Tuning PEDOT:Tos thermoelectric properties through nanoparticle inclusion

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Thermoelectrics Research Group

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Dr. Bruno Lorenzi
Dr. Laura Zulian
Dr. Daniela Galliani

Outline

1. Introduction

- *Conjugated Polymers as Thermoelectric Materials*
- *Conjugated Polymer Nanocomposite*
- *Energy Filtering Effect*

2. Experimental Work

- *Mn_3O_4 Nanoparticles*
- *Nanoparticle Functionalization*
- *Hybrid Film Making*

3. Results

- *Thermoelectrical Characterization*
- *Nanoparticle Influence on Polymer Morphology*
- *Humidity Effect*

4. Conclusion and Further Developments

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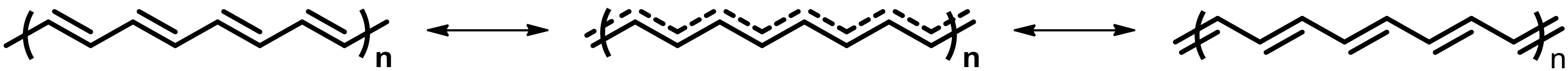
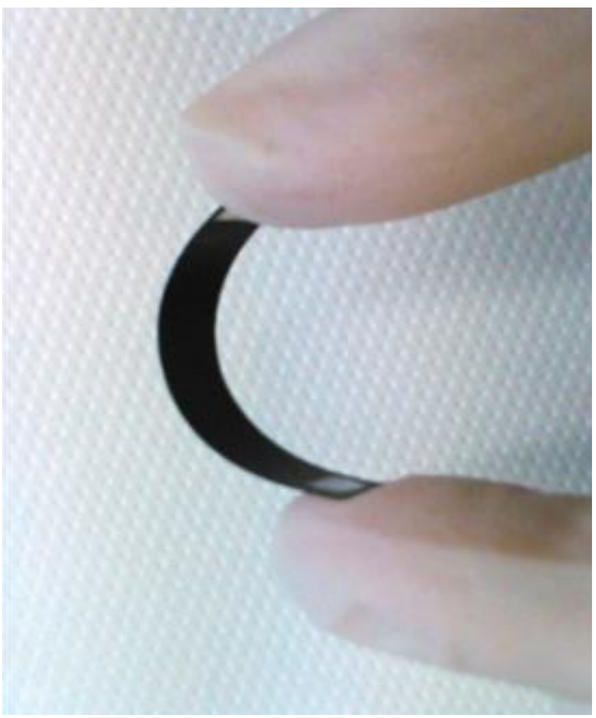
Conjugated Polymers as Thermoelectric Materials





- Low thermal conductivity
- Medium-high electrical conductivity
- Tunable electronic properties
- Easy processing
- Safety
- Environmental stability
- Low cost
- Adaptability to flexible substrate

Elschner, A. *PEDOT: Principles and Applications* CRC Press (2011)
Q. Wei et al., *Materials (Basel).* 8, 732 (2015).

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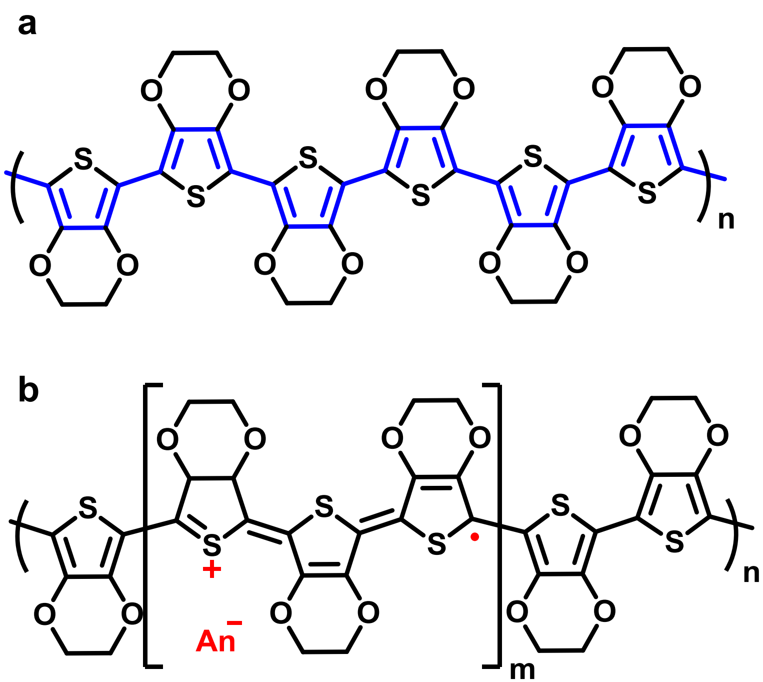
Conjugated Polymers as Thermoelectric Materials

Poly(3.4-ethylendioxythiophene) PEDOT



$An^- = Tos^-, Cl^-, PSS^-$, ecc

Low TE efficiency

Nanostructuration

Bubnova, O. *et al.* Semi-metallic polymers. *Nat. Mater.* **13,** 190–4 (2014)

