the first states of the Kok-Joliot cycle [3-6] and shed light on the possible catalytic mechanism of PSII at atomic level. In the present study, using QM/MM Molecular-dynamics simulations and Minimum-Energy-Path calculations, we elucidated the structural and thermodynamic aspects at the basis of the O-O bond formation, O_2 release and water insertion occurring in the last steps of the Kok-Joliot cycle.

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A new electrochemical platform for fast and efficient determination of dominant non-psychoactive cannabinoids in Cannabis Sativa

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Cannabidiol (CBD), see Figure 1, is a non-intoxicating and non-psychoactive component of the *Cannabis sativa* plant linked to many health-beneficial effects. Hemp, the main source of CBD, has been long known and cultivated for the production of oil, seeds, fiber, and foodstuff. Although many countries, especially in North America and Europe are legalizing cannabis, whether for medical or recreational use, relevant researches lag far behind the needs. Among the knowledge gaps in CBD studies, special and urgent need is seen in sensing and measurement of cannabinoids as a key factor in practical and reliable evaluations. To fill this void and in parallel with a rise in daily cannabis consumption, a variety of analytical approaches have been proposed to measure CDB in a reliable and effective way, based mainly on chromatographic techniques, e.g. HPLC, GC, and LC, which are generally, time-consuming, multistep, costly, and require trained operators. Here, in a preliminary study, we address these challenges by developing an electrochemical platform capable of measuring CBD in an inexpensive, simple, and yet quite sensitive way (Figure 1).

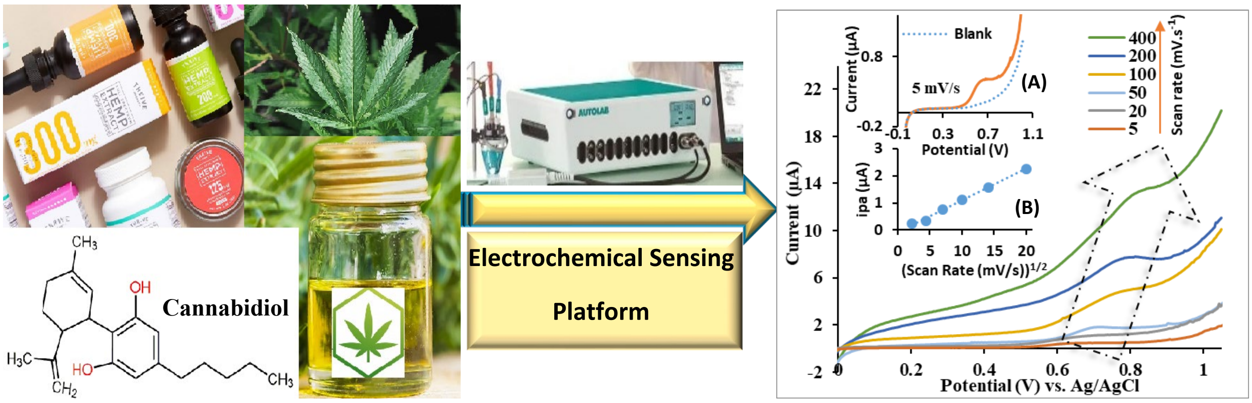

Figure 1. General scheme of the proposed sensor for CBD. Left panel shows chemical structure CBD and natural plant of Hemp. Right panel shows effect of increasing the scan rate on electrochemical behavior of CBD. Inset (A) linear sweep voltammogram of CBD at very low scan rate (5 mV/s). Inset (B) Variation of oxidation peak current of CBD against potential sweep rate.

This electrochemical sensor was designed based on a modified carbon paste electrode in which different carbonaceous materials, i.e. activated carbon, graphene, and multi-wall carbon nanotube were incorporated into the base electrode. The obtained results showed that the presence of these carbon-based modifiers not only changes the sensitivity of the bare electrode, but also substantially alters the peak potential and consequently the selectivity. Linear sweep voltammetry analysis (Figure 1, right panel) clearly shows that in a phosphate buffer solution 0.1 M, a well-defined peak appears for CBD oxidation at the potential of ca. 650-750 mV (vs. Ag/AgCl). Peak currents vary linearly with increasing the potential sweep rate revealing the diffusion-controlled nature of this electrochemical reaction. Furthermore, oxidation peak potentials shift positively as the potential sweep rate increases, suggesting a kinetic limitation in electron transfer between CBD molecules and electrode surface that emerges at higher potential sweep rates. Nevertheless, we demonstrated here that, operating at intermediate sweep rates, e.g. 50 mV s^{-1}, the sensor can successfully measure CBD concentrations.

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Crown ether functionalized graphene quantum dots as electrochemical and fluorescence based sensors for the selective detection of potassium and sodium ions

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Normal physiological functions of the human being are regulated by a fine balance of various trace elements. Among these, sodium and potassium ions are essential electrolytes for human homeostasis and their quantification in body fluids such as serum, sweat and dermis, is of crucial importance in clinical diagnostics.[1] In this work we have explored the electrochemical and optical properties of graphene quantum dots (GQDs),[2] and the selective chelating ability of the crown ethers 15-crown-5 and 18-crown 6[3] with the aim to develop sensitive and selective fluorescent and electrochemical sensors for the determination of sodium and potassium ions. GQDs, synthesized by acidic oxidation and exfoliation of multi-walled carbon nanotubes (MWCNTs) have been covalently conjugated with 15-crown-5 or 18-crown-6 to afford the sensing elements GQDs-15-crown and GQDs-18-crown-6 (Fig. 1).

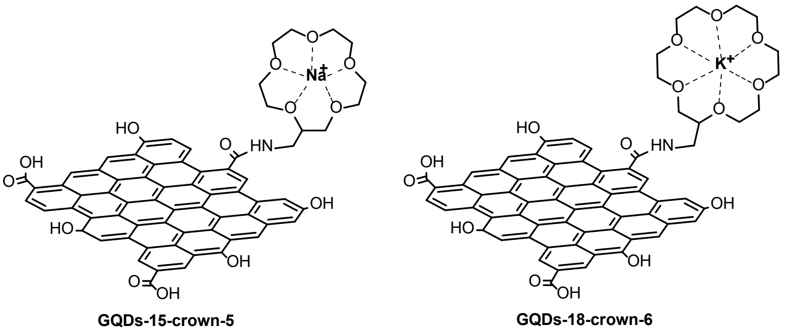

Figure 1. Crown ethers functionalized GQDs for sodium and potassium ions detection.

The electrochemical and photoluminescence performance of the conjugated systems have been evaluated at the concentration range of 1 to 1000 mM in order to investigate the ions selectivity of these. The results of this study have demonstrated that their fluorescence behavior has promising applications for the development of simple, rapid and sensitive optical sensors for the detection of Na^+ and K^+ ions.

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Electrochemical and sensing properties of 2D-MoS$_2$ nanosheets produced via liquid cascade centrifugation at different rate

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Two-dimensional molybdenum disulfide (2D-MoS$_2$) nanosheets are promising electrode materials for advanced applications in the field of electrochemical sensing due to their large specific surface area and charge carrier mobility as compared to bulk material [1, 2]. However, the production of high quality and defect-free MoS$_2$ nanosheets is a big challenge today.

In this communication, layered 2D-MoS$_2$ were prepared via liquid cascade centrifugation (LCC) and their microstructural, morphological and electrochemical characteristics were investigated. The microstructural and morphological characteristics of 2D-MoS$_2$ nanosheets obtained at different centrifugation rate were evaluated by UV-Vis, Raman spectroscopy, and SEM analysis. The 2D-MoS$_2$ nanosheets obtained showed a monotonic decrease of lateral sheet size <L> and layer number <N> with the increase of centrifugation rate (Fig. 1a, b). Screen printed carbon electrodes (SPCE) were modified depositing by drop casting 2D-MoS$_2$ nanosheets from aqueous dispersion obtained at different centrifugation rate. The electrochemical properties of the modified 2D-MoS$_2$/SPCE were assessed by electrical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in $[Fe(CN)_6]^{3-/4-}$ redox probe. Dopamine (DA) and riboflavin (RF) were also tested to investigate the role of <N> and <L> of MoS$_2$ nanosheets in the electrochemical sensing of these two biomolecules.

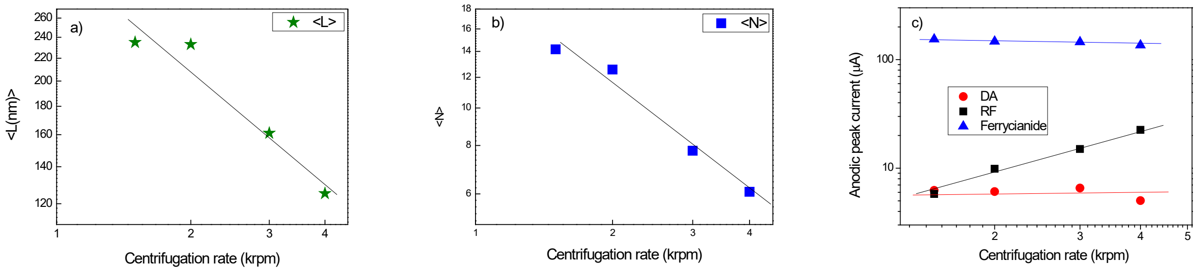

Figure 1. Properties of the MoS$_2$ nanosheets prepared at different centrifugation rate: a) Mean size; b) Mean number of monolayers; c) anodic peak current.

Results demonstrated no significant variations in the electrochemical parameters using the different modified electrodes in the presence of DA. Instead, the electroxidation of RF was found largely promoted with the 2D-MoS$_2$ sample having smaller lateral size and reduced number of layers provided by increasing the centrifugation rate (Fig. 1c).

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Hybrid solar cells operating in aqueous environment

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Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A key aspect to be considered in any PV technology is the operational durability under real outdoor conditions, as well as the sustainability of materials/components and the facile integration with energy storage systems.

In the last five years, dye-sensitized solar cells (DSSCs) with water-based electrolytes have been considered as one of the possible breakthroughs towards DSSCs large-scale diffusion. If opportunely developed and optimized, aqueous solar cells can be truly considered as zero-impact photovoltaic devices fabricated with non-toxic components [1-5].

We show here the possibility of jellying the electrolyte into a solid matrix to boost stability, the possible use of different redox mediators solvated by water, the formulation of TiO_2 pastes for screen-printable photoanodes operating in water, and the replacement of Pt cathodes with more sustainable alternatives.

Overall, we will show how much water-based photovoltaics represents a challenging topic in the current energy scenario, and how it will be able to provide safe, sustainable and easily processable solar cells for building-integrated photovoltaics and portable electronics.

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A new synthetic approach for size-tunable and stable $CsPbBr_3$ nanocubes with near-unity photoluminescence quantum yield

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Cesium lead-halide perovskites nanocrystals (NCs) are composed of cuboctahedral structures with a marked ionic nature and chemical formula $CsPbX_3$, in which Cs^+ is surrounded by eight corner-sharing PbX_6^{4-} octahedra with their vertices occupied by halides.[1] Due to their potential near-unity photoluminescence quantum yields (PLQY), narrow emission profiles, and tunable fluorescence peaks in the green region, $CsPbBr_3$ NCs can be considered the ideal candidates for optoelectronic devices.[2] On this ground, it is of high importance the development of a general synthetic route capable of combining the best of photophysical properties characterizing $CsPbBr_3$ NCs with a sufficient stability, rarely observed in this class of nanomaterials. In this presentation, starting from our recent studies on perovskite NCs,[3] we will describe a synthetic protocol for the obtainment of near-unity PLQY perovskite nanocubes ensuring their size control and, consequently, a narrow and intense emission through the modification of the reaction temperature and the suitable combination ratio of the perovskite constituting elements. The peculiarity of this protocol is represented by the dissolution of the lead precursor ($PbBr_2$) as a consequence of complexation with the bromide anions released by the in situ SN_2 reaction between oleylamine (the only surfactant introduced in the reaction mixture) and 1-bromohexane (Figure 1A). By varying the synthetic parameters, the obtained $CsPbBr_3$ nanocubes exhibited *i*) variable size (ranging from 6.7±0.7 nm to 15.2±1.2 nm), *ii*) PL maxima between 505 and 517 nm, and *iii*) near-unity PLQY with a narrow emission profile (fwhm of 17−19 nm) (Figure 1B-C).

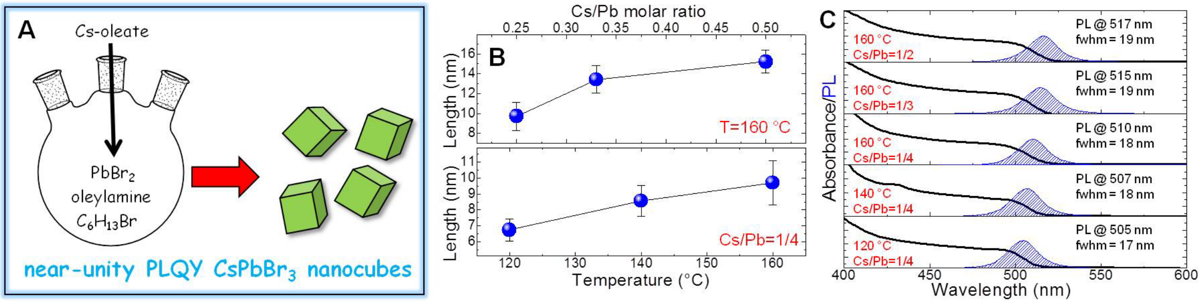

Figure 1. (A) Synthetic scheme, (B) sizes and (C) optical properties of near-unity PLQY perovskite NCs as a function of the experimental conditions.

Additionally, the NCs synthesized by this approach preserved their high PLQYs even after 90 days storage under ambient conditions. Therefore, the proposed synthetic protocol can provide new insights for the direct preparation of differently structured perovskite NCs without resorting to any additional post-synthetic treatment for improving their emission efficiency and stability.

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BMIm-BF_4: a versatile ionic liquid for BF_3 generation and reactions

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Boron trifluoride is a Lewis acid very often used in organic synthesis to carry out acid catalyzed transformations. Nevertheless, its use may be hampered by its high reactivity, volatility and toxicity. [1] Often, to make it easier to handle, complexes of BF_3 and ether are used, but even in these forms there are some drawbacks, such as their corrosive properties, flammability and sensitivity to moisture. [2,3]

For these reasons, we were interested in an alternative and less dangerous source of BF_3, possibly generated *in situ*, without the necessity of storing. The electrochemical oxidation of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF_4) efficiently generates BF_3 from BF_4^-. [4] Thus, we carried out some classical BF_3 catalyzed reactions in anodically oxidized BMIm-BF_4, being this ionic liquid easy to recycle after ethereal extraction.

In comparison with literature data on the use of BF_3-etherate in classical organic solvents, in the investigated reactions analogous or improved results were obtained. Moreover, the noteworthy advantages of the developed method are the *in situ* generation of the BF_3, the possibility to generate the exact amount of required catalyst using the electron as redox reagent, the absence of fumes production, the reduced sensitivity to moisture and the possibility of ionic liquid recycling for subsequent reactions.

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Eco-design of Cellulose NanoSponges for water decontamination

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The design and development of engineered nanomaterials and nanoparticles (ENMs/NPs) for the pollution remediation of water bodies has significantly reached considerable levels of advancement. However, the current lack of knowledge of their fate and transformation once released in the aquatic environment raises concerns in terms of potential impact. To overcome these limits, a safer-by design concept should be followed in developing innovative (nano)-solutions, capable to set at minimum any toxicological effects, while maintaining high efficiency in the remediation action [1]. The correct choice of the starting material and of the synthetic protocol could provide new safe-by-design solutions for this purpose [2].

Herein we report the eco-design strategy used for the development of eco-friendly highly porous cellulose-based nanostructured sponges (CNS), obtained by a thermal cross-linking between TEMPO-oxidized cellulose nanofibers (TOCNF) and branched polyethyleneimine 25 kDa (bPEI) in the presence of citric acid [3]. Ecotoxicology proved to be a useful tool to design the safer solution. CNS resulted to be effective sorbent units for heavy metals removal from both fresh and seawater [4,5], and for the efficient adsorption of organic dyes [6].

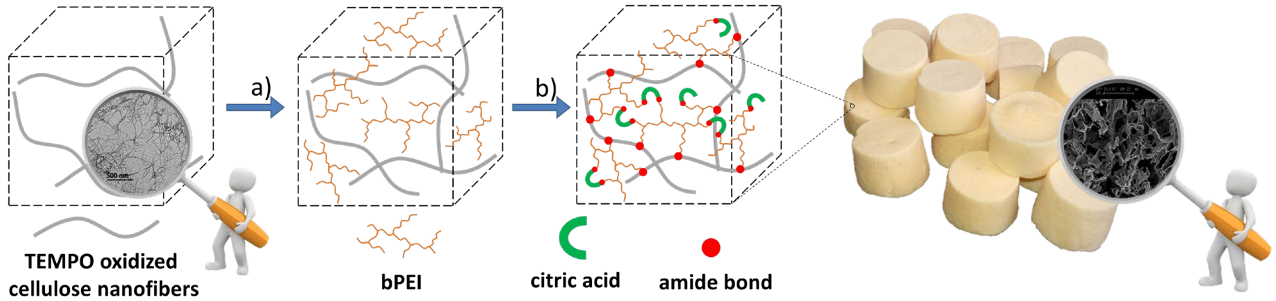

Figure 1. CNS: synthesis and remediation.

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Structural characterization and *in-vitro* anticancer activity of nanovectors for delivery of bioactive coumpounds.

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Since ancient time, it is well known that plant extracts have diverse biological activities and have been used for the treatment of different diseases. Among these extracts there is isofuranodiene (IFD), a lipophilic sesquiterpene isolated from wild celery (Smyrnium olusatrum L., Apiaceae) which proved to have multiple anticancer activities, anti-inflammatory and hepatoprotective effects.

Once isolated in the solid state, IFD is not stable and may undergo a thermal conversion to curzerene which is much less active and for this reason pharmaceutical formulations for its delivery can be considered so to preserve its integrity and to enhance its solubility and bioavailability. Therefore, including the IFD molecule in specific nanocarriers can improve its bioavailability and thus its therapeutic performances. In this study, liquid crystalline vectors such as cubosomes and hexosomes were employed. These new generation drug delivery vehicles enable high drug encapsulating efficiency lipophilic drugs as in the case of IFD which, in our experiments, was encapsulated with more than 90% efficiency. A very good compatibility between the lipophilic drug and the lipid portion of matrix was evident and supported by both structural and chemical characterization carried out through a combination of synchrotron small-angle x-ray scattering (SAXS) and UV Resonance Raman (UV-RR) spectroscopy at Elettra Sincrotrone. Incorporation of the lipophilic IFD in the matrix induced an increase in the volume of the hydrophobic moiety with consequent variation of the spontaneous curvature of the lipid membrane toward a more negatively curved mesophase thus favouring the transition from a cubic *Im3m* to a reverse hexagonal H_{II} phase (Fig. 1a-b). Significant shifts in the components of the IFD Raman spectrum were observed upon its loading in GMO matrix (Fig. 1d) and in particular of those functional groups as the C=C double bonds in IFD molecules which may be influenced by the more hydrophobic environment experienced by encapsulated IFD. Since IFD was found to be an antiproliferative agent towards different kinds of cancer cells and also toward the MDA-MB-231 cells which have the same characteristics of one of the most aggressive subtypes of breast cancer, the TNBC, the *in-vitro* anticancer activity of IFD-loaded nanoparticles was assessed on this particular kind of cancer cells by using the MTT assay. IFD encapsulation in GMO nanoparticles resulted in a significantly enhanced anticancer activity of the loaded nanoparticles compared to the empty ones

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3D integration of pH-cleavable drug-hydrogel conjugates on magnetically driven smart microtransporters

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Targeted drug delivery is a currently challenging but promising approach to overcome some limits of classical pharmaceutical formulations. [1,2] One of the most convenient way to gain control over this type of delivery is the employment of stimuli-responsive materials, able to release drugs only in the site required. [3] An interesting development in the last years involves the use of remotely controlled microdevices in support of this technique. Thanks to this synergy, release can be efficiently controlled both spatially and temporally: devices can be precisely guided to release in targeted locations, whereas temporal control can be achieved by specific functionalization introduced in the stimuli-responsive material. [4, 5]

In this context, the present work describes the functional coating of magnetically controlled microdevices with alginate-based hydrogels able to release drugs mimics at pH values lower than 4.5. The polymers employed have been modified binding the test molecule with cleavable bonds, following an innovative synthetic route. The devices were then magnetically actuated, and their spatial control demonstrated; after the coating process, release from the hydrogels covering the microdevices has been monitored and characterized as a function of the environmental pH, with excellent results. [6]

The here described functional microtransporters have been demonstrated to be particularly promising for *in vivo* applications in body districts where pH gradients are present, like the digestive apparatus.

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Calcium Alginate hydrogels in Semi Solid Extrusion 3D printing: physico-chemical requirements for high printing performance

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Among the polysaccharidic polymers, the alginate, due to its properties i.e. natural source, biocompatibility, biodegradability and pH-dependent solubility is widely studied as pharmaceutical carrier in several innovative drug delivery systems. In particular, the crosslinked network obtained after the interaction of alginate with divalent cation such us calcium or zinc is exploited to produce beads, micro- and nanoparticles [1].

Since 2015, the 3D-printing technologies, a new subset of additive manufacturing processes, are drawing the attention of pharmaceutical compounders, thanks to their rapid prototyping and high manufacturing flexibility, helping to shift from traditional to personalized therapeutic approach [2]. Among them, the semi solid extrusion (SSE) 3D printing can be considered the most promising technology for the bioprinting and drug delivery systems (DDS) production [3]. In the SSE printing process, characterized by mild working conditions and relative ease in obtaining very high drug loads, the 3D objects are obtained through the extrusion of the ink, a polymeric pasta or gel, onto a building plate via a syringe like system. Focusing on the use of gels, and in particular alginate hydrogels, some studies highlighted two critical issues that must be overcome to successfully apply this technology in the pharmaceutical field: the shape fidelity during the printing and the matrix collapsing after drying [4]. Aiming to overcome these issues, several strategies have been proposed, from the post printing curing with divalent cations solutions, to the coupling with other functional excipients such as nanofibrils. In this work, we field another promising strategy as a possible solution to overcome the sodium alginate limits in the SSE process: a pre-crosslinking step of the ink gel with low amount of Ca^{2+}, to improve the hydrogel performance and simplify its use in SSE 3D printing for the development of DDS [5]. To verify this hypothesis, the influence of different Ca^{2+}concentrations (10; 12; 15; 18; 20; and 25mM), leading to different degrees of the crosslinked structure, on physico-chemical properties of alginate gel was investigated and related with the resulting printability. In details, the evaluation of gels extrudability, using pre-set parameters, showed a relationship between the DDS shape retention after printing and the rheological properties of gels and allowed to identify a share thinning behaviour as a fundamental requirement for the successful alginate ink printing. Finally, with the aim to avoid the DDS collapse after drying, several excipients were evaluated (lactose, mannitol, talc, cellulose), with the mannitol being the most promising. In fact, the addition of mannitol improved the shape retention without significantly affecting the rheological characteristics of the gels.

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Mixed oxide Cerium coating for improved titanium nanotubes bioactivity

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Despite the significant contribution of Titanium and its alloys for hard tissue regenerative medicine, some major issues remain to be solved. Implants long term stability is threatened by the poor ability of pure titanium to interact with surrounding tissue and by the consequent scarce osseointegration. Bacteria adhesion and excessive inflammatory response from the host are also to be considered in the design of a device intended to be integrated in the human body.

Fabricating a TiO_2 nanotube array (TiNT) by direct electrochemical anodic oxidation of the titanium substrate responds to the demand for improved cell growth ability. Coating with bioactive materials allows for control and tuning over surface properties which in turn can guide toward high-performance new biomaterials.

Here, a cerium mixed oxide (CeO_x) coating was realized onto optimized TiNT surfaces using a simple layer-by-layer drop casting technique. Surface composition, electrochemical response and *in vitro* ability of inducing hydroxyapatite precipitation were evaluated as a function of the cerium quantity on the surface. The presence CeO_x enhanced the material ability to induce early precipitation of hydroxyapatite (HA) from a simulated body fluid at physiological temperature. When CeO_x concentration exceeds 4%wt, HA maturation in a (poorly) crystalline form, indicating an interesting potential to induce rapid in vivo osseointegration process [1].

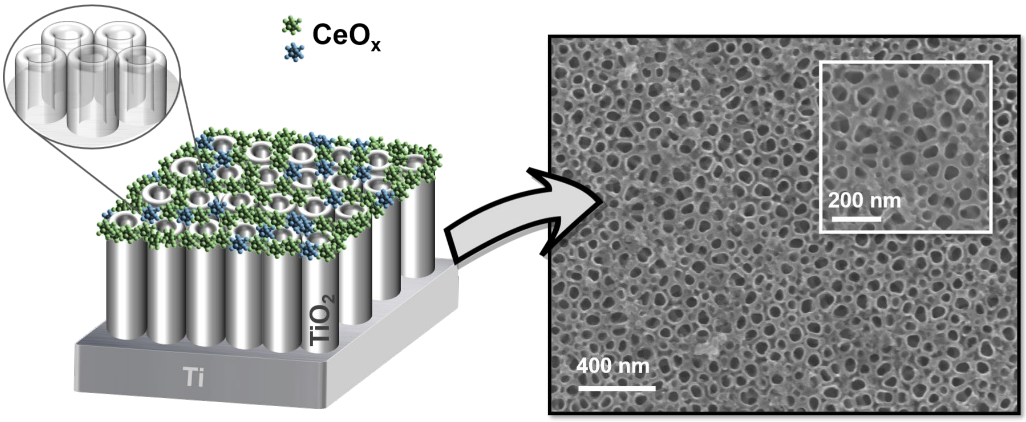

Figure 1. Schematic representation and SEM micrographs of the cerium coated titanium nanotube system

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Adipose stem cell spheroids-laden hydrogels for minimally invasive bone and cartilage regeneration interventions

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Xyloglucan (XG) is a very common hemicellulosic polysaccharide present in the primary cell wall of most vascular plant. It is also a storage polysaccharide in seeds. Xyloglucan extracted from tamarind seeds (TS) is characterized by a β-(1, 4)-D-glucan backbone that is partially substituted by α-(1, 6)-D-xylose. Some of the xylose residues are further substituted by β-(1, 2)-D-galactoxylose. TS-XG is commercially available, biocompatible and FDA-approved for food applications. XG is water-soluble because of the highly branched structure that prevents extensive chain association. Enzymatic cleavage of some of the galactose residues provides XG with temperature-induced gelation properties. In particular, when about 35% of the galactose residues are removed, the aqueous dispersions of this partially degalactosylated xyloglucan (dXG) exhibit both a lower sol-gel (~25 °C) and a higher gel-sol (~100 °C) transition temperature. Hence, dXG can be used as an in-situ gelling polymer at body temperature (37 °C). [1]

In-situ gelling biocompatible polymer solutions laden with stem cells can be very useful for minimally invasive tissue regeneration interventions. They can avoid uncontrolled cell spreading and poor integration with the surrounding tissue. Hydrogels can meticulously look like the native ECM, due to their interconnected pore architecture, high water content and willingness to incorporate biomolecules. Therefore, they offer a 3D-structured environment to host and mechanically support cell growth, and to allow gases, nutrients and cell catabolites exchange. [2]

Adipose-derived mesenchymal stem cells (ASCs) represent a great promise for tissue regeneration as fat is a very abundant source of stem cells and they can self-renew and differentiate into several specific cell types. They are usually cultured as two-dimensional (2D) adherent monolayers, that is not representative of the in vivo condition and often entails lower viability and, more in general, lower "cell quality" in terms of regenerative potential. When ASCs are cultured in low adhesion flasks and with a suitable culture medium, they aggregate in the form of three-dimensional spheroids (SASCs). [3] The incorporation of SASCs into injectable dXG hydrogels, in the presence of properly chosen signaling molecules, has been recently proven to be an effective methodology to grant SASCs viability and preserve their stemness. [4] The most recent advancements of our work demonstrate that by simply modifying the type of signaling molecules present in addition to dXG, the forming hydrogel can actually promote SASC differentiation in either osteogenic or chondrogenic cells. Therefore, these formulations are very promising for the repair of both cartilage and bone defects, that are still a challenge for modern medicine. The biological properties are related to the hydrogels' morphological and rheological properties. The injectability of SASCs-laden formulations is also investigated.

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k- Carrageenan and PVA blends as bioinks to 3D print scaffolds for cartilage reconstruction

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Some polysaccharides have an inherent ability to form strong networks in mild conditions, thanks to their structural composition and self-assembly behavior in aqueous media. k-Carrageenan (k-C) is one of the most noticeable examples [1]. k-C is a sulfated polygalactan obtained from red seaweeds with 25 to 30% of ester-sulfate content and an average relative molecular mass well above 100 kDa. It is formed by alternate units of D-galactose and 3,6-anhydro-galactose (3,6-AG) joined by α-1,3 and β-1,4-glycosidic linkages. The polymer is strongly anionic and, as the free acid is unstable, it is sold as stable sodium potassium and calcium salts or, most commonly, as a mixture of these. It resembles the glycosaminoglycans (GAGs) which are the central constituents of connective tissues. For this reason, k-C can be considered a suitable scaffolding material for tissue engineering.

k-C is water-soluble at temperature above 60 °C and can set into stable gels with decreasing temperature. Networks of k-C are strong, brittle and characterized by a multilamellar morphology. The absence of interconnected porosity may limit the scaffold colonization by cells and the access of nutrients and oxygen. k-C blends with other more resilient polymers, like polyvinyl alcohol (PVA), can improve the mechanical properties and create porosity.[2]

Hydrogels are often used as bio-inks for 3D printing processes that aim to reconstruct the extracellular matrix of relatively soft tissues. The possibility of controlling the printing process on the basis of a computer-aided design (CAD) of the patient's damaged or missing body part holds the promise of manufacturing patient-specific structures. [3] The physicochemical and biological properties of the formed hydrogel have to be harmonized with the viscoelastic behavior of the formulation during and after the extrusion from the printing nozzle. Physically crosslinked hydrogels are often preferred over chemically crosslinked systems because they do not require the presence of initiators and catalysts, that might induce cytotoxicity and require accurate purification.

Our study explores the suitability of aqueous k-C/PVA systems with three different weight ratios between the two polymers for the 3D printing of scaffolds for cartilage reconstruction. Their rheological behavior was investigated for its impact on both processing and product properties. In addition, the mechanical properties and morphological features were investigated for both the hydrogels as prepared and after a freeze-thaw treatment for one day (FT1). The practical printability of the formulations was also tested. Spheroids of Adipose-derived Stem Cells (SASCs) were seeded on the hydrogels and cultured for 21 days in the presence of two different media, the first one that should ensure stemness conditions (SCM) of SASCs and the other one that stimulates stem cell differentiation in chondrocytes (CDM). Cell viability was preserved in SCM for two of the three formulations, while a significant increase in cell viability was observed for all the formulation when cells where cultured in CDM.

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Adducts of functionalized graphene layers with Ag nanoparticles for antimicrobial applications

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Health and environmental impacts of multi-drug resistance (MDR) pathogens are becoming more and more relevant nowadays, thus increasing the need of developing new, safe and effective antimicrobials.

This research was focused on the synthesis, the characterization and the evaluation of the antimicrobial and cytotoxic activity of hybrid nanomaterials made up through a simple and sustainable functionalization of three carbon substrates, namely Graphite, Carbon black and Carbon nanotubes, with a pyrrole moiety (SP) and silver nanoparticles (Ag-NP) [1, 2]. The adducts were analyzed by means of thermogravimetric analyses (TGA), transmission electron microscopy (HRTEM) and X-ray diffraction analyses (WAXD), which confirmed the successful functionalization of raw materials. UV-vis spectroscopy and dynamic/electrophoretic light scattering (DLS/ELS) provided information regarding carbon suspensions stability, particles sizes and surface charge. Results from microbiological tests revealed an outstanding enhancement of the antimicrobial activity promoted by the functionalization with Ag nanoparticles, maintaining unaltered the cytotoxic levels exerted by not-functionalized materials. In the light of these results, a possible bactericidal mechanism based on the synergy between mechanical and oxidative stresses at the bacterial membrane level is proposed.

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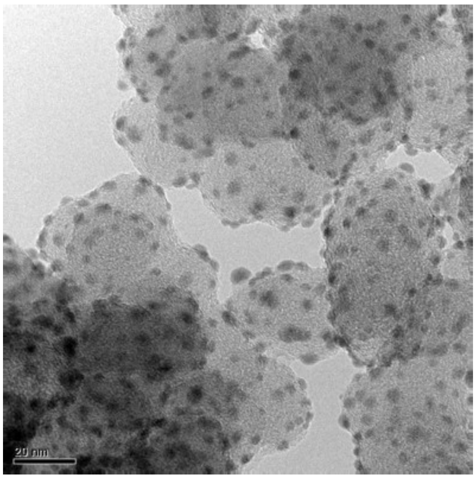

Figure 1 - HRTEM micrograph representing CB functionalized with SP and Ag-NP. Black dots on the surface are Ag NPs.

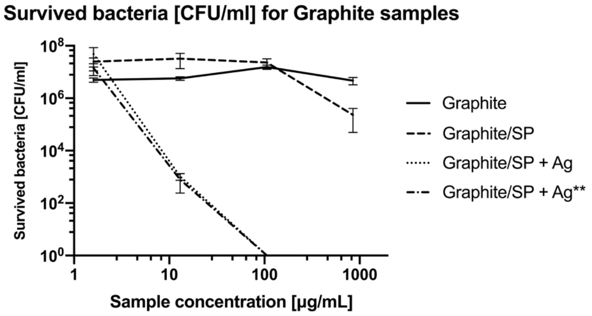

*Figure 2 - Antibacterial activity of Graphite samples represented as number of survived bacteria (Colony Forming Units (CFUs)) after 24h incubation over Sample concentration [μg/mL] (**: higher Ag loading).*

A novel luminescent Europium(III) complexes for citrate detection

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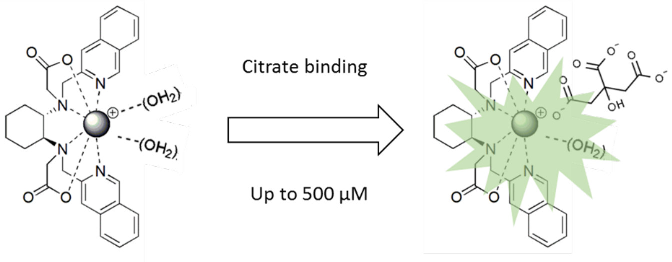
Rationally designed Eu(III) complexes can be exploited as probes in the detection of analytes in biological fluids, by means of luminescence.[1] These complexes must be stable in aqueous solution, absorb and efficiently transfer the UV excitation to the metal ion (*antenna effect*). We succeeded to obtain this goal by including isoquinoline *antenna* into the ligand backbone. In fact, the luminescence of [Eu(bisoQcd)]$^+$ (Figure 1**)** and Eu(isoQC3A) complexes significantly increases in the presence of the main analytes which constitute the interstitial extracellular fluid (*i.e.* hydrogen carbonate, serum albumin (SA) and citrate).[2,3]



Ln(b*iso*Qcd)+

Figure 1. Eu(III) complex suitable for citrate sensing

The optical response of our Eu(III)-based probes is selective towards citrate molecule, when a complex matrix is considered. Citrate molecule is a very important bio-analyte and the monitoring of its concentration is crucial in order to identify the presence of metabolic disease.[4] When a simulated interstitial extracellular fluid is employed, the change of the citrate concentration gives rise to an increase of the Eu(III) luminescence emission intensity of [Eu(bisoQcd)]$^+$. On the other hand, negligible or no change of the luminescence intensity was detected when the concentration of both hydrogen carbonate and SA is changed. This is due to citrate capacity to displace a higher number of water molecules giving a distinctive increase of the luminescence intensity. Moreover, the Eu(III) intrinsic quantum yield of the adduct is higher.
The obtained results candidate our europium complexes as viable probes for luminescence analysis of biofluids with complex matrix.

Acknowledgments: The work was financially supported by PRIN project "CHIRALAB", grant n. 20172M3K5N.

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Co/Pd-based synthetic antiferromagnetic multi-stacks for biomedical applications

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Mesoscale magnetic particles (from few nanometers to microns) are a major class of materials with the potential to revolutionize current clinical diagnostic and therapeutic techniques. They are commonly fabricated by bottom-up chemical synthesis methods; however, recent studies have demonstrated that top-down approaches based on techniques developed for micro/nano electronics can be used to fabricate monodisperse magnetic micro/nanoparticles with a complex structure and shape that are hard to obtain by means of chemical routes [1,2]. In this work, thin film stacks consisting of multiple repeats of single $[Co/Pd]_N/Ru/[Co/Pd]_N$ units with antiferromagnetic coupling and perpendicular magnetic anisotropy were investigated and exploited as a potential starting material to fabricate free-standing synthetic antiferromagnetic microdisks [3]. For this purpose, films were directly grown on a sacrificial optical resist layer (AZ5214) spinned on a thermally oxidized Si substrate, which would serve to obtain free-standing particles after its dissolution. Furthermore, the film stack is sandwiched between two Au layers to allow further bio-functionalization. The samples fulfill all the key criteria required for biomedical applications, i.e., zero remanence, zero field susceptibility at small fields and sharp switching to saturation, together with the ability to vary the total magnetic moment (by changing the number of repetitions of the multi-stack) without significantly affecting any other magnetic features. Moreover, the samples show a strong perpendicular magnetic anisotropy, which is required for applications relying on the transduction of a mechanical force through the particles under an external magnetic field, such as the mechanical cell disruption, which is nowadays considered as promising alternative to the more investigated magnetic hyperthermia approach for cancer treatment [4]. Preliminary results on microdisks will be also discussed.

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Hydrophobin coated superfluorinated nanoparticles for ^{19}F-MRI cell tracking

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^{19}F-MRI has emerged as a promising diagnostic tool providing hot spot imaging along with ^{1}H-MRI. We previously reported a superfluorinated imaging agent, PERFECTA, bearing 36 equivalent ^{19}F atoms and therefore showing a single, intense resonance peak.[1] As most of the superfluorinated contrast agents, PERFECTA is highly hydrophobic, which makes it difficult to be used in biological environment systems. In this work, an amphiphilic protein, hydrophobin (HFBII), which is a natural biosurfactant with filming properties, was used to disperse PERFECTA in aqueous solutions[2]. We optimized a protocol to obtain colloidally stable formulations of PERFECTA. The obtained formulations were characterized by NMR, DLS, microDSC, TEM, ^{19}F-MRI and FTIR. The results showed that these nanoformulations were composed of monodispersed PERFECTA nanoparticles coated by a HFBII shell that also have good NMR relaxation times to be used as ^{19}F-MRI tracking contrast agents [Figure 1]. Cytotoxicity and cellular uptake studies also demonstrated nanoparticle biocompatibility and their ability to label cells. Moreover, hydrophobin protein has been shown to possess stealth properties, thereby reducing the attachment of serum proteins on to the nanoparticles. Thus, the obtained nanoformulation represents a versatile labeling agent that can also be used as delivery vector.

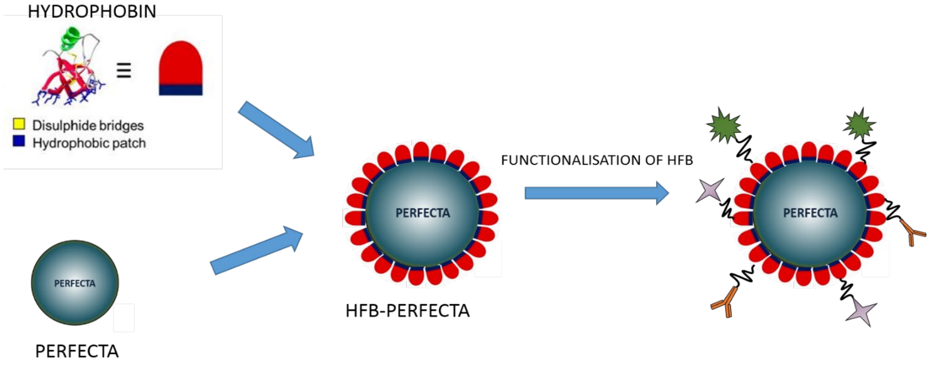

Figure 1: Schematic drawing of the hydrophobin coated superfluorinated nanoparticle.

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Coupling electrospinning and photo-induced crosslinking to produce shape-stable rubber nanofibrous membranes

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Electrospinning is a unique technique to produce fine submicrometric fibers from polymer solution or melt through the application of high electrostatic forces. In particular, the fabrication of rubber nanofibrous membranes by electrospinning has recently attracted significant attention owing to their interesting properties (e.g., superior elasticity, high extensibility, elastic recovery and resilience), and their potential applications in stretchable electronics, (bio)filtration and sensing [1,2]. However, electrospinning of rubbers and the production of rubber fibrous membranes with a stable morphology can be difficult and complicated, due to their high viscoelasticity and low *Tg*.

Herein, butadiene-based nanofiber membranes are obtained by different electrospinning processes (i.e., solution electrospinning, electrospinning of latexes and electrospinning of liquid polybutadienes). A photoinduced thiol-ene crosslinking reaction is then applied (Figure 1a) to increase the stability of the membrane, as well as to enhance and tune its physico-chemical, thermal and mechanical properties [3]. It is demonstrated that high-performance morphologically stable, insoluble, mechanically durable, flexible and stretchable nonwoven nanofibrous materials are obtained (Figure 1b and c).

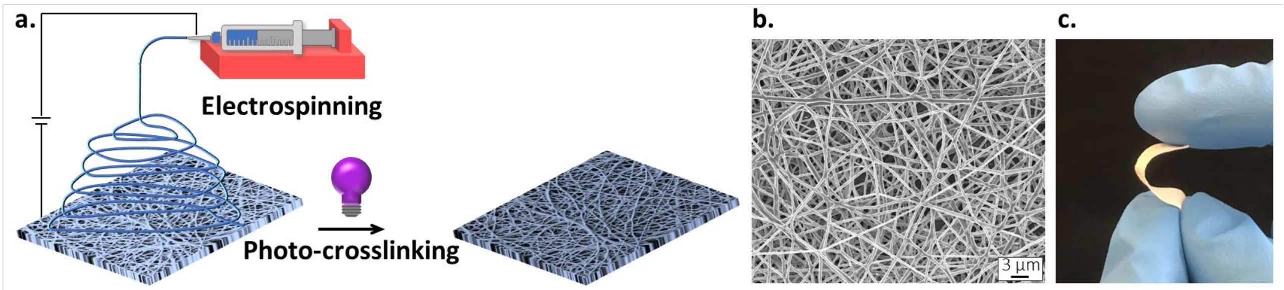

Figure 1. a: Scheme of the process, which couples a first electrospinning step and a subsequent photocrosslinking reaction. b: FESEM image of a rubber photo-cured electrospun mat. c: Picture of a photocrosslinked fibrous membrane showing its flexibility.

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Analysis of the chemical profile of sparkling wines fermented with autochthonous yeast strains using a non-targeted metabolomic approach

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The *Champenoise* technique for the production of sparkling wines is based on "in bottle" re-fermentation carried out by few commercial strains belonging to the *Saccharomyces cerevisiae* species. However, the exclusive use of these strains can cause a flattening of the sensorial profile. In fact, the role of volatile compounds, produced by the yeasts during the fermentative process, is fundamental for sparkling wines produced starting from local grape varieties and, in particular, from those produced in Apulia (Southern Italy), whose economic importance is continually increasing [1]. To the best of our knowledge, only two studies [2, 3], have to date investigated the impact of the autochthonous starter strains on sparkling wine volatiles profile. Furthermore, no information are available on the oenological potential of indigenous grape *cv* Maresco for the production of typical sparkling wine.

This contribution deals with the evaluation of the influence of native selected yeast strains (ITEM deposited in the Microbial Culture Collection of CNR-ISPA) on the chemical profile of sparkling wines through a non-targeted metabolomic approach based on HPLC-HRMS and GC-MS techniques. *Saccharomyces cerevisiae* DV10 (Lallemand, USA) was used as control sample.

The reported results show that:

a) yeast strain affects the levels of some fermentative compounds as well as of polysaccharides, organic acids, phenolic acids and lipids;

b) the control sample was characterized by high values of gluconic acid that adversely affects wine foamability, while lower concentrations of this molecule were detected in sparkling wines produced by the other strains selected in Apulia region;

c) the selected autochthonous yeast strains were able to produce sparkling wines ensuring low volatile acidity (<0.3 g/L), high glycerol content, a good phenolic and acid profile that influences the foam stability and the sensorial quality (body, bitterness and astringency);

d) a map constituting a useful tool to monitor the different patterns of aroma release can be obtained by HPLC-HRMS/GC-MS correlation analysis.

This contribution provides information that will help in modulating the quality of regional sparkling wines obtained from minor autochthonous grape varieties by using selected microbial resources.

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The role of POSS symmetry in polymer matrix dispersion

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Despite their first discovery, dated 1946, the use of polyhedral oligomeric silsesquioxanes (POSSs) as reinforcement for polymeric material has taken hold starting from ‘80. Their characteristics, a nano-sized cage structures, linked with their hybrid (inorganic–organic) nature allow the modification of these molecules according to the particular needs of the host polymer. By combining the low weight and processability of traditional polymers with the property enhancements derived by the inclusion of POSS molecules the resultant nanocomposite can act as self-passivating/self-healing membranes that will dramatically increase the lifetime of orbiting bodies. POSSs may be considered as a nano form of silica, and in their most common form they are comprised of a cubic cage of eight silicon corner atoms and twelve oxygen edge atoms (Figure 1), where each of the eight silicon atoms may carry one of an extremely wide range of functional groups (R), generating hundreds of possible compounds. The aim of this work was to design different POSS structure by changing some of the corner groups and investigate if and how much the symmetry/asymmetry of the POSS structure influences the dispersion in the polymer matric and thus affect the thermal and mechanical properties of the obtained nanocomposites.

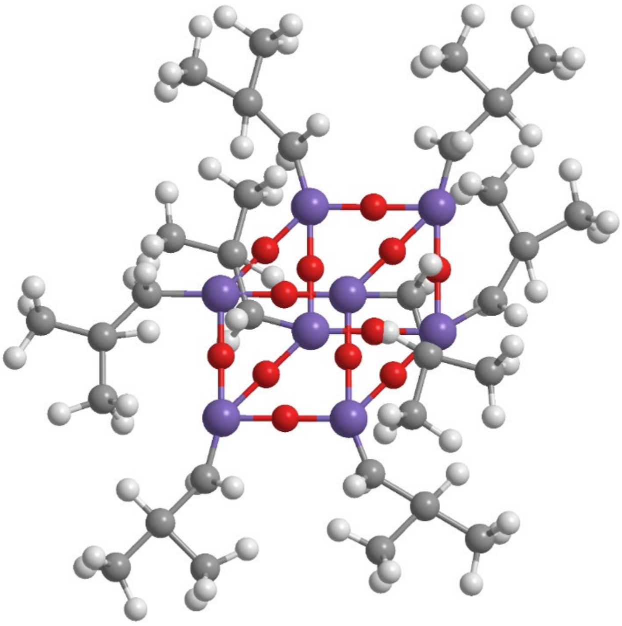

Figure 1. POSS molecular structure

Spectroscopic investigation of the structural evolution of chemically strengthened soda-lime silicate float glass

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The ion exchange process has been successfully exploited since about 60 years for the strengthening of alkali-containing silicate glass. [1] Basically, it consists in the immersion of a glass article in a molten salt where sodium or lithium ions in the glass are exchanged by sodium or potassium from the bath. A diffusion profile with different depth and shape can be generated by changing salt, time and temperature to obtain different final properties. [2, 3, 4] Interestingly, the structural modifications induced by the ion exchange process are still matter of debate.

Therefore, to shed light on the structure-properties relation, different glasses were characterized by means of infrared (FTIR) and solid state nuclear magnetic resonance (NMR) spectroscopies, before and after chemical strengthening. In particular, two soda-lime silicate float glasses with similar density, silica and sodium concentrations but slightly different composition of the other elements were ion-exchanged in molten potassium nitrate.

Both FTIR and ^{29}Si MAS NMR results pointed out some differences between the raw glasses: the shape of the Si-O(-Si)/Si-O$^-$ asymmetric stretching vibration band in FTIR spectra and the resonance belonging to the silica tetrahedra in the ^{29}Si MAS NMR spectra which depend on the amount of bridging/non–bridging oxygens and on the distortion of the silica tetrahedra appeared substantially different [5, 6], very likely because of the different metal cations content in the two glasses. Moreover, after the ion-exchange process, both FTIR and NMR signals show similar evolutions although with different extent for the two glasses (Figure 1). As a matter of facts, a different intensity of the ion exchange process was found for the two glasses from potassium penetration and residual stress profiles measurements.

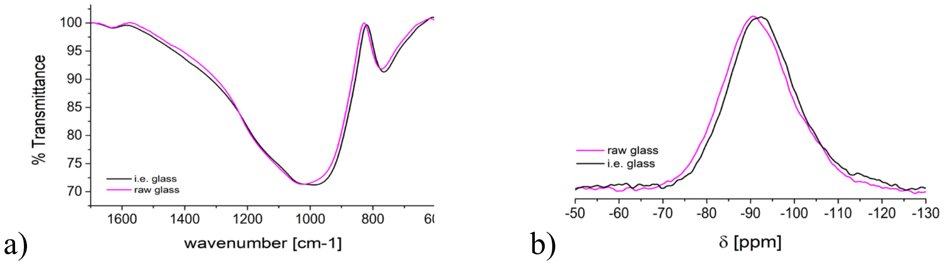

Figure 1. FTIR (a) and ^{29}Si MAS NMR (b) spectra of a representative glass, both raw and after ion-exchange.

The spectroscopic data suggest that a key role is played by the different ability of the exchanged cations to coordinate both bridging and non-bridging oxygens. This affects the bonds angle and length of the silica tetrahedra, thus tuning the capability of the matrix to host the exchanged cations, and, finally, macroscopic properties, such as density and strengthening.

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Synthesis by Sol-Gel process of Silica/Ketoprofen hybrids system: thermal characterization, surface interactions study and drug delivery

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Non-covalent interactions between drug molecules and silica-based materials have a significant influence on the kinetics of release process and toxicology effects. Intermolecular interactions between Ketoprofen molecules and the silica matrix in the hybrids system synthetized by sol-gel process for drug delivery can be studied at atomistic level using Molecular Mechanics (MM) and Molecular Dynamics (MD) methods. Non-covalent interactions between ketoprofen molecules and Silica surface and possible self-aggregation process that can occur at higher drug concentration may play an important role in improving or reducing the bioavailability.

The aim of this work is to synthesize by sol-gel process a system composed by SiO_2 glass and ketoprofen, anti-inflammatory drug. Two percentage of drug (5 and 15 wt%) were entrapped in Silica matrix via sol-gel method and dried materials were analysed through Fourier transformed infrared spectroscopy (FTIR), simultaneous DSC/TGA analysis. The drug loaded amorphous bioactive materials were studied in terms of their drug release kinetics. A theoretical study based on MM and MD simulations is performed to investigate possible surface interactions between the silica-based surface and the ketoprofen drug molecules both at small and higher concentration for useful comparison with experimental data.

Green Polymerization of Conjugated Monomers: Sustainable Solvents for C-H bond activation reactions

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The C−H bond activation reactions are of utmost importance in order to achieve sustainable synthesis of polyconjugated organic materials.[1] Both the tandem Suzuki-Heck as well as the direct arylation polymerizations (DArP) require this activation to be efficient; however, a challenge still resides in the compatibilization of this reaction with environmentally benign solvents. Subject of this presentation is the implementation of sustainable solvents for the synthesis of poly(9,9-dioctylfluorenylene-vinylene) (PFV) and poly(3-hexylthiophene) (P3HT). For PFV, the aim was the assessment of green solvents (anisole and propylene carbonate) as media for the tandem Suzuki–Heck polymerization using the traditional $Pd(AcO)_2/P(o\text{-}Tol)_3/NEt_3$ catalytic system, reaching a suitable compromise between molecular weights and polymer regioregularity. The catalyst performances were improved by carrying out the reaction in anisole, while the resulting poly(arylene-vinylene) regioregularity, which was determined by ^1H-NMR, could positively be influenced by the polarity of the sustainable medium, introducing propylene carbonate as reaction cosolvent.

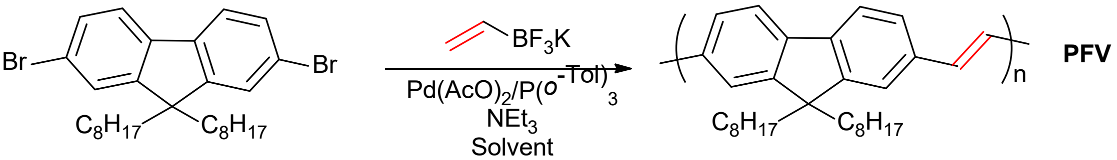

Figure 1. Reaction conditions for the polymerization of 2,7-dibromo-9,9-dioctylfluorene (PFV).

Conversely, the DArP of 2-bromo-3-hexylthiophene could not be carried out in propylene carbonate, while it is found that catalyst performances in anisole (see Figure 2) requires a careful choice of the palladium source used. In terms of molecular weights of the polymer, the best conditions are obtained using $PdCl_2(PPh_3)_2$ as the precatalyst, affording a highly regioregular P3HT (98%, assessed by ^1H-NMR spectroscopy) in quantitative yields and high molecular weights (26.7 kg mol^{-1}). Moreover, UV-Vis investigation will be shown, that indicate that the polymers obtained under these conditions maintained unaltered their optoelectronic properties.

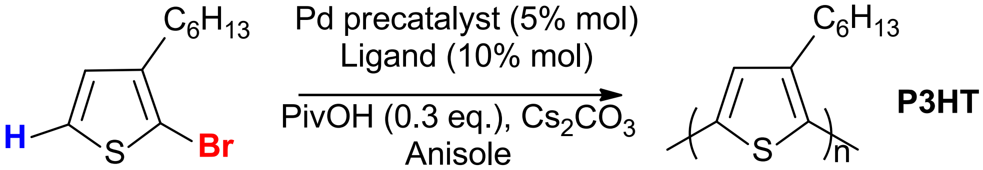

Figure 2. Reaction conditions adopted for the DArP of 2-bromo-3-hexylthiophene (P3HT) in anisole.

The results of this investigation[2] will contribute to the full understanding and exploitation, in every available instance, of the potentialities of green solvents, in particular for polymerization protocols regarding conjugated monomers.

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INCREASE: Innovative Nanostructured CaRbon based delivery system for photothermal triggered drug release.

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The interest on carbon-based nanostructures has grown constantly by their chemical, optical and electrical properties, showing great promise for a wide variety of biomedical and technological applications including drug delivery, photothermal therapy and photodynamic therapy.[1,2] The ***INCREASE*** project,[3] funded by the University of Catania - Italy (Piano di Incentivi per la ricerca di Ateneo 2020/2022 - Pia.ce.ri.) aims to develop innovative and biofriendly nanocomposites, based on Carbon nanomaterials such as carbon nanodots (CDs), graphene oxide sheets, carbon-polymer composites, properly functionalized for an effective photothermal and photodynamic (PTT and PDT), through the delivery of drugs triggered by light stimuli. Innovative CDs synthetic and doping strategies will be implemented to prepare “smart-doped-CDs” with a remarkable red-shift optical absorption in order to obtain a strong photothermic and dynamic efficiency at therapeutic region (700-980nm). In this scenario N, P, B, S and other species have been considered as doping agents. The correlation between the doping agent amounts with optical and photothermal properties have been investigated by experimental and modelling simulation approaches. Photothermal triggered drugs release has been investigated by fluorescence approaches. Computational studies have been implemented to investigate the delivery efficiency enhancement by polymer coverage density to improve the photothermal efficiency upon light absorption in the therapic window for a light-induced therapy application. The calculations have carried out within the framework of both molecular mechanics and quantum mechanics approaches.

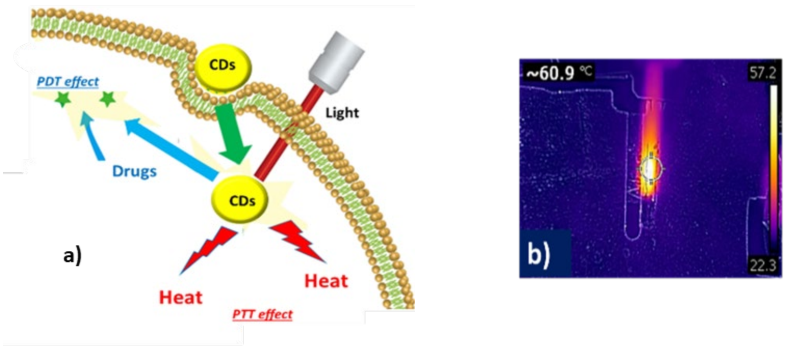

Figure. a) Emission spectra of CDs, b) photothermic effect of CDs and c) scheme of dual PPT-PDT effects.

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Water-soluble bis-cationic push-pull fluorophores

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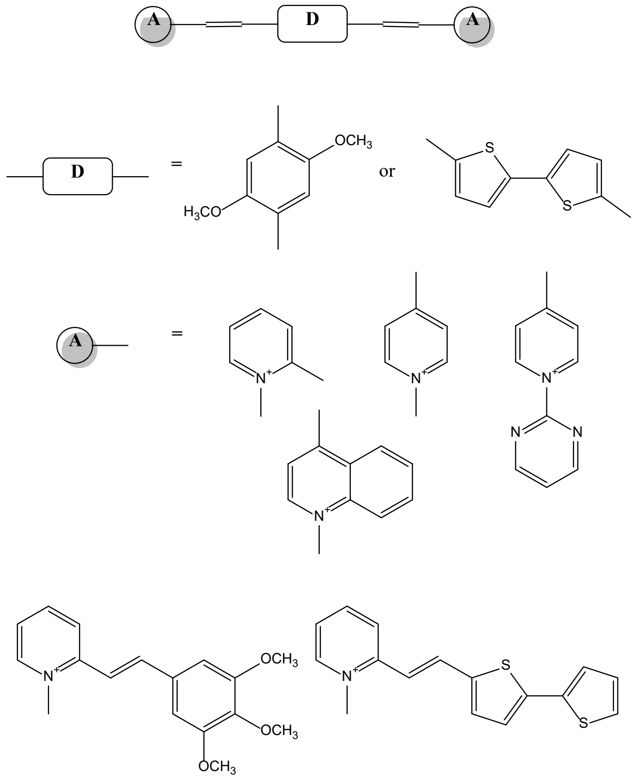
Recently, a great research effort has been dedicated to the study of organic nonlinear optical (NLO) materials because of their potential applications in many fields.[1]

Organic molecules are preferred to inorganic materials, thanks to their adaptability, flexibility of design, environment-friendly nature and low-cost of production. A family of organic chromophores with NLO activity are push-pull compounds, consisting of electron-donor D (*push*) and electron-acceptor A (*pull*) moieties, held together by a π-conjugated system.[2]

Their NLO response is very sensitive to the nature of the moieties (donor/acceptor strength or dipolar character) and to the extension and nature of the π-conjugated system.[3] In fact, absorption and emission properties of the system can be finely tuned by changing the nature of the donor and/or acceptor groups or the length of the π-bridge. This approach makes it possible to obtain families of dyes, whose absorption and emission abilities can span all the UV-Vis spectral range.



The opportunity of covering the whole spectral window is indeed an attractive feature to be pursued: panchromatic absorption, coupled with high absorption coefficients, is ideal for organic photovoltaics applications while panchromatic fluorescence can be exploited in organic light-emitting diodes (OLEDs).The advantages of introducing a positive charge in the molecular system lays in the increased acceptor strength, which implies higher NLO response, but also in increased water solubility, which becomes necessary for biological and medical applications.

In order to find novel biosensors with enhanced NLO activity, a new series of *all-trans* six styryl-azinium derivatives (Figure 1), characterized by an extended $^{+}$A-π-D-π-A^{+} structure, has been synthesized. Diverse pairs of central donors (dimethoxybenzene rings rather than bi-thienyl units) and lateral acceptors (*ortho/para* methyl-pyridinium, methyl-quinolinium or pyridinium-pyrimidin moieties) have been studied in order to explain the dependence of different photophysical properties on the molecular structure of the six dyes.

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PbS quantum dot-based chemiresistive device for vapor explosives detection

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Rapid and accurate detection of explosives is an important issue in many fields, including monitoring during production and storage, environmental surveillance, and homeland security. Despite being quite accurate, techniques currently available for trace explosives detection require bulky instruments, time-consuming procedures, and trained technical staff, thus imposing severe limitation to the desirable systematic monitoring of sensitive areas. The development of small-sized systems, with high sensitivity, low power consumption, and suitable for mass production is thus a pressing need to grant security, especially for uncontrollable environments such as entry points to public places and transport networks.

Colloidal quantum dots (QD) have been gaining attention as interesting building blocks for gas sensors [1] since the strong quantum confinement effects experienced by semiconductor nanoparticles leads to unique electronic and optical properties that couple with size-controlled tunability and excellent processability enabling facile integration on silicon platforms [2].

Here we demonstrate a high-performance chemiresistive sensor based on colloidal QD for the room temperature detection of nitroaromatic explosives. The sensor was fabricated via simple and effective layer-by-layer spin coating of a PbS QD solution under ambient atmosphere, followed by in-situ ligand exchange with ethylenediamine (EDA) to partially replace the original oleic acid coating. Scanning electron microscopy characterization (SEM) of the QDs film morphology revealed the presence of small cracks, facilitating the penetration of gas molecules (figure1). The amine-capped sensors exhibited a very large sensitivity towards nitrobenzene (NB), selected as representative of the nitroaromatics compounds, with lowest measured concentration of 65 ppb and a limit of detection estimated to 2.4 ppb. Response time of 9.6 min and recovery time of 8.7 min were assessed for the sensors. Easy fabrication, room temperature detection, high sensitivity, and full recovery upon gas release of the PbS QD sensors here presented make them quite promising for nitroaromatic explosive detection applications.

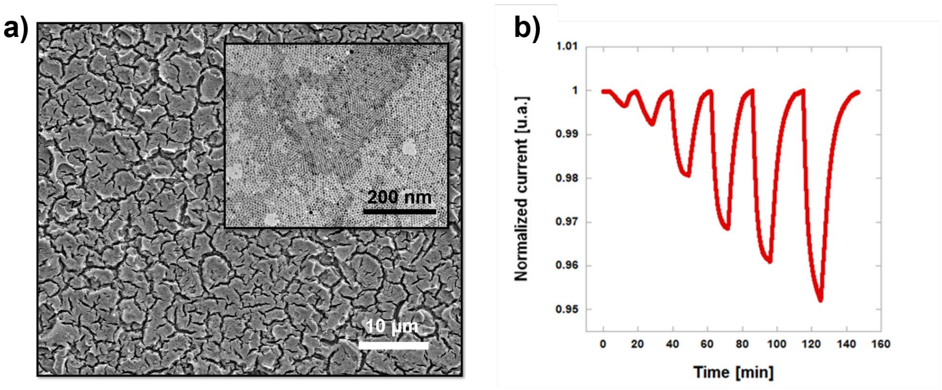

Figure 1. SEM image of the PbS QD film (a), TEM image of the precursor solution (inset) and normalized current curves towards different concentrations of NB as a function of time (b).

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A preliminary investigation on MoS_2 as an anode for potassium batteries

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Future renewable energy integrated grid systems require rechargeable batteries with low cost, high safety and long cycle life. The much higher abundance and fair distribution of potassium compared to lithium in Earth crust indicates that rechargeable potassium batteries can represent an attractive replacement for lithium-ion counterparts. Rechargeable potassium batteries have gained tremendous attention during the past decade [1]. However, the development of rechargeable potassium batteries is still in its infancy.

Due to the large atomic radius of potassium, some electrode materials that are commonly used in Li-ion systems are not suitable for potassium batteries. Thus, new anode materials for these energy storage systems have been developed [2]. The most performing are mainly based on carbon materials, metal alloys, metal dichalcogenides and potassium metal. On the other hand, cathode materials can be divided into three categories: Prussian blue and its analogues, layered metal oxides and polyanion oxides.

Among transition metal dichalcogenides, layered MoS_2 offers a suitable 2D diffusion pathway for K^+ ions, since the layered are stacked together by van der Waals interactions and the interlayer distance can be modulated [3]. Herein, we reported a preliminary study on MoS_2 as anode material in potassium batteries. When deposited on copper as current collector, it ensured, at 0.1 A/g, an initial charge and discharge specific capacity of 102.7 and 106.7 mAh/g, respectively and Coulombic efficiency of 96.3%. After 100 cycle, it exhibited 94% capacity retention, with a Coulombic efficiency approaching 100%.

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TiO_2-organic hybrid materials: dark oxidative activity through the easy generation of reactive oxygen species

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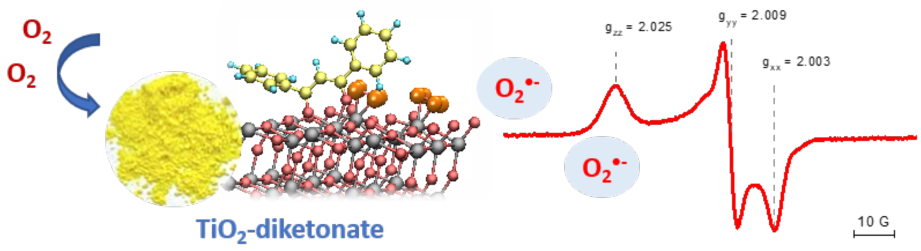
The controlled production of reactive oxygen species (ROS), highly active derivatives of O_2, allows their exploitation for the decontamination of water (by so-called Advanced Oxidation Processes), purification of air, disinfection, and even anticancer therapy [1]. Metal oxide surfaces can generate ROS such as superoxide radical anions ($O_2^{\bullet-}$) and hydroxyl radicals ($^{\bullet}OH$) upon specific activation (e.g., light irradiation or reducing treatments), however their short lifetime makes the handling and storage of these species very challenging.

We established a convenient sol-gel route for the synthesis of TiO_2- and ZrO_2-based hybrid materials with specific organic ligands, forming charge transfer complexes with the metal ions, in particular β-diketones such as acetylacetone (2,4-pentanedione) and dibenzoylmethane (1,3-diphenyl-1,3-propanedione). These amorphous dried gels are able to spontaneously generate superoxide radicals on their surface and preserve them stably adsorbed for exceptionally long times (years). As a consequence, they show remarkable performances in the oxidative degradation of various organic pollutants in water without any light irradiation [2-4].



Schematic representation of superoxide ion formation on the surface of a TiO_2-dibenzoylmethane hybrid; electron paramagnetic resonance (EPR) spectrum of a TiO_2-dibenzoylmethane sample showing the signal of $O_2^{\bullet-}$.

To deepen the understanding of the mechanism and electronic features related to this unusual behaviour, we complemented the spectroscopic characterization of our materials with DFT calculations. The results revealed that the molecular structure of the organic ligand, its interaction with the metal and the presence of surface O vacancies are key factors in promoting the adsorption of O_2, its reduction and eventually the stabilization of $O_2^{\bullet-}$.

The intrinsic oxidative potential of these hybrid materials makes them promising not only for water remediation, but also for the development of active air filters and antimicrobial coatings.

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Molecular dynamics simulation method to predict drug encapsulation into biodegradable nanoparticles: the case of Quinine encapsulation

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Small molecule-based therapies have shown to improve outcomes in COVID-19 patients diagnosed with severe pneumonia [1]. In this context, the natural alkaloid Quinine (QN) is considered as a safer and well-tolerated medicine compared to Cloroquine (CQ) and Hydroxixhloroquine (HCQ). The reformulation of QN to improve its pharmacokinetics and safety profile may be helpful to support its use to treat COVID-19 patients. Among all the available strategies, the use of biodegradable/biocompatible polymeric nanoparticles (NP) may help to reduce QN side effects and improve its therapeutic efficiency. In this regard, Poly-(glycolic acid) (PGA) and poly-(lactic acid) (PLA) along with the copolymer poly-(lactic-co-glycolic acid) (PLGA) are the most popular among the various available FDA approved biodegradable polymers [2]. In this study, a full atomistic molecular dynamics (MD) simulation approach has been used to investigate the use of PLA, PGA, and PLGA polymers as potential drug delivery systems for lipophilic QN (logP = 2.51), with the final aim to gain knowledge about the mechanism of QN encapsulation and release at the atomic/molecular level.

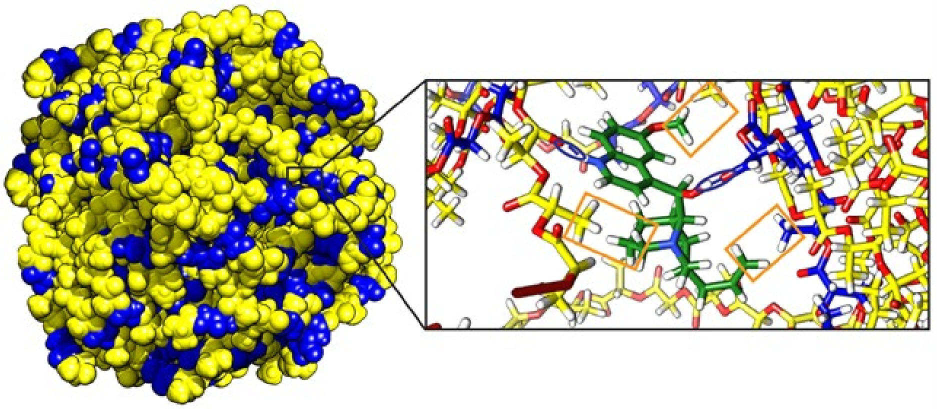

Figure 1. PLGA-QN system. The polymer chains are shown in blue (glycolic acid) and yellow (lactic acid) spheres, while the C, O, N and H atoms of the QN molecules are shown in green, red, blue and white, respectively. The blue circles and the orange rectangles highlight the hydrogen bonds and the nonpolar interactions observed between quinine and copolymer respectively.

MD results have shown that QN molecules remained strongly aggregated inside the PLA core through QN-QN π-stacking and Hydrogen Bonding interactions, which could detrimentally affect QN release and bioavailability. In contrast, the observed weak QN-PGA interactions and the greater free volume found in PGA matrix promoted a fast diffusion of QN molecules to the water phase. On the other hand, in PLGA system, QN was found to be homogeneously distributed (Fig.1), establishing site specific nonpolar and hydrogen bonds drug-polymer interactions. This peculiar drug accommodation into PLGA matrix may be expected to provide a controlled QN release as a function of polymer erosion rate, which could promote a safer and effective therapeutic use of QN against SARS-CoV-2.

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Revisiting Platinum-diphosphine Complexes as Pre-Catalysts for Oxidation Reactions: Seeking Improvement Through Confinement

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Oxidation reactions rank amongst the most important classes of chemical transformations, with numerous well-known industrial processes falling into this category. Many of these reactions make use of homogeneous pre-catalysts, and to this end, we have previously reported on the platinum catalysed oxidation of alkynes,[1] alkenes,[2,3,4] and ketones,[5] in each case making use of supporting diphosphine ligands and benign oxidants (Figure 1, *i* to *iii*). We now revisit this established chemistry, seeking to improve the reactions with respect to classical catalytic metrics (selectivity, activity, longevity), by confining the well-defined pre-catalysts in well-defined spaces, such as capsules, micelles, and nanoparticles. We hope that this complementary approach, which brings together organometallic, supramolecular and heterogeneous methodologies, will allow for a direct improvement with respect to the systems investigated, in addition to opening up chemical space that is yet to be fully exploited.

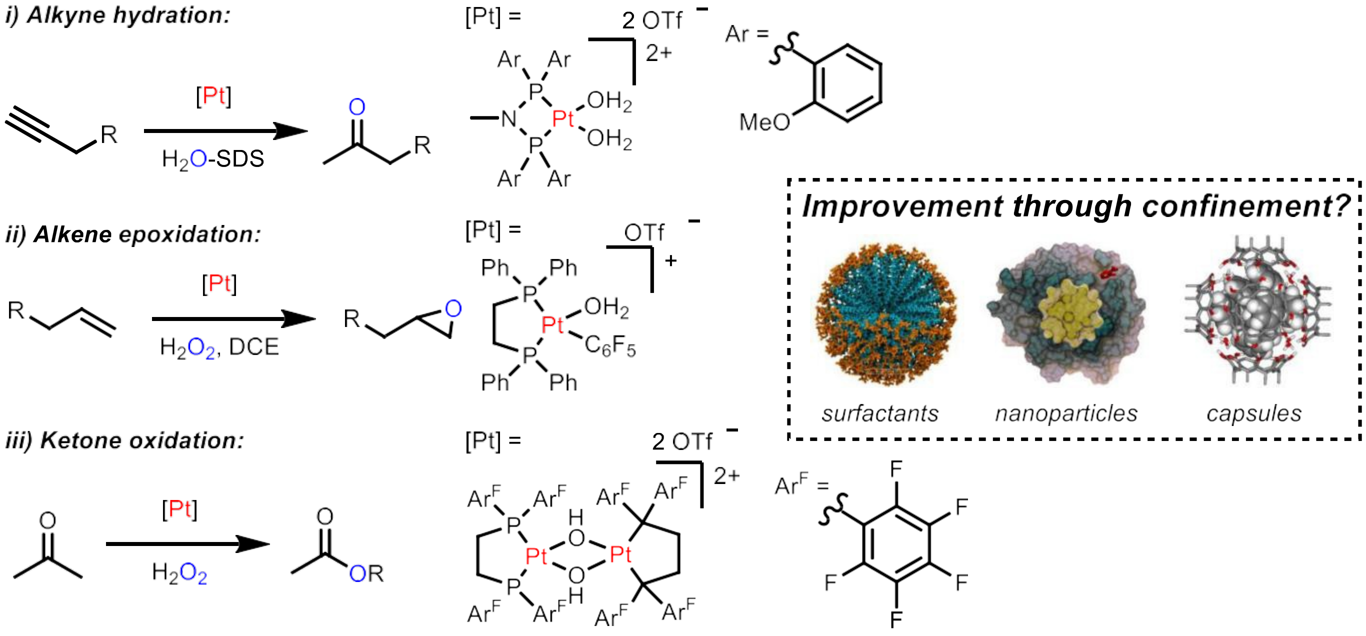

Figure 1: Previously reported oxidation reactions of i) alkynes, ii) alkenes and iii) ketones, using platinum-disphosphine pre-catalysts and benign oxidants. In this work, we hope that confinement of the pre-catalysts in well-defined spaces (as shown at right) will allow for improvements with respect to activity, selectivity and longevity. SDS = sodium dodecyl sulphate; DCE = dichloroethane; OTf = trifluoromethanesulphonate.

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An overview on Li-N_2 cells for ammonia production

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Electrochemical N_2 reduction reaction (E-NRR) is studied as a sustainable and renewable energy-based process to replace the well-established Haber-Bosch process (HB) for NH_3 production, one of the top-3 chemicals produced worldwide, at the base of fertilizers synthesis and a viable green energy carrier, since it is easier transportable and safer than H_2. Operating in harsh conditions (at least 450 °C - 200 atm), the HB process is responsible of about 1% of the global greenhouse gas emissions (about 400 Mtons/year of CO_2 are released) [1]. Even using "green" or "blue" H_2, the HB process is viable only in huge centralized plant and would reach no more than 40% energy efficiency, remaining highly energy-consuming [1]. Thus, to reach independence from fossil energy sources, it is quite urgent to find a sustainable process working in mild conditions and driven by abundant even if discontinuous renewable energy sources.

Li_3N is the only stable nitride of alkali metals and its formation is thermodynamically favored also in ambient conditions. Li-mediated NRR was demonstrated in 1994 [2] and it has recently demonstrated promising results, both in continuous systems with Li^+ ions and a proton donor in the same cell, and in discontinuous processes involving Li_3N formation and subsequent protonolysis into NH_3. In the first setup, E-NRR carried out in aqueous or ethanol environments has been proposed and a recent study demonstrated a Faradaic efficiency (FE) of around 30% [3], far greater than that of standard E-NRR. In the second approach, cell design is similar to that of Li-air batteries and shows an intriguing possibility, i.e. to avoid the main competitive reaction (hydrogen reduction reaction); in this way, it is possible to reach FE higher than 60% [4].

This poster gives an up-to-date overview of Li-N_2 electrochemical systems for NH_3 synthesis.

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C_3N_4 based materials for photo-reforming of aqueous solution of oxygenated organic compounds

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Photocatalysis based on the use of semiconductors has gained, during the recent years, increased attention as promising sustainable process for H_2 and fine chemicals production, given the possibility of activating such photocatalysts by visible light radiation [1,2]. Photocatalytic treatments devoted to the conversion of organic substances contained in wastewaters into chemical compounds of high interest, such as hydrogen, represents a new strategy to recover chemical energy and an innovative route to decontaminate wastewaters. The photo-reforming of aqueous solutions containing oxygenated organic compounds combines photocatalytic water splitting with the oxidation of organic substrates in a single process occurring at ambient conditions. The generated H_2 comes both from water-splitting and from organic substrate dehydrogenation [3]. Unfortunately, the most active photocatalysts are active under UV irradiation, so further studies are necessary to improve the solar light absorpion ability of the semiconductors. In this presentation, both bare and composite materials based on carbon nitride and niobium oxide are used as photocatalysts for the photo-reforming of water solution of both triethanolamine and ethanol. The choice of these two materials arises from the fact that their appropriate heterojunction can lead to lower recombination between the photo-generated electrons and holes. Furthermore, the potential of the conduction and valence bands of the two semiconductors are suitable for both the formation of hydrogen and the oxidation of organic compounds. Moreover, due to its favorable band gap, carbon nitride exhibit high visible light absorption.

In this work, C_3N_4 has been prepared by thermal condensation of melamine and a successive thermo-exfoliation. Nb_2O_5 and Nb_2O_5/C_3N_4 composite materials have been prepared by hydrothermal synthesis followed by a thermal treatment at different temperatures of the obtained powder. The photo-reforming activity has been measured under UV-LED irradiation and natural sunlight illumination. Moreover, the effect on the photo-reforming performances of graphene deposited on the catalyst surface as well as the presence of metallic Ag or Pt as co-catalysts was studied.

The obtained results are encouraging, particularly under natural sunlight irradiation, because in some cases the hydrogen formation resulted higher than 2000 $\mu mol \cdot g^{-1} \cdot h^{-1}$ with an apparent quantum yield of ca. 7 %.

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Edge functionalization of graphene layers with a 2-pyrone

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Conversion of hydrolyzed biomass, mainly composed by carbohydrates, into suitable building blocks is one of the major purposes of Green Chemistry, defined as ‘‘the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances” [1].
2-pyrones (**Fig. 1**) are a class of unsaturated heterocyclic C-6 sugar derivatives, prevalent in many natural products and, due to their versatile chemical reactivity, intriguing building blocks in organic and polymer chemistry [2,3].

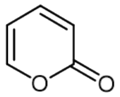

Figure 1. Chemical structure of 2-pyrone

In this work, a green and efficient procedure for the preparation of 2-pyrone is presented, starting from galactaric acid [4], also known as mucic acid, easily obtained from galactose or galacturonic acid. A 2-pyrone derivative, 5-hydroxy-6-oxo-6H-pyran-2-carboxylic acid ethyl ester (Pyr-COOEt, **Fig.2**) was used for the functionalization of nano-sized graphite with high surface area (HSAG).

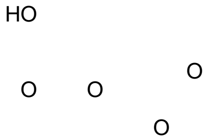

Figure 2. Chemical structure of 5-hydroxy-6-oxo-6*H*-pyran-2-carboxylic acid ethyl ester

Adducts of Pyr-COOEt with HSAG were prepared by means of a simple and sustainable method [5, 6], with the help of either thermal or mechanical energy. Functionalization yield was in all cases larger than 90%. After the functionalization reaction, the bulk structure of HSAG remained substantially unaltered, thanks to the edge functionalization. Few layers graphene were easily obtained by means of a mild sonication of a water dispersion of the HSAG/Pyr-COOEt adducts.

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Transition metal nanoparticles on pyrrole-decorated sp^2 carbon allotropes for selective Hydrogen Isotopic Exchange.

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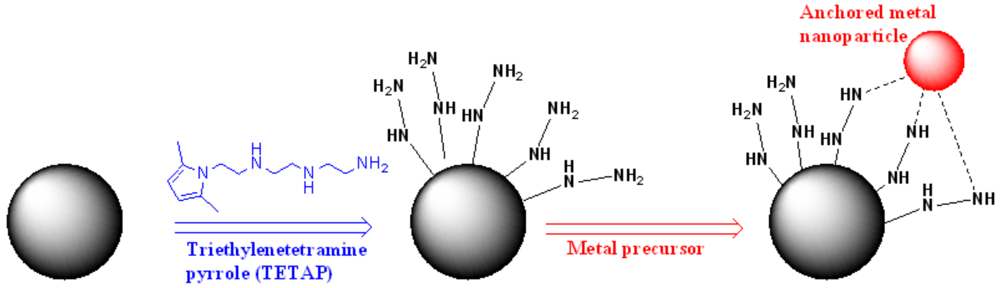
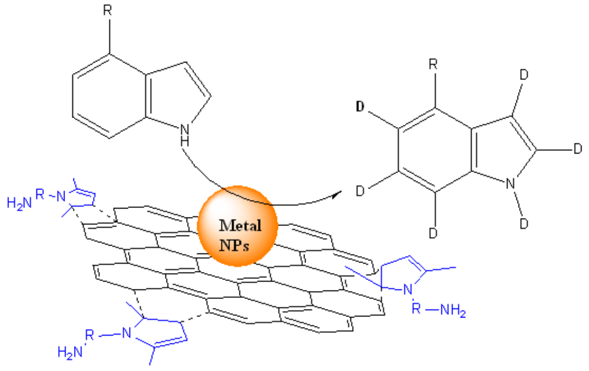
Compared to homogeneous catalysts, heterogeneous systems possess more attractiveness in the chemical industry because of the easier separation from the reaction products, lower amount of wastes, larger recyclability, and lower toxicity and corrosiveness.
Objective of this research was to prepare more efficient and more selective heterogeneous catalysts, by anchoring transition metal cations and nanoparticles on nitrogen decorated sp^2 carbon allotrope (CA), which were functionalized with pyrrole compounds. Triethylenetetramine pyrrole (TETAP) was selected as the pyrrole compound: it was synthesized and grafted onto multiwalled carbon nanotubes and high surface area graphite with efficient and viable methodology [1-3].
The CA/TEPAP adduct was used as the support of transition metal nanoparticles.



It is here reported the example of ruthenium supported catalyst [4], investigated by means of elemental and surface area analyses, X-ray diffraction, transmission electron microscopy. The catalyst was used for the Hydrogen Isotopic Exchange (HIE) of aromatic compounds of pharmaceutical interest.



Outstanding selectivity was obtained.