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Conjugated Polymer Nanocomposite

Materials	S (μV/K)	PF (μW/m K^2)	*ZT*	Year
PEDOT:PSS/SWCNT	30	25	0.02	2013
PEDOT:PSS/MWCNT	70	500	-	2010
PEDOT:PSS/Bi_2Te_3	60	130	0.1	2010
PEDOT:PSS/Te	163	70.9	0.1	2013
PEDOT:PSS/Au NPs	26.5	51.2	~0.1	2014
PEDOT:PSS/Au nanorods	12	30	-	2014
PEDOT:PSS/Ge	~50	165	0.1	2014

Wide variety of materials!

Nanomaterial

Synthesis Method

CHOOSING CRITERIA

Q. Wei, M. Mukaida, K. Kirihara, Y. Naitoh, and T. Ishida, *Materials (Basel).* 8, 732 (2015).

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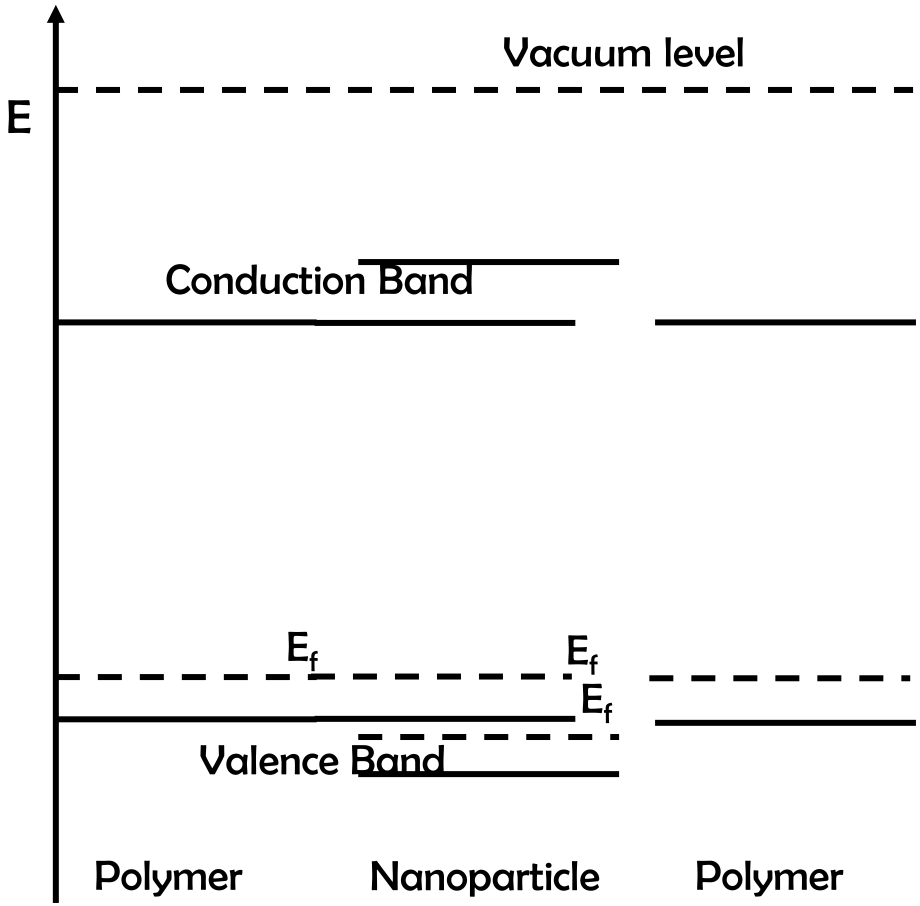
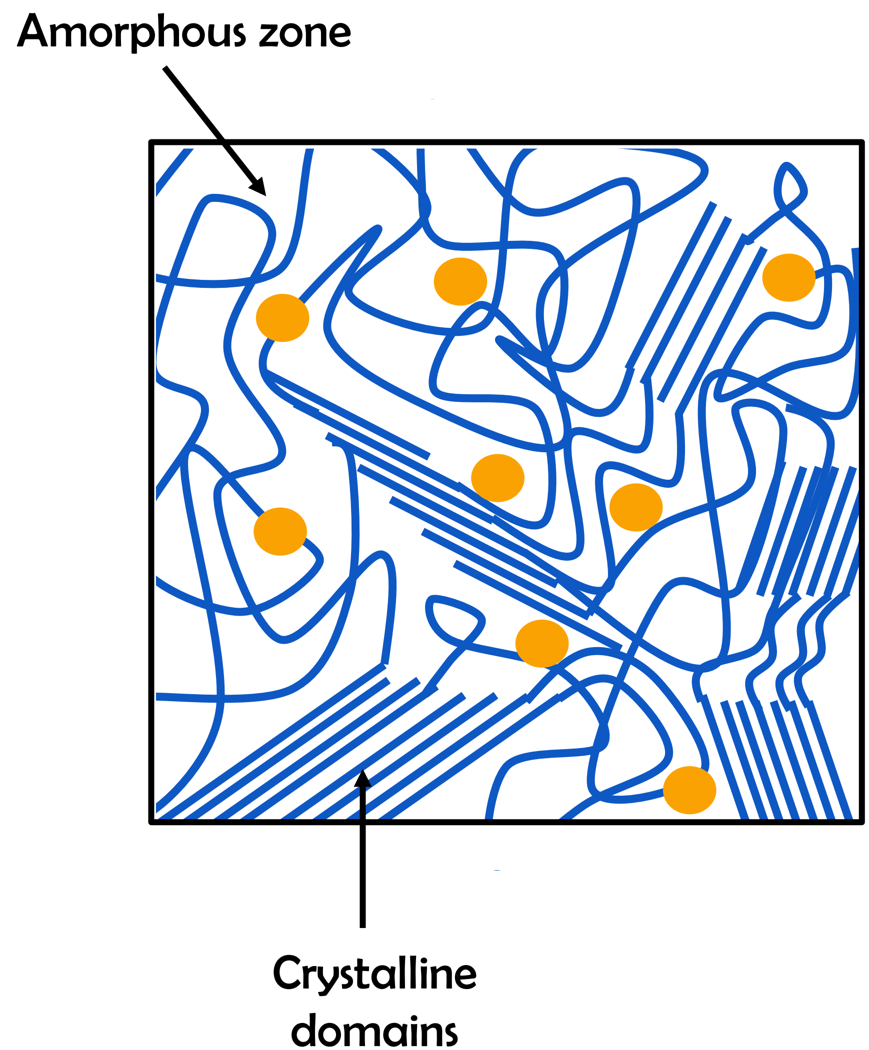
Energy Filtering Effect