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Nanoparticle self-assembly towards functional hybrid suprastructures

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Metal nanoparticles (NPs) assemblies have been emerging as a new class of functional nanomaterials for several high-end applications. Our work in this field is focused on the design of different NPs self-assembly strategies to obtain innovative nanoscale hybrid suprastructures. At this aim, we devised bioreducible supraparticles (SPs) obtained *via* gold nanoparticles (GNPs) self-assembly into spherical suprastructures and their stabilization by the film-forming protein hydrophobin II.[1] Obtained SPs efficiently encapsulated hydrophobic drug molecules that could be released intracellularly upon hydrophobin II film dismantling by the reducing action of glutathione. A similar strategy was employed to develop fluorous gold supraparticles obtained *via* the self-assembly of fluorinated GNPs, driven by fluorophobic effect. The newly developed SPs were endowed with fluorous compartments that could host high payloads of partially fluorinated drugs.[2] Moreover, we recently reported chiroptically active peptide-gold suprastructures. We conceived iodination as a strategy to strengthen the gold-reduction capability of the amyloidogenic peptide DFNKF and combine it with its distinctive self-assembly features. Owing to gold-mediated C-I activation on the phenylalanine iodobenzenes, the resulting peptides yielded efficient Au-reduction ability promoting the synthesis of GNPs, and simultaneously working as templates for their spontaneous assembly into spherical suprastructures endowed with chiroptical activity.[3]

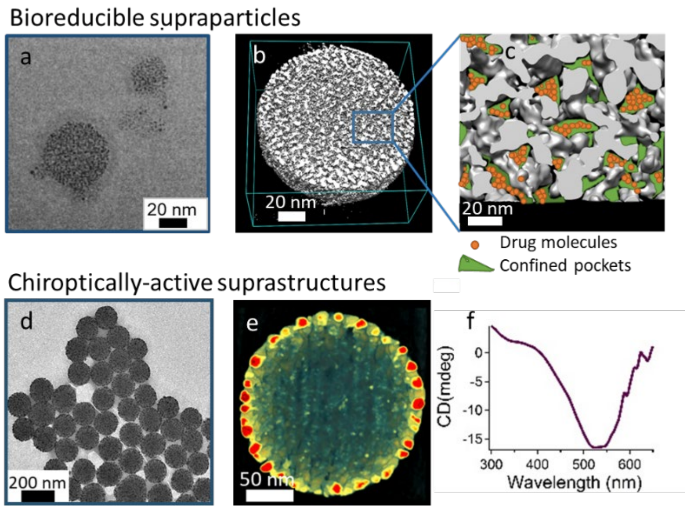

Figure 1: TEM image (a) and tomography reconstruction (b) of bioreducible supraparticles. Schematic representation of drug molecules encapsulation in the bioreducible supraparticles (c). TEM image (d), tomography reconstruction (e) and CD spectrum (f) of chiroptically-active gold-peptide suprastructures**.**

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The Synthesis, Characterization and Catalytic Properties of Novel Gold(I) Complexes Bearing Alkylated PTA Ligands

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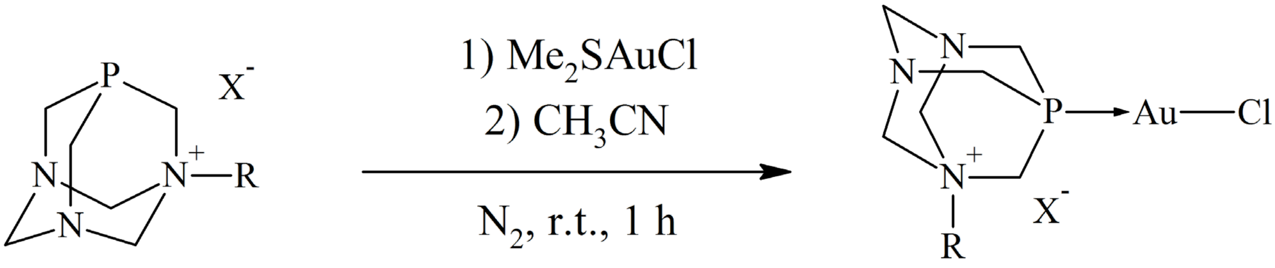
Organophosphines are among the most common ancillary ligands used in organometallic chemistry, owing to their ability to stabilize low metal oxidation states and their capacity to influence both the steric and electronic properties of the metal center upon coordination. The monodentate, adamantane-like phosphine PTA (1,3,5-triaza-7-phosphaadamantane) and its derivatives have been the subject of interest over the last two decades due to their relatively small cone angle (103°) and the availability of nitrogen atoms for further functionalization. This, together with their chemical and thermal stability as compared to PMe_3 and PEt_3, which are sterically similar yet are known to oxidize easily and spontaneously ignite in air, makes them attractive ligands for use in synthesis and catalysis.[1] With these factors in mind, and considering the variety of reactions catalyzed by gold(I) phosphine complexes,[2] we synthesized four different gold(I) long chain-N-alkylated PTA complexes

(Scheme 1) bearing methyl (**Me**), hexyl (**Hex**), octyl (**Oct**), and dodecyl (**Dod**) alkyl substituents. The complexes were subsequently used as pre-catalysts in model addition reactions, such as the hydroarylation of alkynes and the cyclopropanation of alkenes. The effect of both the alkyl side chain and the counterion on the solubility and reactivity in different solvents is analyzed. Furthermore, the stability of the ligands and the resultant complexes is evaluated.



R-PTA X

(R-PTA X)AuCl

R = **Me**, **Hex**, **Oct**, **Dod**

X = $\mathbf{PF_6^-}$, $\mathbf{BF_4^-}$

Scheme 1

[1] Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M., *Coord. Chem. Rev.* **2004**, *248*, 955-993.
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Microplastic/nanoplastic removal by membrane processes

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Plastic pollution represents a major concern considering the disastrous impact that it has on the environment and humans. The world plastic production is constantly increasing with a production rising from 335 million tons in 2016 to 348 million tons in 2017 [1]. The significant increase and widespread in worldwide production of plastics produces huge amount of plastics waste on land that enters in the aquatic environment causing growing alarms [2]. Furthermore, as microplastic (MP)is able to adsorb other common environmental contaminants, such as metals, pharmaceuticals, and others, it can cause diseases such as cancer, malformations in animals and humans, reduced reproductive activity, reduced immune response [2].

Nowadays, the 98% of MP is retained from wastewater treatment plants (WWTPs) but MP with a size smaller than 20 μm and NP is not retained, therefore WWTPs plants are supposed to be one of the major responsible for the plastic pollution in wastewater effluents [2]. A removal efficiency of 98% is achieved by the tertiary treatment, producing an effluent of almost drinking-water quality. However, the limited application of tertiary treatments in the WWTPs coupled with the huge amount of treated wastewaters to obtain water with different quality are a source of plastic in the effluents. Among the tertiary treatment processes, membrane operations can offer an effective solution to the microplastic and nanoplastic pollution in the effluents. To date, the application of membrane technology in the removal of microplastic is still limited, the last year registers a certain increase of study in which conventional membrane separation process and MBR are combined with the other existing treatment processes to reach a more effective removal of microplastic contaminants from wastewaters. In this work the removal of microplastic/nanoplastic contained in the wastewater of a domestic dryer by membrane processes was investigated. The removal of MP/NP was studied using polymer membranes of different material and pore size. The performance of membranes was evaluated and compared in terms of permeability and fluxes. Furthermore, the fouling index (IF%) and the cleaning efficiency (EC%) after suitable washing operations were evaluated.

Preliminary studies suggest that membrane technology may represent a useful solution in well-designed treatment processes to limit plastic pollution.

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Fabrication and properties of mixed multilayer electrodes based on Ruthenium and Copper oxide

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The combination of two or more transition metal oxides greatly enhances the electrocatalytic properties of electrodes used in oxidative processes. Many metallic oxides have been prepared and tested with this aim.

In the last few years [1], we have addressed our research towards the development of mixed oxide electrodes containing mainly Ru but combined with several other metal oxides (for example manganese). In this work, thin-film electrodes coated with ruthenium (RuOx) and copper oxide (CuOx) were fabricated by thermal decomposition. The organic solutions containing the precursor salts were drop-cast on titanium foils (Ti) with a layer-by-layer approach. The coating consisted of some layers (from 1 to 3) of mixed oxide deposited on two layers of pure RuOx. In order to investigate the possible synergistic effect due to the co-presence of both metals on the electrocatalytic properties, different ratios of precursors' concentration were adopted. A comparison with samples obtained by all mixed oxide layers was also performed. The effect of the pre-treatment of the titanium foil was also considered.

To obtain insights into the surface morphology and structure, the prepared electrodes were characterized by scanning electronic microscopy (SEM) and X-ray diffraction (XRD). The stability and the electrochemical activity were investigated by accelerated life tests under galvanostatic conditions, potentiodynamic polarization, cyclic voltammetry, and electrochemical impedance spectroscopy (EIS).

The electrodes were then tested as anodes for the oxidation of molecules of environmental concern with a focus on the electrogeneration of dangerous by-products in the presence of chlorides. The addition of scavenger species was used to clarify the produced oxidants.

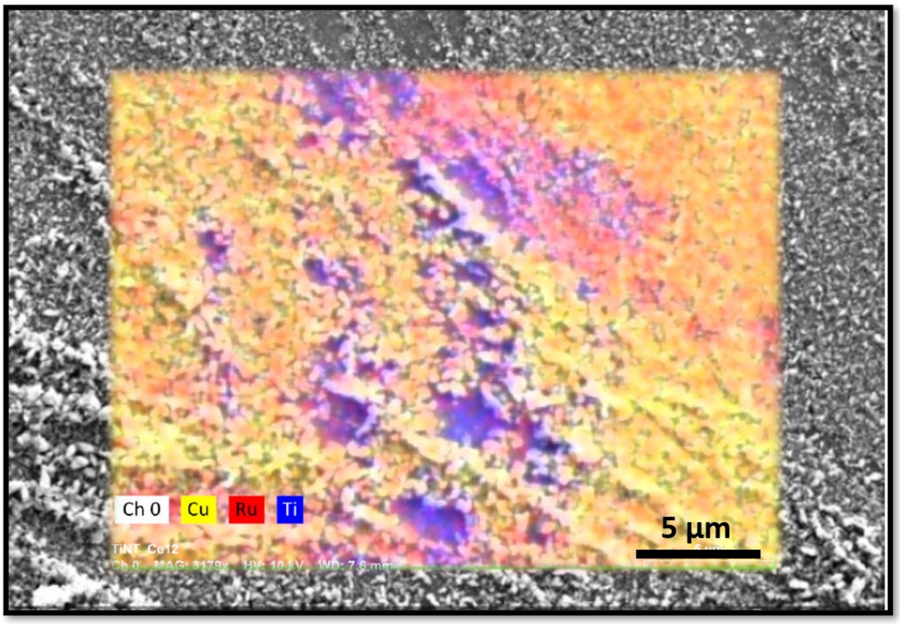

Figure 1. *FE-SEM for a thypical RuO_x-CuO_x coated Ti electrode. with the corresponding EDX maps as insets.*

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Functionalized carbon black for elastomeric composites with low dissipation of energy

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The most important application of elastomeric composites, tire compounds, relies on the following dynamic-mechanical properties: dynamic rigidity and hysteresis. For car tires, hysteresis is tuned as a function of temperature: high at low temperature and low at medium-high temperature, to promote traction on wet roads and low energy dissipation (rolling resistance), respectively. To obtain these properties, amorphous precipitated silica is used as reinforcing filler. The strengths of silica are: nano dimensions and the possibility of incorporating and establishing chemical bonds with the elastomers' chains. Carbon black (CB), which is also largely used in tire compounds, does not have functional groups able to promote chemical bonds with the rubber matrix. It would be highly desirable to functionalize the surface of carbon black with such functional groups: a CB with a cradle to gate LCA comparable if not even better than silica's LCA could be used in replacement of silica in tire compounds.

In this work, a pyrrole compound (PyC) was used for functionalizing CB by applying the so-called "pyrrole methodology" [1-3]. The selected PyC contained a thiol group which was expected to react with the sulphur-based crosslinking system, thus forming chemical bonds with the rubber chains [4]. The synthesis of the PyC and the functionalization reaction were characterized by high atom efficiency. A poly(styrene-co-butadiene) copolymer from anionic solution polymerization was used as the main rubber for the compound preparation. The crosslinked composite material filled with functionalized CB revealed substantial improvements with respect to the composite with pristine CB, in particular: high rigidity and low hysteresis at high temperature. These findings seem to confirm the formation of the expected rubber-filler chemical bond and are even comparable to those of silica-based rubber composites.

The results here reported pave the way to CB-based rubber composites with a low environmental impact.

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[4] International patent application No. PCT/EP2019/061707, filed on November 5th, **2019**

Insights into the reproducibility of non-targeted NMR procedures in food analysis

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In last years, non-targeted metabolomics based on 1D ^{1}H Nuclear Magnetic Resonance spectroscopy (NMR) combined with chemometrics has being experienced an increasing number of applications, such as in food quality control and fraud detection [1]. To date, no internationally agreed guidelines are available to regulate the procedures for non-targeted spectroscopic analyses over different laboratories. Also, no official analytical parameters have been established so far to determine the repeatability and reproducibility of the applied protocols in this field. We recently made some contributions organizing multiple inter-laboratory studies and elaborating the big amounts of data deriving from. A particular focus was dedicated to evaluating the reproducibility of the NMR analyses performed through different spectrometers and by many operators, by developing common calibration lines and validated classification models [2, 3]. The effect of processing of data was investigated towards the development of more efficient chemometric analysis [4]. Nevertheless, the variability induced by the operator during the preparation of the NMR sample is still understudied. In the present work, as part of a collaborative research project (Istituto Poligrafico Zecca dello Stato – Politecnico di Bari), this aspect was taken under deep investigation. Thus, 65 samples of tomato collected from different Italian regions were subjected to the same strict analytical protocol encompassing the sample preparation and the subsequent NMR analysis. Such a protocol was performed by two different operators and utilizing two diverse spectrometers. A classification model was developed through the chemometric elaboration of the data produced by the first laboratory and it was tested utilizing, as a test set, the data provided by the second laboratory. The study provided useful insights into the effect of variations in the sample preparation, the protocol of analysis, and the processing of data on the reproducibility of the results. The results described herein, introducing some concepts of good practice, may help to realize the far-sighted project designed to induce a more widespread use of non-targeted spectroscopic methods in food analysis.

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Hierarchical Iron-Nitrogen-Carbon Electrocatalysts for Oxygen Reduction Reaction

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COFs (covalent organic frameworks) are organic polymers known for their high surface area which find applications catalysis, chemical separation, and gas storage.[1] Tuning synthesis parameters allowed obtaining different structures and morphology leading to extraordinary electrocatalytic performance and stability toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). In this context, the development of electrocatalysts based on transition metals embedded on COFs is of fundamental importance to achieve new generation energy systems.[2,3]

In this work the synthesis of a class of COFs with a 3D spherical hierarchical structure has been developed and optimized. The synthesis was carried out through the polymerization reaction of two monomers, such as phenol (P) and melamine (M), followed by a hydrothermal treatment. During this process, a soft template, Pluronic F127 (F127), is added to modulate the microporosity [4]. After that, the phenolic resin has been impregnated with different amount of iron and pyrolyzed at 900 °C in NH_3 atmosphere. Changing the mass ratio of P, M and F127, nanostructured samples with different morphologies have been obtained (Figure 1a,1b and 1c). The prepared materials showed a large specific surface area (around 850-1100 m^2/g) and hierarchical porosities composed of mesopores and micropores. Furthermore, due to its structure, chemical composition, porous structure and high specific surface area, these materials exhibited a good electrocatalytic performance and stability toward ORR in alkaline electrolyte, with an onset and half-wave potential of 0.89 V and 0.82 V vs RHE, respectively, which are comparable to commercial Pt/C catalyst taken as reference.

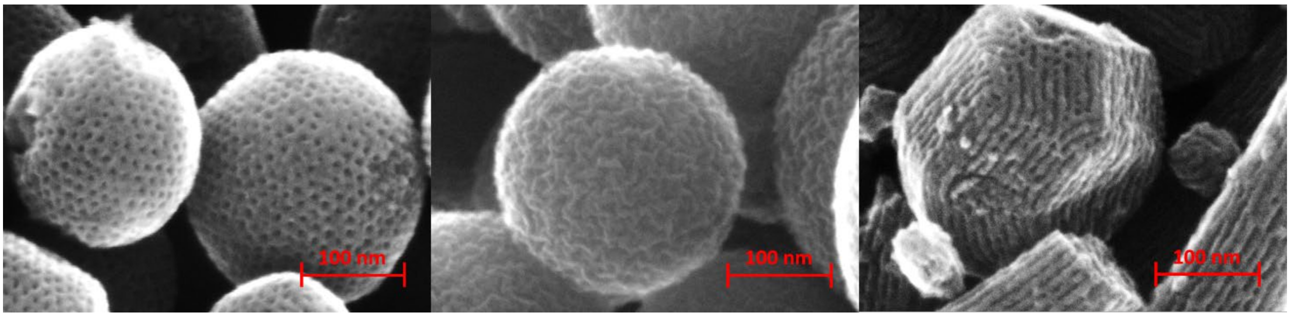

Figure 1. SEM comparison of three phenolic resin compounds (PMR) with different synthetic conditions a) PMR homogeneously distributed micropores; b) PMR without micropores and c) PMR asymmetric structure with pores and linear grooves.

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Environmental assessment of levulinic acid obtainment from residual Cynara Cardunculus biomass

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This work was performed in the framework of the PRIN 2017 project titled "Development and promotion of the Levulinic acid and Carboxylated platforms by the formulation of novel and advanced PHA-based biomaterials and their exploitation for 3D printed green-electronics application", the acronym of which is VISION [1].

Particularly, the obtainment of levulinic acid from lignocellulosic residual biomass from Cynara Cardunculus residual biomass, after a steam explosion pretreatment was studied. Indeed, levulinic acid represents a versatile platform chemical, classified by the United States Department of Energy as one of the top-12 promising bio-based building blocks.

The optimized experimental procedure was accurately and objectively quantified in terms of its environmental impact by applying the Life Cycle Assessment (LCA) methodology from the cradle to the grave perspective, thus starting from the crop production, up to the levulinic acid extraction from steam exploded residual biomass.

The environmental and human health impacts were modeled using the software Simapro v. 9.1.1.1 [2], with Ecoinvent 3.6 as the reference database for the inventory analysis [3].

The impact assessment was performed by the IMPACT 2002+ evaluation method [4].

The IMPACT 2002+ assessment method was modified by creating a new impact category named "Fertility of the soil" related to the nitrogen content in the humus characterizing the soil. This allowed for the first time to comprise in the environmental impact also the quality of the soil after the Cynara Cardunculus crop production.

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Pt^{II}-nitrile complexes: An experimental and computational study

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New spectroscopic (through FT-IR, UV and multinuclear NMR in solution and in the solid state determinations), structural (through X-ray structures redetermination) and computational (by DFT methods) studies have been carried out to clarify the nature of the N-Pt^{II} bond in a series of *cis*-/*trans*-$(RNC)_2PtCl_2$ (R = Me, Ph, CH_2Ph, *p*-Ph-CF_3, *p*-Ph-CH_3, *p*-Ph-OCH_3) nitrile complexes. This bond is characterized by both $N\rightarrow Pt^{II}$ σ and $N\leftarrow Pt^{II}$ π contributions, the latter corresponding to about 30-40% of the total orbital interaction. The significant (50-60 cm^{-1}) ν_{CN} blue-shift (apparently counterintuitive considering the depletion of electron density along the C-N axis and the π-back-donation involving virtual anti-bonding π^* orbitals) is in agreement with the calculated increase of k_{CN} force constants mainly deriving from an inversion of polarization of the CN bond with respect to the free ligands [1]. It was proved that the red-shift effect of the $N\leftarrow Pt^{II}$ π–back-donation buffers the effect of CN polarization, lowering the magnitude of the ν_{CN} blue-shift [1]. The $\delta(^{13}C_{CN})$ were in all cases highfield-shifted or unchanged with respect to the free ligands, both in solution and in the solid state, apparently in contrast with the susceptibility of the nitrile carbon to nucleophilic attack. DFT calculation in solution showed that for $\delta(^{13}C_{CN})$, spin-orbit contributions are very small for the free ligands (0.5 ppm), while as large as 6 ppm for the complexes [2]. This confirms that $\delta(^{13}C_{CN})$ experiences a moderate Heavy Atom Light Atom (HALA) effect, being in β to the Pt^{II}. The improved reactivity of Pt^{II}-nitrile complexes towards nucleophiles was extensively reported in the literature [3]. It was shown that the nitrile activation in *trans*-$[Pt^{II}Cl_2(NCMe)_2]$ is induced by the LUMO energy decreasing when moving from the free ligand to the complex [4]. Recently,[5] a DFT mechanistic study of the nucleophilic addition of NH_3 to *trans*-$[Pt^{II}Cl_2(NCMe)_2]$ to achieve the cationic *trans-Z,Z*-$[Pt^{II}Cl(NH_3)\{HN{=}C(NH_2)Me\}_2]Cl$ complex has been carried out. The reaction gives different products depending on the experimental conditions: the neutral bis-amidine derivative at high temperature and in the presence of $NH_{3(aq)}$ excess, the cationic bis-amidine derivative in CH_2Cl_2, with $NH_3(g)$ from 0° to RT, and a mixture of neutral and cationic derivatives in THF with $NH_{3(aq)}$ at RT [5]. The hierarchy between the substitution reaction (*via* preliminar chloride substitution by NH_3 on the Pt center) and the direct nucleophilic attack of NH_3 on the coordinated NCMe, has been studied. Results shows that the substitution reaction followed by the nucleophilic addition is highly favored. The amidine formation occurs by a mechanism involving six-membered transition states with a water molecule as an effective proton shuttle. The influence of the R moiety in *cis*-/*trans*-$(RNC)_2Pt^{II}Cl_2$ (R = *p*-Ph-CF_3, *p*-Ph-CH_3, *p*-Ph-OCH_3) complexes on the reactivity with NH_3, from both the synthetic and theoretical point of view is under investigation.

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Solid acids for green chemistry: is the hydrolytic sol-gel route a suitable synthesis strategy?

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Solid acids are the green alternative for heterogeneous acid catalysis, in particular for industrial processes exploiting biomass. Nb–P-Si oxides are valid candidates owing to their specific acidic properties and tolerance to water, despite the intrinsic instability to hydrolysis of Si-O-P bonds in wet atmosphere. Besides the high temperature techniques, sol-gel synthetic methods are a viable alternative not only because they represent a lower cost technology but also because they allow the preparation of high purity materials with a homogeneous distribution of components on the atomic scale. Recently, innovative hydrolytic sol-gel routes, distinguished by the easy manipulation of precursors and wholly performed at room temperature, were established allowing obtaining amorphous Nb-P-Si mixed oxide materials, with SiO_2 content equal to 95 and 92.5 mol% and Nb/P molar ratios equal to 1 and 2. [1-3].

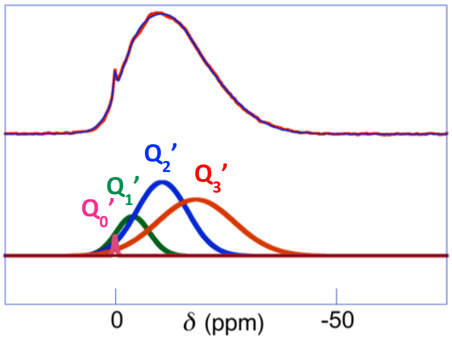

Figure 1. ^{31}P MAS NMR spectrum of 5Nb5P90Si dried gel (upper) and corresponding curve fitting (below).

Si–O–Nb bridges were formed which allowed phosphorus to be anchored stably through Nb–O–P bonds within the gel (see Figure 1). These materials showed remarkable acidic characteristics exhibiting both Brønstend and Lewis sites and showing excellent catalytic performances in different reactions such as the hydrolysis of inulin [2, 4], the esterification of oleic acid with polyalcohols [2], fructose dehydration [5], gas-phase ethanol conversion to ethylene [3].

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Emerging properties of resilin-inspired peptides upon halogenation

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Resilin is a natural elastomeric protein found in the exoskeleton of insects, having a key role in their flight and jumping skills[1,2]. This protein shows remarkable resilience and noteworthy energy storage. Indeed, it is commonly used in tissue engineering and other fields, *e.g.*, drug delivery.[3] We demonstrated the huge impact of halogenation on the supramolecular properties of some biologically relevant biomolecules. Here, we focused on the impact of this modification on a short fragment of Resilin, with the aim to confer to this sequence the same elastomeric properties of the full-length protein. The need to use this reductionist approach[4] is that the macromolecule is particularly complex and difficult to produce on a large scale with inevitable negative feedback from the economic and applicability points of view. Our studies demonstrate that halogenation amplifies the intermolecular interactions, promoting the self-assembly of this peptide.[5-9] Introduction of halogen atoms on the tyrosine residue of the peptide promotes the formation of resilient fibril-like aggregates, which are not formed in the non-modified sequence. Through molecular dynamics studies, we further testified how the presence of bromine, in particular thanks to the halogen bonds, gives great structural order to the peptide, favoring the fibrillar aggregation. Studies of mechanical properties through rheology showed how the material has acquired important properties such as elasticity. This work shows how it is possible, even only through small modifications on a small fragment derived from resilin, to introduce unique properties to a material (absent in the natural sequence). The unique properties of this halogenated peptide make it a promising candidate for manifold applications, *e.g.*, elastomers.[10]

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Mass spectrometry monitoring of organic reactions: a gas-phase study to highlight the reaction mechanism of the Knoevenagel condensation

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The creation of carbon–carbon bonds is still highly required topic in organic chemistry for the capacity to give a wide variety of new products of industrial value. The Knoevenagel reaction represents an important reaction to obtain carbon-carbon bonds. [1] Imidazole-based ionic liquids are widely used as catalysts in the Knoevenagel condensation reaction. [2] These catalysts can operate through different reaction paths, through different intermediates. Therefore, the studies of these intermediates can create new research opportunities with respect to the type of catalytic activity, and the precise knowledge of the intermediates involved in the Knoevenagel mechanism is also important to design new specific catalysts. Mass spectrometric techniques were used to capture from the condensed phase the ionic reactants, intermediates, and products of the reaction. The progress reaction was monitored over time with atmospheric pressure (AP) ionization techniques, such as electrospray ionization and AP chemical ionization, coupled to mass spectrometry (ESI-MS and APCI-MS) to check the formation of the reaction products, detect the key intermediates of the process and elucidate the catalyst role in reaction mechanism. [3] Considering the debate existing on the Knoevenagel mechanism, the precise knowledge of the intermediates involved in the reaction is crucial to design task-specific catalysts. To this end, we have exploited the speed and sensitivity of the mass spectrometric techniques to efficiently "fish" from the condensed phase the ionic reactants, intermediates, and products of the reaction and carry them in the gas-phase environment for structural and reactivity investigations. Collision-induced dissociation experiments, performed by an ion-trap mass spectrometer and consisting in subsequent steps of ion isolation and fragmentation, have been employed to characterize intermediates and products of the Knoevenagel condensation. These techniques have long-term contributed to provide mechanistic information about important organic reactions. [4-6]

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Effect of $BaTiO_3$ nanoparticles functionalization on structural and piezoelectric properties of polymer-ceramic nanocomposites

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The last ten years have been characterized by a growing interest in the field of flexible, lead-free, piezoelectric nanocomposites for energy harvesting and sensor applications. These composites are usually made of a piezoelectric ceramic filler (e.g., $BaTiO_3$, $KNbO_3$, $Na_{0.5}Bi_{0.5}TiO_3$) embedded in a suitable polymeric matrix [1]. One of the main problems in the production of such composites consists in the poor affinity between the inorganic filler and the organic matrix [2]. This results in difficult and non-homogeneous filler dispersion in the matrix, in particular caused by the high volumetric fraction of the filler required to obtaining high performance composites. Surface functionalization of ceramic nanofillers can improve the chemical affinity between the organic matrix and the inorganic moiety of the composite, resulting in improved filler-matrix interaction and, hopefully, in enhanced piezoelectric response. The aim of this work consists in the surface functionalization of barium titanate nanoparticles, produced by hydrothermal synthesis, with different molecules, according to the host polymeric matrix. The particles' surface is chemically activated in order to increase the amount of reactive groups, and then functionalized by reacting with different organosilanes, such as (3-glycidyloxypropyl)trimethoxysilane (GPTMS) or (3-aminopropyl)triethoxysilane (APTES) [3] functionalized nanoparticles are characterized by FTIR and solid state NMR spectroscopy [Figure 1], and TG/DTA analysis to assess the process effectiveness. Pristine and functionalized nanoparticles are embedded (up to 20-30% vol fraction) in different polymeric matrices such as epoxy resin and poly-dimethylsiloxane. Nanocomposites are characterized by SEM imaging [Figure 2] and both FTIR and solid state NMR to evaluate nanoparticles dispersion and filler-matrix interaction. The piezoelectric response (d_{33} constant) is measured using a Berlincourt type piezo-d_{33}-meter and correlated to the structural features of the nanocomposites.

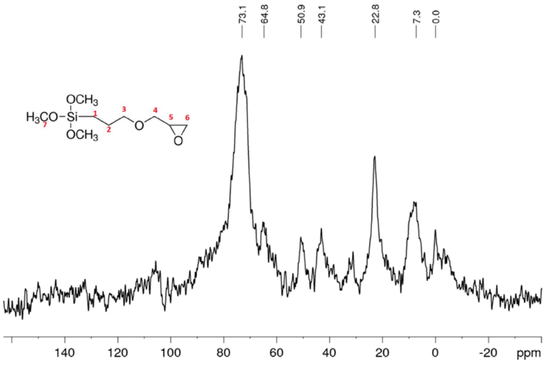

***Figure 1** ^{13}C CPMAS NMR spectrum of GPTMS-functionalized BaTiO3 nanoparticles (inset: C labeling of GPTMS molecule)*

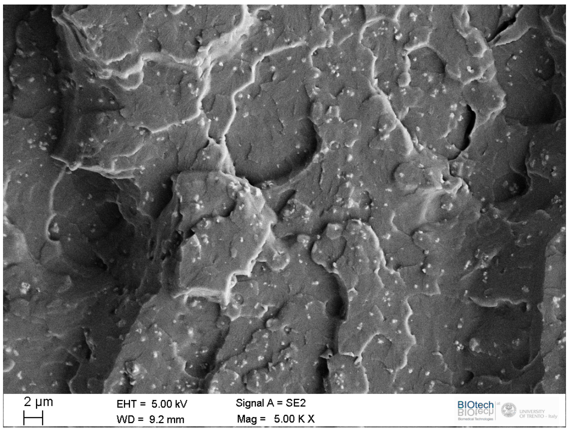

***Figure 2** SEM micrograph of epoxy-based nanocomposite*

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Società Chimica Italiana

SCI2021

TECNOLOGIA FARMACEUTICA (TFA)

- Orals
- Posters

Lipid and dendrimer-based nanomedicines for siRNA

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Nanomedicines have recently led to major successes in the delivery of nucleic acids. Regarding the latest, several drugs have been launched on the market or in clinical trials for liver diseases or local applications (ophthalmic or pulmonary). During this presentation, I will describe our contribution to overcome the remaining barriers to extend the scope of nanomedicines. I will be discussing three types of nanomedicines that my group has been designing in recent years.

- Cationic phosphorus-containing dendrimers and dendrons were applied to the delivery of an anti-TNF-α siRNA by inhalation for the first and by intravenous administration for the second. Characterization of siRNA interaction with the cationic pyrrolidinium end group was studied. As a result of this interaction, cellular internalization was increased as well as the efficacy of the siRNA. Both systems were able to strongly reduce lipopolysaccharide-induced lung inflammation in mice and arthritis score in the CIA murine model.
- We also designed systems for the targeted delivery of siRNA to CD44 expressing cancer cells. The most efficient one called “aptasome” was composed of a core made of a siRNA:protamine complex surrounded by a lipid membrane-bearing anti-CD44 aptamers. On a breast cancer model expressing CD44 and transfected with luciferase gene, our system was shown to block in vitro and in vivo protein expression due to their stronger cellular specificity and better accumulation in tumor.

In conclusion, our three delivery platforms have improved drug efficacy taking into account the pathophysiological changes in each disease but also improving the biopharmaceutical properties of carried drugs.

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Adenovirus based technology and the GRAd-COV2 vaccine

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ReiThera Srl – previously Okairos – was founded by an experienced team which pioneered the development, manufacture and early clinical testing of non-human origin adeno-vectored vaccines for major infectious diseases such as hepatitis C, malaria, HIV, Respiratory Syncytial Virus, and Ebola. With fully-equipped, state of the art R&D laboratories and GMP production facility located in Rome, and auxiliary laboratories in Naples, ReiThera delivers reliable solutions at every step of early development to engineering and industrial process. From early development to final QP release, we provide tailored and effective solutions to meet the industry's demanding regulatory standards and the expectations of the fast-growing market of gene-delivery technologies.

ReiThera's facility is dedicated to GMP lot production in support to clinical development consisting of 870 m^2 cGMP production suites, 170 m2 quality control laboratory, and more than 700 m^2 of GMP and research support service space, inclusive of filling suite equipped with an oRABS isolator with a fully automated aseptic filling machine. In this area, ReiThera produces GMP viral cell culture, up to a 200L scale and supports fill finish of DP lots for clinical trials.

Starting form early 2020, ReiThera promptly reacted to the COVID-19 pandemic by using its most advanced technologies to quickly develop an adenoviral-based vaccine, GRAd-COV2, to tackle the global vaccine demand. To do this, ReiThera also built a new GMP facility that could support the manufacturing of the vaccine on large scale.

The new commercial scale facility (500 m^2) is equipped with state-of-the-art single use technologies, both Upstream and Downstream, that has a potential full capacity of 100 million doses of vaccine per year. The virus production room is equipped with a 200 L Single Use Bioreactor which works in perfusion through ATF (Alternate Tangential Flow) technology, one 1000 L and one 2000 L Single Use Stirred Bioreactors. This manufacturing capacity based on single use technology is unique in Italy.

GRAd-COV2 vaccine has successfully completed clinical trials of Ph1 and Ph2 demonstrating its safety and efficacy on hundreds of volunteers.

ReiThera has developed a technological platform based on proprietary reagents and manufacturing processes that can be easily scaled up and transferred to support global and local vaccine demands.

A lesson from Vitamin B12: from the biological issues to the design of a nutraceutical formulation

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Vitamin B12 (VitB12) is an essential micronutrient needed for life. It is synthesized exclusively by certain bacteria and archaea and, thanks to their interaction with animals and plants, VitB12 can enter the food chain of human beings.

The deficiency of VitB12 is determined by several causes that include for example the malabsorption due to transitory gastrointestinal diseases or exclusion of specific food such as in the case of a strictly vegan diet. Furthermore, a life-long administration of VitB12 is needed in the case of inborn errors of VitB12 metabolism or congenital diseases that affect its absorption.

Deficiency of VitB12 determines several impairments including bone and heart disease, depression, neurological disorders, infertility, abnormal embryo development, and cancer, while VitB12 treatment is crucial for survival in inborn errors of VitB12 metabolism.

VitB12 is administrated through intramuscular injection, thus impacting the patients' lifestyle, although it is known that oral administration may meet the specific requirement even in the case of malabsorption. Furthermore, the high-dose injection of VitB12 does not ensure a constant dosage, while the oral route allows only 1.2% of the vitamin to be absorbed in human beings.

Nanocarriers are promising nanotechnology that can enable therapies to be improved, reducing side effects. Today, nanocarrier strategies applied at VitB12 delivery are at the initial phase and aim to simplify administration, reduce costs, improve pharmacokinetics, and ameliorate the quality of patients' lives. The safety of nanotechnologies is still under investigation and few treatments involving nanocarriers have been approved, so far.

Here, it is made the point regarding the biological issues linked to VitB12 absorption or specific supplementation and discusses the needed or desirable features of nanocarriers to ameliorate VitB12 bioavailability towards an improved nutraceutical formulation.

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Using magnetic stimulus to bioengineer tendon tissue and tissue models: new tools to understand and stimulate regenerative pathways

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Despite the limited knowledge on tendon development and healing processes, it is known that inflammation plays a key role in tendon tissue healing. Persistently increased inflammatory cytokine levels have been associated to tendon degeneration and/or scar tissue formation upon injury and therefore may provide a target for assisting new therapeutic strategies. However, the molecular and cellular mechanisms involved are poorly understood requiring further insights.

In previous studies, we showed that magnetic actuation modulates the behaviour of tendon cells exposed to IL-1□, a pro-inflammatory cytokine, and that magnetically actuated membranes could hold immunomodulatory properties when implanted in a rat exposed to an external magnetic field [1]. Therefore, we have been focusing efforts on understanding possible uses of magnetic stimulus, in combination with magnetic responsive materials, to modulate inflammation in tendon/tendon cells, which can provide an additional valuable tool to trigger tissue regeneration instead of simple repair.

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Inflammation in wound Healing: the role of drug delivery

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The inflammatory phase is a crucial step in wound healing. Recently there was more attention to this aspect in terms of diagnostic procedures and therapeutic strategies.

The goal of caregiver should be to better understand when there is a necessity to provide the wound bed and surrounding skin with an anti-inflammatory therapy. The role of exudate on this matter is fundamental and more and more information have been provided to characterize the various cytokines in the exudate. In the last few years there was an increasing interest about correcting-rebalancing the inflammation in various type of chronic wounds. The treatment ideally should by pass the systemic side effects of immunosuppressive agents considering the patient general status, which is most of the time affected by several other co-morbidities. Topical agents with anti-inflammatory action have shown potential positive effects on chronic wounds. The range of topical agents in use at this time will range from matrix metallo proteases inhibitors, anti TNF alfa drugs, anti-inflammatory non-steroid agents. Careful evaluation of wound bed and sometime pathological assessment with a biopsy are mandatory before starting treatment. Level of pain will benefit also from those treatments according to the relation between pain and inflammation.

Microfluidic preparation and characterization of iRGD-functionalized solid lipid nanoparticles for targeted delivery

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For the past years, research has been conducted to utilize solid lipid nanoparticles (SLNs) as alternative to colloidal drug delivery system, such as lipid emulsions, liposomes and polymeric nanoparticles. SLNs combine the advantages of different colloidal carriers and avoid some of their disadvantages. Microfluidic nanoparticle synthesis strategies have been developed with the goal of providing a successful approach to scale-up the nanoparticle synthesis process in a reliable and reproducible manner. Efficient mixing and rapid chemical reaction at the nanoliter to picoliter scales allow microfluidic devices to better control the synthesis parameters, and thus, the nanoparticles size and properties [1]. The production of SLNs using microfluidics was recently published as the first platform [2]. In this work we produced SLNs by microfluidics technique and paclitaxel (PTX) was loaded into SLNs as a potential model drug for the treatment of glioblastoma. However, in order to improve the biodistribution and efficacy of PTX the affinity ligands, such as peptides and antibodies that bind to tumor-associated markers, can be used. A new class of targeting peptides, tumor-penetrating peptides, that home to tumors are actively transported into extravascular tumor parenchyma. Cell and tissue-penetration of this class of peptides requires the C-terminal exposure of the C-end rule (CendR) motif. The CendR receptor, neuropilin-1 (NRP-1), is overexpressed in many tumor cells lines in vitro and in tumor and stromal cells in vivo. The prototypic CendR peptide RPARPAR binds to NRP-1 and NRP-2 and triggers cellular internalization, extravasation, and tissue penetration of the peptide and payloads coupled to it [3]. iRGD peptide (CRGDKGPDC) is a composite of the RGD avintegrin- binding motif and an RGDK cryptic CendR motif. In this study, the PTX loaded-SLNs produced by microfluidics were functionalized with the iRGD peptide. The SLNs proved to be stable in aqueous medium and are characterized by a Z-average under 150 nm, a polydispersity index below 0.2, a zeta potential between −20 and −35 mV and a drug encapsulation efficiency around 40%. Moreover, *in vitro* cytotoxic effects and cellular uptake have been assessed using 3D tumour models of U87 glioblastoma cell lines.

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Response Surface Methodology for the optimization of Nanogels Polyelectrolyte Complex intended for Ovalbumin nasal delivery

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The development of a new pharmaceutical formulation is a laborious process that largely relies on empirical methods to control the critical quality attributes of the final product. As a result, it can be time-consuming, costly and with high risk of failure. Response surface methodology (RSM) consists of an experimental strategy to optimize the formulation composition and the manufacturing process of such drug delivery product to furnish the desired quality traits obtaining the best quality of information with minimum effort [1]. RSM was used to design and optimize physically crosslinked nanogel (nGEL) based on Dextran sulfate (DS) and ε-Poly-L-lysine (εPL) polyions as antigen carrier for nasal vaccine delivery. Nasal delivery of vaccine offers an easily accessible route to the immune system inducing both mucosal and systemic immunity; the overall features of nGEL, in terms of particles size and charge, represent a key role to achieve maximum immunological effect [2]. In light of these considerations, the effect of DS concentration and the polyanion (DS) to polycation (εPL) ratio at three different levels was investigated on nGEL mean size, polydispersity (PDI) and zeta potential (ZP). A total of 14 formulations were prepared, nGEL were formed spontaneously in water based on the electrostatic interactions between the two strong polyions DS and εPL. Prediction of the optimal formulation was performed using the desirability function. The optimized formulation showed similar theoretical and experimental values, confirming the predictive ability of the mathematical model. Cytotoxicity analysis proved the safety of the optimized nGEL toward Human keratinocyte (NCTC 2544), human fibroblast (HFF1) and human airway epithelial (Calu-3) cell lines, respectively selected as skin, nasal and bronchial/tracheal airway epithelium cell-based in vitro models, confirming the potential application of nGEL for nasal administration. Evaluation of nGEL behaviour in cell culture media was evaluated by DLS and Turbiscan® AG Station after incubation at 37°C for 24 h to assess particles physical stability. The optimized formulation was successfully loaded with ovalbumin (OVA) as a model antigen and furtherly characterized for thermal behaviour, encapsulation efficiency and *in vitro* release profile in phosphate buffer solution pH 5.8 to simulate the intranasal milieu. Loaded nGEL released nearly 43% of OVA within 72 h, assuring prolonged release to maximize exposure to the immune system. Preliminary data show that nGEL and OVA-loaded nGEL are not able to stimulate the inflammatory response in both human primary monocytes and monocyte-derived macrophages in terms of cytokine production (*i.e.*, IL-6, TNF-alpha, IL-10). The lack of reactivity also proved the absence of endotoxin contamination being these cells highly sensitive to minimal amount of LPS (0.01 ng/ml). Moreover, they do not interfere with the physiological inflammatory response to LPS from *E. coli*. Otherwise, the OVA antigen is specifically recognised by an OVA specific hybridoma when OVA-loaded nGEL are internalised and processed by murine dendritic cells. Further studies are ongoing to assess the potential application of OVA-loaded nGEL after intranasal administration to enhance the immunological response.

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Cellulase as active excipient in HPMC prolonged-release matrices: a novel approach to zero-order kinetics

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Introduction Zero-order release kinetics provided by oral Drug Delivery Systems (DDSs) is needed to obtain constant drug plasma levels, which are more desirable than peak and valley plasma concentration profiles as they lead to lower incidence of side effects and frequency of administration[1]. Hydrophilic matrices, which are the most common type of extended-release DDSs[2], do not enable achievement of this kinetics unless proper changes are introduced into the formulation and/or in their geometry. In fact, the initial “burst” effect, due to drug release not yet controlled by the polymer, along with the progressive reduction of the release rate, due to changes undergone by DDSs during the interaction with fluids, result in a non-linear release profile.

Activity of cellulase on HPMC has already been demonstrated by the use of the enzyme in the formulation of a time-controlled DDS[3]. In hydrophilic matrices, cleavage operated by the enzyme could bring about a progressive weakening of the gel layer possibly resulting in an increased diffusivity of the loaded drug as well as in increased extent of erosion phenomena. The typical decrease in drug release rate that affects the linearity of the profiles in their final portion could be mitigated through an increased diffusion and lower increase in the diffusional pathway. In this study, the impact of the addition of cellulase into HPMC-based hydrophilic matrices formulations was studied by means of concomitant release tests and mass loss experiments, to assess possible changes in the release performances.

Methods A mixture of Acetaminophen and HPMC (Methocel®K4M) in a 1:1 weight ratio was used as such or with the addition of different percentages (0.5%, 1%, 5%, 10% w/w with respect to HPMC) of an enzyme-containing product (Sternzym®C13030, 2500 u/g enzymatic activity) to prepare cylindrical matrices (Ø 2,49 cm, nominal weight 1,5 g, crushing strength 70-100 N). The compacts have been coated on all the surface except for one base with an impermeable film, consisting in a 15% w/v CAP solution in acetone. These matrices were tested for mass loss and release tests (n=3) by a Eur. Pharm. 10.0 dissolution Apparatus 2 (500 mL distilled water, 37 °C, $\lambda = 243$). The milligrams of Acetaminophen released have been plotted against time to build cumulative curves. For mass loss experiments, at fixed time points, 50 ml of fluid was withdrawn, replaced with fresh medium, and dried at 80°C to constant weight. The milligrams of solids recovered after drying of each fluid sample were plotted against time to build cumulative curves.

Results An increase in mass loss rate was observed as a function of the percentage of enzyme added. When the enzymatic product was added at 1%, mass loss rate was more than doubled, which would indicate a marked hydrolytic activity of cellulase even when present at low concentrations. The linearity of the release profiles also increased with the percentage of enzyme. The enhanced permeability of the swollen gel layer promoted by cellulase, led to a higher release rate that would not only counteract the release rate decrease but also “mask” the burst phase. The latter could be due to alignment of release rates in the burst and following portions of the curve. Moreover, the greater extent of erosion promoted by cellulase could be effective in limiting the progressive increase of drug diffusion pathway.

These preliminary results may represent a promising basis for a broader study of the proposed strategy in oral prolonged-release matrices based on hydrophilic derivatives of cellulose.

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Remote magneto-mechanical actuation of magnetoliposomes by alternating or pulsed magnetic fields

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Stimuli-responsive liposomes are a promising drug nanocarrier with potential for controlled drug release. Smart behavior of stimuli-responsive liposomes is reflected by their various macroscopic modification under the effect of internal or external stimuli triggers. Their structure, permeability and other characteristics can be altered under certain stimuli, such as heat, light, magnetism and pH changes. Among all investigated stimuli-responsive liposomes, early efforts focused on the use of magnetic field as external trigger and magnetic nanoparticles (MNPs) to control drug delivery from liposomes. The combination of MNPs and liposomes produces the so called magneto-liposomes (MLs). Depending on the characteristics of the magnetic field, MNPs can act as a nano – heater, when the magnetic energy is dissipated as heat energy, or they can serve as a magneto-mechanical actuator, when the magnetic field is converted into a mechanical effort. Usually, MNPs are used to generate heat either from hysteresis losses or from Néel or Brownian relaxation processes. This magnetic hyperthermia can be obtained when MNPs are exposed to appropriate magnetic fields (amplitudes of kA/m and frequencies from tens to hundreds of kHz), and it has been used to trigger release of drugs from MLs. This approach exploits MNPs as nano-heaters to produce a modification in the physical state and permeability of MLs. Therefore, the successful application of the magneto-thermal approach requires the use of temperature-sensitive liposomes, with a T_m in the range from 39°C to 42°C.

More recently, the attention has begun shifting towards a different actuation of MLs. Specifically, it has been observed that it is possible to obtain controlled drug release from MLs even, using non-heating alternating magnetic field (AMF) or pulsed electromagnetic field (PEMF) of appropriate intensity and frequency. Under these conditions, MNPs have demonstrated to be able to convert the energy of the magnetic field into mechanical deformation of the liposomal bilayers. This approach represents an interesting and alternative method to overcome the drawback of the magneto-thermal actuation, that are related to the generation of eddy currents. This alternative approach does not involve heat dissipation by the MNPs, but their vibration or rotation produces a mechanical destabilization of lipid membranes of MLs. It follows that MNPs in a non thermal magnetic field can act as a suitable nano-mechanical actuator.

The efficacy of this approach has been proved with MLs containing hydrophilic MNPs using both low-amplitude AMF, produced by a laboratory device, and PEMF, generated by a device already used in therapy [1],[2],[3]. However, it was shown that the co-entrapment of MNPs and hydrophilic drugs in the internal space of liposomes can reduce the entrapment of the active molecule, due to the co-presence of MNPs within the same volume. To overcome this issue, the magneto-mechanical approach could be proposed using MLs containing small hydrophobic MNPs (5 nm in diameter) within the membrane. In this way, the potentialities of the magneto-mechanical actuation induced by non-thermal MF can be exploited without affecting the drug loading. The aim of this work is to study the phenomena of the release from the MLs and understand how the phospholipid composition, the lateral packing and organization within the membrane of MLs may influence the effectiveness of the magneto-mechanical actuation.

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Controlled and tunable polymeric micro/nano particles production using membrane technology

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Polymeric micro and nanoparticles have broad utility as vehicles for drug delivery and form the basis of several therapies approved by the US Food and Drug Administration. In the early 1990s, membranes have been introduced for the production of micro and nanoparticles with a narrow particle size distribution and controlled size [1,2]. In the so-called membrane emulsification process, two immiscible phases are separated by the membrane and a high interfacial tension exists between the membrane surface and the droplet-forming phase. More recently, an innovative method for the production of polymeric nanoparticles by combining membranes with the well-known nanoprecipitation has been introduced [3]. In this case, two miscible phases are separated by the membrane and meet each other at the pore exit where the mixing of the polymer solution (in an organic solvent, i.e., acetone) with the non-solvent phase (i.e., water) occurs.

Herein, two case studies will be presented to demonstrate the powerful of membrane technology in pharmaceutical particles development: 1) PLGA-PEG microparticles production by *MEMBRANE EMULSIFICATION* and solvent diffusion-evaporation method [4] and 2) PVA nanoparticles production by *MEMBRANE NANOPRECIPITATION*. PLGA-PEG, one of the most common polymers used in drug delivery applications, has been used as carrier material for the production of microparticles for dexamethasone encapsulation. The impact of different solvents used for polymer dissolution (Ethyl Acetate or Dichloromethane), fluid-dynamics and operating conditions applied during membrane emulsification and solidification steps, respectively, on size distribution, particles morphology and green performance scores were investigated. In particular, the sustainability assessment of the process was evaluated by considering the properties of the polymeric particles produced (size, size uniformity and drug encapsulation efficiency) together with the energy consumption. Hydrogel nanoparticles have attracted considerable attention as promising drug carriers for therapeutic applications. They are currently produced starting from emulsion templates while the use of nanoprecipitation for hydrogels is still limited and the application of membrane nanoprecipitation has never been reported. PVA nanoparticles have been produced by using water and an alcohol (ethanol and methanol) as solvent and non-solvent, respectively. The influence of parameters related to formulation composition (i.e. solvent, polymer concentration, phases ratio, non-solvent) and operative conditions (shear stress, flux) to develop a scalable formulation method for the production of highly uniform hydrogel nanoparticles by using membrane nanoprecipitation has been investigated. Results demonstrated that membrane technology is an environmentally improved method for the production of drug delivery systems with enormous impact in terms of formulation quality, energy consumption reduction and waste minimization. The simplicity and versatility of the method combined with the use of green solvents hold much promise for the development of a sustainable chemical manufacturing industry. Considering that a broad spectrum of micro-nanostructured materials with predictable and controllable sizes, different chemical compositions, morphologies, and functionalities can be produced by using the proposed method, membrane-based technologies represent a valuable alternative to the conventional particles manufacturing methods.

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Crocetin as both neuroprotective agent and cross-linker for sericin for obtaining new nasal bioactive nanoparticles

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Crocetin is a carotenoid constituent of saffron that has shown significant potential as an antitumor, neuroprotective, anti-inflammatory, and antiangiogenetic agent as well as it can inhibit amyloid β fibril formation [1,2]. Crocetin is water-insoluble and has low oral bioavailability [2]. Sericin is a water-soluble and globular silk protein derived from Bombyx mori cocoons; it possesses ROS-scavenging, anti-inflammatory, and in vitro immunomodulatory activities [3,4]. This research aimed to use crocetin as a new bioactive natural cross-linker for sericin for obtaining bioactive nanoparticles intended for nasal administration. Nanoparticles were prepared to exploit the in situ crocin's hydrolysis into crocetin, and characterized in terms of physicochemical properties, ROS scavenging activity, cytocompatibility, and cytoprotective effect against oxidative stress. Glutaraldehyde/sericin nanoparticles have been prepared as a control. The reaction between sericin and crocetin was confirmed by FT-IR and thin-layer chromatography. The yield was 98.61 ± 1.03% versus 90.69 ± 2.06% of glutaraldehyde/sericin nanoparticles. Crocetin/sericin nanoparticles had 248.33 ± 6.10 nm diameter and spherical-like shape with a smooth surface studied by Transmission Electron Microscope (TEM) and Atomic Force Microscope (AFM). Nanoparticles remained stable in dispersion at 4 °C for 28 days, and no aggregation occurred after freeze-drying with 0.1% w/v of trehalose. The use of crocetin as a natural cross-linker significantly improved the in vitro ROS scavenging ability of crocetin/sericin nanoparticles with respect to glutaraldehyde/sericin nanoparticles. Both formulations were cytocompatible at all the concentrations tested on human fibroblasts and Caco-2 cells and protected them against oxidative stress damage.

The results obtained support the employment of crocetin as a new cross-linker for sericin and nanoparticles as nasal formulations. After nasal administration, crocetin could reach the brain directly and exert the neuroprotective effect enhanced by the antioxidant activity of sericin.

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Rifampicin loaded liposomes for *Mycobacterium abscessus* infection treatement: intracellular uptake and antibacterial activity evaluation

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Mycobacterium abscessus (Mabs) is an opportunistic pathogen, responsible for severe pulmonary infections in immunocompromised patients, such as Cystic Fibrosis patients [1]. Treatment of pulmonary infections caused by Mabs are extremely difficult to treat as this species is naturally resistant to many common antibiotics. Liposomes are self-assembled vesicular nanocarriers, suitable for hydrophilic and lipophilic drug loading, able to deliver drugs to the target site and successfully used in different pharmaceutical applications [2]. Moreover, liposomes are biocompatible, biodegradable, and nontoxic vesicles. Nebulized liposomes are reported in literature to be efficient to target antibacterial agents to macrophages. Aim of the present study is to formulate rifampicin-loaded liposomes (RIF-liposomes) for lung delivery, in order to increase the local concentration of the antibiotic. Unilamellar liposomal vesicles composed of anionic DPPG mixed with commercial HSPC for rifampicin delivery were designed, prepared and characterized. Samples were prepared using thin film hydration method [3]. Rifampicin loaded and unloaded liposomes were deeply characterized in terms of size, ζ-potential, bilayer features, stability over time and in different biological media. Rifampicin entrapment efficiency and release were also evaluated. Finally, biological activity of RIF-loaded liposomes in Mabs-infected macrophages was evaluated. The results show that RIF-loaded liposomes induced a significantly better microbicidal effect in comparison with free drug, as assessed in terms of intracellular mycobacterial growth by means of CFU assay. Altogether, our results suggest that liposome formulation of rifampicin may represent a valuable strategy in order to enhance the local activity of the drug.

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An affordable approach to scalable nanomedicine manufacturing: 3D printed microfluidics

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One of the main issues for the translation from the bench to the clinic of innovative drug delivery nanosystems is the scale up of the manufacturing process. Microfluidics is a technique that can overcome this drawback thanks to high reproducibility, low batch-to-batch variation, better control over particle characteristics, and higher production rate compared to conventional bench techniques such as the thin layer hydration method [1]. Nevertheless, the predominant barriers for new microfluidics users are access to expensive equipment and device fabrication expertise. 3D printing technology promises to be an enabling new field that helps to overwhelm these obstacles expanding the realm of microfluidics [2].

Here, we are presenting two different microfluidic chips designed to obtain a passive micromixing by a "zigzag" bas-relief and by the presence of "split and recombine" channels. The two designs were first evaluated with computational fluid dynamic studies to assess the mixing potential and then 3D printed in polypropylene using the fused deposition modeling technique. Polypropylene was selected among other 3D printable materials since it is chemically inert and resistant to most of the organic solvents such as ethanol, acetone, and acetonitrile. Cannabidiol loaded PLGA nanoparticles and liposomes were manufactured using the developed chips and the influence of production parameters over the final characteristics was studied applying a design of experiment approach.

The 3D printed microfluidic devices resulted compliant with the original design and both the chips showed an effective production of nanocarriers with tunable characteristics and with a good loading degree. The design of experiment approach helped to understand the main manufacturing parameters that affected the final nanocarrier characteristics.

These polypropylene-based microfluidic chips could represent an affordable and low-cost alternative to common microfluidic devices for the effective manufacturing of nanomedicines (both polymer- and lipid-based) after appropriate tuning of manufacturing parameters. This has the potential to widen accessibility further by eliminating the design barrier in addition to the fabrication barrier largely limiting access to microfluidic technology at present. This is an initial approach to this opportunity that can lead to further designs to improve the characteristics of the microfluidic system. The compromise between resolution and material choice will certainly continue to define the preference for either technology.

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Development and Characterization of a Novel Redox-responsive Core-shell Structure Nanohydrogel as Intracellular Delivery System

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INTRODUCTION

Redox-responsive nanocarriers are of increasing interest in intracellular delivery to achieve specific payload release inside cells by using the concentration difference of reducing agent between extracellular and intracellular environment [1, 2]. In this study, a novel redox responsive core-shell structure nanohydrogel was prepared using two biocompatible synthetic polymers: i) vinyl sulfonated poly (HPMAm-lac$_{1-2}$)-PEG-poly(HPMAm-lac$_{1-2}$) triblock copolymer (Trib-sulf) and ii) thiolated hyaluronic acid (HA-SH) in order to develop an intracellular drug delivery platform for different pharmaceutical applications.

MATERIALS AND METHODS

Trib-sulf copolymer with DS 12% and HA-SH with DS 27% were synthesized according to our previous work [3]. The core-shell structure nanohydrogel was prepared by water in oil (W/O) nanoemulsion method. The HA-SH was dissolved in MilliQ water as water phase and dropped in organic phase which was prepared by dissolved Trib-sulf copolymer in chloroform supplemented with lecithin along with homogenization as surfactant. Subsequently, formed nanoemulsion was transfer to 37 °C incubator under gentle stirring for cross-linking. The nanohydrogel was washed by chloroform to remove lecithin and unreacted Trib-sulf then isolated as white powder by lyophilization. Two model protein cytochrome C (CC) and bovine serum albumin (BSA) differing in Mw were encapsulated in to the nanohydrogel separately by dissolving into water phase before the homogenization step of nanohydrogel preparation.

RESULTS AND DISCUSSION

The particle size, PDI and zeta potential of the nanohydrogels were characterized by DLS and summarize in Table 1. The nanohydrogel presented an appropriate particle size around 250 nm with a narrow distribution. The morphology of the NanoC was characterized by SEM which indicated a regular spherical shape with smooth surface (Figure 1.a). The nanohydrogel was confirmed cross-linked by three different ways: disulfide cross-linked HA core, thermal gelation on the shell induced by the thermal sensitive HPMA segment from Trib-sulf and a Michael addition reaction on the interface between the core and the shell. The core-shell structure of the NanoC was directly observed by TEM (Figure 1.b), and further confirmed by Raman spectroscopy from a standpoint of chemical composition that the presence of peaks assigned to new formed –S–S– and –C–S– bonds. The particle size of the protein-loaded nanohydrogel was increased compared with the blank ones. The surface zeta potential kept consistent with the blank ones which indicated that the protein was entrapped into the hydrophilic core. The nanohydrogel showed good encapsulation efficiency (approximately 90%) for both BSA and CC. The protein can be rapidly released into reducing environment via nanohydrogel degradation triggered by redox responsiveness. Significantly, the peroxidase activity of CC was both highly retained after encapsulation and showed a typical Michaelis-Menten kinetics. The nanohydrogel was demonstrated to have a very good cytocompatibility by LDH cytotoxicity assay and can be efficiently internalized into macrophages observed by confocal microscopy.

Table 1. Characterization of empty and protein loaded nanohydrogels

Payload	Particle Size (nm)	PDI	Zeta Potential (mV)	Encapsulation yield	Loading capacity
Blank	251.30 ± 5.74	0.12 ± 0.04	−12.7 ± 0.60	--	--
BSA	319.37 ± 13.10	0.21 ± 0.04	−12.3 ± 0.44	93.41 ± 5.49 %	18.68 ± 1.10 %
CC	321.73 ± 7.95	0.20 ± 0.01	−12.2 ± 0.40	90.78 ± 4.37 %	18.16 ± 0.87 %

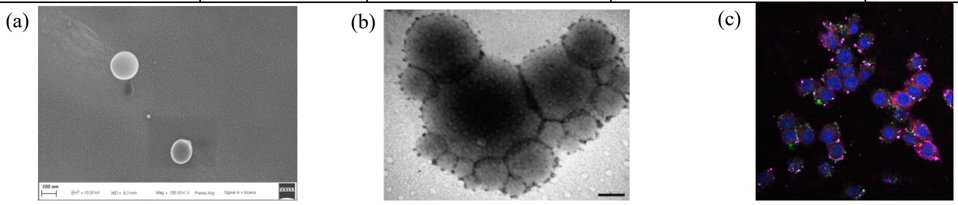

Figure 1. Imagines of the nanohydrogel: (a). SEM; (b). TEM and (c). Confocal images of RAW264.7 cells treated by FITC loaded nanohydrogel (merge channel)

CONCLUSION

In conclusion, the appropriate particle size, the good encapsulation ability for macromolecules and the redox-sensitive release behavior, make the developed NanoC technology a promising tool for the potential intracellular delivery for different pharmaceutical applications, including cancer therapy and beyond.

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Crystallization of stable doped mannitol polymorphs and *in vitro* assessment of their safety as carriers for lung delivery

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The aerosolization performance of dry powder inhalers (DPIs) for the administration of micronized APIs at low dosage depends, among other parameters, on the nature and solid-state properties of the carrier. Mannitol, being non-reducing and non-hygroscopic, is a promising compound to be used as carrier, since it is useful to overcome limitations of lactose, in particular with reference to patients' intolerance and incompatibility with APIs carrying amino groups [1].

On these bases, it is interesting to investigate the effect of different polymorphs on DPIs performances, provided that kinetically stable mannitol polymorphs are obtained, preferably by a simple and reproducible method. To this purpose, doping polymers [2], namely PVA 22K® and PVP K30®, were introduced into mannitol solutions to induce its recrystallization. Different amounts of doping agents were tested, and the minimal amount needed to obtain α and δ form identified. The lowest concentration of PVA 22K® necessary to obtain α form from saturated methanol solution was 2% w/w, with respect to mannitol, while δ form could be obtained with 1% w/w of PVP K30®, by using acetone as antisolvent. Powder X-ray diffraction and differential scanning calorimetry were used to monitor the stability of polymorphs which was confirmed up to 12 months of storage in accelerated conditions (40°C and 75% R.H.). Despite the low amount of doping agents, concerns may be raised about their safety as excipients for lung administration.

For this reason, in vitro assays were performed on two models of the airways, namely Calu3 and A549 cell lines, as a preliminary indication of cytocompatibility. The range of concentration tested was selected considering, on one side, the highest amount of respirable solid, that was obtained by *in vitro* aerosolization of the content of a capsule of 20 mg of sole excipients, i.e. 2 mg, and, on the other side, the estimated volume of lung lining fluid (10 to 30 mL) [3]. On these premises, cells were exposed to different doped polymorphs of mannitol at concentrations up to 16 times higher than the worst-case-scenario (0.2 mg/mL). Viability with respect to β mannitol or untreated cells was evaluated by MTT assay. PVP K30® and PVA 22K® were also tested alone up to a concentration of 64 μg/mL.

No significant differences in viability were observed on both cell lines at all concentrations tested, and viability never decreased below 80% with respect to control, providing substantial evidence of the safety of these substances as useful excipients for inhalation.

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Multicomponent nanosuspension for the bronchial asthma inhalation therapy

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Corticosteroids and bronchodilator agents represent a first line therapy for bronchial asthma treatment [1]. Nevertheless, natural active ingredients have shown a wide variety of promising pharmacological activities and, among others, curcumin exhibited an extraordinary efficacy as an add-on ingredient in asthma treatment, due to its immunomodulatory and anti-inflammatory activity [2]. However, its low water solubility and bioavailability lead to a poor therapeutic effect, which can be overcome by its formulation as nanocrystals. Nanocrystals are nanoparticles of pure drug, which can be prepared as colloidal nanosuspensions, in both water and non-water media, stabilised using surfactants or polymers [3].

The aim of this study was to prepare a multicomponent formulation for the delivery of curcumin (CUR) and beclomethasone dipropionate (BDP) into the lungs as water-based nanosuspensions. Three different formulations were prepared, namely CUR nanosuspension, BDP nanosuspension and the multicomponent nanosuspension (CUR+BDP). The formulations were prepared using a wet ball media milling technique and a non-toxic surfactant as stabiliser. Physical-chemical characterization of nanoparticles and in vitro studies of pulmonary delivery efficiency with Next Generation Impactor (NGI, Apparatus E Ph. Eu.) were carried out. The three different formulations exhibited a nanocrystal diameter in the range 200-240 nm and a low polydispersity index. Furthermore, nebulization tests showed optimal aerodynamic parameters and MMAD < 5 µm.

Table 1. Composition and dimensional analysis of the three studied formulations.

	Composition			**Dimensional Analysis**	
	Curcumin (% p/p)	Beclomethasone dipropionate (% p/p)	Poloxamer 188 (% p/p)	Average diameter (nm)	PDI
CUR-NS	1%	-	0.5 %	206 ± 5	0.250 ± 0.02
BDP-NS	-	1%	0.5 %	241 ± 2	0.236 ± 0.01
CUR+BDP-NS	0.5 %	0.5 %	0.5 %	220 ± 7	0.253 ± 0.02

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Spray patch based on hyaluronic acid and chitosan microparticles medicated with olive leaf extract

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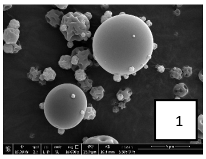
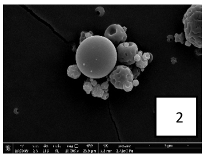
Wound Healing Society described a wound as the result of "disruption of normal anatomic structure and function". Recently, different strategies have been developed to make the wound healing process faster and less painful. Several scientific publications explain the function of chitosan (CS) as a wound healing accelerator. This ability could be associated by its effects of enhancing the functions of inflammatory cells, such as fibroblasts, polymorphonuclear leukocytes and macrophages [1]. Hyaluronic acid (HA) is an important component of the extracellular matrix of the skin. HA is involved in wound healing and tissue repair processes owing to its ability to maintain a humid environment favourable to healing and the stimulation of growth factors, cellular constituents, and the migration of various cells essential for healing [2]. In order to prepare a formulation able to improve the process of wound repair with antimicrobial activity, microparticles loaded with olive leaf extract (OLE) were projected. OLE is used in traditional medicine as a food supplement for a variety of beneficial effects, including anti-inflammatory, antioxidant and antimicrobial. Based on these considerations, microparticles of hyaluronic acid (MpHA-OLE) and chitosan (MpCS-OLE) both loaded with OLE extract were prepared by the spray-drying technique. Polyphenols content determination and degradation assay of OLE was performed. A morphological analysis was conducted on the microparticles using scanning transmission electron microscopy (STEM). Both microparticles types have a smooth surface and a size of about 5 µm (figures 1, 2). The cytotoxicity and wound healing tests were performed on fibroblasts (cell line balb/3T3 clone A31), as fundamental cells involved in the wound healing process [4]. Different types of mixtures were tested on fibroblasts: MpCS-OLE 100%; MpHA-OLE 100%; MpHA-OLE 50%:MpCS-OLE 50%; MpHA-OLE 75%:MpCS-OLE 25%; MpHA-OLE 25%:MpCS-OLE 75%. The mixture composed by MpHA-OLE 25%:MpCS-OLE 75% was the most effective in the wound repair process (figure 3).





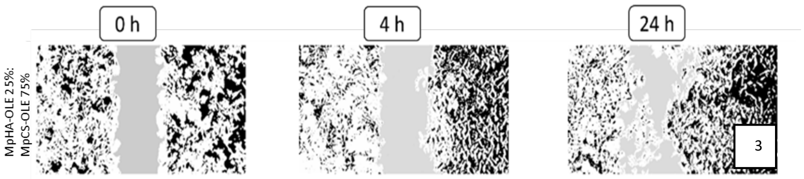


Figure n. 1: STEM micrograph of CS-OLE (16000X magnification)
Figure n. 2: STEM micrograph of HA-OLE (16000X magnification)
Figure n. 3: In vitro wound closure observed after 4 and 24 h for untreated cells (CTR) and for cells treated with different microparticles mixtuters (cell line balb/3T3 clone A31) (4X magnification)

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EtoGel: combined systems for new ethosomes application in joint diseases treatments.

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Rheumatic diseases are often degenerative joint diseases, e.g., osteoarthritis (OA) and rheumatoid arthritis (RA), and to date they are treated with oral, parenteral and intra-articular therapies. The oral administration route has the best patients' compliance but the administered dose is limited by the hepatic first pass effect and some drugs can cause gastrointestinal side effects. Instead, intra-articular drug administration seems to be the most effective approach to treat joint diseases, because the local drug delivery is able to minimize side effects of drugs which are often administered through the systemic route. On the other hand, the current intra-articular treatments require frequent and repeated injections due to a rapid degradation of injected drugs caused by the micro-environment of the joint and as a consequence they entail a high financial burden and reduction in patients' compliance and quality of life. Based on these evidences, the aim of this research work was to propose Ethosomes®, nanocarriers typically used for skin drug delivery, as potential intra-articular drug delivery devices, in order to obtain a longer residence time of the delivered drug in the knee joint. To make ethosomes compatible with administration other than cutaneous, the conventional composition and preparation method were modified. Ethosomes® were prepared by using a low ethanol concentration and carrying out a vesicle extrusion during the preparation. We have demonstrated that the modified composition did not affect the deformability of ethosomes®, a typical feature of this colloidal vesicular topical carrier. The maintenance of sufficient deformability bodes well for an effective ethosome® application in the treatment of joint pathologies because they should be able to cross the pores of the dense collagen II network. The investigated ethosomes® were inserted in a three-dimensional network of thermo-sensitive poloxamer gel (EtoGel) to improve the residence time in the joint. A rheological investigation evidenced that EtoGel could allow an easy intra-articular injection at room temperature and hence transform itself in gel form at body temperature into the joint (Figure 1).

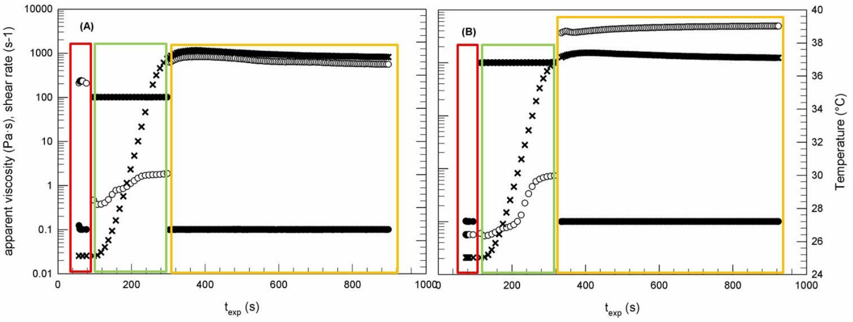

Figure 1. Syringe test carried out to evaluate the viscosity curve of poloxamer gel (A) and EtoGel (B) as a function of temperature and the stage of intra-articular injection (shear rate).

Furthermore, EtoGel seemed to be able to support the knee joint during walking and running, maintaining their gel characteristics without undergoing a gel–sol transformation following stress. In fact, the G′ values are kept above the G″ values throughout the experimental frequency range for both analyzed samples. Moreover, no crossover frequency, at which the storage and loss moduli were equal, was observed. In vitro studies, carried out on two chondrocytes cell lines, demonstrated that the amount of used ethanol did not affect the viability of human chondrocytes and nanocarriers were also able to suitably interact with cells.

Castanea sativa waste as dermo-functional ingredient into a topical delivery system: from the design and development of the formulation to *in vitro* stability and *in vivo* skin tolerability and efficacy

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Chestnut harvesting generates a high number of wastes, mostly spiny burs, that are usually burned or left to rot in the woods by the farmers [1]. In the last years, the new tendency in skin-care formulations is the use of ingredients with antioxidant, immunomodulatory, or photoprotective purposes, obtained from natural products as well as food by-products or agricultural wastes. As matter of fact, food "waste" is the new up and coming commodity and trend in the healthy industry. Technological innovation, to reuse resources, acts for the healthy industry as a sort of catalyst to improve the products quality and business models as it fits with the circular economy concept. The wellness industry has a great interest in antioxidant polyphenols-rich natural extracts, useful in topical application, for their efficacy in reducing oxidative stress and inflammatory phenomena. They can exert protection from damaging free radicals produced when skin is exposed to ultraviolet light or allowed to age naturally. Moreover, never before consumers had such an attentive in selecting products with a high content of natural ingredients and low environmental impact, such as green products [2-4]. Thus, in the present study, *C. sativa* bur extract was used as the active ingredient, in topical delivery system (O/W creams) evaluating its dermal application also proving chemical-physical stability, *in vitro* skin permeation profile, and tolerability, and *in vivo* efficacy by clinical trials. In a previous study, the hydroalcoholic extract, aqueous ethanol 50% (CSE), was found to be rich in polyphenols and with a strong *in vitro* free radical scavenging activity [1]. Based on this promising antioxidant activity and cytotoxicity, 0.1% w/w CSE extract was added to the O/W cream (B). A blank cream (A) was prepared as a control. pH and viscosity values were acceptable for cutaneous application. The cream microstructure resulted homogenous and stable over time. A and B creams showed a typical pseudoplastic non-Newtonian behavior. The presence of CSE affected the B viscosity value by reducing it, giving a desirable feature for easy skin application of the cream. The B cream was able to enhance the *in vitro* CSE skin permeation also preserving its functionality. It resulted non-irritating, with a zero value of total skin irritation and edema index. B had a significant moisturizing effect on 20 Caucasian female volunteers, increasing the skin barrier function. The formulation unchanged the sebum, pH, and erythema values. The results of the sensory evaluation showed that B cream met consumer appeal and acceptance requirements also with great sustainability profiles that consumers value very much.

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Development of topical formulations using hydrolyzed keratin as an alternative to the commonly employed emulsifying agents

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Keratin hydrolysates are water soluble peptides obtained by chemical or enzymatic processes, starting from different organic sources as hair or nails in humans and feathers, horns, claws and hooves in animals. These hydrolysates have been found promising applications in several fields including biomedical, cosmetic, agriculture and packaging ones [1-2]. Specifically, they are known in cosmetics with the INCI name of hydrolyzed keratin (HK) and are employed as skin moisturizing, hair repairing, nail hardening and conditioning agents in a large variety of commercial formulations [3]. Despite their large use in cosmetics, HK can be also employed as an excipient in pharmaceutical formulations intended for a topical application, thanks to its valuable chemical-physical properties as surface adsorption and thickening ability. The aim of the present work is to develop a topical cream formulation containing the antifungal drug ketoconazole using HK extracted and purified from human hair as an emulsifier and a stabilizer without the addition of any other synthetic or natural surfactant. Firstly, HK was extracted from human hair by alkaline hydrolysis, purified by precipitation and dialysis and characterized both at a solid state (differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy) and in aqueous dispersion (tensiometry, conductivity, dynamic light scattering and rheological analyses). Then, its emulsifying properties in comparison to those of polysorbate 80 were screened using vegetable (almond and sunflower oil) or synthetic oils (isopropyl myristate, ethyl oleate, glycerol monooleate type 40) commonly employed in pharmaceutical products. Finally, an oil in water cream formulation was optimized for the topical delivery of 1% w/w ketoconazole.

HK was able to decrease surface tension as a function of concentration down to around 50 mN/m, acting as an amphiphilic macromolecule able to be adsorbed at water/air interface. The apparent CMC value determined by tensiometry, conductimetry and dynamic light scattering was around 2-2.5 mg/mL. On the other side, the thickening ability in water was scarce, providing aqueous dispersions with a viscosity only slightly higher than water. This is probably related to the low molecular weight of keratin-derived peptides (<10 kDa) obtained from hydrolysis, as evidenced by gel-electrophoresis. All emulsions prepared with the same percentage of HK and oily phase (up to 10% of each component) resulted to be stable for at least 2 months at 4 °C. Phase separation occurred, instead, when the amount of HK in the formulation was lower than that of the oily phase. Glycerol monooleate was the oily phase with the highest solubilization capacity for ketoconazole. Therefore, an emulsion formed by a 10% w/w of HK and 10% w/w of glyceryl monooleate containing the drug was prepared and thickened using a pre-neutralized polyacrylate crosspolymer. A stable cream was obtained for the topical delivery of ketoconazole intended for the treatment of skin infections.

Overall, these findings demonstrate the possibility of using HK extracted and purified from human hair as a stabilizer for pharmaceutical formulations such as emulsions or creams without the addition of any other surfactant or emulsifier.

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Biodegradable microparticles for the treatment of the posterior eye segment diseases

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The therapy of posterior eye segment disorders [1], which are often chronic and degenerative [2] is generally performed by intravitreal (i.v.) drug administration of anti-growth factors. This route of administration is associated to severe adverse effects, such as retinal detachment, hemorrhages and vison loss [2]. Thus, the sustained i.v. release of the therapeutic agent may help reducing the injection frequency the related risk of adverse effects. Here, biodegradable poly(lactic-co-glycolic acid) (PLGA)-based microparticles (MPs) externally decorated hyaluronic acid (HA) were produced by a modified double emulsion-solvent evaporation. Briefly, an aqueous BSA solution (0.4% w/v) was emulsified with an organic solution composed of PLGA and F68/F127 poloxamers (PLGA:poloxamers weight ratio was 90:10 and 70:30; the formulations were named P70 and P90, respectively) in dichloromethane (DCM) (20% w/v overall polymer concentration). The obtained emulsion was further homogenized with an external aqueous phase containing HA (Mw=1600 kDa; 0.75% w/v) and poloxamers (overall 0.0375% w/v). DCM was evaporated and the hardened MPs were washed and lyophilized for 24 h. Control PLGA-only (P100) MPs were produced. MP morphology was studied by SEM and BSA release evaluated in simulated vitreous body (SVB).

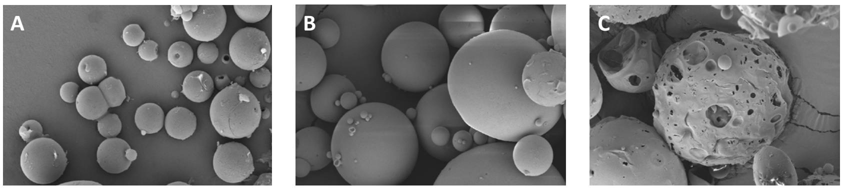

Fig. 1: SEM images of (A) P70 (B) P90 and (C) P100.

P100 MPs were porous, while P70 and P90 formulations possessed a smooth surface. Moreover, all MP formulations could sustain BSA release for at least four weeks, with a limited burst effect when poloxamers were present.

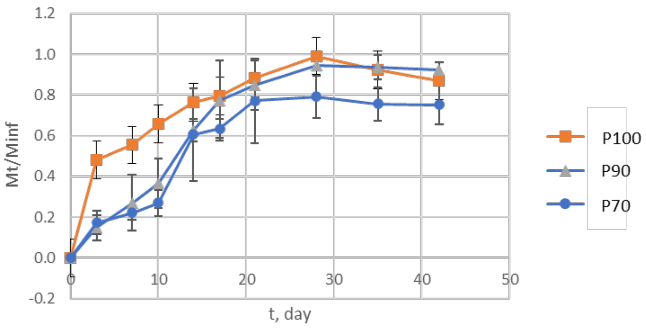

Fig. 2: Released BSA fractions for the three formulations.

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Poloxamer– and poloxamine-based hydrogels as biocompatible systems for the delivery of active compounds

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Hydrogels are hydrophilic macromolecular networks able to retain a significant amount of water or biological fluids [1]. Despite their multiple benefits such as biocompatibility, low toxicity, and similarity to the native extracellular matrix, the implantation of these materials requires an invasive surgical procedure that can cause pain and discomfort for the patient. Thermosensitive hydrogels can overcome these drawbacks. They can easily be prepared and administered in liquid form and undergo gelation in the body, allowing a prolonged and sustained drug release, thus reducing the frequency of administrations and improving the compliance of patients [2]. Poloxamers and poloxamines, nonionic surfactants made up of poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) moieties, are the most widely-used stimuli-sensitive materials for drug delivery applications [3].

Poloxamers are linear PEO-PPO-PEO triblock copolymers that were introduced in the late 1950s and have been proposed for various pharmaceutical applications [1,2]. Our research team recently demonstrated the feasibility of using poloxamer 407 (P407)-based hydrogels for the *in situ* administration of rutin, a flavone glycoside contained in many plants and characterized by various pharmacological activities [4]. However, its bioavailability is compromised by a poor water solubility. The addition of rutin to P407 solutions (20%, w/w) did not compromise the physico-chemical properties of the resulting hydrogels up to a drug concentration of 0.1% w/w. The rheological profiles of systems prepared with rutin as a powder were comparable to those obtained using an ethanol solution of the active compound, thus demonstrating a plausible administration of the flavone glycoside without co-solvents and hence avoiding potential adverse effects.

Poloxamines are X-shaped amphiphilic block copolymers made up of an ethylenediamine central portion linked to four chains of POP-POE [3]. The presence of two tertiary amines confers thermodynamic stability and pH sensitivity to these derivatives and favors their chemical modification as a function of the required need. Among these, poloxamine 908 (P908) exhibits reversible gelation at temperatures close to that of human body. We investigated the suitability of P908 to develop *in situ*-forming injectable hydrogels. P908 aqueous solutions above 25% w/w of copolymer were characterized by a $T_{sol-gel}$ around body values, a useful shear-thinning behavior that could promote their injection into the body and a significant physical stability. The *in vitro* drug release studies using rhodamine B and ovalbumin as model compounds showed the potential applications of P908-based hydrogels as systems for the sustained release of hydrophilic molecules and proteins. Moreover, the inclusion of various colloidal systems did not affect the characteristics of P908 systems, by enabling the development of nanocomposite hydrogels that combine the advantages of both carriers to improve the drug delivery efficiency.

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Printing of cutaneous patches loaded with propranolol for the treatment of infantile hemangiomas

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Topical propranolol (PR) has been used in clinics for treating cutaneous infantile hemangiomas, but frequent applications of semi-solid preparations are required to maintain therapeutic PR concentrations in the skin layers over time. The design of cutaneous patches is attractive to simplify the regimen and to maximize the residence of the dosage form at the absorption site. Indeed, cutaneous patches are designed to provide a prolonged drug delivery through the skin to achieve a local effect. Usually, they are drug-in-adhesive systems, in which the drug is dispersed and/or dissolved in a pressure-sensitive adhesive (PSA) matrix. This manufacturing approach requires expansive equipment that is not easily adaptable to the preparation of small or personalized batches. This work aims to study the preparation of cutaneous PR patches by hot-melt ram extrusion printing, a novel technique suitable for the personalization of such dosage forms [1]. This technology allows defining easily both the patch geometry and the dose according to the patient's need avoiding any manipulation (i.e., the dosage form cutting). To prepare patches, three simple technological operations were required: i) mixing of a poly-ammonium methacrylate polymer (EuRL) with a suitable amount of plasticizer (i.e., acetyl triethyl citrate, ATEC); triacetin or tributyl citrate, TBC), and the drug (propranolol base, PR-B or hydrochloride, PR-Cl); ii) the melting in the ram extruder, and iii) the printing on the backing layer foil. The printed patches were characterized in terms of adhesive properties (i.e., tack, shear adhesion, and 180°-peel adhesion), other than drug content, in vitro drug release, and skin permeation.

The final thickness of the patches (50±10 μm), and the drug contents were uniform, exception made for the TRI-based formulations which were too-fluid to allow a reproducible deposition of the adhesive matrix on the backing layer. On the contrary, all ATEC and TBC formulations exhibited suitable adhesive properties. The tack of placebo ATEC-based patches resulted significantly higher than those obtained from TBC ones ($p < 0.01$), whereas shear adhesion resulted in a comparable pattern. The drug did not significantly affect the adhesive properties of the patches plasticized with TBC and ATEC. The in vitro release results demonstrated that PR was rapidly released from all formulations, suggesting that the thermodynamic activity of the drug at the cutaneous patch/stratum corneum interface should be guaranteed during the application on the skin. The flux (J) values, calculated from the in vitro skin permeation experiments, followed the rank order: ATEC/Pr-Cl < TBC/Pr-Cl < TBC/Pr-B, < ATEC/Pr-B ($p < 0.001$; one-way ANOVA). The PR retained amounts were similar for almost all tested formulations ($Q_{ret} \approx 14$ μg/cm^2). The overall results suggested that patches made of EuRL and TBC and containing 1% PR-Cl were the most promising formulation for ensuring the PR retention on the human epidermis ($Q_{ret}/J = 1.32$) and, therefore, it can be selected when a superficial infantile hemangioma had to be treated. Conversely, patches made of EuRL and ATEC and containing 1% PR-B ($Q_{ret}/J = 0.09$) in the case of deep infantile hemangiomas.

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Polysaccharides based scaffolds for skin tissue engineering

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Wound healing process is complex. Biopolymer-based scaffolds represent an attractive three-dimensional substrate for wound regeneration, for mimicking the dermal extracellular matrix.

The aim of the work was the development of polysaccharide scaffolds intended for skin reparation. In particular, chitosan (CH) and pullulan (P) in association with glycosaminoglycans (either chondroitin sulfate - CS or hyaluronic acid – HA) were considered for scaffolds preparation via electrospinning. The nanofibers were prepared starting from aqueous/acetic polymer solutions to obtain insoluble membranes in aqueous fluids, able to act as a support for cell migration and proliferation. A multidisciplinary approach has been used to characterize the scaffolds including chemico-physical characterization (SEM, SAXS, thermal analysis, zeta potential) and preclinical evaluation (fibroblasts and endothelial cells adhesion/proliferation onto scaffolds and in vivo evaluation in murine burn model) that allowed to obtain integrated information.

The nanofibrous scaffolds prepared were entirely based on polysaccharides, including also polymers having opposite charges (CH, cationic, and CS/HA, anionic) and citric acid was used as crosslinker (activation by heating at 150°C 1 h).

The nanofibers show regular shape and smooth surface [1]. The resistance of scaffolds to solubilization in aqueous fluids seems attributable to the creation of amide bonds (mainly in the CH scaffold, while hindered by the formation of PEC in CH/CS and CH/HA scaffolds) and felting, occurring when water is released from the electrospun scaffold, resulting in local physical multi-entanglement between fibers, that cannot be released by simple hydration. CH/CS scaffold shows the best performance in allowing the skin healing in vivo (murine burn model) and correspondingly, it evidences the best proliferation properties in vitro (fibroblasts and HUVEC). The physico-chemical analysis suggests that the CH/CS scaffold offers more adaptability in terms of swelling and fiber roughening once hydrated, thus conceivably allowing for optimal cell adhesion and migration. In addition, the macroscopic feature of a pronounced deformability pointed at the CH/CS scaffold as a good protective cover for non-flat or irregular surfaces.

To render the scaffolds effective against microbials infections, they were loaded with norfloxacin [2, 3] or with Ag nanoparticles [4]. Moreover, the chondroitin sulfate based scaffolds were also loaded with clay minerals (montmorillonite or halloysite) to enhance the healing process [5].

Although a more extensive preclinical study should be performed, the preliminary results suggested that the scaffold composition and their morphology associated to the loading of active/functional ingredients are key factors to achieve skin reparation.

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Development and Optimisation of a Locally-acting Microemulgel to Improve the Biopharmaceutical Properties of Cannabidiol for Dermatological Delivery

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Recently, the usage of cannabinoids in treating various dermatological conditions is gaining increasing interest. Cannabinoids exert anti-inflammatory and anti-pruritic activities, due to their interaction with CBD2 endocannabinoid receptors localized in the skin cells [1, 2]. Cannabidiol (CBD) is a non-psychotropic phytocannabinoid, which demonstrated a role in modulating skin inflammatory response [3]. In this study CBD was formulated in a microemulgel, in order to control its cutaneous absorption and retention [4]. The microemulsion was prepared by the aqueous titration method and a pseudo-ternary diagram was constructed in order to define the microemulsion existence range. Microemulsion components were carefully selected for their biopharmaceuticals properties and their safety profile in cutaneous applications: isopropyl myristate (5%) was chosen as oily phase, Solutol HS 15 (20%) as non-ionic surfactant, whereas Transcutol P (9%) was selected as cosolvent. Globules of the obtained microemulsion had sizes around 35 nm and PdI less than 0.25; these values also did not change after loading 1% w/w CBD. CBD-microemulsion was then incorporated in Sepigel 305, well known as excellent rheology modifier and selected as gelling agent because it formed a clear and homogeneous microemulgel (CBD-MEgel). Analysis of CBD-MEgel by dynamic light scattering, as well as scanning and transmission electron microscopy, showed the stability of the microemulsion droplets in the gelled formulation. Viscosity was evaluated by the rotational digital viscometer at both 21±2 °C and 35±2 °C, and pH (*ca.* 6.5) was found to be suitable for cutaneous application. The release properties of CBD by the microemulgel were also investigated using vertical diffusion Franz cells and cellulose nitrate membranes: the microemulgel presented a slower CBD release compared to the conventional hydrogel. Accordingly, preliminary permeation studies, carried out by the skin-PAMPA™, demonstrated a lower permeability of the *stratum corneum* for CBD formulated in CBD-MEgel, and these findings were confirmed by permeation studies performed using the Franz cell system with rabbit ear skin. Physical and chemical stability of both CBD-microemulsion and CBD-microemulgel was evaluated over a period of 3 months, showing optimal shelf-life of both formulations at the storage conditions (4±1 °C and 21±2 °C). In conclusion, developed formulation had suitable rheological, stability and permeability features for a locally-acting dermatological delivery of CBD.

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Engineered tubular scaffold for full-thickness esophageal replacement

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Congenital esophageal malformations such as severe atresia, and acquired such as malignant esophageal cancer, requires esophagectomy resulting in full thickness resection which cannot be left untreated. The limitations of the current surgical procedures that use autologous conduit highlight a critical need for tissue engineered circular grafts for esophageal full-thickness wall reconstruction. Polymeric tubular scaffolds cellularized with Mesenchymal Stem cells (MSCs) are proposed as engineered substitutes to promote and speedup regeneration process [1],[2].

Copolymer Poly-L-lactide-co-poly-ε-caprolactone (PLA-PCL) 70:30 ratio and 85:15 ratio were chosen to prepare electrospun tubular scaffolds. Electrospinning apparatus equipped with rotating mandrels was used to collect polymeric nanofibers. Two different types of mandrel were used: cylindrical (∅ 10mm) and asymmetrical (∅ 10 mm and ∅ 8mm) (**Figure 1a and b**). Asymmetric geometry was selected in order to suit surgical implantation. Electrospining process was carried out on PLA-PCL 20% w/v solution in methylenchloride:dimethylformammide 70:30 v/v ratio. Electrospinning parameters set up were: voltage 30 kV, flow-rate 0.5 ml/h, needle 18G and speed of rotating mandrel 1500 rpm
Cylindrical scaffolds were characterized for their morphology, permeability towards glucose (180Da Mw) and mechanical properties.
The scaffolds were engineered with MSCs from pig bone marrow. Different cells seeding methods (vertical and horizontal) were tested on both cylindrical and asymmetrical scaffolds (**Figure 1 d and e**). Biological characterization was performed by MTT test after 7 and 14 days incubation while cells distribution was analysed by Dapi staining and Scanning Electron Microscopy (SEM) analysis.
Preliminary polymeric scaffold *in vivo* surgical implantation was performed on porcine model and after 14 days histological analysis was performed on resected esophageal tissue.

Morphological analysis performed by SEM and processed by ImageJ software showed that fibers in a nanometer size range (700 ± 0.30nm) were collected using both mandrel types. Using the asymmetrical one more aligned fibers were collected on junction section (**Figure 1 c**).
After 24h incubation the asymmetrical tubular scaffolds showed higher glucose permeability rate (98.94 ± 16.00 %) than the cylindrical ones (60. 41 ± 1.77 %).
Results of mechanical tests showed values of Young's Modulus for the asymmetric tubular scaffolds (0.52 ± 0.28 MPa) closer to those obtained for pig's esophagus used as reference control (0.22 ± 0.014MPa). The asymmetrical tubular scaffolds geometry resulted to improve mechanical properties with respect to cylindrical tubular geometry. The result could be related also to the higher fibers alignment in asymmetrical tubular scaffolds, caused by higher surface charge density.
Cell viability was always higher than 80% in all scaffolds analyzed. Horizontal cell seeding method demonstrated more uniform and homogeneous cell distribution along the whole scaffold surface as confirmed by Dapi and SEM analysis (**Figure 1 f**).
Data of *in vivo* experiments showed suitable interaction between polymeric scaffold and tissues ensuring structural support. A mild inflammatory response was observed in the explanted tissues.

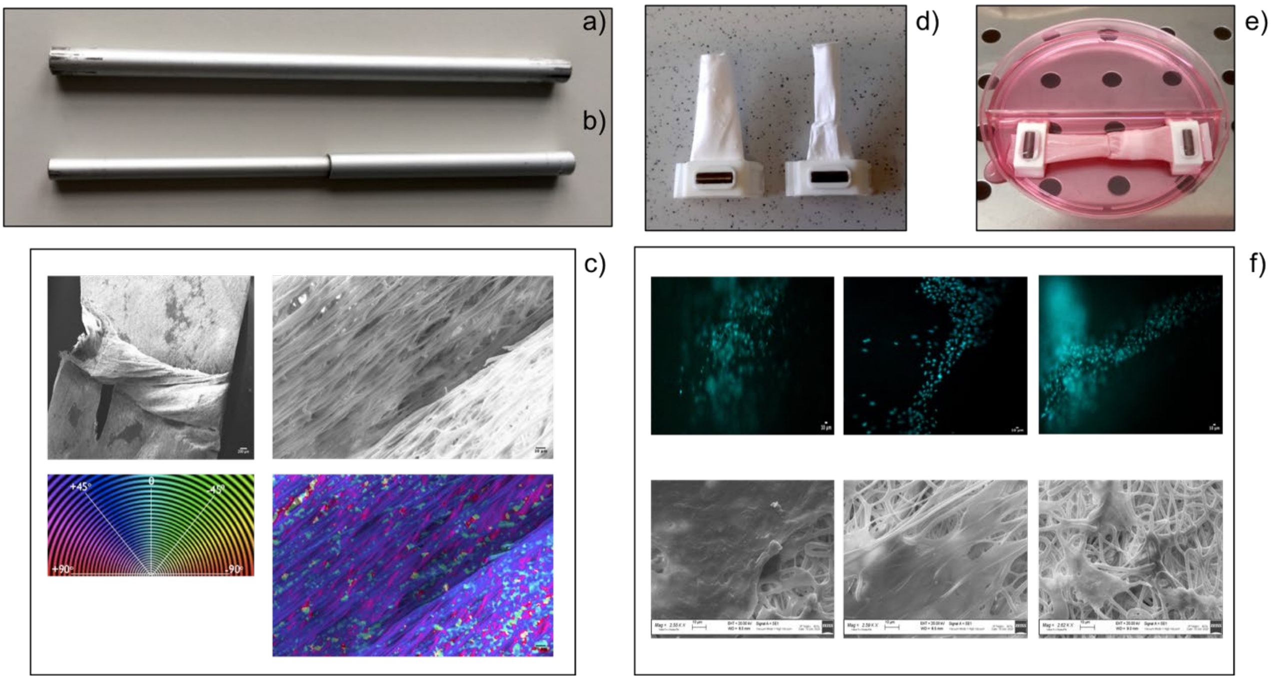

Figure 1: a) cylindrical tubular mandrel; b) asymmetric tubular mandrel; c) morphological characterization and orientation analysis of asymmetric tubular scaffolds. Images of tubular asymmetric scaffold incubation: d) vertical cell seeding; e) horizontal cell seeding. f) Dapi staining and SEM analysis of asymmetric tubular scaffold.

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Harnessing Nrf2-targeting siRNA loaded nanobubbles to overcome melanoma resistance

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The siRNA-mediated inhibition of the Nuclear factor E2-related factor 2 (Nrf2) can be an attractive approach to overcome chemoresistance in various malignant tumors, including melanoma [1]. However, siRNAs are prone to quickly enzymatic degradation and have very poor ability to cross cell membranes. Considering these limitations, the use of nanocarriers have been studied to protect siRNA from degradation during systemic circulation, and deliver siRNA to target cells avoiding nonspecific effects [2]. Interestingly, polymer-shelled nanobubbles (NBs) have shown a great potential as nanoplatform for efficient nucleic acid delivery [3]. This work aims at designing a new type of chitosan-shelled nanobubbles for the delivery of siRNA against Nrf2. siRNA was encapsulated in aqueous droplets within the NB core by means of a preparation method, based on a water-oil-water (W/O/W) double-emulsion, purposely tuned. The NB formulations were *in vitro* characterized determining the physico-chemical parameters (average diameter, polydispersity index, zeta potential), morphology, loading capacity and stability over time. The gel retardation assay using electrophoresis on agarose gel was carried out to confirm the incorporation of the siRNA within the NB. Fluorescent NB formulations were then prepared labelling the core with 6-coumarin to investigate their cellular uptake. *In vitro* transfection efficiency and specificity of siNrf2-NB for Nrf2 were determined by Western blot. The ability of siNrf2-NBs in reducing drug resistance was checked in melanoma M14 cells, by analyzing cytotoxicity. Stable ultra-fine NB formulations were obtained, having sizes of about 100 nm and positive surface charge. siRNA was efficiently encapsulated in NBs, reaching an encapsulation efficiency of about 90%. Its incorporation within the NBs was also confirmed by gel retardation assay using electrophoresis on agarose gel. The fluorescent-labelled NBs were rapidly internalized into M14 cells. siNrf2-NBs were able to down-regulate the target gene in M14 cells, sensitizing the resistant melanoma cells to the cisplatin treatment. Based the results, nanobubbles have shown to be a promising tool for siRNA delivery, able to overcome chemoresistance in melanoma cancer.

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Functionalization of polyacrylic hydrogel scaffold for 3D cell culture

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Traditionally, cell cultures have been performed on 2-dimensional surfaces, but recent evidences have demonstrated that 2D-cultured cells are morphologically different from natural cells, which may induce alterations in cellular biochemical processes and trafficking. On the contrary, in a 3D culture, cells retain their shape and the relevant microenvironment, more similar to the *in vivo* one, favors greater culture stability and longer lifespans [1].

We have recently patented a new hydrogel scaffold based on Carbopol® 980, obtained by compression of a mixture of the polyacrylic polymer with the porogen agents $NaHCO_3$ and NaCl and subsequent thermal treatment, which leads to the formation of a continuous matrix; finally, a leaching process removes the water-soluble components and turns the matrix into a transparent, porous hydrogel scaffold, which can be autoclaved. The 3D scaffold has been successfully tested for culturing various cell types [2].

Our current research has focused on the functionalization of the polymer network by exploiting its acidic groups for covalent tethering of molecules that might further improve cell adhesion and proliferation. On this purpose, the carboxylic functions have been activated by EDC/NHS coupling, followed by reaction with ethylenediamine (EDA), to generate free amino groups suitable for further binding with acidic molecules, and with glycine (GLI), as a proof of concept to verify the feasibility of functionalization with peptides or proteins (Figure 1). The functionalized scaffolds, after lyophilization, have been characterized by IR spectroscopy, which confirmed the formation of amide bonds. The degree of functionalization has been quantified by hydrolysis in acidic medium, followed by titration of released EDA/GLI by ninhydrin reaction [3]. In the case of EDA, the amount of amine groups present of the scaffold surface has also been measured by reaction with 4-nitrobenzaldehyde [4]. Finally, the functionalized scaffolds have been analysed for their mechanical and swelling properties in aqueous medium, in comparison with neat ones.

Further research is ongoing to functionalize the neat scaffold with RGD peptides, and the EDA scaffold with chondroitinsulfate, both known as effective biomolecules for scaffold surface modification.

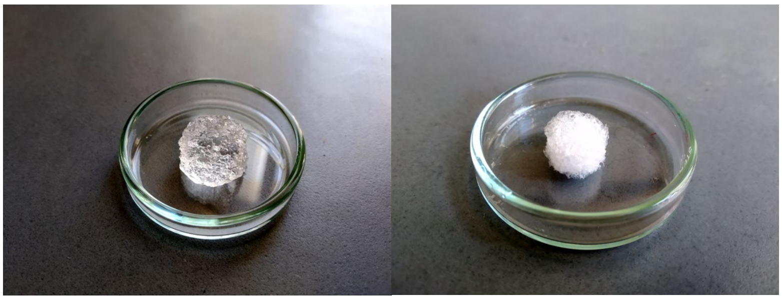

Figure 1. Images of a scaffold functionalized with GLI: wet (left) and lyophilized (right).

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Preparation of Vitamin E D−〈-Tocopheryl Polyethylene Glycol Succinate (TPGS)-based mixed micelles for the enhancement of Fenretinide solubility

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Neuroblastoma is an embryonal tumour originating from the simpatico-adrenal lineage of the neural crest. It approximately accounts for about 15% of all paediatric oncology deaths. Metastatic Neuroblastoma tumours at diagnosis remains a clinical challenge, despite advances in multimodal therapy. Retinoids are a class of compounds known to induce both terminal differentiation and apoptosis/necrosis of neuroblastoma cells. Among them, fenretinide (4-HPR), has been considered one of the most promising chemopreventive agent but it is partially efficacious due to both a low water solubility and a rapid metabolism. Here, we have developed a novel micellar 4-HPR formulation by which the drug was encapsulated into mixed micelles formed by 1,2-distearoyl-glycero-3-phosphoethanolamine-N-[methoxy(polyethyleneglycol)-2000] (DSPE-PEG) and Vitamin E D-α-Tocopheryl polyethylene glycol 1000 succinate (TPGS) in 1:2 molar ratio. These amphiphilic molecules, able to self-assemble above the critical micellar concentration (CMC) in nanometric aggregates of about 13 nm (Figure 1), are characterized by a hydrophilic corona and a hydrophobic core which can host poorly soluble drugs. The loaded micelles were prepared according to the solvent casting method by dissolving 4-HPR in chloroform at different drug: micelle forming material w:w ratios (from 1:10 to 1:50) [1]. Then the film was rehydrated with Milli-Q water and the drug content in solution was assessed after filtration (0.22 μm) to remove the excess non-encapsulated drug and used for further characterizations. Aliquots of each sample were diluted in methanol to disrupt the micelles and release the drug. The organic solutions were then spectrophotometrically analyzed to assess 4-HPR total solubility and drug entrapment efficiency (EE %). The particle sizes as well as polydispersion indexes and zeta potential of the preparations were measured by a Malvern Nano ZS90 light scattering apparatus. Size analysis was performed on both fresh dispersions and on rehydrated freeze-dried powders. The thermal properties of lyophilized 4-HPR micelles, free 4-HPR and TPGS-DSPE-PEG, and of physical mixtures of the raw materials were studied. The obtained results showed the considerable effect of TPGS-DSPE-PEG on 4-HPR total solubility. At the maximum ratio tested, total drug solubility reached the value of about 1.35 mM, establishing an improvement by 314 folds.

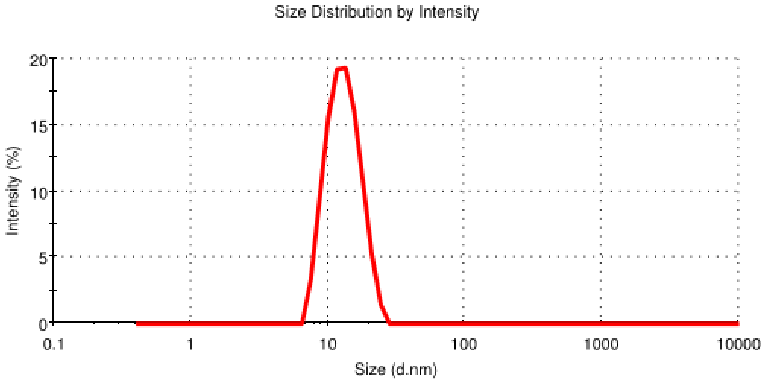

Figure 1. Representative size distribution of loaded mixed micelles.

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Cerium oxide loaded polyurethane scaffolds for tendon tissue engineering

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INTRODUCTION: Tendon pathologies are medical conditions that include ruptures and overuse injuries, accompanied by inflammatory and degenerative alterations, such as tendinopathies. These pathologies can be greatly debilitating, causing pain, loss of muscle function, joint instability and abnormal movements, adversely affecting the patient's life. Chronic injuries often require a surgical treatment, but many common surgical techniques for tendon repair produce poor results, despite recent advancements in orthopaedic surgery [1]. For this reason, new approaches need to be explored. Biopolymers based scaffolds have been proposed in tissue engineering to replace and restore tendon tissue, due to their ability to mimic the structural, biomechanical, and biochemical functions of the extracellular matrix (ECM), consequently mimicking the native tissues. Moreover, inorganic materials have been studied in the last decades as biocompatible components in tissue repair [2]. Given these premises, the aim of this work was the design and development of tubular scaffolds, by means of electrospinning technique, based on thermoplastic polyurethane (TPU) and combined with chondroitin sulphate (CS), a glycosaminoglycan effective in wound healing, and cerium oxide nanoparticles (CeO_2), able to increase the mechanical strength of the scaffold and enhance the tissue healing potential [3, 4].

MATERIALS AND METHODS: To obtain a continuous jet that allows the generation of uniform nanofibers, TPU was solubilized in water/acetic acid in different concentrations keeping the electrospinning parameters fixed. The fine formation of nanofibers was obtained for 12% w/w, for this reason it was selected for the loading of CS (1% w/w) and CeO_2 (1 mg/ml), alone and combined. The final blends were electrospun using an electrospinning apparatus equipped at first with a flat collector to evaluate the characteristics of the loaded fibers, and in a second moment with a rotating drum to obtain scaffolds with a tubular shape. The obtained scaffolds were dried in a vacuum at 60°C for 6 h to make sure the removal of any remaining solvent [5]. The systems morphology was assessed using SEM and TEM analysis to evaluate the fibers conformation and the inclusion of CeO_2 nanoparticles. Moreover, the fibers dimensions were calculated by means of ImageJ software. The contact angle of the scaffolds was measured by means of a contact angle meter and the weight loss in physiological medium was evaluated. The scaffolds mechanical properties were thereafter evaluated by means of a Texture Analyzer, and the force at break (Fmax), elongation % and Young modulus (YM) were calculated.

RESULTS: The morphological analysis of the systems obtained from blends with different TPU percentages confirmed that 12% w/w was the optimal concentration to obtain a continuous jet and uniform fibers. The presence of CS and CeO_2 did not affect the electrospinning process and the obtained scaffolds were insoluble in water. All systems were characterized by nanometric dimensions, moreover the fibers collected in tubular shape presented an aligned structure, mimicking the collagen nanofibrils typical of native tendon tissue. CS and CeO_2 were also visible incorporated into the structure. The contact angle measurements demonstrated the hydrophobicity of the surface, which has been demonstrated to enhance the protein absorption suitable for new tissue formation. Moreover, the systems showed a progressive weight loss in physiological medium, demonstrating a degradation capability. The mechanical properties of both randomly oriented and aligned scaffolds confirmed that the presence of CeO_2 increased the Fmax and the Young modulus of the systems, and the scaffolds loaded with both CS and CeO_2 possessed the highest Young modulus. Moreover, the scaffolds collected in tubular aligned shape reached Fmax values of 13 MPa, which is comparable to that of the native tendon (12 MPa).

CONCLUSIONS AND FUTURE PERSPECTIVES: In conclusion, electrospinning was successfully used to prepare scaffolds based on TPU in association with CS and CeO_2. The obtained systems were characterized by a nanofibrous regular structure, and the ones collected in tubular shape presented an aligned conformation, similar to the collagen fibrils of the native tissue. Moreover, the scaffolds possessed mechanical properties comparable to that of the tendon, representing a promising structure to stand the mechanical loads during the tissue regeneration. Further analyses are ongoing to test the cell adhesion and proliferation onto the scaffolds and their ability to produce ECM.

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"Oleo-ethosomes": new nanocarriers obtained from the combination of oleic acid, phospholipids and ethanol.

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"Oleoethosomes" are nanocarriers obtained thanks to the combination of oleic acid, phospholipids and ethanol. Oleic acid is able to form unilamellar vesicles in a pH range between 8 and 10 and it is highly sensitive to pH variation. This pH sensitivity is responsible for a lack of stability of the oleic vesicles. The aim of this research project is to obtain a more stable nanosystems based on oleic acid, counterbalancing the pH instability with other amphiphilic or surfactant compounds. For this purpose, we decided to evaluate whether the presence of ethanol can both improve the vesicular and maintained a certain vesicular deformability, a chemical-physical aspect essential for some practical application, i.e. percutaneous delivery. Namely, ethanol and oleic acid are recognized as permeation enhancers and they are already used for the preparation of vesicles and for transdermal administration. In fact, ethanol is the main constituent of deformable and flexible ethosomes. We wanted to prepare oleo-ethosomes characterized by similar physicochemical and technological features to ethosomes but with significant lower amount of ethanol thus increasing the potential application routes beside skin one and, at the same time, reducing the oleic acid-induced vesicular instability.

	Formulation A	**Formulation B**	**Formulation C**	**Formulation D**	**Formulation E**	**Formulation F**
Ethanol (% w/w)	25	20	15	25	20	15
Molar ratio Oleic acid:phospholipon 90G	1:1	1:1	1:1	1:0.5	1:0.5	1:0.5

The oleo-ethosomes were prepared using the same preparation method of the ethosomes [1,2] with compositions as reported in the Table. DLS analysis showed that each sample had mean size ranging from 120 to 200 nm, a narrow size distribution (a polydispersity index value lower than 0.3) and a negative zeta-potential value ranging between -28 and -38 mV. The delta back scattering and delta transmittance profiles were constant throughout the analysis duration (1 h), thus showing a suitable stability at 25 °C and 37 °C. The results of serum stability at 60 and 70 % of FBS showed that the mean size and polydispersity index increased up to 24h, thus suggesting a possible interaction with plasma proteins. Whereas the net surface charge has preserved the negative values. The results of pH stability showed a gradual reduction of the mean size above all at pH 10. Promising results were obtained in terms of encapsulation efficiency and release profile over time. Taking into consideration these encouraging preliminary results, future goals will propose to carry out *in vitro* and *in vivo* studies on suitable animal model.

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Cardiac delivery of therapeutics via injectable thermosensitive hydrogel

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Many genes and pathways have been indicated to play essential roles during heart regeneration and manipulation of these pathways using mRNAs or small molecules have been shown to be promising therapeutic strategies [1-2]. For this, a dual delivery system composed of mRNA polyplexes and micelle-containing thermosensitive hydrogel, previously complexed with CHIR99201 (a small hydrophobic GSK3 inhibitor and Wnt agonist), was designed allowing local sustained release of mRNA as well as small molecular weight drugs (Fig.1). In this study, the synthesis of mPEG-pDMAEMA (PD) diblock copolymer was optimized via RAFT polymerization and this polymer was used as polymeric carrier for mRNA condensation. Condensed mRNA polyplexes showed an average size of 146 ± 11 nm (N/P charge ratio 10) with a positive zeta potential (10.1 ± 0.3 mV). Subsequently, the loading of mRNA polyplexes into a thermosensitive pNIPAM-PEG-pNIPAM (NPN) hydrogel was evaluated to facilitate local and sustained mRNA release. The NPN triblock copolymer synthesized by ATRP polymerization, was used as a loading carrier for CHIR99021 (CHIR) by forming flower-like micelles that encapsulate the hydrophobic drug via heat-shock procedure [3]. The CHIR-NPN gel was then formulated by increasing the CHIR-NPN polymer content, reaching the final concentration of 20% w/w. After 15 days, NPN placebo hydrogels were fully dissolved while drug-loaded hydrogels exhibited much longer degradation times (up to 54 days). This proves that the presence of CHIR affects the stability of the hydrogel, presumably due to its interaction with the dehydrated pNIPAM blocks. Experimental studies revealed a sustained release of the drug over 54 days, demonstrating release kinetics mainly governed by hydrogel erosion. Placebo and CHIR-loaded gels showed temperature-sensitive behavior with a gel point below 37 °C, proving their injectability and *in situ* gelation upon administration, as previously demonstrated [4]. The final dual delivery system, composed of mRNA polyplexes and CHIR-loaded NPN hydrogel, showed the same mechanical properties as the CHIR-NPN gel and demonstrated injectable features at room temperature. In conclusion, the synergistic release of mRNA polyplexes and CHIR-NPN micelles offers a promising therapy for myocardial regeneration. The next steps in our research will focus on the use of this dual delivery system as a tool for local treatment for myocardial infarction.

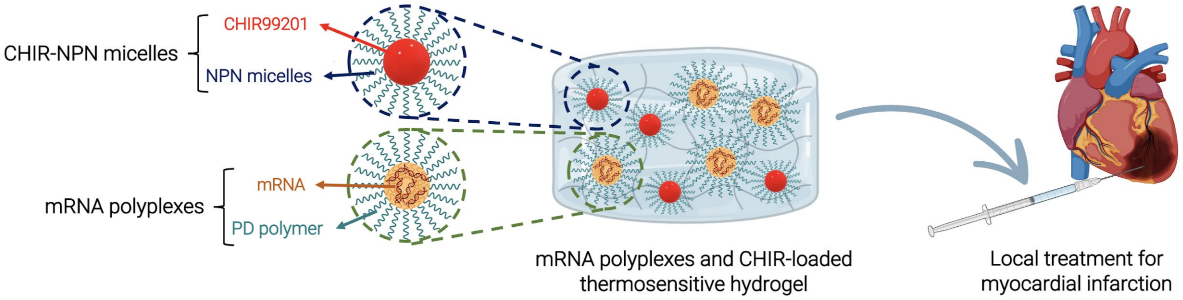

Figure 1. *Schematic overview of the designed dual delivery system for heart regeneration.*

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Inclusion of pterostilbene in natural cyclodextrins: complex preparation and solid-state characterization

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Pterostilbene (3,5-dimethoxy-42-hydroxystilbene, PTB) is a natural dietary polyphenol, occurring primarily in blueberries and Pterocarpus marsupium heartwood [1]. In recent years, this compound has attracted increasing interest owing to its antioxidant, anti-inflammatory and anticarcinogenic properties and its capacity to reduce and regulate cholesterol and sugar blood levels [2]. The low aqueous solubility of pterostilbene is one factor that limits its utility; the aim of this study is the use of cyclodextrins (CDs) as complexation agents to improve the solubility and stability of this drug [3,4]. CDs are natural macrocyclic oligomers composed of 〈-D-glucose units linked by 〈-1,4 glycosidic bonds to form torus-shaped molecules. This conformation is responsible for inclusion complex formation with organic molecules, the latter generally being included within the hydrophobic CD cavity. In this study, various methods used to prepare inclusion complexes between PTB and three natural cyclodextrins (α-CD, β-CD and γ-CD) are described. The characterization of all the solid phases isolated was performed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), hot-stage microscopy (HSM), X-ray diffraction (XRD), FT-IR and ^{1}H NMR spectroscopy.

The results indicating little or no evidence of the affinity of PTB to complex with α-CD. However, with the higher homologues β-CD and γ-CD a definitive indication of complexation was first evident from thermal analysis and subsequently corroborated by FT-IR and ^{1}H-NMR spectroscopy, as well as PXRD and single-crystal X-ray diffraction methods.

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Association of a quercetin nanosuspension and chitosan oleate emulsions

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A novel approach to improve the dermal bioavailability of poorly soluble molecules, such as quercetin, developing nanocrystals has been recently increase attention [1,2]. The interest for quercetin, like for other polyphenols, is related to its anti-inflammatory, antioxidant and antimicrobial properties, useful in different cutaneous disorders [2].

In the present study, a quercetin nanosuspension stabilized with a poloxamer, was associated with an emulsion stabilized with the amphiphilic chitosan oleate (CS-OA), prepared according to previous studies [3]. As oil phase an isopropylmiristate (IPM) and clove oil mixture (9:1) was selected to associate the absorption enhancement properties of IPM to those of CS-OA, and to exploit the analgesic effect of clove oil. Aim of the study was to assess the relevance of the preparation method on the interaction between the two disperse systems and on the physical stability of the formulation. A two steps association method involved the addition of the quercetin nanosupension to preformed emulsion by stirring for different times (either 5 minutes or 1 hour). A one step method was also evaluated, involving the emulsification of the oil phase in an aqueous dispersion of the quercetin nanocrystals. In both cases the emulsion was obtained by means of an Ultraturrax apparatus. Emulsions without quercetin were characterized at different oil concentrations between 3.8 and 10% (w/w) showing D_{90} between 3 and 3.5 µm. An accelerated stability test performed by centrifugation showed creaming effect decreasing with the increase of the oil concentration. The different behaviours were evaluated also by a FT-IR analysis whose spectral data were analysed by PCA. The most concentrated dispersion showed the lowest sensitivity to centrifugation and the highest stability with respect to creaming effect. This result was explained with the rheological behaviour of the emulsions, whose viscosity increases with the oil content. The physical stability in normal conditions confirmed these results, showing no creaming after 30 days for 10% oil concentration.

The associations between emulsions and nanosuspension showed in all cases good physical stability under visual inspection up to 30 days, with reduced creaming effect with respect to the emulsion and reduced sedimentation with respect to the suspension. Under centrifugation, a different behaviour depending on the preparation method, was quite clearly evidenced by FT-IR and PCA analysis, suggesting a higher sensitivity to centrifugation for the system obtained with one step method. However, the granulometric analysis and the microscopic visualization suggested for this sample a higher degree of association between the nanosuspension and the emulsion droplets, with respect to the samples prepared with the two steps method.

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Camouflage nanosystems based on chitosan and cellular membranes for the rivastigmine delivery to the brain

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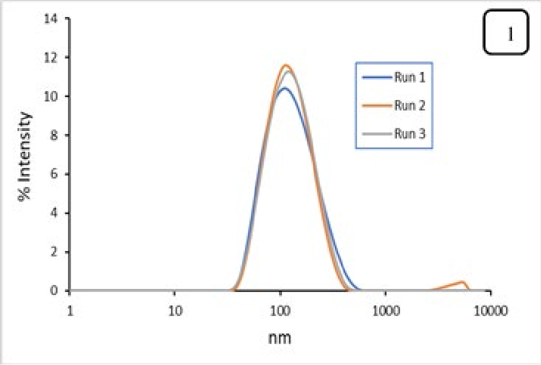
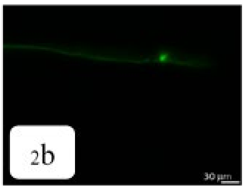
Targeting to the Central Nervous System (CNS) is an open challenge for pharmaceutical technology. The blood brain barrier (BBB) is extremely selective and drastically limit the permeation of actives. Presently, nanomedicine offers new strategies for CNS delivery, including those related to treatment of neurodegenerative diseases, such as Alzheimer's disease [1]. The aim of this work is to develop a homoselective targeting toward the BBB by using the cell membrane camouflage approach [2]. A nanocarrier prototype was prepared, displaying a central core made of depolymerized chitosan, loaded with rivastigmine (NP) and a lipid shell consisting of either synthetic lipids (NP-SL) or extracted from murine endothelial (bEnd.3) cell membranes (NP-ML). The prepared NPs had an encapsulation efficiency about 20% and a size diameter of 150 nm (figure 1). The cell membrane isolation was performed and immunostaining studies confirmed the maintenance of cell adhesion molecules within the collected cell membranes (vascular cell adhesion molecules-1, V-CAM 1, vascular endothelial cadherin, VE-cadherin) (figures 2a, 2b). NPs were coated by thermal controlled co-extrusion, resulting in size increment and reduction of the Zeta potential value. The NP-SL and NP-ML size and Zeta potential were similar each other. The coating was confirmed by immunostaining studies (figure 3). The in vitro targeting efficacy of the developed carrier is presently under investigation.





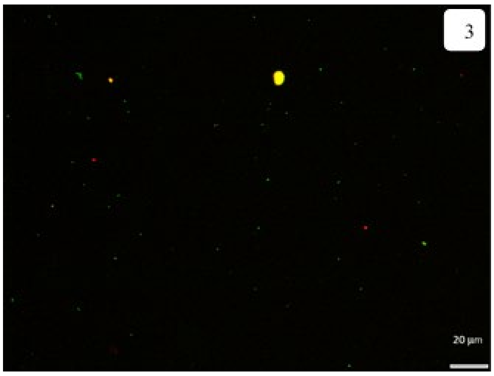


Figure n. 1: Size distribution of NP.
Figure n. 2a: Micrograph of V-CAM1 (RED) obtained from isolated membranes of bEnd.3 cells (40X magnification).
Figure n. 2b: Micrograph of VE-cadherin (GREEN) obtained from isolated membranes of bEnd.3 cells (40X magnification).
Figure n. 3: Micrograph of VE-cadherin (GREEN) and V-CAM1 (RED) obtained from NP-ML.

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Calcium phosphate-coated nanoparticles for bone delivery

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Due to their similarity to bones, calcium-phosphate (CaP) systems have recently received a lot of research attention due to their biocompatibility and their ability to bond directly to bone [1]. Several researchers described application of nanoscale CaP coatings on implants to enhance their bioactivity and to facilitate osteointegration with natural bone. In addition, based on data reported in the literature, these inorganic systems have potential in drug delivery [2]. As regards the drug delivery, nanotechnologies (from nanoparticles to nanostructured scaffolds) have been widely studied to increase efficacy and specificity in the treatment of bone diseases including cancer bone metastasis, osteosarcoma, bone infections and inflammatory diseases, osteoarthritis, as well as bone regeneration. They offer the advantages of protecting the cargo and increasing its retention time and carrying the drug to its destination achieving a specific delivery via surface modification [3]. Although lipid NPs have been widely applied as nanocarriers for drug delivery [4], thanks to their superior biocompatibility, kinetic and physical stability, up today only CaP-coated liposomes and polymeric nanoparticles have been proposed to be used as drug delivery systems for bone diseases [5].

Recently, we developed trilaurin-lecithin solid lipid nanoparticles (SLNs) using the "cold dilution of microemulsion (μE)" technique [6] to be proposed as carriers of doxorubicin (DOXO) for the treatment of bone diseases like osteosarcoma. The main purpose of the present study is to increase SLNs' uptake by osteosarcoma cell lines by an alternate layering of calcium and phosphate ions on their charged surface (CaP-SLNs). Briefly, after SLNs preparation, CaP coating was obtained by a simple and reliable method that exploits the localization of calcium and phosphate ions on SLN surface. Zeta potential and particle size were monitored by dynamic light scattering as a function of the alternatively added calcium and phosphate ions. After each addiction a slight and progressive particle size increase from 280 to 340 nm was noted. Moreover, the initially negative Zeta potential value increased upon the first calcium addiction and decreased after the addiction of phosphate with a trend which was continued upon following additions of calcium and phosphate. The presence of CaP coating was also confirmed by SEM analysis. Moreover, energy dispersive X-ray spectroscopy (EDS) analysis of CaP-SLNs showed an increase of phosphorus amount and the presence of calcium, which is lacking in uncoated SLNs. Also, TEM and infrared spectroscopy (FT-IR) analyses confirmed the presence of CaP coating. Another aspect we considered was the stability of CaP-SLNs. The use of freeze-drying in the presence of different cryoprotectants improved the stability of these systems. Furthermore, we assessed the potential ability of CaP-SLNs to deliver drugs in bone tissues. With this aim, a lipophilic DOXO derivative (DOXO dodecyl ester) was synthesized and then entrapped in the lipid matrix of SLNs with an entrapment efficiency % (EE%) of 75% after CaP coating.

Preliminary studies on osteosarcoma U2OS cells line revealed the biocompatibility of the CaP-SLNs and an increased cellular uptake of DOXO dodecyl ester, entrapped in SLNs.

Considering these positive preliminary results, these CaP-SLNs may be proposed as an innovative carrier for drug delivery to bone tissue. Further studies are required to understand the time of drug release e the efficacy of CaP-SLNs performing *in vitro* and *in vivo* tests.

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Solid lipid nanoparticles for sorafenib ophthalmic delivery

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Uveal melanoma represents one of the most common malignant tumor of the eye, showing the ability to metastasize, especially in the liver (90%), inducing mortality in 50% in one year [1]. Sorafenib (SRF) represents a potential treatment because of two main mechanisms: firstly, it is able to inhibit Raf kinases – within the mitogen-activated protein kinase (MAPK) pathway, constitutively active in most uveal melanoma tumors; moreover, it acts on vascular endothelial growth factor (VEGFR) and platelet-derived growth factor receptor (PDGFR), causing the inhibition of tumor angiogenesis [2]. Despite this interesting anti-cancer activity, its clinical use is limited by its severe side effects and its poor water solubility [2]. These drawbacks could be overcome through its encapsulation into solid lipid nanoparticles (SLN). In this study, the influence of two different solid lipids, Softisan (A) and Suppocire (B), at different concentrations (5, 7, 8, 9 % w/V) on nanoparticles mean size and homogeneity was investigated. SLN prepared by the PIT method were purified through ultra-centrifugation: the pellet redispersed in phosphate buffer saline was sterilized by filtration using PVDF filters. Homogeneous nanoparticles were obtained at the highest lipid concentrations (8 and 9% w/v) with A8, B8 and B9 showing particles mean diameter lower than 200 nm, adequate for the ophthalmic administration [3]. The physical stability of A8, B8 and B9 at 25, 40 and 60 °C was investigated by Turbiscan® for 30 days. B8 showed the occurrence of significant instability phenomena ($\Delta T>20\%$) due to particles aggregation, as confirmed by the increase of polydispersity index (PDI) during storage. A8 and B9 showed a great stability confirmed by the absence of transmission variation. *In vitro* cell viability on rabbit corneal epithelial cell line (SIRC) was evaluated by MTT assay in "wash" and "no wash" conditions. B8 induced a cell mortality by 56 ± 1.09 % and 78 ± 0.98 % in "wash" and "no wash" conditions, respectively. Interestingly, A8 and B9 showed a promising cytocompatibility profile even when tested in the "no wash" condition, although this is a very extreme testing condition that may provide potential false positives for cytotoxic effects. SLN A8 was selected as the optimal formulation for SRF loading (0.8 or 1.0 % w/v). Results demonstrated that SRF was successfully encapsulated (75%) without modifying nanoparticles size and homogeneity. *In vitro* release studies using the Franz-type diffusion cells showed a controlled and prolonged SRF release, with a delivery lower than 25% during the first 24 hours and less than 50% in 72 hours. Taken all together, these results suggest that SRF encapsulation in SLN represents a potential valid strategy to be further investigated for the treatment of uveal melanoma.

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Overcoming lung barriers to siRNA delivery in cystic fibrosis through inhalable lipid/polymer hybrid nanoparticles

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In the last few years, the down-regulation of genes directly involved in the pathogenesis of severe lung diseases, such as cystic fibrosis (CF), through siRNA delivery to the lung has gained tremendous research interest. Nevertheless, naked siRNAs have a very short half-life and are often unable to penetrate across cellular and extracellular barriers imposed by the CF lung [1]. To overcome this issue, the development of inhalable delivery platforms able to cross the mucus barrier lining epithelium and to gain access to the underlying epithelial cells is imperative.

Here, we propose mucus-penetrating hybrid lipid/polymer nanoparticles (hNPs) for pulmonary delivery of siRNA consisting of a poly(lactic-co-glycolic acid) (PLGA) core surrounded by a biocompatible lipid shell.

siRNA-loaded hNPs, comprising or not poly(ethylenimine) (PEI) as third component, were prepared by an emulsion/solvent diffusion technique [2], employing dipalmitoylphosphatidylcholine (DPPC) or 1, 2-Distearoyl-sn-glycero-3-phosphoethanolamine-poly(ethylene glycol) (DSPE-PEG), as lipid shell, to obtain non-PEGylated and PEGylated nanoparticles. The developed hNPs showed a mean hydrodynamic diameter lower than ~180 nm, low polydispersity index (~ 0.1), a negative ζ potential (-23/-28 mV) and appropriate aerosolization properties for lung administration. A siRNA pool against nuclear factor-kB (NF-κB), one of the main post-transcriptional factors involved in the CF inflammatory response, was entrapped with high efficiency (higher than the 80%) and released with a peculiar triphasic kinetics up to 10 days.

Particular attention was focused on the ability of hNPs to assist and to improve the diffusion of siRNA across the mucus layer. The diffusion assay was carried out by a Transwell® multi-plate assay, employing both artificial mucus (AM) and sputa derived from a heterogeneous and representative set of CF patients. The diffusion profiles of hNPs through mucus were highly influenced by the composition (i.e., DNA and mucin content) and viscosity of the sputum samples, which resembled the health conditions of the corresponding donor patient [3]. Noteworthy, the presence of PEG on hNP surface significantly increased the permeation rate only through poorly colonized CF sputa (isolated microorganisms<2), while a lower boosting effect of PEGylation on hNP permeation was observed in more complex samples (isolated microorganisms>2). Furthermore*, in vitro* studies on mucus-covered Calu-3 monolayers grown at air-liquid interface demonstrated that DPPC engineered hNPs were more efficient than their PEGylated counterpart in improving cell uptake of siRNA. *In vivo* preliminary data show that siRNA-loaded DPPC hNPs can significantly reduce neutrophil lung infiltration after intratracheal administration in LPS-challenged rats.

Overall, results highlight the great potential of the developed hNPs as carriers for pulmonary delivery of siRNA for local treatment of CF-related lung inflammation.

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THE EASY GOV – LABORATORY MANAGEMENT PLATFORM

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The European Project EASY GOV [1] is developing a simplified and assertive LABORATORY MANAGEMENT PLATFORM, based on common guidelines to motivate and increase the efficiency of human resources within the academic institutions.

This web-platform will help the management of all laboratorial needs and facilities such as laboratory equipment, chemicals, collections of microorganisms, laboratory wastes, laboratory material, laboratory spaces, services, laboratory safety and training taking into account the innovative practices to be adopted face to the COVID-19 pandemic.

As an example, among the laboratorial needs, the development of a dynamic and interactive platform where all chemicals can be managed, and the development of method to check expiration dates by means of warnings and indicates the priority of their use, would allow Target Groups to be able to organize their work in advance, without having to be in the laboratories.

During the development phase, pilot tests will be applied with about fifty participants from each partner university (department/centres directors, teachers, lab technicians and researchers), who work in laboratories.

In conclusion, the PLATFORM will increase the efficiency of the use of the human resources of the universities and will contribute to the strengthening of the productivity and competitiveness too.

EASY GOV Laboratory Management Platform

Co-funded by the
Erasmus+ Programme
of the European Union

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A preliminary technological study for diagnostic use of manganese

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Recently, diagnostic imaging research has led to the development of multimodal imaging techniques such as positron emission tomography (PET) / magnetic resonance imaging (MRI) which allows to obtain at the same time metabolic information provided by PET and morphological information provided by MRI [1]. A fundamental prerequisite for obtaining a real fusion between the two imaging modalities is the use of chemically identical radioactive and paramagnetic contrast agent. In this regard, the transition metal manganese appears to be the ideal candidate as a potential bimodal contrast agent but due to its high dose toxicity, it is not currently used in diagnostics. In order to overcome toxicity problems, in the present study the production and characterization of anionic liposomes, as delivery systems for manganese were investigated.

Negatively charged liposomes were produced using the direct hydration method followed by extrusion [2]. Particularly, four different anionic surfactants were considered, namely sodium docusate, N-lauroylsarcosin sodium salt, Protelan AG8 and sodium lauroyl lactylate.

The obtained formulations were then characterized in terms of size, surface charge, efficiency of encapsulation and stability over time. The extruded liposomal dispersions are homogeneous and monodisperse with an average particle diameter not exceeding 200 nm. The measure of Z potential confirmed the presence of a negative surface charge. Preparations with N-lauroylsarcosin sodium salt and sodium lauroyl lactylate were considered to be the most stable over time and the presence of manganese did not affect their size distribution. Liposomal systems with Protelan AG8 and sodium docusate were instead excluded from the discussion due to their instability.

The two selected anionic liposomal systems were then tested for their in vitro antiproliferative effect on the human keratinocyte cell line (HaCaT) by MTT assay. The obtained results highlighted that both formulations are not toxic. Liposomes containing N-lauroylsarcosin sodium salt or sodium lauroyl lactylate were loaded with two manganese compounds with different water solubility.

The actual concentration of manganese in each formulation was determined by mean of atomic absorption spectroscopy demonstrating that the manganese compound with hydrophilic characteristics is retained almost completely within liposomes, whilst lipophilic manganese compound is loaded around the 60-70%. Moreover these formulations showed a dose - dependent antiproliferative effect on HaCaT cell cultured in vitro.

Currently, the present study is still in progress with the aim of investigating the interaction between manganese and the negative charges of the surfactant and determining the magnetic properties of the obtained liposomal system, a relevant factor for the potential application in diagnostic imaging.

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pH-responsive Oleic Acid based nanoformulation: effect on human melanoma cell line

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In recent years, the burden of cancer incidence and mortality is growing rapidly around the world, in fact cancer is the first or second cause of death before age 70 [1]. Therapeutic approaches for cancer treatment are generally characterized by high toxicity and low capability of drugs to penetrate tumors at concentration suitable to achieve the widest level of bio-distribution and persistence. Tumor microenvironment is one key obstacle for drug efficacy, being characterized by hypoxia, low blood pressure and acidic pH [2]. The effect of this adverse microenvironment is the lack of adequate treatments often associated with the onset of resistance [3]. Since 2019, the incidence of melanoma has been rapidly increasing all over the world; improvement of both target and immune therapies against the advanced stage of melanoma is counterbalanced by a high percentage of either non-responder patients or suffering of severe drug-related toxicity.

To overcome these problems, pH-sensitive nanoemulsions and niosomes, able to load lipophilic or hydrophilic drugs, are designed, prepared and deeply characterized. pH-sensitive Oleic Acid (cis-9-octadecenoic acid, OA)-based nanocarriers could be able to release entrapped drug in response to external stimuli (eg pH decrease) and they could be employed for the treatment of cancer disease [4]. Nanoemulsions and niosomes can be administered by parenteral or pulmonary route. Looking to pulmonary administration, nanocarriers have been coated by Chitosan, a mucoadhesive agent in order to enhance the nanocarrier lung residence time.

A deep physical chemical characterization of niosomes and nanoemulsions was carried out evaluating size, ζ-potential, stability over time and in culture media, fluidity, microviscosity and polarity. Moreover, nanocarriers pH-sensitivity was evaluated by fluorometric assay employing different probes. Cytotoxicity and cellular uptake were assessed on both normal fibroblasts and human melanoma cell line.

Different studies confirm the suitable nanometric size for the desired administration, the stability of Nanoemulsion and Niosomes in buffer and in culture media and the pH-sensitivity of the nanosystems, investigated as a function of pH and confirmed by DLS data, probe release studies and fluidity, polarity and microviscosity evalution. Overall, nanocarrier cell treatment in vitro resulted not toxic; furthermore, nanostructure melanoma cell uptake and retention were efficient and no morphological difference was appreciable as a function of nanocarrier compositions. Probably, the demonstrated pH sensitivity at acidic pH is due to the presence of oleic acid as pH sensitive moiety, so the choice of these nanocarriers will allow us to exploit oleic acid activity combined with its pH-sensitiveness. It will help to convey drugs to the tumor microenvironment, with the goal of reaching the metastatic sites extremely difficult to treat.

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Natural *vs* synthetic polymer-based systems containing rutin: a comparison between zein and PLGA as biomaterials

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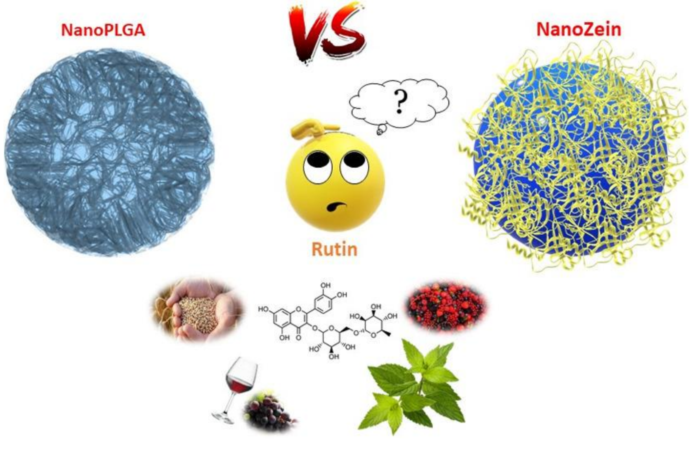
The increasing demand of the market for active compounds characterized by great efficacy and specificity requires the development of a modern approach to improve both pharmacological and functional properties of therapeutic agents. In this context, zein, a natural protein obtained from corn characterized by a lipophilic nature, has been widely employed in the development of nanoparticles, favoring the retention of poorly water-soluble compounds, avoiding the use of harmful chemical cross-linkers. The US Food and Drug Administration approved the protein as a Generally Recognized as Safe material for drug delivery applications. In particular, our research team recently demonstrated that it is possible to combine zein with several non-ionic and anionic surfactants with the aim of obtaining high stable colloidal particles [1,2]. In this investigation, the ability of zein nanoparticles to retain and release rutin, a polyphenolic bioflavonoid, was investigated and compared with systems made up of poly(lactic-co-glycolic acid) (PLGA), one of the most successfully used biodegradable biomaterials. Briefly, the protein matrix and the use of the ionic surfactant sodium deoxycholate promoted a great entrapment efficiency of rutin favoring a controlled and prolonged release of the bioactive compound with respect to PLGA nanoparticles which showed a lesser ability to retain the drug. Moreover, rutin-loaded zein nanocarriers exerted a greater antioxidant effect on human cells (C-28 and NCTC2544) than the active compound, especially at drug concentrations of 5 and 10 μM, suggesting a synergistic action between the intrinsic antioxidant activity of the protein and the pharmacological properties of the bioflavonoid [3]. The results demonstrate the possibility of the proposed nanosystems to provide a high level of stabilization for sensitive and labile active compounds.



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Thiolated hydroxypropyl- β-cyclodextrin as a promising mucoadhesive tool to prolong poorly soluble drugs ocular residence time

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Therapeutic efficacy of powerful active ingredients, which could cure most eye diseases, is limited by poor eye bioavailability (often less than 5%) mostly due to blinking reflex and nasolacrimal drainage (1). The purpose of this study was to synthesize a mucoadhesive thiolated hydroxy-propyl-β-cyclodextrin (HPβCD) in order to prolong the ocular residence time of the non-soluble model drug dexamethasone (Dex).

The thiolation was carried out using a microwave-assisted method with thiourea in acid conditions. A new purification method using size exclusion column was proposed. The structure of the obtained HPβCD-SH was confirmed by ^{1}H NMR spectroscopy. The modified β-CD was evaluated for thiol content, and drug inclusion properties. Moreover, the viscoelastic behavior of the modified oligomer was investigated via rheological and microrheological studies, whereas mucoadhesive properties were evaluated on excised porcine eye. In the end, an Irritation test (modified Draze test) and the elimination kinetics test from tear fluid, have been performed on New Zeland albino rabbits.

HPβCD-SH oligomer displayed 150 ± 50 µmol thiol groups per gram. The thiolated product did not show any cytotoxicity to Caco-2 cells at a concentration of 0.5% (m/v) within 24 h. The dynamic viscosity was increased up to 2.2-fold within 60 minutes at 37 °C, and these results have been confirmed by microrheological tests. Moreover, HPβCD-SH displayed long mucoadhesion in *ex-vivo* assays, with more than 80% of product retained on the ocular surface after 2 h 30 min. *In vivo* tests in rabbits confirmed *in vitro* results as mean residence time (MRT) and maximum residence time (RT max) were increased 4- and 6-fold, respectively, compared to pristine HPβCD.

According to these results, thiolated HPβCD might be a promising auxiliary tool to provide prolonged ocular residence time of poorly soluble drugs like Dex. *In vivo* evaluations of drug corneal permeation are currently in progress.

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Thiolated 2-methyl- β-cyclodextrin as a mucoadhesive excipient for poorly soluble drugs: synthesis and characterization

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Out of the several bioavailability limitations of topically administered drugs, solubility and low retention time are surely among the most relevant. Cyclodextrins are well known excipients, able to form inclusion complex with hydrophobic poorly soluble drugs and increase their apparent solubility (1). Methyl-β-cyclodextrin is freely soluble in water unlike non methylated β-cyclodextrins, therefore its increasing solubility properties are emphasized. Cyclodextrins can be further functionalized by adding thiol moieties, which lead to the establishment of transient covalent mucoadhesive interaction with mucosal tissues (2). This additional biopharmaceutical property is essential to increased retention times on absorption sites and improve drug therapeutic regimes. The aim of this study is to propose for the first time the microwave assisted synthesis of a highly thiolated 2-methyl-ß-cyclodextrin (MCD-SH) and to characterize the functional excipient in terms of mucoadhesion and complex capability by using the model drug dexamethasone (Dex).
A screening of microwave assisted synthesis at different pHs, reaction times and with different quantitative of the reagent thiourea, was performed in absence of organic solvents. The thiolated product (MCD-SH) was isolated by size exclusion chromatography and deeply characterized via proton and bidimensional NMR spectroscopies.
Out of the microwave synthesis screening, resulted that pH conditions and reaction time are crucial factors. The thiolation reaction has shown to be significantly more effective in the range $0.5 < pH < 1.5$. Moreover, the product obtained with the two hours synthesis displayed 20% higher thiol functionalization with respect to shorter synthesis times. The better obtained compound in terms of thiolation and yield, was selected and deeply characterized and a thiolation degree of 67.4% was determined. Diffusion measurements evidenced the presence of momomeric cyclodextrins and ruled out the massive oxidation of the cyclodetrins into linked dimers or trimers.
Host-guest complexing capability were evaluated by using dexamethasone (DEX) as model drug, mucoadhesion features were assessed by micro-rheology evaluations, and a cytotoxicity screening on BALB/3T3 clone A31 is in progress. With this preliminary as well as promising results, we can already assess that the present study offers a quick and easy microwave thiolation method, able to provide a high thiolation degree on 2-methyl-β-cyclodextrin. The obtained thiolation degree has to be considered of great impact also seeing that the cyclodextrin is already functionalized on a reactive position (OH-C2).

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Biopharmaceutical study of ionic liquids as solubilizing agents and stabilizers, for the formulation of antimicrobial eye drops containing diacerein

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Diacerein is an anthraquinone drug used as a slow-acting symptomatic active principle in osteoarthritis, authorized in countries of the European Union, Latin America and Asia. Its main mechanism of action is the inhibition of interleukin-1 signaling pathway. Moreover, diacerein has recently been evaluated as a potential antimicrobial agent in bacterial keratitis [1].

Despite the numerous pharmacological activities, diacerein shows poor solubility in biological fluids and is easily degraded to its deacetylate derivate rhein at physiological pH. These behaviours drive to reduced bioavailability. Ionic liquids (ILs) are organic salts generally obtained from the combination of cations of organic nature and anions of various kinds. Their melting point is below 100 °C while some of them are liquid already at room temperature. ILs are emerging as powerful solubilizing and stabilizing agents, with potential but still low pharmaceutical applicability [2]. The aim of this study is to prepare an eye drop formulation with diacerein and ILs for the treatment of bacterial keratitis. This study proposes the use of (2-hexyloxy- 2-oxoethyl)-trimethylammonium bromide ([C6bet]Br) or (4-hexyloxy-2-hydroxy-4-oxobutyl)-trimethylammonium bromide ([C6carn]Br) as functional excipients, capable of forming nanometric aggregates that increase the apparent solubility of diacerein and its stability at hydrolysis. The dimensional distribution and the zeta potential of ILs nanoaggregates in aqueous conditions were determined. The stability of diacerein at 37 ° C with and without ILs was evaluated, as well as the apparent solubility. A microrheological evaluation assessed the mucoadhesion properties of the nanoaggregates and the biocompatibility of the system was assessed on murine fibroblasts cell line Balb 3T3 A31. Finally, in vivo tolerability and elimination kinetics studies were carried out on New Zealand albino rabbit.

The apparent solubility of diacerein heightens progressively with increased concentrations of ILs and the solubilizing power becomes more pronounced after overcoming their critical aggregation concentration (CAC). The simulation of diacerein degradation under physiological condition was performed. Diacerein resulted completely degraded to rhein in a few minutes, the selected concentrations of [C6Bet]Br and [C6Carn]Br preserved the active principle for at least 6h, up to 70% and 30% respectively. Micro-rheological analysis showed a substantial increase on the viscosity of mucin solutions at concentrations above the CAC for both ILs. Cytotoxicity tests confirmed that diacerein has a lower toxicity than rhein, while IC50 of the two ILs, [C6bet]Br and [C6carn]Br were 8.7 mg/ml and 13.5 mg/ml respectively. In vivo Draize tests showed good ocular tolerability of both the eye drop solutions. Finally, preliminary results from elimination kinetics studies showed that the eye drops containing ILs are able to prevent diacerein fast degradation, as only diacerein is detected in the lacrimal fluid of ILs treated eyes. Antimicrobial assessment of IL/diacerein eye drops is presently on-going.

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Neem oil nanoemulsions + Resveratrol: *in vitro* activity on human T24 bladder cancer cells

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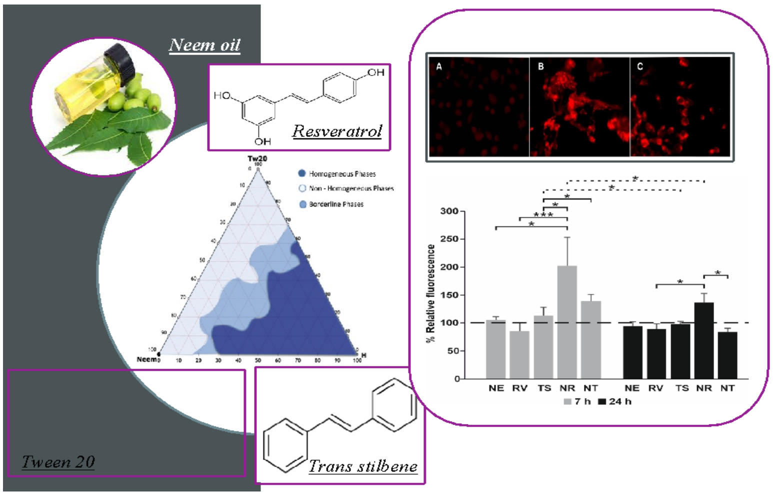
Resveratrol (RV), a natural polyphenol product, is used in plant defense from fungal and microbial aggression. It is found naturally, especially in plants such as grapes, peanuts, and berries.
In the last decades, several researchers have extensively demonstrated its chemo-preventive potential against bladder cancer [1].
Unfortunately, the physicochemical properties of RV, in particular its high reactivity and low solubility in aqueous phase, limited its bioavailability and the *in vivo* efficacy.
In order to overcome these limitations, the inclusion in a drug delivery system can promote to enhance the therapeutic usage of this molecule.
For this reason, oil-in-water (O/W) nanoemulsions (NEs) have been considered the ideal candidates for RV encapsulation [2].
Firstly, since surfactant and oil composition can strongly influence NE features and their application field, a ternary phase diagram was constructed and evaluated to select a suitable surfactant/oil/water ratio [3]. Then, the selected sample was deeply characterized in terms of physical chemical features, stability, release capability and cytotoxic activity.
Results showed a significant decrease in cell viability after the incubation of bladder T24 cancer cells with RV loaded NEs, compared to free RV. Selected NE formulation was able to preserve and improve RV cytotoxic activity by a more rapid drug uptake into the cells.
In conclusion, the obtained results have demonstrated that the encapsulation of this molecule into O/W NEs can represents an effective approach to improve RV bioavailability and cellular uptake.



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Production of polydioxanone (PDO) microfibers obtained by centrifugal spinning technology as skin/tendon tissue substitutes

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Fiber spinning technologies attracted a great interest since the beginning of the last century and, over time, the number of patents concerning new production methods grow considerably. One of the most effective techniques relies on the use of the electrospinning, however, this apparatus is not entirely suitable for the industrial scale due to low fiber yield, safety problems, high energy consumption and material or solvent intrinsic drawbacks [1]. Alongside electrospinning, other fiber manufacturing methods are devised and patented, such as melt blowing, template synthesis, island in the sea and Forcespinning® otherwise known as centrifugal spinning [2]. Now centrifugal spinning represents a versatile method which implements the type of materials that can be used for the design of fibers. In this research work a centrifugal spinning apparatus was set-up by means of a commercial cotton candy machine. The original equipment was properly modified and adapted to apply the same theoretical principles of the patented Forcespinning®. The aim was to achieve fibers from melted polyesters, in particular from Polydioxanone (PDO). Polydioxanone (PDO) is a bioabsorbable polyester derived from p-dioxanone monomers which recently gained particularly interest in biomedical field thanks to its peculiarity such as optimum biocompatibility, modular degradation rate, and excellent mechanical properties. PDO was successfully designed as electrospun scaffold and employed as substitute in tendon tissue repair [3]. However, due to the challenge in gaining fibers from nontoxic mixtures or melted PDO, no works upon centrifugal-spun PDO fibers were published to date. In this study two different deep eutectic solvents (DES) were employed as polymer plasticizers to improve the capability of PDO to be spun in melt form. Choline chloride/citric acid (ChCl/CA) and betaine/citric acid (Bet/CA) DES were respectively employed. Physical mixtures were prepared by blending different polymer/DES weight ratios and maintaining the DES (ChCl/CA or Bet/CA) molar ratio equal to 1:1. The physical mixtures were then poured into the spinneret and melted at 140°C for 5 min. After complete melting, the blends were spun for 1-2 min at 700 rpm. Except for PDO alone, all PDO/DES mixtures spun using the handmade centrifugal spinning apparatus gained fibers and the suitability of DES as plasticizer agent was demonstrated. Scanning electron microscopy analysis (SEM) showed smooth and continuous fibers with heterogeneous dimensions ranging from 10 to 20 μM and the hydration did not affect the fiber structure. Microfibers were assembled in aligned and random macro structures and the mechanical behaviors were assessed. Both macro conformations exhibited excellent elastic nature and high tensile strengths (600 MPa). PDO/DES microfibers resulted biocompatible on normal human fibroblasts ensuring cellular proliferation within 18 days of culture. Confocal analysis showed exceptional fibroblasts spreading and adhesion on both PDO/DES microfibers, demonstrating their ability in supporting cell growth and proliferation. Finally, thanks to the excellent mechanical behaviors and the good biocompatibility, the resultant microfibers can be envisioned as optimal biomedical devices to treat, depending on their macro-conformation, skin (random, cotton-like structure) or tendon (aligned, high tough woven band) lesions.

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Extraction of the antioxidant phytocomplex from wine-making by-products and sustainable loading in phospholipid vesicles specifically tailored for skin protection

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Grape pomace, one of the most abundant winery-making by-products, is a valuable source of bioactives, such as anthocyanins, stilbenes or gallate derivatives, that can be easily exploited in food, cosmeceutical and pharmaceutical fields thanks to their various activities, such as antioxidant, anti-bacterial, anti-inflammatory and anti-aging (1). Their biological activities mainly rely on their radical scavenging activity, which allows them to prevent the oxidative damage caused by ROS (Reactive Oxygen Species) (2). Among the different nanocarriers developed as a carrier for different actives, liposomes and nanovesicles specifically modified, represent the preferred choice for skin delivery, as they are composed of biocompatible and safe ingredients (3).

The present study is aimed at valorizing grape pomace, by extracting the main bioactive compounds from the skin of pomace and using them to manufacture innovative nanoformulation capable of both avoiding skin damages and promoting skin care. The phytochemicals were recovered by means of maceration in hydroethanolic solution. Catechin, quercetin, fisetin and gallic acid, which are known for their antioxidant power, were detected as the main compounds of the extract. Liposomes and phospholipid vesicles modified with glycerol, or Montanov 82®, or with a combination of both, were used as carriers for the extract. The vesicles were small (~183 nm), slightly polydispersed (PI ≥ 0.28), and highly negatively charged (~-50 mV). The extract was loaded in high amounts in all the vesicles (~100%) irrespective of their composition, Table 1. The antioxidant activity of the extract, measured by means of the DPPH (2,2-Diphenyl-1-picrylhydrazy) test, was 84%±1, and slightly increased when loaded into the vesicles (~89%, P<0.05). The grape pomace extract loaded vesicles were highly biocompatible and able to protect fibroblasts (3T3) from the oxidative stress induced by hydrogen peroxide.

Table 1. Mean diameter (MD), polydispersity index (PI), zeta potential (ZP) and entrapment efficiency (E%) of the vesicles. Mean values ± standard deviations are reported (n≥3). The same symbol (§) indicates the same values (p>0.05).

	MD (nm)	PI	ZP (mV)	E (%)
Liposomes	§183±24	0.33	-52±12	101±1
Montanov-liposomes	§214±19	0.30	-51±5	100±1
Glycerosomes	§194±25	0.37	-39±3	99±2
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Chitosan/SBE-β-CD NPs with external coating of thiolated hyaluronic acid for ophthalmic delivery of Indomethacin

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Indomethacin is topically administered for the treatment of conjunctivitis, uveitis and inflammation of posterior segment. It is currently available as 0.1% 2-Hydroxypropyl-beta-cyclodextrin (HP- β-CD) eye drop, however subjected to the major drawbacks that hamper its bioavailability: nasolacrimal duct draining, reflex blinking and low volume of conjunctival sack. Aim for the project was the creation of nanoparticulate system to improve residential time of Indomethacin in the conjunctival sack, enhancing the solubility, stability and permeability of the drug[1]. The nanoparticles (NPs) were obtained through ionotropic gelation technique[2], exploiting interaction between positively charged amino group of chitosan and negatively charged sulphate group of Sulfobutylether-β-Cyclodextrin (SBE-β-CD). Chitosan was used for its biosimilar properties and the cyclodextrin for its well-known advantages derived from host-guest complexation[3]. The NPs were external coated with Thiolated Hyaluronic acid to improve their mucoadhesive properties[4]. The free thiol groups of cysteamine derivatives are able to form disulphide bonds with cysteine rich domains of mucin, hence enhancing the residential time of the delivery system in the conjunctival sack. The NPs were morphologically characterized through Size (340 ± 7 nm), Z-potential (+18,3 ± 0,4 mV), NMR, IR, DSC. The mucoadhesive properties of the NPs were evaluated using texture analyser with ex-vivo studies on chicken's trachea and oesophagus. Further studies were conducted with Curcumin loaded NPs for fluorescence studies after artificial tear wash-off. The irritability and toxicity effects of NPs were disclaimed with HECAM and ICE tests. NPs improved drug permeability, while maintaining a similar release profile, sustained over time, to the commercially available cyclodextrin based eye drop. The developed NPs show increased residential time in conjunctival sack, drug stability and permeability, no irritancy and toxicity for local administration, making them an optimal and innovative drug delivery system for ocular release.

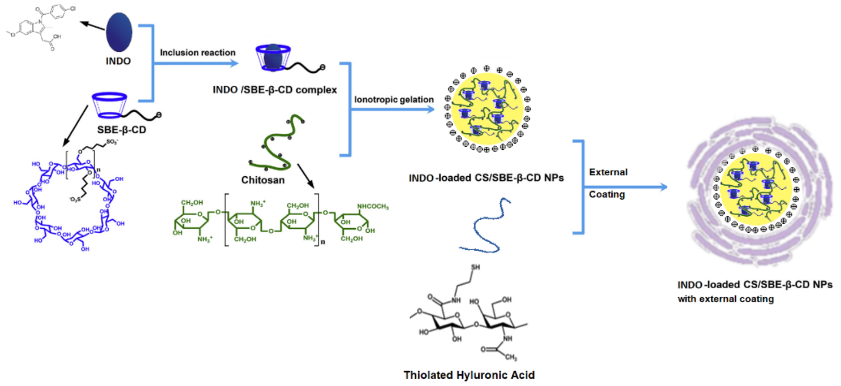

Figure 1: NPs Creation through Ionotropic Gelation

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Polymeric Nanoparticles Delivering Ferulic Acid for Potential Ocular Application

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Antioxidant substances such as Ferulic acid (FA) have been shown to be effective in treating/preventing the age-related macular degeneration and diabetic retinopathy [1]. Due to its phenolic structure, FA can form resonance-stabilized phenoxy radicals, thus suppressing the production of reactive oxygen species and their harmful effects. FA poor solubility in aqueous solutions its limits therapeutic efficacy. Polymeric nanoparticles (NPs) have long been explored to overcome these constraints. In this study, two polymeric materials were investigated to load FA into NPs prepared by the nanoprecipitation method [2]: poly(lactic acid) (NPA) and poly(lactic acid)/poly(lactic acid-co-glycolic acid) (NPB). A preliminary in vitro study on retinal pericytes and endothelial cells was carried out to ascertain the absence of cytotoxicity of the unloaded carriers. The two drug-loaded nanocarriers were characterized by photon correlation spectroscopy to detect the mean size, polydispersity index and zeta potential. Purification studies by centrifugation and dialysis were carried out to remove any residual surfactant or unloaded drug and to select the suitable purification methods considering the preservation of the physico-chemical characteristics of the starting nanoformulations and FA purification yield. The encapsulation efficiency of the systems was evaluated and in vitro release profile up to 48 h was evaluated by High Performance Liquid Chromatography. Morphological systems analysis was performed by Scanning Electron Microscope. The final formulations were cryoprotected with hydroxypropyl-β-cyclodextrin and freeze-dried to maintain the integrity of the systems. The physical and chemical stability of the resuspended systems was followed for 28 days of storage at 5 °C. The freeze-dried samples were analyzed by Differential Scanning Calorimetry and Fourier-Transform Infrared spectroscopy. The results showed the production of homogeneous (PDI < 0.2) NPs with an optimal size for ocular delivery (< 250 nm), a smooth spherical surface, a negative ZP (from -23.80 to -33.70 mV), tolerated pH values (7.3), osmolarity isotonic with tear fluid (258-265 mOsm/Kg), an encapsulation efficiency between 64.86 and 75.16% and a controlled release profile. Thermal and spectroscopic analyses confirmed the encapsulation of FA in the polymer matrix. The data obtained from the cell viability assays demonstrated the tolerability of the blank carriers in the concentration range 0.25-1 mg/ml on endothelial cells and 0.25-2.5 mg/ml on pericytes. The systems obtained could therefore be promising strategies for ocular drug delivery, although further in vitro biological tests are under study on FA-loaded NPs to confirm efficacy and safety and their potential application.

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Polysaccharides-based spray-dried microparticles in tissue engineering

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Infections in non-healing wounds remain one of the major challenges. In this work, antibacterial nanoparticles (CuO and ZnO NPs) were encapsulated in spray-dried microparticles based on polysaccharides, in order to combine antimicrobial and wound healing properties to prevent/treat wound infection that could delay and impair the healing process.

Briefly, two different polymeric blends were prepared by mixing maltodextrin (MD) or dextran (DX) with a mixture of amino acids (Thr, Cys and Gly) in aqueous solution and citric acid was used as cross-linking agent. Analogously to unloaded solutions, ZnO or CuO NPs were loaded to each solution. Microparticles were prepared using a Buchi 190 mini spray drier and the microparticles were then cross-linked by heating. The morphology of the microparticles were analyzed by means of SEM and particle size distribution was determined using Malvern Mastersizer 3000E granulometer. The crush test was carried out by means of a TA.XT plus Texture Analyzer and the biocompatibility of microparticles was evaluated using normal human dermal fibroblasts. The hemostatic activity of microparticles was evaluated using rat whole blood pooled from 6 male rats (Wistar 200–250 g).

The morphological analysis shows that all the microparticles were spherical and with smooth surfaces, and the loading of the NPs did not modify their morphology. Moreover, the crosslinking by heating did not significantly change the microparticles morphology and particle size distribution. In particular, the microparticles were characterized by narrow size distributions, as highlighted by the SPAN Index values, and particle size analyses indicated that microparticles had d[4,3] values of 19–26 µm. The hydration of microparticles were expressed as Swelling Index (SI): MD microspheres showed SI values (0.9-1.2) remarkable lower than the microspheres containing DX (1.8-3.5). The crushing test shows that the NPs loaded microparticles, in comparison with unloaded microparticles, were less elastic while no significant differences were observed on the rupture forces. Moreover, unloaded microparticles were characterized by high biocompatibility and, the encapsulation of NPs in microparticles increased the cytocompatibility compared to the free NPs, suggesting that the systems were able to prevent the negative effect of CuO and ZnO towards the fibroblasts. Microparticles accelerated blood coagulation merely by mixing with the whole blood of rats and SEM images showed that microparticles aggregate with blood components such as fibrin networks, probably due to their capability to extract fluid from blood when applied to an active bleeding site, causing proteins, platelets, red blood cells and other effective compositions of blood to concentrate on material surface.

The spray-dryer was successfully used to obtain microparticles with regular shape and smooth surface. Due to their capability to support fibroblasts proliferation and to prevent CuO and ZnO cytotoxicity, these microparticles are promising to prevent/treat nonhealing wound infection. Further investigations are ongoing to evaluate the antimicrobial properties of the systems and to assess their efficacy on a murine excisional wound healing model

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Magnetic versus Plasmonic Nanotags for Histamine Biodetection in Wine

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Histamine is a biogenic amine present in different fermented foods. Due to this fact, fish, meat, cheese, vegetables, chocolate, beer or wine may have a certain amount of histamine, that could even increase during the maturation time. 1% of the population is intolerant to histamine, but even in healthy individuals a high amount of histamine could cause increased gastric acid secretion and heart rate, headache, urticaria, pruritus and tachycardia, bronchospasm or cardiac arrest [1].
The determination of histamine is usually done following complex and time-consuming methods, such as chromatography, enzymatic and ELISA tests [2]. However, the control of histamine on-site during the fermentation processes would be an interesting option for food industries, in order to manage the quality of their products. In this work, a rapid, cheap and simple test for the detection and quantification of histamine in wine is presented. A competitive lateral flow immunoassay (CLFI) has been designed by using two types of labels: magnetic (iron oxide) and plasmonic (gold) nanoparticles. In the former case, the quantification of the test relies on the superparamagnetism of the particles measured by a high frequency magnetic sensor [3,4], while in the latter it is done by reflectance measurements using a commercial optical strip reader. CLFIs are the preferred format to detect small molecules in lateral flow immunoassays. In these, a synthetic complex of the antigen–protein to be detected is immobilized on the nitrocellulose membrane of the strip forming the test line. These latter will compete with histamine present in the sample for the binding sites of the anti-histamine antibody which is added to the sample. When flowing by capillarity, only the free antibodies will get trapped by the histamine immobilized on the test line. Afterwards and as a developing step, a solution with one of the two labels conjugated with protein G is run through the strip. This protein has a high affinity for the Fc chains of the antibodies and gets therefore trapped at the test line. Its signal will be either magnetic or coloured but its intensity is for both inversely proportional to the concentration of histamine in the sample.
This methodology was followed to analyse histamine in wine samples, with a range concentration from 10-6 to 10-1 mg/mL for both types of labels. The conclusion is that, although gold nanoparticles are easier to functionalise, the magnetic test enables a better quantification which is absolutely independent of the teint that the wine (mainly red or rose wine) give to the membrane strip.

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Tuning microfluidic mixer parameters to produce ovalbumin-lipid nanoaggregates

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Microfluidic mixing has emerged as a reproducible and scalable technique for the production of a variety of nanoparticles. The possibility to finely modulate process parameters (such as the flow rates) as well as the concentration of input materials, allows to fabricate nanoparticles with very diverse properties [1]. Recently, microfluidic mixing has been employed to formulate liposomes loaded with subunit antigens to improve their stability and immunogenicity [2]. In previous works, the amount of organic solvent employed in the microfluidic process was kept below a defined threshold to avoid the unfolding and precipitation of proteins. In this work, we cross that threshold to obtain ovalbumin nanoaggregates (OVA-NAg) stabilized by lipids. We explored the formulation space by systematically changing the process parameters and the starting concentration of lipids and OVA, to identify the determinants driving the formation of nanoaggregates vs the formation of liposomes.

The formulations were composed of OVA and dipalmitoylphosphatidylcholine (DPPC), cholesterol and dialkyldimethylammonium bromides (DDAB) with alkyl chains of 14, 16 or 18 C. Mixtures of DPPC, cholesterol and DDAB in methanol were rapidly mixed with an OVA solution in PBS at different flow rate ratios (1:3; 3:5; 1:1) using a Nanoassemblr Benchtop (Precision Nanosystems), and the organic solvent was subsequently removed by dialysis against PBS. Neither the flow rate ratio nor DDAB chain length had an impact on the size and polydispersity index of nanoparticles, as determined by dynamic light scattering. It was possible to purify OVA-NAg from liposomes by applying different centrifugation or ultracentrifugation protocols. As expected, higher flow rate ratios between the organic and the water phase enhance the formation of OVA-NAg due to OVA precipitation. The ratio between OVA-NAg and liposomes (determined by TEM) can be further increased by rising the OVA:lipid input ratio. The morphology of OVA-NAg was observed by cryo-TEM. The amount of OVA in the NAg or entrapped within liposomes was determined by BCA. Preliminary biocompatibility and cell uptake by RAW 264.7 marcophages showed that DDAB with shorter alkyl chains are more toxic than longer counterparts, and OVA-NAg prepared with C18 DDAB are rapidly taken up by macrophages with no evident toxicity.

Overall, we demonstrated the possibility of obtaining lipid-stabilized protein nanoaggregates by microfluidic mixing. The higher immunogenicity of nanoparticulate antigens compared to soluble antigens, makes NAg a promising platform for vaccination [3].

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Delivery of proteins to the brain: the case study of enzyme-loaded solid lipid nanoparticles by microfluidic technique

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Diseases involving the Central Nervous System (CNS) are one of the most exciting challenges for the scientific community in the world. In fact these disorders, although characterized by different etiologies, are united by therapeutic difficulties due to the presence of the blood-brain barrier. This physiological barrier isolates the brain compartment, making it very difficult for small molecules to reach it and almost completely preventing the entry of macromolecules.[1] For these reasons there is a need for innovative non-invasive formulations capable of conveying the drug to the CNS in a safe and controlled way. In this context, solid lipid nanoparticles (SLNs) have gathered wide interest due to some features that allow them to overcome the limitations of other innovative formulations.[2] However, the production of SLNs in a conventional "bench-top" method still faces several critical challenges, such as the lack of reproducibility, which restricts it from being widely adopted in the pharmaceutical industry. The microfluidic technique has enabled the synthesis of nanoparticles with narrower size distributions, improved batch-to-batch reproducibility, and higher drug loadings and enabling one industrial scale-up[3]. Herein, a microfluidic device was primed to optimize the SLNs and compared to the bench top method. Lysozyme was loaded into SLNs as a potential model enzyme for the delivery of macromolecule to the brain. The developed nanosystems were characterized and they showed Z-average under 200 nm, a polydispersity index below 0.2, a zeta potential between +30 and −15 mV and a drug encapsulation efficiency around 50%. However, the data obtained showed that the SLNs obtained by microfluidics had smaller size and a lower polydispersion index. Cryogenic transmission electron microscopy (Cryo-TEM) was used to determine the morphology of SLNs and the localization of the model enzyme. Studies concerning the release profile of the enzyme have been carried out. The results seemed to show a biphasic release profile, with a first fast release of the enzyme adsorbed on the outer shell of the SLNs then a sustained release of the enzyme from the core of SLNs. Moreover, the investigative tests of enzyme activity were performed on *Micrococcus Lysodeikticus* cultures, and the data exhibited that the enzyme retains its biological activity after being released. This study is innovative as it aspires to gain new formulations capable of delivering to the brain biological macromolecules usually unavailable in therapy due to restrictions linked to the BBB, using a new production technique that is suitable for industrial scale-up.

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Co-delivery of bergamot essential oil and ammonium glycyrrhizate using ultradeformable liposomes: promising feature for topical anti-inflammatory activity

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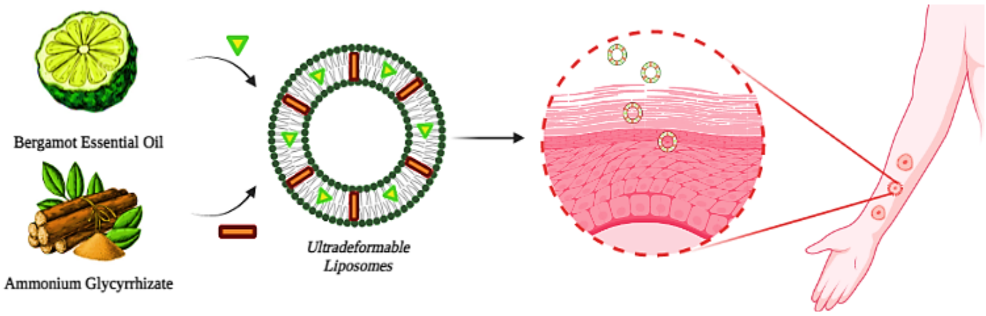

Figure 1. Created with BioRender.com

Ultradeformable liposomes are known for their ability to increase the drugs permeations through the skin, thanks to their passage as intact vesicles through the *stratum corneum*. Bergamot essential oil and ammonium glycyrrhizate are two natural compounds, which share anti-inflammatory, anti-itching, healing and soothing properties [1,2,3]. In this investigation bergamot essential oil (BEO) and ammonium glycyrrhizate (AG) were co-encapsulated within ultradeformable liposomes and hence formulations were investigated for the potential treatment of inflammatory skin disease. For each sample, DLS analysis showed a mean size value lower than 140 nm, a narrow size distribution (a polydispersity index values <0.2) and a negative zeta-potential ranging from -30 to -47 mV. Delta transmission and delta backscattering profiles confirmed the absence of coalescence, sedimentation, flocculation or clarification events, thus evidencing a suitable formulation stability. HPLC and UV-Vis methods were used to evaluate the entrapment efficiency (EE%) of AG, bergamottin and bergapten as well as the drugs' release. The EE% were respectively 65% and 27% for AG and bergamottin/bergapten. The release experiments showed that the presence of BEO influenced the AG release, i.e. AG-loaded-vesicles released the drug more rapidly (100% within 72 h) than BEO-AG-co-loaded vesicles (70% AG released after 9 days), thus evidencing a prolonged drug release from the co-loaded formulations. The findings of deformability test showed suitable deformability index for the various investigated formulations. Interestingly, the deformability index decreased at high concentrations of AG, probably due to its amphipathic nature. The *in vivo* anti-inflammatory activity of BEO-AG-loaded ultradeformable liposomes was tested on human healthy volunteers, who were pre-treated with methyl-nicotinate, thus mimicking skin inflammation under controlled conditions. The results demonstrated that the multidrug-loaded ultradeformable liposomes decreased the skin inflammation more than AG-loaded ones and AG solution. Altogether these findings suggest a promising combination of natural active compounds for the treatment of inflammatory skin disorders using ultradeformable liposomes.

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Development of flexible and mechanical strain resistant membranes as promising guide conduits for nerve repair

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Peripheral nerve injury is one of the most debilitating pathologies that severely impairs patients' life. Although many efforts have been made to advance in the treatment of such a complex disorder, successful strategies to ensure full recovery are still scarce. In the last two decades tissue engineered tubular scaffolds, namely neural guide conduits (NGCs), have emerged as potential systems for neural regeneration [1, 2].

Given these premises, the aim of the present work was to develop flexible and mechanical strain resistant membranes intended to act as support and guide for neural cells during the regeneration process. For this purpose, multichannel poly (lactic-co-glycolic acid) (PLGA)-based membranes (MC-Mb) were designed and manufactured. In particular, the MC-Mb preparation provided the coating of water-soluble fibers (Fbs) with a PLGA-based film. The subsequent immersion in water of the fibers-containing film allowed the formation of inner channels and the obtainment of the multi-channel membranes.

Firstly, aligned-interconnected electrospun water soluble Fbs were obtained *via* electrospinning process (STKIT-40 Linari Engineering, I) from a solution composed of alginate medium viscosity (1% w/w), poloxamer (2% w/w) and two different grades of poly(ethylene oxide) (PEO), PEO 600 kDa (1% w/w) and PEO 4000 kDa (2.2% w/w). In particular, the fibrous mat obtained showed aligned fibers characterized by a mean diameter of about 5-10 μm interconnected by a randomly oriented nanofibrous network (SEM analyses, ImageJ software).

Subsequently, various PLGA 50:50 (lactide-glicolide)-based solutions in ethyl acetate were prepared with the aim of achieving several films via solvent casting; the addition of poly(D,L-lactide) (PDLLA) and poly(ethylene glycol) (PEG), at different molecular weights, to PLGA solution was considered to improve films mechanical properties. Different PLGA, PDLLA and PEG concentrations were considered too. Films obtained after solvent casting were characterized in terms of mechanical resistance, flexibility, resistance to suture (TA.XT Plus Texture Analyzer, Stable Micro System, UK) and wettability (Contact Angle Meter/Goniometer - DMe 211, In). The solution that gave the best film in terms of mechanical properties and wettability was used as coating solution for Fbs, in order to obtain an insoluble polymeric platform. Finally, coated Fbs were soaked in water to allow the dissolution of soluble components and the formation of an insoluble biodegradable membrane (MC-Mb) with aligned-interconnected empty channels. MC-Mb morphology, mechanical properties and wettability were evaluated. In conclusion, the multi-step process developed has proved to be simple and effective, resulting in the formation of a promising innovative biodegradable multi-channel platform. Biocompatible matrices, based on collagen or alginate, containing neuroprotective compounds, will be considered as functional fillers.

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Spermidine as multifunctional agent in the design of innovative tools for nervous tissue repair

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Nervous tissue injuries affect more than one billion people worldwide and dramatically impact on the patient's quality of life. Such lesions are characterized by the loss of neurons and/or neuroglial cells, which leads to a disruption of the neural network and, thus, to an impairment of some fundamental system functions [1]. The present work aimed at developing two novel anionic polysaccharide-based nanosystems, specifically nanogels and nanofibers, as innovative tools for nervous tissue repair. Spermidine (SP), a biologic polyamine, was used as multifunctional agent for the preparation of both nanosystems. SP cationic nature at physiological pH makes it an ideal cross-linking agent for anionic polysaccharides, such as alginate (ALG) and gellan gum (GG). Moreover, SP is characterized by a neuroprotective activity: it preserves neurons from oxidative damage and modulates the over-expression of pro-inflammatory cytokines at the injury site [2].

Nanogels (NGs), consisting of ALG and SP, were developed as promising filler of neural guide conduits or multichannel scaffolds in the treatment of peripheral nerve injuries. NGs were prepared by ionotropic gelation: a SP solution was continuously extruded from a syringe into an ALG solution maintained under magnetic stirring (900 rpm). A two-level full factorial design was employed to investigate, on a statistical basis, the influence of three factors (ALG concentration, ALG viscosity grade and ALG: SP w/w ratio) on the response variable (NG hydrodynamic diameter). According to the 2^3 design, eight NG dispersions were prepared and analyzed by means of Dynamic Light Scattering (Litesizer 500; Anton Paar, I). Results showed that ALG concentration and viscosity grade had a statistically positive effect on NG diameter, while ALG: SP w/w ratio, in the range considered, did not significantly influence the response variable. The ionotropic gelation method has proven to be robust and able to produce spherical particles in the range of 0.4-4 μm (SEM analyses) with a zeta potential lower than -10 kV (Electrophoretic Light Scattering; Litesizer 500). NGs characterized by the lowest hydrodynamic diameter was selected for the continuation of the work: further studies are on-going to evaluate NG mechanical properties by means of AFM indentation test.

Nanofibers (NFs), containing GG and SP, were proposed as novel neural scaffold, endowed with both neuroprotective and neuroregenerative potential; after local application at the site of nervous injury, NFs should support and guide axonal outgrowth and their slow degradation should be responsible for SP controlled release. Mixtures, containing GG and increasing SP concentrations, were prepared and characterized in terms of viscosity and viscoelasticity (Modular Compact Rheometer 102, Anton Paar, I): more and more structured GG/SP mixtures were obtained by increasing SP amount, proving its cross-linking potential. NFs, containing GG, SP, two grades of polyethylenoxide, as spinnable polymers [3], and poloxamer, were prepared by electrospinning. The resulting NFs, subjected to a tensile test (TA.XT Plus Texture Analyzer, Stable Micro System, UK), underwent a plastic deformation without structure break, suggesting a good mechanical resistance when applied at the injury site. Moreover, NFs were insoluble in aqueous media and able to form a thin gel layer after hydration.

Actually, *in vitro* studies on a model cell line (Schwann cells) are on-going to investigate the cytotoxicity, the antioxidant and anti-inflammatory potential of the most promising nanosystems (NGs and NFs) developed.

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Brij O2-stabilized gliadin nanoparticles as innovative vegetal protein-based drug carriers

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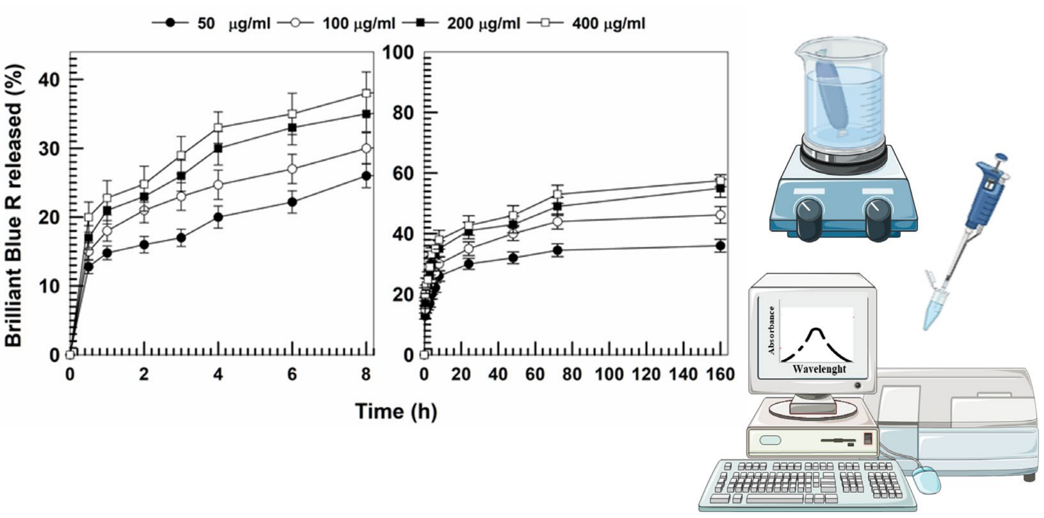
The exploitation of proteins as polymers significantly increased in recent years. Indeed, their intrinsic biocompatibility, biodegradability and spontaneous self-assembly into nanostructures has favored the development of various pharmaceutical formulations [1]. In this investigation, gliadin, the prolamin-rich protein from wheat grains, was used as raw material for the development of a novel vegetal-based nanoformulation. In detail, gliadin-based nanoparticles were obtained following the nanoprecipitation of different amounts of biopolymer (0.2-1.6 mg/ml) previously dissolved in a hydroalcoholic solution. The organic phase was mixed to the aqueous one by means of an Ultraturrax homogenizer and the suspension was placed on a magnetic stirrer to promote the evaporation of the organic solvent. The physico-chemical features of gliadin nanostructures were characterized by means of photon correlation spectroscopy and their time- and temperature-stability by static multiple light scattering. Among the various surfactants used, the addition of 0.1% w/v of the Super Refined grade Brij O2 (SR BO2) promoted the formation of negatively charged nanostructures of ~150 nm characterized by a narrow size distribution. Furthermore, the emulsifier enhanced the stability of samples when incubated at different pH and temperature values (up to 50 °C). Freeze-drying experiments showed that mannose (10% w/v) is a useful cryoprotectant. The gliadin matrix promoted the entrapment and a controlled release of model compounds characterized by different physico-chemical features. In particular, *in vitro* release test showed a biphasic leakage of entrapped compounds with an initial burst effect, followed by a gradual release of both hydrophilic and lipophilic molecules. SR BO2-stabilized gliadin-based nanoparticles showed a low cytotoxicity on normal and tumor cell lines up to 25 µg/ml of biopolymer. The obtained results demonstrated that gliadin nanostructures can be exploited as potential drug carriers [2].



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Release study of food-grade polymeric colonic drug delivery systems: evidence of pH-dependent behavior by Scanning Electron Microscopy

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Colon-targeted drug delivery systems (cDDS) are designed for the oral administration of active ingredients. These systems can protect the cargo from the stomach and small intestine environment, ensuring a selective release in the colon area.

These systems are, therefore, ideal for a local therapeutic action against IBD (inflammatory bowel disease) or to improve the systemic effect of active agents sensitive to the environments of the previous tracts of the digestive system.

Following previous studies of ours, in which the food-grade copolymers Eudraguard® Biotic and Control have been proposed for the production of microparticles loaded with natural compounds (nutraceuticals) [1] [2], in this study we aimed to acquire a microscopic evidence of the process of degradation of the above polymers in gastric, enteric and colon pH conditions. The systems were formulated using an ESE technique (emulsion-solvent evaporation) and were loaded with Resveratrol as a model drug.

To perform the Scanning Electron Microscopy (SEM) analysis, specimens of each cDDS were maintained under magnetic stirring at different pH conditions: for 1 h in simulated gastric fluid (SGF), for 3 h in simulated intestinal fluid (SIF) or for 4 h in simulated colonic fluid (SCF). The microscopic behavior of the systems was correlated with *in vitro* drug release studies, carried out under a pH-change protocol between pH 1.2 to 7.4 [1].

SEM pictures confirmed that all the systems ensured a limited gastric release of resveratrol (below 20% of the loaded dose), as evidenced by the presence of small pores in the surface of microparticles kept in SGF.

The system constituted by Eudraguard® Biotic only showed the maximum release in the colon environment, and SEM analysis confirmed the presence of completely degraded microparticles in these conditions.

The systems produced with pure Control allowed a sustained drug release over time and in SCF showed only partially degraded microparticles.

Using the mixed polymeric matrices, with increasing the percentage of Eudraguard® Control the systems progressively lost the colon release capacity and gave a sustained over time with a plateau in the small intestine conditions.

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Stability of pre drawn syringes of Corminaty®
for an efficient Covid-19 mass vaccination

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The first vaccine approved in the EU and the US for the prevention of COVID19, caused by the SARS-CoV-2 virus, is based on mRNA-loaded lipid nanoparticles (LN) dispersed in an aqueous medium. This formulation is commercialized as a deep-frozen concentrate for dispersion (Pfizer-BioNTech COVID-19 Vaccine in the US or Comirnaty® in EU), which is diluted (upon thawing) just before injecting a 0.3-mL dose intramuscularly. Due to the intrinsic innovative aspects of both the active ingredient (i.e., mRNA) and drug delivery system (i.e., lipid nanoparticles) in clinical applications, limited information can be retrieved in the "Summary of Product Characteristics" or literature about the vaccine stability [1, 2].

In attempt to fill the gap of background information which would help to rationalize handling (i.e., administration components and timing) and transport, we investigated the stability of LN and mRNA of two baches of Comirnaty® stored in either glass vials or 1-mL plastic syringes [made of poly(propylene) or poly(carbonate)], both kept in cold chain (i.e., 2-8 °C), or room temperature (25 °C) over 5 h. The impact of road transportation for 30 km in a suburban area using temperature stabilizing medium was explored. Physical stability of Comirnaty® was assessed by dynamic light scattering (DLS) and nanoparticle tracking analysis (NTA), while mRNA stability was assessed by gel electrophoresis.

LN of leftovers analyzed by DLS resulted in D_H ranging between 80 and 100 nm with a relatively narrow polydispersity (< 0.2). Small differences, but not statistically significant, were observed between the two batches (#1 vs #2; p-value = 0.2476). The particle size distribution derived from NTA analyses and expressed in terms of D_{10}, D_{50} and D_{90} was superimposable for batch #1 and #2 (D_{10}: 56±1 nm and 59±4 nm; D_{50}: 78±5 nm and 78±4 nm; D_{90}: 124±9 nm and 124±6 nm for batch #1 and #2 leftovers, respectively).

Both DLS and NTA data evidenced that physical features of LN did not significantly change upon storage in syringes for 24 h between 2 and 25 °C. Moreover, the unmodified value of nanoparticle concentration confirmed the physical stability of particles that do not undergo aggregation or absorption during storage in syringes (or vial transportation).

Regarding mRNA, the loading quantification by UV-Vis based nanodrop confirmed a very consistent and reliable mRNA concentration in the range from 178 to 185 ng/μL. After quantification, gel documentation highlighted the high stability of mRNA after 1 and 5 hours of incubation at 4 °C. This was confirmed by the presence of a uniform band in both the samples stored within the glass vials and the syringes for injection.

In conclusion, mRNA-loaded LN are physically and chemically stable in syringes made of different materials, when subjected to mechanical and thermal stresses of relatively low intensity and short duration. In the context of the current pandemic situation, it implies that an aseptic technique (preferentially in a dedicated area or room) should be utilized to preserve the microbiological stability of single doses before being transport to the point of administration.

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Water-Soluble Terpenoids Loaded on Halloysite Clay with Wound-Healing Properties

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Recently mineral healing clays gained much attention for wound dressing applications. Here, we selected halloysite (HAL) clay as biocompatible, non-toxic material useful as drug delivery system to enhance healing properties of the water-soluble terpenoids [1-3] (**T1-3**). Terpenoids-loaded HAL clay (**TH1-3**) were prepared and characterized by adsorption equilibrium studies, X-ray powder diffraction (XRPD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy and release studies. Results revealed that **T1-3** were adsorbed to the HAL surface with good efficiency. The prevalent mechanism of drug retention is due to the adsorption via electrostatic interactions between the cationic groups of the **T1-3** and the HAL external surface. Release studies demonstrated that **T3** was released in higher percentage (>60%) compared to **T1-2** (≈50%). Additionally, **TH1-3** were assessed for their antimicrobial activity and capability to promote the re-epithelialization of scratched HaCat monolayers, through the time-kill test and the wound healing assays, respectively. Results revealed that all the tested formulations were able to reduce the microbial growth already after 1 h of incubation and they ensured the complete wound closure after 48 h. Furthermore, at the concentration of 1 µg/mL, **TH3** exhibited 45% wound closure at 24 h, compared to **TH1** (27%) and **TH2** (30%), resulting the best candidate in making the tissue repair process easier and faster.

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Ultrasound-assisted extraction of cannabinoids from Cannabis sativa for medicinal purpose

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The therapeutic benefits of cannabis are more and more recognized at the scientific level. Moreover, the need to improve expertise on the use of cannabis-based medicinal products and their clinical effects is increasing. Due to the limited availability of industrial products, patients must be treated with pharmaceutical preparations, compounded in a pharmacy in accordance with a medical prescription [1]. At present, cannabinoid extraction performed by pharmacists is mainly based on maceration in oil [2]. Ultrasound-assisted extraction can be a promising alternative to maceration. Even if the method has already been used with cannabis [3], extraction conditions need to be further investigated. In this work, direct sonication at fixed ultrasound frequency of 26kH (Hielscher UP200St Ultrasonic homogenizer, Seneco Srl, I) was considered and the effect of amplitude and sonotrode size (Hielscher Sonotrode 2mm, S26d2, for samples from approximately 2mL up to 50mL; 7mm, S26d7, for samples from approximately 20mL up to 500mL), sonication time (10, 20, 30min) and volume of the solvent (20 or 50mL) were evaluated.

The standardized medicinal cannabis FM2 or Bedrocan and olive oil, as a solvent, were used at the ratio 1:10. To obtain decarboxylated cannabinoids, cannabis inflorescence was heated in an oven at 115°C for 40min before extraction [2]. Analyses of the samples were performed on a HPLC/UV Shimadzu Prominence-i LC-2030C.

Preliminarily, samples of pure oil were sonicated (amplitude 60%, 2mm sonotrode) at different sonication times to monitor temperature changes. The measured temperature was related to solvent volume: after 30 min of sonication, in 20mL samples the oil temperature was over 83°C, while it was near 70°C in the larger volume. 20mL volume was selected to continue the evaluation. At the intermediate time (20min - oil temperature: 80°C), FM2 samples were prepared without decarboxylation step. It was shown that cannabinoids in acidic form were still present (CBDA 0.67±0,03% w/w; THCA 0.24±0,02% w/w). Thus, the effect of ultrasounds on extraction efficiency at the three sonication times were evaluated using FM2 previously decarboxylated in an oven (n=3). After each considered time step, differences in total CBD (T=10, 0.66±0.08% w/w; T=20, 0.64±0.06% w/w; T=30, 0.65 ± 0.04% w/w) and total THC (T=10=20=30, 0.26±0.02% w/w) contents were found to be not statistically significant ($p>0.05$). Considering that CBD and THC were almost completely extracted, the shorter sonication time can be considered suitable to obtain a high level of extracted cannabinoids, comparable to those obtained after a maceration phase of 40min at 100°C (T=10, total CBD: 0.59±0.04% w/w; total THC: 0.26±0.02% w/w; n=3).

The effects of ultrasounds on extraction efficiency were also verified using Bedrocan, one of the most used Cannabis variety, containing high level of THC. 50mL samples (amplitude 30%, 7mm sonotrode) were prepared. Total extracted THC measured after 10min sonication (1.90±0.07% w/w; n=3) was higher ($p=0.02$) with respect to those obtained after 40min maceration (total THC: 1.62±0.18% w/w; n=19).

In conclusion, ultrasound-assisted extraction yielded a cannabinoid content similar or even higher than those obtained after maceration, with the advantage of minimizing extraction time. The decarboxylation step remains necessary to avoid the presence of acidic forms, CBDA and THCA.

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New proposals for the photoprotection and controlled delivery of diclofenac

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The light sensitivity of Diclofenac (DC) is well known and the formation of impurities as 1-(2,6-dichlorophenyl)indolin-2-one and other quinone derivatives has been reported in several papers [1-2]. In previous studies, we have defined the photodegradation profile of DC in solution and semi-solid commercial specialties and proposed satisfactory photostabilization systems by adding chemical UV-absorbers or by incorporating the drug into cyclodextrin matrices [3] and niosomes in presence of 5% ascorbic acid [4].

In this work, new matrices were studied to improve both drug delivery and light stability. Solid lipid particles (SLPs) based on biocompatible lipids were developed by using membrane technology in combination with solvent-induced precipitation. SLPs are increasingly used for the encapsulation of labile hydrophilic and hydrophobic drugs, minimizing their degradation in the body and providing their sustained release [5]. Membrane technology is a high throughput micro-nanomanufacturing process that permits to design micro-nanostructured multi-material components for bioactive molecules encapsulation with target size, size distribution and complex 3D structures [6, 7]. The method has unique feasibility for formulations containing bioactive labile molecules and it is recognized also among the most sustainable, clean, and safe manufacturing processes [8]. Photodegradation tests were made according to the international ICH rules [9]. The degradation process was monitored by spectrophotometric analysis and the data were processed by Multivariate Curve Resolution (MCR) to estimate spectra and concentration profiles of the involved components. Light scattering system was used to characterize the SLPs in terms of particle size and particle size distribution. Morphological features of SLPs were examined by Scanning Electron Microscopy (SEM). The encapsulation efficiency (EE) and drug loading efficiency (DLE) of DC were calculated using an indirect method. In *vitro* drug release studies were also performed to evaluate the release mechanism.

Photodegradation rate of DC in solution was found very fast, with a residual content of 90% after 2.52 min, under a radiant exposure of 450 Wm^{-2}. In contrast, the first results obtained showed promising capacities for the proposed formulations both in the photoprotection of the drug and in its controlled release compared to the usual pharmaceutical formulations.

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INDICE COMUNICAZIONI ORALI

Astolfi	Paola	TEC OR042
Atzori	Matteo	INO OR025
Audisio	Davide	ORG OR003
Avola	Tiziana	ANA OR086
Ayaz	Nazeeha	TEC OR027
Aye	Yimon	FAR KN005
Bacchiocchi	Riccardo	IND OR058
Baccolo	Giacomo	ANA OR034
Bach	Anders	FAR KN009
Badetti	Elena	ABC OR007
Baglio	Vincenzo	ELE OR57
Baglioni	Michele	FIS OR076
Baldassarre	Francesca	TEC OR041
Baldelli	Francesca	FIS OR067
Baldini	Laura	ORG OR087
Ballarotto	Marco	ORG OR019
Balliana	Eleonora	ABC OR002
Balsamo	Stefano Andrea	IND OR047
Bandiera	Tiziano	FAR KN011
Baratta	Mariafrancesca	FIS OR107
Barbanente	Alessandra	INO PZ008
Barbera	Vincenzina	TEC OR021
Barberis	Elettra	MAS OR005
Barbieri	Luisa	ABC OR054
Barbieri	Pierluigi	ABC OR058
Bardi	Brunella	FIS OR103
Barlocco	Ilaria	INO OR002
Barola	Carolina	MAS OR011
Baron	Marco	INO OR019
Barone	Laura	ANA OR114
Barreca	Marilia	FAR OR011
Bartella	Lucia	MAS OR010
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Battistuzzi	Gianantonio	CSB OR003
Begni	Federico	FIS OR088
Bella	Federico	IND OR036
Bellassai	Noemi	ANA OR068
Bellavita	Rosa	FAR OR042
Bellia	Francesco	CSB OR022
Bellina	Fabio	ORG OR069
Bellini	Marco	INO OR041
Belloni	Alessia	INO OR048
Bellotti	Denise	ANA OR087
Bellotto	Ottavia	CSB OR002
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Bernini	Roberta	ORG OR005
Bertani	Marco	TEO OR001
Bertinetti	Stefano	ANA OR060
Berto	Silvia	ANA KN010

Bertucci	Alessandro	ANA OR069
Bertuletti	Susanna	ORG OR117
Bertuzzi	Giulio	ORG OR108
Bettini	Simona	FIS OR080
Biagini	Denise	ANA OR035
Biagiotti	Giacomo	ORG OR027
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Bianchi	Federica	ANA OR076
Bianco Prevot	Alessandra	ANA IL005
Biancolillo	Alessandra	ANA KN004
Biasi	Pierdomenico	IND KN003
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Biffis	Andrea	INO OR022
Bifulco	Aurelio	TEC OR017
Biggio	Deborah	ANA OR115
Bigogno	Alessandra	ABC OR006
Bisag	Denisa	ORG OR118
Biscaglia	Francesca	FIS OR064
Bizzarri	Bruno Mattia	ORG OR020
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Bloise	Ermelinda	TEC OR004
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Boldrini	Chiara Liliana	ORG OR080
Bollella	Paolo	ANA KN009
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Bonfio	Claudia	CSB PZ002
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Brandi	Jessica	ANA OR095
Brandiele	Riccardo	ELE IL31
Bretti	Clemente	ANA KN002
Brilloni	Alessandro	ELE OR67
Brufani	Giulia	ORG OR119
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Brunelli	Andrea	ABC OR015
Brunetti	Leonardo	FAR OR009
Brunsveld	Luc	CSB KN003
Budroni	Marcello	FIS OR122

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Busato	Matteo	FIS OR094
Buscemi	Gabriella	ORG OR081
Cabri	Walter	IND KN002
Cademartori	Davide	ELE OR56
Caflisch	Amedeo	CSB KN006
Calà	Elisa	ANA OR063
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Calandra	Pietro	ABC OR055
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Calcaterra	Andrea	ORG OR006
Calcio Gaudino	Emanuela	ORG OR120
Calgaro	Loris	ABC OR056
Calogero	Francesco	ORG OR121
Calvano	Cosima Damiana	ANA IL004
Calvini	Rosalba	ANA OR132
Calvino	Martina Maria	FIS OR118
Campagnolo	Filippo	INO OR024
Campanella	Beatrice	ANA OR116
Campiani	Giuseppe	FAR KN001
Campisciano	Vincenzo	ORG OR122
Campisi	Sebastiano	FIS OR034
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Capone	Matteo	TEO OR015
Cappai	Rosita	ANA OR088
Caprioglio	Diego	ORG OR021
Capriotti	Anna Laura	ANA IL009
Caputo	Paolino	FIS OR040
Cara	Claudio	FIS OR105
Caratelli	Veronica	ANA OR134
Carbone	Daniela	FAR OR013
Cardoso Gomes	Guelber	TEO OR016
Carena	Luca	ANA OR061
Carmignani	Alessio	FIS OR099
Carpanese	Maria Paola	ELE OR48
Carpentieri	Maria Antonietta	DID OR002
Carucci	Cristina	FIS OR063
Caruso	Manfredi	TEC OR005
Casini	Angela	CSB KN005
Castiglione	Franca	TEC OR010
Casula	Luca	TFA OR011
Cataldo	Salvatore	ANA OR089
Catani	Martina	ANA PZ004
Catelli	Emilio	ANA OR064
Catto	Marco	FAR OR031
Cavalera	Simone	ANA OR096
Cavazza	Antonella	ANA OR025
Cavuoto	Denise	IND OR002
Cecchi	Teresa	DID OR010

Cecconi	Daniela	MAS OR001
Ceccucci	Anita	TEC OR045
Cefali	Manuel Amedeo	ABC OR059
Centomo	Paolo	INO OR033
Cerrato	Andrea	ANA OR097
Cerri	Luca	TFA OR012
Cesari	Cristiana	INO OR035
Chelazzi	David	FIS OR 129
Chenet	Tatiana	ANA OR026
Chiarcos	Riccardo	IND OR027
Chiarello	GianLuca	FIS OR030
Chino	Marco	INO OR032
Chiodo	Fabrizio	ORG OR007
Chirizzi	Cristina	FIS OR081
Ciacci	Luca	ABC OR003
Ciccola	Alessandro	ABC OR008
Cinti	Stefano	ANA OR071
Cioffi	Nicola	ANA IL010
Cipriano	Domenico	ABC OR045
Cirillo	Martina	ORG OR008
Clemente	Ilaria	FIS OR065
Cleto Bruzzese	Paolo	INO OR027
Colella	Marco	ORG OR022
Colella	Maria Francesca	FIS OR115
Collini	Elisabetta	FIS OR047
Colloca	Stefano	TFA IL002
Colozza	Noemi	ANA OR135
Comis	Silvia	ELE OR43
Condorelli	Marcello	FIS OR009
Consentino	Luca	IND OR015
Conte	Francesco	IND OR045
Contente	Martina	FAR OR018
Conti	Luca	INO OR023
Coralli	Irene	ANA OR077
Corbisiero	Dario	ORG OR023
Cordaro	Massimiliano	ORG OR024
Corinti	Davide	INO OR063
Corno	Marta	FIS OR101
Corradini	Danilo	ANA OR024
Corrente	Giuseppina Anna	FIS OR035
Corrieri	Matteo	ORG OR132
Cosentino	Ugo	DID OR015
Costa	Maria	DID OR003
Costanzo	Paola	ORG OR061
Cozzolino	Antonietta	IND OR028
Cristiano	Maria Chiara	TFA OR013
Cristina	Tealdi	ELE KN68
Crivellaro	Giovanni	ELE OR07
Crocetti	Letizia	FAR OR006
Cucinotta	Lorenzo	ANA OR003
Cupellini	Lorenzo	TEO PZ005

Curti	Claudio	ORG OR059
D’Ambrosio	Valeria	ABC OR022
D’Imperio	Nicolas	ORG PZ012
Da Pian	Marta	ORG OR034
D’Agata	Roberta	ANA OR117
Dai	Yasi	TEO OR018
Dal Bello	Federica	ANA OR028
Dall’Anese	Anna	INO PZ002
D’Alterio	Massimo Christian	INO OR004
D’Amato	Alfonsina	ANA OR105
Damiano	Caterina	INO OR016
Damin	Alessandro	FIS OR126
Danielis	Maila	IND OR005
D’Aria	Federica	FIS OR018
Darjazi	Hamideh	ELE OR72
Davighi	Maria Giulia	ORG OR010
de Araujo Lima e Souza	Giselle	TEC OR011
De Bon	Francesco	ELE OR16
De Bonis	Angela	FIS OR097
De Castro	Cristina	ORG OR011
De Ceglie	Cristina	ABC OR017
De Filpo	Giovanni	FIS OR082
De Gennaro	Gianluigi	ABC OR001
De Grazia	Gemma	ANA OR004
De Leo	Vincenzo	FIS OR019
De Luca	Chiara	ANA OR106
De Marchi	Fabiola	MAS OR008
De Santis	Roberto	FIS KN012
De Santis	Serena	TEC KN003
De Zotti	Marta	CSB OR001
Deganello	Francesca	INO OR039
Degli Esposti	Lorenzo	FIS OR021
Del Coco	Laura	INO OR061
Del Galdo	Sara	TEO OR022
Del Giudice	Alessandra	FIS OR053
Del Giudice	Daniele	ORG OR088
Del Grosso	Erica	ANA OR072
Della Pelle	Flavio	ANA KN011
Dell’Edera	Massimo	FIS OR113
Deng	Siyuan	TFA OR009
Desantis	Jenny	ORG OR012
Dettin	Monica	FIS OR096
Di Capua	Angela	ANA OR098
Di Carlo	Gabriella	FIS KN010
Di Carluccio	Cristina	ORG OR013
Di Carmine	Graziano	ORG OR035
Di Donato	Francesca	ANA OR036
Di Fidio	Nicola	IND OR053
Di Giulio	Tiziano	ANA OR018
Di Guida	Rossella	ORG OR014
Di Liberto	Giovanni	FIS OR028

Di Liberto	Giovanni	TEO PZ003
Di Maiolo	Francesco	TEO OR029
Di Maro	Mattia	ORG OR110
Di Maro	Salvatore	FAR OR039
Di Matteo	Paola	TEC OR025
Di Muzio	Simone	FIS OR071
Di Nardo	Fabio	ANA OR099
Di Noja	Simone	ORG OR031
Di Pietro	Maria Enrica	TEC OR012
Di Porzio	Anna	CSB OR029
Di Terlizzi	Lorenzo	ORG OR063
Dibenedetto	Carlo Nazzareno	FIS OR001
Dichiara	Maria	FAR OR021
Dichiarante	Valentina	TEC OR031
Dilonardo	Elena	TEC OR028
Dini	Danilo	ELE OR17
Dispenza	Clelia	TEC OR046
Distefano	Alessia	CSB OR009
Dogra	Raghav	ANA OR009
Domestici	Chiara	INO OR042
Donà	Lorenzo	TEO OR030
Donati	Greta	TEO PZ001
Donato	Paola Agata	ANA OR030
Donnarumma	Danilo	ANA OR118
Donnoli	Maria Irene	DID OR011
D’Onofrio	Mariapina	ORG OR009
Dozzi	Maria Vittoria	FIS KN009
D’Urso	Alessandro	CSB OR010
Econdi	Stefano	IND OR011
El Fadil	Dounia	ANA OR107
Elbaz	Lior	ELE KN55
Elkhanoufi	Sabrina	CSB OR008
Elliani	Rosangela	ANA OR005
Erba	Alessandro	TEO PZ002
Ermini	Elena	ORG OR036
Escolano Casado	Guillermo	FIS OR069
Esposito	Anna	ORG PZ014
Esposito	Germana	ORG OR037
Esposito	Roberto	INO OR020
Esposito	Rodolfo	FIS OR106
Esposito	Tiziana	TFA OR014
Espro	Claudia	TEC KN001
Estima Gomes	Manuela	TFA IL005
Fabbiani	Marco	FIS OR006
fabbri	Debora	ANA OR029
Fabiani	Laura	ANA OR019
Facchetti	Giorgio	INO OR031
Facchin	Alessandro	ELE OR35
Facchin	Alessandro	ELE OR51
Faginas-Lago	Noelia	TEO OR008
Fagiolari	Lucia	IND OR061

Fagnani	Francesco	INO OR007
Falco	Marisa	ELE OR62
Falletta	Ermelinda	IND OR048
Famulari	Antonino	INO OR062
Fanizza	Elisabetta	FIS OR014
Fanti	Federico	MAS OR004
Fasano	Valerio	ORG OR116
Fasolini	Andrea	IND OR040
Fasulo	Francesca	TEO OR009
Fattal	Elias	TFA IL001
Federico	Bella	TEC OR038
Felletti	Simona	ANA OR078
Fenti	Angelo	ABC OR009
Ferdeghini	Claudio	ORG OR032
Ferdinando Summa	Francesco	TEO OR023
Ferlenghi	Francesca	FAR OR019
Fermi	Andrea	INO OR045
Fermo	Paola	ANA IL006
Feroci	Marta	ELE KN045
Ferracane	Antonio	ANA OR006
Ferrari	Giorgio	IND OR065
Ferraro	Giovanni	FIS OR011
Ferrauto	Giuseppe	INO OR051
Ferrazzano	Lucia	ORG OR064
Ferrero	Luca	ABC OR005
Ferretti	Francesco	INO OR021
Fidaleo	Marco	TFA IL004
Filippin	Ilaria	TFA OR003
Fiorentini	Carlo	DID IL002
Fiorentino	Antonino	ABC OR034
Fiorenza	Roberto	IND OR016
Fiorito	Daniele	ORG OR060
Fischer	Peter	ELE KN06
Forchetta	Mattia	ORG OR082
Fornari	Fabio	ANA OR037
Fornasier	Marco	FIS OR016
Forni	Alessandra	FIS OR044
Fortino	Mariagrazia	TEO OR010
Fortunati	Alessia	ELE OR21
Foschi	Francesca	ORG OR123
Francesconi	Oscar	ORG OR089
Franchina	Flavio	ANA KN001
Franchino	Allegra	ORG OR067
Franco	Francesca	ORG OR076
Franzini	Roberta	ORG OR038
Frateloreto	Federico	ORG OR133
Freccero	Riccardo	INO OR069
Frosi	Ilaria	FAR OR017
Froudakis	George	FIS KN007
Funicello	Maria	ORG OR015
Gabas	Fabio	FIS OR058

Gaeta	Massimiliano	CSB OR021
Gaggero	Elisa	ABC OR035
Gaggiotti	Sara	ANA OR124
Gagliardi	Anna	IND OR049
Galantini	Luciano	FIS KN011
Galassi	Rossana	INO OR047
Galeotti	Marco	ORG OR039
Galletta	Micaela	ANA OR007
Galloni	Melissa Greta	IND OR017
Gambassi	Francesca	INO OR049
Garbarino	Gabriella	IND OR006
García Lascurain	P. Guzmán	ABC OR046
Garello	Francesca	INO OR054
Gaspa	Silvia	ORG OR070
Gatti	Lucrezia	ABC OR028
Gatto	Emanuela	FIS KN003
Gazzola	Silvia	ORG OR138
Gazzotti	Stefano	IND OR023
Gelain	Arianna	FAR OR014
Gelli	Rita	FIS OR052
Geninatti	Simonetta	INO OR084
Gentile	Luigi	FIS KN004
Gentili	Dario	ORG OR016
Gentili	Pier Luigi	FIS OR038
Gessner	Viktoria	INO IL001
Ghedini	Elena	IND OR070
Ghini	Veronica	CSB OR006
Ghini	Veronica	INO OR070
Ghirga	Francesca	ORG OR041
Giacalone	Francesco	ORG PZ007
Giambastiani	Giuliano	IND OR063
Giannetto	Marco	ANA OR073
Giedroc	David	INO IL003
Gilda Ritacca	Alessandra	TEO OR020
Gioiello	Antimo	FAR KN006
Giordana	Alessia	INO OR030
Giorgi	Silvia	IND OR057
Giorno	Lidietta	CSB OR004
Giovanni	Falcone	TEC OR044
Giovannini	Tommaso	FIS OR060
Girlando	Alberto	FIS OR090
Girolametti	Federico	ANA OR010
Giuffrè	Ottavia	ANA OR090
Giuliano	Elena	TFA OR017
Giurlani	Walter	ANA OR119
Giustiniano	Mariateresa	FAR PZ002
Gobbo	Pierangelo	ORG PZ004
Gobetto	Roberto	INO OR001
Gois	Pedro	FAR KN012
Golla	Manohar	IND OR029
Goracci	Laura	ORG OR042

Gori	Alessandro	TEC IL003
Gorla	Giulia	ANA OR120
Goti	Giulio	ORG OR083
Grattieri	Matteo	ELE OR18
Grigioni	Ivan	IND OR035
Groppo	Elena	FIS KN005
Gualandi	Andrea	ORG OR134
Gualandi	Isacco	ANA KN007
Gubitosa	Jennifer	FIS OR024
Guerra	Giulia	ABC OR036
Gugliuzza	Annarosa	ABC OR043
Guidoni	Leonardo	TEO OR013
Guidotti	Giulia	ABC OR021
Guidotti	Matteo	IND OR067
Gullifa	Giuseppina	ANA OR079
Guzman	Hilmar	ELE OR23
Hajareh Haghighi	Farid	INO OR066
He	Xiufang	ELE OR39
Hernandez	Simelys	IND OR034
Hessel	Volker	IND KN007
Hirsch	Anna	FAR KN008
Hmoudah	Maryam	IND OR071
Iaccarino	Nunzia	CSB OR027
Iammarino	Marco	ANA OR031
Ianni	Federica	FAR OR016
Illiano	Anna	ANA OR008
Illuminati	Silvia	ANA OR062
Impemba	Salvatore	INO OR052
Imperatore	Concetta	ORG OR043
Inaudi	Paolo	ANA OR044
Intagliata	Sebastiano	FAR OR028
Interino	Nicolò	ANA OR100
Irto	Anna	ANA OR091
Jacobson	Kenneth	FAR MD001
Joseph	Edith	ABC KN001
Jurinovich	Sandro	DID OR004
Kaveh	Moulaee	TEC OR035
Keserű	György	FAR KN002
Khalid	Shahid	ELE OR75
Koper	Marc	ELE KN19
Kuhnert	Nikolai	MAS PL003
La Nasa	Jacopo	ANA OR080
La Regina	Giuseppe	FAR OR004
La Tella	Roberta	ANA OR081
Labarile	Rossella	FIS OR015
Labate	Maria	ABC OR025
Lacarbonara	Giampaolo	ELE OR08
Lambruschini	Chiara	ORG OR040
Lamuraglia	Raffaella	ABC OR029
Lancellotti	Isabella	TEC OR018
Larisa	Lvova	TEC IL002

Laudadio	Gabriele	ORG PZ015
Laurati	Marco	FIS KN001
Laus	Michele	IND KN004
Lazzara	Giuseppe	ABC OR050
Leccese	Mirko	FIS OR102
Lenci	Elena	DID OR012
Lenci	Elena	ORG PZ009
Lenzi	Alessio	ANA OR108
Leonardo	Duranti	ELE OR49
Leone	Linda	INO OR005
Leonelli	Cristina	TEC OR016
Lesch	Andreas	ANA OR045
Li	Min	ANA OR121
Liccardo	Letizia	INO OR055
Licen	Sabina	ABC OR010
Licen	Sabina	ANA OR038
LiDestri	Giovanni	FIS OR002
Lipparini	Filippo	TEO OR025
Lippi	Martina	TEC OR033
Lisuzzo	Lorenzo	FIS OR072
Litti	Lucio	FIS OR078
Lo Porto	Chiara	FIS OR108
Lo Vecchio	Carmelo	ELE OR03
Locatelli	Marcello	ANA OR082
Lodesani	Federica	TEO OR031
Lodi	Giulia	ABC OR032
Loianno	Valerio	FIS OR086
Lombardi	Dora Stella	DID OR005
Lombardo	Marco	ORG OR135
Lopreside	Antonia	ANA OR074
Losi	Niccolo	ABC OR060
Lovison	Denise	INO OR056
Lucantonio	Stefania	IND OR060
Lucarini	Marco	ORG PZ005
Lucarini	Simone	FAR OR024
Lucenti	Elena	INO OR014
Lufrano	Ernestino	ELE OR65
Lunardon	Marco	INO OR072
Lupi	Michela	ORG OR136
Lupidi	Gabriele	ORG OR145
Luque	Rafael	IND KN006
M. Fiore	Ambra	TEC OR019
Maccarone	Giuseppina	MAS PL001
Macchia	Eleonora	ANA OR020
Magnaghi	Lisa Rita	ANA OR039
Magni	Mirko	ELE OR26
Mai	Antonello	FAR MD002
Maiuolo	Loredana	ORG OR074
Malacaria	Luana	ANA OR092
Malegori	Cristina	ANA KN005
Malferrari	Marco	ELE OR37

Malitesta	Cosimino	ANA OR136
Mameli	Valentina	FIS OR010
Manca	Gabriele	INO OR057
Mancinelli	Michele	ORG OR075
Mancini	Alessandro	ABC OR061
Manfredi	Marcello	ANA OR109
Manfredi	Norberto	ORG OR084
Mangini	Anna	ELE OR66
Mangraviti	Domenica	ANA OR051
Mannias	Giada	INO OR075
Mantovani	Marco	ABC OR020
Manzoli	Maela	IND OR051
Marasco	Daniela	INO OR060
Marassi	Valentina	ANA OR101
Marchesi	Stefano	FIS OR110
Marchiò	Luciano	INO OR077
Marcì	Giuseppe	TEC OR029
Marcolin	Giampaolo	FIS OR043
Maresca	Giovanna	ELE OR74
Maria Squeo	Benedetta	ORG OR106
Mariani	Federica	ANA OR021
Mariconda	Annaluisa	INO OR068
Mariotti	Nicole	IND OR032
Marittimo	Nicole	ANA OR052
Marotta	Angela	TEC OR009
Martella	Daniele	IND OR031
Martelli	Giulia	ORG OR137
Martina	Bortolami	TEC OR040
Martini	Francesca	FIS OR048
Martí-Rujas	Javier	INO OR006
Maruccia	Elisa	ELE OR20
Marullo	Salvatore	ORG OR111
Marussi	Giovanna	ANA OR065
Marzo	Tiziano	INO OR011
Mascolo	Giuseppe	ABC OR037
Mascolo	Giuseppe	ABC OR038
Masi	Marco	ORG OR044
Massari	Serena	FAR OR036
Massaro	Arianna	TEO OR002
Massaro	Marina	ORG OR054
Mastrangelo	Rosangela	FIS OR074
Mattarozzi	Monica	ANA OR102
Maturi	Mirko	ORG PZ013
Mauriello	Francesco	IND OR059
Mauriello	Francesco	TEC OR002
Mazzapioda	Lucia	ELE OR52
Mazzaracchio	Vincenzo	ANA OR022
Mazzariol	Chiara	INO OR080
Mazzei	Luca	CSB PZ001
Mazzoni	Rita	INO OR043
Mazzucato	Marco	ELE OR12

McLean	John	MAS PL002
Medici	Fabrizio	ORG OR071
Medves	Marco	FIS OR061
Melchior	Andrea	TEC KN004
Melinte	Gheorghe	ANA OR023
Memboeuf	Antony	MAS PL005
Mendolicchio	Marco	TEO OR026
Meninno	Sara	ORG PZ011
Merlo	Francesca	ANA OR110
Mero	Angelica	ORG OR112
Messa	Francesco	ORG OR072
Messina	Grazia	FIS OR007
Messore	Antonella	FAR OR038
Metrangolo	Pierangelo	ORG PZ003
Mezzetta	Andrea	ORG OR062
Mezzomo	Lorenzo	ELE OR63
Micalizzi	Giuseppe	ANA OR111
Miceli	Mariachiara	TEC OR024
Micheletti	Cosimo	IND OR043
Miglio	Vanessa	FIS OR036
Miglione	Antonella	ANA OR046
Migliorati	Valentina	FIS OR121
Migliore	Rossella	ANA OR093
Milanese	Chiara	FIS OR026
Miletto	Ivana	FIS OR062
Milite	Ciro	FAR PZ001
Minella	Marco	ANA OR011
Minero	Claudio	ANA PL001
Minguzzi	Alessandro	ELE KN15
Minnelli	Cristina	ORG OR045
Mocci	Rita	ORG OR066
Moedlinger	Marianne	FIS OR125
Monaci	Linda	MAS KN002
Monciatti	Elisabetta	ORG OR113
Mondello	Luigi	ANA PZ002
Monica	Fabrizio	TEC KN002
Montalbano	Marco	FIS OR114
Montali	Laura	ANA OR125
Montero	Jorge	ELE OR09
Montesarchio	Daniela	ORG PZ006
Montini	Tiziano	IND OR041
Montone	Carmela Maria	ANA OR002
Morandi	Sara	FIS OR077
Moretta	Alma	DID OR006
Morillas Becerril	Lucía	ORG OR046
Moro	Miriam	ELE OR22
Mosconi	Edoardo	INO PZ010
Mostoni	Silvia	INO OR073
Motta	Stefano	TEO OR019
Moyano	Encarnación	MAS PL004
Mulas	Gabriele	FIS OR037

Munzi	Gabriella	TEC OR032
Mura	Monica	FIS OR020
Muraglia	Marilena	FAR OR027
Murgolo	Sapia	ABC OR040
Musazzi	Umberto	TFA OR018
Muscolino	Emanuela	TEC OR047
Musella	Simona	FAR OR005
Musolino	Maria Grazia	IND OR037
Mussini	Patrizia	ANA OR047
Mussini	Patrizia	ELE KN01
Mustorgi	Eleonora	ANA OR133
Musumeci	Francesca	FAR OR003
Nacci	Angelo	ORG OR139
Nale	Angeloclaudio	ELE OR46
Nannuzzi	Chiara	FIS OR112
Nardelli	Francesca	ABC OR012
Nardiello	Donatella	ANA OR012
Narzi	Daniele	TEC OR034
Navacchia	Maria Luisa	ORG OR047
Naviglio	Daniele	ANA OR112
Neese	Frank	INO PZ001
Negri	Fabrizia	TEO KN003
Neri	Giulia	ORG OR055
Nervi	Carlo	INO OR017
Nieto Fabregat	Ferran	ORG OR048
Nomellini	Chiara	FIS OR089
Nori	Valeria	ORG OR065
Notaro	Anna	ORG OR049
Oliva	Eleonora	ANA OR054
Oliveri	Valentina	CSB OR024
Olivieri	Diego	INO OR082
Olivo	Giorgio	ORG OR090
Operamolla	Alessandra	ORG OR056
Orian	Laura	FIS OR100
Orlandi	Manuel	ORG PZ010
Ostacolo	Carmine	FAR OR007
Pagano	Rita	CSB OR020
Pagot	Gioele	ELE OR47
Palazzi	Sergio	DID OR009
Palazzi	Sergio	DID OR014
Palmieri	Sara	ANA OR083
Palmioli	Alessandro	ORG OR050
Panniello	Annamaria	FIS OR050
Panza	Nicola	INO OR013
Paolantoni	Marco	FIS OR116
Paone	Emilia	IND OR038
Papa	Veronica	IND OR069
Pappalardo	Valeria	IND OR055
Pargoletti	Eleonora	ELE OR58
Parmeggiani	Camilla	IND OR030
Parnigotto	Mattia	ELE OR13

Parodi	Adriano	ORG OR030
Parrino	Francesco	TEC OR015
Pascale	Raffaella	MAS OR013
Pasini	Mariacecilia	ORG OR052
Passarini	Fabrizio	ABC KN002
Pastore	Andrea	ANA OR126
Patamia	Vincenzo	ORG OR053
Pavan	Cristina	INO OR003
Pavlos	Nikolaou	ELE OR42
Pavone	Michele	ELE KN64
Pecoraro	Adriana	FIS OR059
Pecoraro	Tania	INO OR034
Peddis	Davide	DID OR007
Peddis	Davide	FIS OR003
Pedone	Alfonso	TEO KN002
Pedrazzani	Riccardo	INO OR046
Pedretti	Silvia	MAS OR002
Pelagatti	Paolo	INO OR053
Pellegrino	Francesco	ANA KN003
Pelosi	Chiara	FIS OR119
Penconi	Marta	FIS OR057
Perathoner	Siglinda	IND KN008
Perego	Carlo	IND KN005
Perinelli	Diego	TFA OR015
Perrella	Fulvio	TEO OR027
Perrone	Daniela	ORG OR051
Peruffo	Nicola	FIS OR046
Petralito	Stefania	TFA OR004
Petri	Elisabetta	ELE OR02
Petrone	Alessio	TEO OR012
Pettazzoni	Luca	ORG OR057
Phan Huu	Andrea	TEO OR032
Piacentini	Emma	TFA OR005
Piacenza	Elena	FIS OR023
Picca	Rosaria Anna	ANA OR066
Picci	Giacomo	INO PZ003
Piccinni	Marco	ELE OR04
Piga	Isabella	MAS OR003
Pigani	Laura	ANA OR048
Pinto	Gabriella	ANA OR013
Pintus	Anna	INO OR044
Pinzi	Luca	FAR OR029
Piovano	Alessandro	FIS OR051
Piovano	Alessandro	IND OR025
Piovesana	Susy	ANA IL001
Pipitone	Giuseppe	IND OR022
Pippione	Agnese	FAR OR001
Pirali	Tracey	FAR KN003
Piras	Federica	ABC OR041
Pirola	Carlo	IND OR068
Pironti	Concetta	ABC OR042

Pirota	Valentina	ORG OR100
Pirro	Fabio	INO PZ006
Pisani	Michela	CSB OR017
Pisani	Silvia	TFA OR021
Pither	Molly	ORG OR092
Platella	Chiara	CSB OR012
Plutino	Maria Rosaria	FIS OR087
Podda	Edoardo	IND OR026
Poggi	Giovanna	FIS OR075
Poli	Federico	ELE OR27
Polo	Annalisa	ELE IL32
Polo	Annalisa	FIS OR032
Ponte	Fortuna	INO PZ004
Porpora	Francesca	ABC OR030
Porto	Michele	FIS OR095
Pota	Giulio	TEC OR013
Potenti	Simone	ORG OR101
Pratesi	Debora	ORG OR093
Prati	Silvia	DID OR013
Pravatto	Pierpaolo	TEO OR033
Prejanò	Mario	INO OR059
Prete	Prisco	IND OR046
Previti	Santo	FAR OR025
Prosa	Mario	FIS OR084
Punta	Carlo	TEC OR003
Punzo	Angela	ANA OR127
Quaglio	Deborah	ORG OR094
Quinto	Maurizio	ANA IL007
Quivelli	Andrea Francesca	ORG OR140
Rabuffetti	Marco	ORG OR141
Radi	Marco	FAR KN004
Ragazzini	Ilaria	ANA OR137
Ragno	Daniele	ORG OR142
Rainer	Alberto	TEC IL001
Ramacciotti	Francesca	ABC OR047
Ranallo	Simona	ANA OR128
Ranaudo	Anna	TEO OR007
Rancan	Marzio	INO OR050
Rapino	Stefania	ELE KN40
Rassu	Giovanna	TFA OR006
Rau	Julietta	FIS KN013
Ravasio	Nicoletta	IND KN001
Ravera	Enrico	INO PZ005
Ravera	Mauro	INO OR029
Rayhane	Zribi	TEC OR037
Reato	Mattia	ELE OR14
Rebeccani	Sara	ELE IL28
Regina	Serena	TEC OR007
Renai	Lapo	ANA OR103
Riccardi	Claudia	CSB OR005
Ricci	Michele	ORG OR102

Ricci	Simona	FIS OR008
Ricciarelli	Damiano	INO OR040
Riela	Serena	ORG OR058
Rigamonti	Luca	INO OR083
Rigon	Carolina	ABC OR031
Rinaldi	Federica	TFA OR007
Ripani	Lorenzo	ELE IL30
Ritacco	Ida	TEO OR005
Riva	Laura	TEC OR006
Rivoira	Luca	ANA OR014
Rizzi	Federica	FIS OR066
Rizzi	Vito	FIS OR039
Rizzo	Carla	ORG OR104
Rizzo	Giorgio	ORG OR143
Rizzuti	Antonino	TEC OR052
Roberto	Grisorio	TEC OR039
Robotti	Elisa	ANA OR040
Rocco	Daniele	ELE OR05
Roda	Barbara	ANA KN012
Rojo	Teofilo	ELE KN73
Roletto	Jacopo	ORG PZ008
Romanelli	Alessandra	CSB OR013
Romanelli	Marco	TFA IL006
Romanucci	Valeria	CSB OR018
Romerio	Alessio	CSB OR014
Rosa-Gastaldo	Daniele	ORG OR091
Rosciardi	Vanessa	FIS OR073
Rossano	Carmelina	IND OR056
Rossetti	Arianna	TEC OR043
Rossetti	Ilenia	IND OR050
Rossi	Christian	INO OR076
Rossi	Federico	FIS OR117
Rossi	Roberto	ORG OR095
Rossin	Andrea	INO OR036
Rossino	Giacomo	FAR OR022
Rosso	Francesca	IND OR062
Rotundo	Laura	ELE IL33
Rovaletti	Anna	TEO OR021
Roverso	Marco	ANA OR084
Ruffino	Roberta	FIS OR012
Ruggieri	Silvia	INO OR010
Russina	Olga	FIS OR123
Russo	Laura	ORG OR096
Russo	Luigi	CSB OR007
Russo	Patrizio	ORG OR144
Russo	Vincenzo	IND OR019
Sabbatini	Luigia	ANA PZ001
Sabbatini	Simona	TEC OR008
Sabuzi	Federica	ORG OR103
Sacchetti	Annalisa	IND OR012
Sacco	Giovanni	ORG OR097

Sacco	Pasquale	FIS OR055
Saielli	Giacomo	TEO OR011
Sainas	Stefano	FAR OR032
Salafia	Fabio	ANA OR032
Salerno	Tania	ANA OR055
Saliu	Francesco	ABC OR018
Salvestrini	Stefano	FIS OR120
Salvino	Rosachiara Antonia	FIS OR045
Salvitti	Chiara	INO OR009
Sanadar	Martina	TEC OR049
Sandri	Giuseppina	TFA OR019
Sangiorgi	Nicola	IND OR042
Sanna Angotzi	Marco	FIS OR091
Sannino	Gennaro	ELE OR38
Sannino	Gennaro	ELE OR38
Sansoni	Simone	FIS OR031
Santalucia	Rosangela	FIS OR104
Santamaria	Monica	ELE KN24
Santi	Cristina Manuela	ORG OR098
Santini	Saul	ANA OR015
Santino	Federica	ORG OR099
Santoro	Antonio	INO OR079
Santulli	Federica	INO OR028
Sarcina	Lucia	ANA OR075
Sardella	Roccaldo	ANA IL008
Sartori	Andrea	ORG OR124
Sartori	Emanuela	FIS OR027
Sassi	Paola	FIS KN002
Satira	Antonella	TEC OR014
Sawssen	Slimani	ABC OR014
Sbrascini	Leonardo	ELE OR70
Scala	Angela	ORG OR125
Scalarone	Dominique	ABC OR051
Scalvini	Laura	FAR OR008
Scattolin	Thomas	INO OR015
Scavetta	Erika	ANA IL002
Schiavo	Eduardo	TEO PZ004
Sciacca	Claudia	ORG OR077
Sciarrone	Danilo	ANA OR056
Sciutto	Giorgia	ANA OR041
Scoditti	Stefano	INO OR026
Scognamiglio	Monica	ORG OR126
Scorciapino	Andrea	FIS KN015
Scroccarello	Annalisa	ANA OR129
Scuderi	Debora	FIS KN006
Serafini	Ilaria	ABC OR013
Serafini	Martina	IND OR033
Sessoli	Roberta	INO PZ009
Severini	Leonardo	FIS OR127
Sfragano	Patrik	ELE OR44
Sgaravatti	Elena	CSB KN004

Sgherza	Damiano	ABC OR053
Sicilia	Emilia	TEO KN001
Siciliano	Giulia	FIS OR109
Silipo	Alba	ORG OR127
Silveri	Filippo	ANA OR024’
Silvestri	Teresa	TFA OR016
Simari	Cataldo	FIS KN014
Simeone	Felice	ABC OR016
Siracusa	Laura	ORG OR128
Slimani	Sawssen	FIS OR005
Sole	Roberto	IND OR007
Sologan	Maria	ORG OR105
Sorbelli	Diego	TEO OR028
Sorbi	Claudia	FAR OR033
Spadavecchia	Serena	ABC OR052
Spanu	Davide	ANA OR094
Speghini	Adolfo	INO OR078
Spinaci	Andrea	FAR OR002
Spinello	Angelo	CSB OR026
Spitaleri	Luca	INO OR012
Sportelli	Maria Chiara	ANA OR122
Spyrakis	Francesca	FAR OR035
Staffolani	Antunes	ELE OR54
Stefania	Rachele	ORG OR129
Stefanucci	Azzurra	FAR OR040
Stener	Mauro	TEO KN004
Stevenazzi	Andrea	FAR KN007
Straniero	Valentina	FAR OR026
Stucchi	Marta	INO OR081
Tabanelli	Tommaso	IND OR003
Tabasso	Silvia	IND OR052
Taddeo	Francesco	IND OR009
Tadini-Buonisegni	Francesco	CSB OR016
Taghavi	Somayeh	IND OR021
Tamborini	Lucia	FAR OR015
Tanini	Damiano	ORG OR078
Tartaglia	Angela	MAS OR012
Tasinato	Nicola	TEO PZ006
Tassone	Giusy	CSB OR015
Tatini	Duccio	FIS OR124
Tavani	Francesco	FIS OR083
Tecilla	Paolo	ORG PZ002
Terraneo	Giancarlo	CSB OR025
Terraneo	Giancarlo	TEC OR030
Terzi	Alberta	FIS OR017
Tesauro	Diego	INO OR065
Tessore	Francesca	INO OR067
Testa	Edoardo	TEC OR048
Testoni	Antonio	DID OR008
Tiboni	Mattia	TFA OR008
Tiecco	Matteo	ORG OR114

Timoncini	Andrea	ABC OR026
Tira	Roberto	CSB OR019
Tocci	Elena	TEO OR014
Tocco	Davide	FIS OR054
Toffanin	Stefano	FIS OR079
Toigo	Christina	ELE OR69
Tomassi	Stefano	FAR OR041
Torrini	Francesca	ANA OR130
Toso	Alessandra	IND OR013
Tosoni	Sergio	TEO OR004
Tranchida	Peter	ANA OR057
Travagliante	Gabriele	CSB OR028
Tribbia	Michele	ELE OR76
Tricase	Angelo	ANA OR049
Trifiletti	Vanira	FIS OR029
Tripaldi	Laura	TEC OR023
Trovato	Emanuela	ANA OR033
Tseberlidis	Giorgio	INO OR038
Tsurumaki	Akiko	ELE OR61
Tubaro	Cristina	INO OR018
Tuccillo	Mariarosaria	FIS OR033
Tuccitto	Nunzio	FIS OR013
Turano	Paola	CSB KN002
Turco	Lucilla	FAR OR030
Turnaturi	Rita	FAR OR010
Turrini	Federica	ANA OR042
Tursi	Antonio	FIS OR042
Uliassi	Elisa	FAR OR034
Vacca	Paolo	IND KN009
Valente Chavez Lozano	Marco	ABC OR049
Valenti	Giovanni	ELE KN10
Valentini	Federica	ORG OR115
Valgimigli	Luca	ORG OR130
Valsecchi	Cecile	ANA OR058
Vanni	Matteo	INO PZ007
Vanti	Giulia	TFA OR020
Vanzan	Mirko	TEO OR003
Varvaro	Gaspare	TEC OR050
Vasa	Kristian	ORG OR107
Velino	Cecilia	ABC OR004
Velino	Cecilia	ABC OR024
Venanzi	Mariano	DID IL001
Venditti	Iole	INO OR064
Venezia	Virginia	TEC OR001
Ventimiglia	Alessia	IND OR054
Vento	Fabiana	IND OR018
Ventura	Giovanni	ANA KN008
Vercelli	Barbara	ELE OR36
Versaci	Daniele	ELE OR71
Vezzù	Keti	ELE OR60
Vincenti	Flaminia	MAS OR015

Vitale	Alessandra	TEC OR051
Vitiello	Rosa	IND OR066
Vitola	Giuseppe	ABC OR044
Vitone	Daniele	CSB OR023
Vivado	Davide	ANA OR016
Vizza	Martina	ANA OR050
Volanti	Mirco	ABC OR039
Vona	Danilo	ORG OR131
Voronov	Aleksandr	IND OR008
Vottero	Eleonora	FIS OR093
Vottero	Eleonora	IND OR004
Weidenkaff	Anke	INO IL002
Wetzl	Cecilia	ELE IL29
Winter	Roland	FIS KN008
Xiufang	He	ELE OR39
Zanardi	Chiara	ANA IL003
Zanchin	Giorgia	ORG OR073
Zani	Lorenzo	ORG OR085
Zanini	Roberta	ABC OR027
Zanut	Alessandra	ELE OR41
Zarrelli	Armando	ABC OR019
Zelenay	Piotr	ELE IL50
Zendri	Elisabetta	ABC OR048
Zennaro	Federtica	ABC OR057
Zianni	Rosalia	MAS OR007
Ziccarelli	Ida	ORG OR146
Zippilli	Claudio	ORG OR079
Zoccali	Mariosimone	ANA PZ003
Zoli	Maddalena	ELE OR25
Zoppi	Giulia	IND OR044
Zucca	Antonio	INO OR071
Zuliani	Alessio	FIS OR041

INDICE COMUNICAZIONI POSTER

Begni	Federico	FIS P0004
Belay	Masho	ANA P0010
Bella	Federico	ELE P0001
Bellomo	Chiara	INO P0009
Bellomo	Chiara	INO P0010
Benedetti	Michele	INO P0011
Benzi	Alice	ORG P0011
Bernardini	Massimo	IND P0003
Berto	Silvia	ANA P0017
Bertuletti	Susanna	ORG P0012
Bertuletti	Susanna	ORG P0111
Bevilacqua	Matteo	INO P0012
Bhela	Irenepreet	FAR P0002
Bianchi	Eleonora	TFA P0004
Bianco	Mariachiara	MAS P013
Bianco	Mariacristina	ANA P0072
Biancolillo	Alessandra	ANA P0031
Bianconi	Elisa	FAR P0022
Bianconi	Tommaso	FIS P0005
Billeci	Floriana	ORG P0013
Bisbal Lopez	Lydia	ORG P0014
Blanco	Ignazio	TEC P0001
Bocchinfuso	Gianfranco	FIS P0006
Bona	Beatrice	FIS P0007
Bonasera	Aurelio	FIS P0008
Bonciarelli	Stefano	ORG P0015
Bortolamiol	Enrica	INO P0013
Boselli	Monica	ORG P0016
Bosi	Adele	ABC P0001
Bozza	Desiree	ANA P0004
Brandiele	Riccardo	ELE P0002
Brigliadori	Andrea	IND P0041
Brouziotis	Antonios Apostolos	ANA P0097
Brucoli	Jacopo	ORG P0017
Brugnetti	Gabriele	ELE P0003
Bruno	Maria Chiara	TFA P0005
Bufano	Mariana	FAR P0003
Bugatti	Kelly	ORG P0018
Buonocore	Michela	FAR P0023
Buratti	Alessandro	ANA P0044
Bussoli	Guido	INO P0014
Cafiero	Claudia Maria	CSB P0006
Calamante	Massimo	ORG P0019
Calì	Federico	FIS P0009
Callone	Emanuela	TEC P0002
Camarero Gonzalez	Patricia	ORG P0020
Cambiotti	Elena	FIS P0010
Camillo Testa	Maria Rita	ANA P0092
Campanella	Beatrice	ANA P0032
Campolucci	Marta	FIS P0011
Cantarini	Mattia	FAR P0004

Cappitti	Alice	IND P0004
Cardellicchio	Francesco	ABC P0002
Cardellicchio	Francesco	ABC P0003
Cardellicchio	Nicola	ABC P0015
Cardiano	Paola	ANA P0062
Carignani	Elisa	FIS P0012
Carnamucio	Federica	ANA P0073
Carraro	Massimo	ORG P0021
Carrozza	Debora	INO P0015
Carta	Paola	FIS P0013
Casadidio	Cristina	TFA P0006
Casale	Monica	ANA P0033
Casiello	Michele	ORG P0022
Casini	Andrea	FIS P0014
Casiraghi	Antonella	FAR P0024
Casiraghi	Antonella	TFA P0036
Castagnotto	Elena	ABC P0036
Castellaneta	Andrea	MAS P001
Castiglioni	Michele	ABC P0029
Catauro	Michelina	TEC P0003
Catenacci	Laura	TFA P0007
Catenacci	Laura	TFA P0008
Catinella	Giorgia	FAR P0025
Catinella	Giorgia	ORG P0023
Cattaneo	Stefano	INO P0016
Cavalleri	Matteo	INO P0017
Cecinato	Angelo	ABC P0023
Cecinato	Angelo	ABC P0025
Cecinato	Angelo	ABC P0026
Cerra	Sara	INO P0018
Cerri	Luca	TFA P0009
Cerveri	Alessandro	ORG P0024
Cescon	Mirco	ANA P0045
Chen	Cheng Giuseppe	FIS P0015
Chiarcos	Riccardo	IND P0005
Chiarello	Matteo	ANA P0078
Chilla	Giuseppe	FIS P0016
Chindamo	Giulia	TFA P0010
Chino	Marco	INO P0019
Chirco	Gabriella	ABC P0004
Ciaffaglione	Valeria	FAR P0005
Ciamaritaro	Veronica	FIS P0017
Cianciusi	Annarita	FAR P0006
Cicchi	Stefano	ORG P0025
Cicco	Luciana	ORG P0026
Ciccola	Alessandro	ABC P0037
Ciccone	Lidia	FAR P0045
Cimino	Cinzia	TFA P0011
Cinelli	Giuseppe	FIS P0018
Cipriano	Alessandra	FAR P0046
Claudia	Claudia	CSB P0005

Clemente	Mariangela	ORG P0027
Cofelice	Martina	FIS P0019
Cogliano	Tommaso	IND P0006
Colaiezzi	Roberta	INO P0020
Compagnucci	Tommaso	ORG P0028
Comparini	Lucrezia Margherita	ORG P0029
Conelli	Daniele	TEC P0004
Coniglio	Davide	MAS P005
Consiglio	Giuseppe	TEC P0005
Consiglio	Giuseppe	TEC P0006
Consumi	Marco	ANA P0005
Conte	Francesco	IND P0007
Conte	Gemma	TFA P0012
Coppola	Carmen	ORG P0030
Coppolino	Carmelo	ANA P0046
Coppolino	Carmelo	ANA P0047
Corazzari	Ingrid	INO P0021
Corradini	Danilo	ANA P0023
Corradini	Danilo	ORG P0031
Corrente	Giuseppina Anna	FIS P0020
Corsini	Maddalena	TFA P0013
Cortesi	Rita	TFA P0014
Costa	Jessica	FIS P0021
Costanzo	Giuliana	FAR P0047
Costi	Maria Paola	FAR P0026
Crescenzi	Maria Assunta	MAS P024
Cressoni	Chiara	INO P0022
Croce	Lucia	ANA P0024
Cucciniello	Raffaele	ABC P0016
Curri	M. Lucia	FIS P0068
Curti	Federica	ORG P0032
D’Amore	Teresa	MAS P014
D’Auria	Maurizio	ORG P0033
De Angelis	Martina	ORG P0034
De Beni	Eleonora	ABC P0009
De Castro	Federica	INO P0023
De Luca	Erik	INO P0024
De Santis	Serena	TEC P0007
De Soricellis	Giulia	INO P0025
De Zotti	Marta	ORG P0035
Decandia	Gianfranco	ORG P0036
Decandia	Modesto	FAR P0048
Decavoli	C.	ORG P0037
Del Regno	Rocco	ORG P0038
Deleo	Alessandro	FAR P0007
Dell’Accantera	Davide	ORG P0039
Della Valle	Maria	CSB P0007
DellaLatta	Elisa	FIS P0022
Denti	Vanna	MAS P010
Di Bello	Elisabetta	FAR P0008
Di Berto Mancini	Marika	ORG P0040

Di Lecce	Roberta	ORG P0041
Di Lorenzo	Flaviana	ORG P0042
Di Matteo	Francesca	FAR P0049
Di Natale	Giuseppe	MAS P007
Di Pietro	Roberto	ANA P0011
Di Sarno	Veronica	FAR P0053
Di Vito Nolfi	Giuseppe	ORG P0043
Diego	Diego	CSB P0002
Dilauro	Giuseppe	ORG P0044
Dolla	Tarekegn	INO P0026
Donadio	Anna	INO P0086
Donato	Paola Agata	ANA P0048
Donato	Simone	IND P0008
Duro	Ida	MAS P023
Fabbri	Debora	ANA P0025
Fabbri	Lorenzo	ANA P0036
Fabbri	Lorenzo	ANA P0037
Fabbri	Roberta	ORG P0112
Facchinetti	Irene	ELE P0004
Faggiano	Antonio	ABC P0033
Fagiolari	Lucia	TEC P0008
Falgiani	Annamaria	ANA P0012
Fallica	Antonino Nicolò	FAR P0059
Fanizzi	P. Francesco	INO P0028
Farinini	Emanuele	ANA P0034
Fasano	V.	ORG P0045
Faverio	C.	ORG P0046
Feoli	Alessandra	FAR P0027
Fermo	Paola	ABC P0005
Ferracane	Antonio	ANA P0049
Ferrara	Chiara	ELE P0005
Ferrauto	Giuseppe	INO P0029
Ferrone	Vincenzo	ANA P0050
Ferrone	Vincenzo	ANA P0051
Fioco	David	INO P0030
Fiore	Luca	ANA P0079
Forghieri	Giulia	IND P0009
Forgione	Rosa	ORG P0047
Forleo	Tiziana	ANA P0018
Formaggio	Fernando	CSB P0008
Formaggio	Fernando	ORG P0048
Fornarini	Simonetta	INO P0031
Forte	Jacopo	TFA P0015
Foschi	Martina	ANA P0035
Fouad Manar	Ahmed	INO P0032
Franca	Marina	INO P0033
Francesca	Francesca	ABC P0038
Franchina	Flavio	ANA P0052
Frassati	Stefano	ANA P0013
Fratoddi	Ilaria	INO P0034
Fresch	Elisa	FIS P0024

Gabano	Elisabetta	INO P0035
Gagliardi	Agnese	TFA P0016
Galletti	Gabriele	IND P0010
Gallucci	Noemi	FIS P0025
Gandini	T.	ORG P0049
Gazzillo	Erica	ORG P0050
Gazzurelli	Cristina	INO P0036
Gentile	Antonio	ELE P0006
Geppi	Marco	FIS P0026
Giacobello	Fausta	FIS P0027
Giacomantonio	Roberto	ORG P0051
Giacomazzo	Gina	INO P0037
Giancaspro	Mariangela	FIS P0028
Giannessi	Giulio	FIS P0029
Giavazzi	Davide	TEO P0001
Gigli	Matteo	INO P0038
Gili	Marilena	MAS P015
Giovanna	Valentino	CSB P0020
Giurlani	Walter	ANA P0038
Gobbo	Alberto	INO P0039
Gottuso	Alessandro	FIS P0030
Gramazio	Pio	IND P0011
Grandinetti	Bruno	IND P0012
Grassiri	Brunella	TFA P0017
Grassiri	Brunella	TFA P0018
Grassiri	Brunella	TFA P0019
Grecchi	Sara	ANA P0039
Grifagni	Deborah	CSB P0009
Grilli	Davide	FIS P0031
Grillo	Giorgio	IND P0013
Grillo	Giorgio	IND P0043
Guaragnone	Teresa	FIS P0032
Guglielmero	Luca	INO P0040
Guidotti	Matteo	IND P0014
Gullo	G.	ORG P0052
Hanieh	Patrizia N.	TFA P0020
Herbrik	F.	ORG P0053
Iammarino	Marco	ANA P0026
Ielo	Ileana	FIS P0033
Imparato	Claudio	TEC P0009
Ioele	Giuseppina	TFA P0037
Iovino	Pasquale	ABC P0017
Iucci	Giovanna	INO P0041
Izzi	Margherita	ANA P0093
Jiritano	Antonio	ORG P0054
Jorea	Alexandra	ORG P0055
Krstic	Milena	ORG P0056
La Gatta	Salvatore	INO P0042
La Parola	Valeria	IND P0015
La Tella	Roberta	ANA P0053
Lagostina	Valeria	INO P0043

Lamanna	Giuseppe	FAR P0052
Landi	Noemi	FIS P0034
Lando	Gabriele	ANA P0074
Landrini	Martina	INO P0044
Lanza	Valeria	CSB P0010
Laudadio	Emiliano	TEC P0010
Lembo	Antonio	ORG P0057
Leonardi	Costanza	ORG P0058
Lettieri	Mariagrazia	ANA P0080
Licen	Sabina	ANA P0081
Lievore	Giulio	ANA P0007
Ligorio	Simona	MAS P009
Lippolis	Martina	ORG P0059
Livolsi	Simone	IND P0016
Lo Vecchio	Carmelo	ELE P0007
Locardi	Federico	FIS P0036
Locatelli	Marcello	ANA P0054
Locatelli	Marcello	ANA P0082
Lombardi	Lorenzo	ORG P0060
Longo	Alessandra	FIS P0037
Longo	Edoardo	ORG P0061
Longo	Lilia	IND P0017
Longobardi	Francesco	ANA P0101
Lopresti	Ludovica	CSB P0011
Loro	Camilla	ORG P0062
Luciani	Lorenzo	INO P0045
Luckham	Stephen	TEC P0011
Lusardi	Matteo	FAR P0009
Macchioni	Alceo	INO P0046
Madabeni	Andrea	FIS P0038
Magnano	Greta	ANA P0098
Maisuradze	Mariam	ANA P0094
Maletti	Laura	ANA P0027
Mandato	Maria	MAS P016
Mandrioli	Roberto	FAR P0028
Manetto	S.	ORG P0063
Manfredi	Marcello	MAS P008
Manghi	Maria Chiara	ABC P0039
Mangini	Anna	TEC P0012
Mangraviti	Domenica	ANA P0028
Manzotti	Mattia	INO P0047
Maramai	S.	ORG P0064
Marassi	Valentina	ANA P0083
Marchesi	Elena	ORG P0065
Marchesi	Massimo	ABC P0022
Marchetti	A.	ORG P0067
Marchetti	Roberta	ORG P0066
Marchettini	Nadia	ABC P0012
Marcì	Giuseppe	TEC P0013
Margani	Fatima	TEC P0014
Mari	Matteo	INO P0048

Marino	Carmen	FAR P0029
Marseglia	Angela	ORG P0068
Martinuzzi	Stefano	ANA P0040
Martinuzzi	Stefano	ANA P0041
Marzano	Simona	CSB P0012
Mascolo	Giuseppe	ABC P0030
Maspero	Marco	FAR P0030
Massardo	Sara	FIS P0039
Maurelli	AnnaMaria	FIS P0040
Mazzariol	Chiara	INO P0049
Mazzilli	Valerio	FIS P0041
Mazzoccanti	G.	ORG P0069
Mazzotta	Elisabetta	ANA P0042
Mazzotta	Sarah	FAR P0010
Mazzucato	Marco	ELE P0009
Mecarelli	Enrica	MAS P006
Melchiorre	Massimo	INO P0050
Meneghetti	Fiorella	FAR P0031
Mentana	Annalisa	MAS P017
Mercadante	Alessandro	ORG P0070
Mercuri	Giorgio	INO P0051
Merlo	Francesca	ANA P0055
Messori	Alessandro	INO P0052
Miele	Dalila	TFA P0021
Migliore	Claudio	IND P0018
Milana	Paola	INO P0053
Milanesi	Francesco	ORG P0071
Milani	Barbara	INO P0054
Milardi	Danilo	CSB P0013
Milone	Marco	ORG P0072
Mingoia	Francesco	FAR P0011
Mizzoni	Silvia	INO P0055
Molteni	Letizia	ORG P0073
Monopoli	Antonio	ORG P0074
Montanari	Serena	FAR P0032
Monti	Marta	TEO P0002
Moreira	Miguel	ORG P0075
Morelli	Carlo F.	ORG P0076
Morena	A.	ORG P0077
Moretti	Elisa	INO P0056
Moretti	Giulia	FIS P0043
Mori	Matteo	FAR P0012
Moriggi	Francesco	TEC P0015
Morina	Riccardo	ELE P0010
Moscone	Danila	ANA P0019
Muccilli	V.	ORG P0078
Musci	Pantaleo	ORG P0079
Mustorgi	Eleonora	ANA P0029
Nacci	Tommaso	ABC P0027
Nagendra	Baku	IND P0019
Napolitano	Ettore	ORG P0080

Nardi	Alessandro Nicola	FIS P0044
Nardiello	Donatella	ANA P0064
Nardiello	Donatella	ANA P0065
Natali	Daniele	IND P0020
Naviglio	Daniele	ANA P0008
Negro	Enrico	ELE P0011
Nicosia	Angelo	IND P0021
Nigro	Maria	ABC P0032
Niknam	Fatemeh	INO P0057
Nocchetti	Morena	INO P0005
Noormohammadi	Eshagh	ELE P0012
Notardonato	Ivan	ANA P0030
Notardonato	Ivan	ANA P0087
Notarstefano	Valentina	INO P0058
Nottoli	Michele	TEO P0003
Oliveri	Valentina	CSB P0014
Olivito	Fabrizio	ORG P0081
Omelyanchik	Alexander	FAR P0033
Omelyanchik	Alexander	FIS P0045
Ottolini	Michela	FIS P0046
Oulad El Majdoub	Yassine	ANA P0006
Pagano	Flavia	ANA P0099
Pagano	Rosanna	FIS P0047
Pagliaricci	Noemi	INO P0059
Pagliero	Marcello	IND P0022
Pajer	Nicolò	INO P0060
Palagi	Lorenzo	CSB P0015
Palermo	Carmen	ANA P0066
Palucci	Benedetta	ORG P0082
Pampararo	Giovanni	INO P0061
Panunzi	Paola Anna	ELE P0013
Paoletti	Fabiola	MAS P018
Papa	Ester	ABC P0035
Paparo	Rosanna	ANA P0088
Papucci	Costanza	ORG P0083
Parise	Angela	INO P0062
Passarini	Fabrizio	ABC P0040
Pavan	Cristina	INO P0063
Pavletić	Pegi	FAR P0050
Pavoni	Elena	ANA P0014
Peddis	Davide	FIS P0048
Pellis	Giulia	ABC P0006
Pepe	Angela	MAS P020
Pepe	Giacomo	FAR P0034
Perego	Jacopo	IND P0023
Perra	Matteo	TFA P0022
Peruffo	Nicola	FIS P0049
Petrilli	Marzia	ORG P0084
Pianta	Nicolò	ELE P0014
Pierini	Adriano	TEO P0004
Pierri	Martina	ORG P0085

Pietracci	Lorenzo	INO P0064
Pietrobon	Luca	IND P0024
Pietrobon	Luca	IND P0025
Pigliacelli	Claudia	TEC P0016
Pilato	Serena	ORG P0086
Pinna	Marco	ANA P0015
Pinzi	Luca	FAR P0054
Pirodda	Gabriele	TEC P0017
Pirola	Carlo	IND P0026
Pisano	Luisa	ORG P0087
Pittalà	Valeria	FAR P0055
Pizzolato	Marco	IND P0027
Poerio	Teresa	TEC P0018
Pogni	Rebecca	FIS P0051
Porcelli	Francesco	TEC P0019
Porpora	Francesca	ABC P0007
Porporato	Silvia	ELE P0017
Prestia	Tommaso	ORG P0088
Preti	Lorenzo	ORG P0089
Prioglio	Gea	TEC P0020
Priola	Emanuele	INO P0065
Pro	Chiara	INO P0066
Protti	Michele	FAR P0035
Prozzi	Marco	ANA P0016
Puxeddu	Michela	FAR P0056
Quaglia	Giulia	FIS P0052
Quinto	Maurizio	ANA P0056
Quinto	Maurizio	ANA P0089
Racaniello	Giuseppe F.	TFA P0023
Ragone	Rosa	TEC P0021
Rama	Francesco	TFA P0034
Rando	Giulia	FIS P0053
Rando	Maria	INO P0067
Rapacciuolo	Pasquale	ORG P0090
Rapino	Alessandra	TFA P0035
Raspolli Galletti	Maria Anna	IND P0028
Rebeccani	Sara	ELE P0015
Renno	Giacomo	IND P0029
Renzi	Emilia	INO P0068
Riboni	Nicolò	ANA P0067
Ricci	Paola	INO P0085
Ricciardi	Beatrice	TEC P0022
Ricciardi	Maria	ABC P0034
Rigante	Elena	ANA P0063
Rigoletto	Monica	ABC P0041
Ripani	Lorenzo	ELE P0016
Rispoli	Francesco	ORG P0091
Rivoira	Luca	ABC P0018
Rizzardi	Ilaria	IND P0030
Rizzi	Rosanna	FAR P0057
Rizzo	Marco	FAR P0013

Rizzo	S.	TFA P0033
Rizzo	Serena	MAS P019
Roda	Barbara	ANA P0020
Romanelli	Alessandra	CSB P0016
Romani	Daphne	INO P0069
Romano	Giammarco Maria	INO P0070
Romanucci	Valeria	ORG P0092
Rombolà	Alessandro G.	ANA P0057
Romeo	Alessia	TFA P0024
Romeo	Isabella	FAR P0014
Rosa	Roberto	TEC P0023
Rosati	Marta	ORG P0093
Rosetti	Alessia	FAR P0036
Rossi	Ruggero	IND P0031
Ruggeri	Marco	TFA P0025
Russo	Camilla	FAR P0058
Russo	Francesca	ABC P0013
Russo	Simona	INO P0071
Russo	Stefano	TEO P0005
Sabatino	Leonardo	ANA P0090
Saiano	Filippo	ANA P0058
Saladino	Marialuisa	FIS P0054
Salafia	Fabio	ANA P0091
Salamone	Tommaso	INO P0072
Salerno	Alessandra	FAR P0051
Salha	Mohammed	INO P0073
Saliu	Francesco	ABC P0010
Saliu	Francesco	ABC P0011
Saliu	Francesco	MAS P022
Salvador	María	TFA P0026
Salvini	Antonella	IND P0032
Samorì	Chiara	ORG P0094
Sandri	Francesco	IND P0033
Sandri	Francesco	IND P0042
Santarsiere	Alessandro	ORG P0095
Santonoceta	Giuseppina	ANA P0075
Santoro	Angelo	FAR P0037
Sanz	Ines	FAR P0038
Sarti	Elena	ABC P0031
Sartirana	Marta	IND P0034
Satta	Giuseppe	ORG P0096
Saviano	Michele	CSB P0017
Scala	Maria Carmina	FAR P0039
Scandurra	Cecilia	ANA P0084
Scarperi	Andrea	FIS P0055
Schifano	Fabio	INO P0074
Schlich	Michele	TFA P0027
Sciacca	Michele	CSB P0018
Scibetta	Lorenzo	ABC P0024
Scognamiglio	Antonia	FAR P0015
Sebastiani	Jessica	FAR P0060

Secci	Fausto	FIS P0056
Semeraro	Paola	FIS P0057
Severini	Leonardo	FIS P0058
Sfameni	Silvia	FIS P0059
Sgarbossa	Paolo	TEC P0024
Sica	Alfredo	FAR P0040
Sica	Filomena	FIS P0060
Silla	Alessia	ANA P0085
Silvestri	Brigida	TEC P0025
Sirignano	Marco	INO P0075
Smaldone	Gerardina	FAR P0016
Smith	Andrew	MAS P002
Sommonte	Federica	TFA P0028
Sonzini	Paolo	INO P0076
Sorato	Andrea	ORG P0097
Sori	Lorenzo	TEC P0026
Spada	Lucia	ABC P0019
Sparaco	Rosa	FAR P0017
Spatola	Emanuele	ORG P0098
Speciale	Immacolata	ORG P0099
Speltini	Andrea	ANA P0068
Speltini	Andrea	ANA P0086
Sportelli	Maria Chiara	ANA P0095
Squadrone	S.	INO P0027
Stabile	Rita	FAR P0018
Staccioli	Maria Paola	FIS P0067
Stevanin	Claudia	ANA P0059
Stoccoro	Sergio	INO P0077
Tali Shandiz	Shiva	FAR P0019
Taliani	Sabrina	FAR P0061
Tallarida	A. Matteo	ORG P0100
Tammaro	Olimpia	IND P0035
Tarsitano	Martine	TFA P0029
Tartaglia	Angela	MAS P003
Tartaglia	Angela	MAS P004
Tassone	Giusy	CSB P0019
Tesser	Riccardo	IND P0036
Ticali	Pierfrancesco	FIS P0061
Tieuli	Sebastiano	IND P0037
Toma	Lorenzo	ANA P0100
Tomassetti	Mauro	ANA P0021
Tombesi	Alessia	INO P0078
Torta	Gianluca	ABC P0020
Toscanesi	Maria	IND P0038
Tresin	Federica	INO P0079
Tricomi	Jacopo	ORG P0101
Tricomi	Jacopo	ORG P0102
Trilli	Jordan	FAR P0041
Troiani	Anna	MAS P021
Troiani	Anna	TEC P0027
Troiano	Cassandra	FIS P0062

Troiano	Rubina	INO P0080
Truzzi	Cristina	ANA P0060
Tudino	Valeria	FAR P0020
Turco	Rosa	IND P0039
Turrini	Federica	ANA P0069
Vagnoni	Flavio	ANA P0061
Valentini	Francesca	ORG P0103
Valentino	Caterina	TFA P0030
Vanacore	Adele	ORG P0104
Varsalona	Maria	FIS P0063
Venanzi	Mariano	FIS P0064
Vento	Federica	ANA P0070
Verdicchio	Federico	INO P0081
Veronese	Eleonora	ORG P0105
Versaci	Daniele	ELE P0018
Vezzoni	Carlo Alberto	ORG P0106
Vicente-Garcia	Cesar	ORG P0107
Vida	Veronica	ORG P0108
Vigani	Barbara	TFA P0031
Villa	Stefania	FAR P0062
Viteritti	Eduardo	ANA P0071
Vivenzio	Giovanni	FAR P0021
Viviano	Monica	FAR P0063
Vizza	Martina	ANA P0043
Voccia	Maria	IND P0040
Voci	Silvia	TFA P0032
Volanti	Mirco	ABC P0014
Vomeri	Alessandro	INO P0082
Wafa	Aidli	ELE P0019
Xhafa	Sonila	INO P0083
Yousif	Dawod	ORG P0109
Zamperlin	Nico	TEC P0028
Zampieri	Daniele	FAR P0044
Zani	Veronica	FIS P0066
Zecca	Marco	ORG P0110
Zuccaccia	Daniele	INO P0084

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