N. Neophytou, X. Zianni, H. Kosina, S. Frabboni, B. Lorenzi, and D. Narducci, *Nanotechnology* 24, 205402 (2013).

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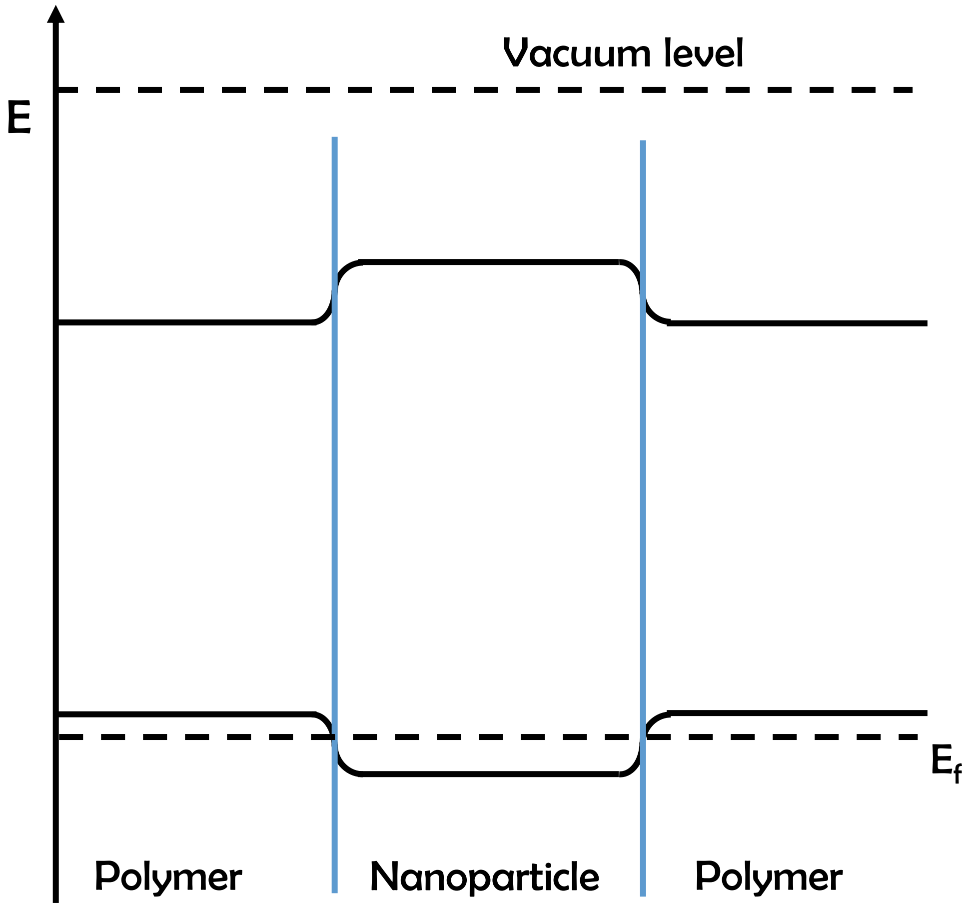
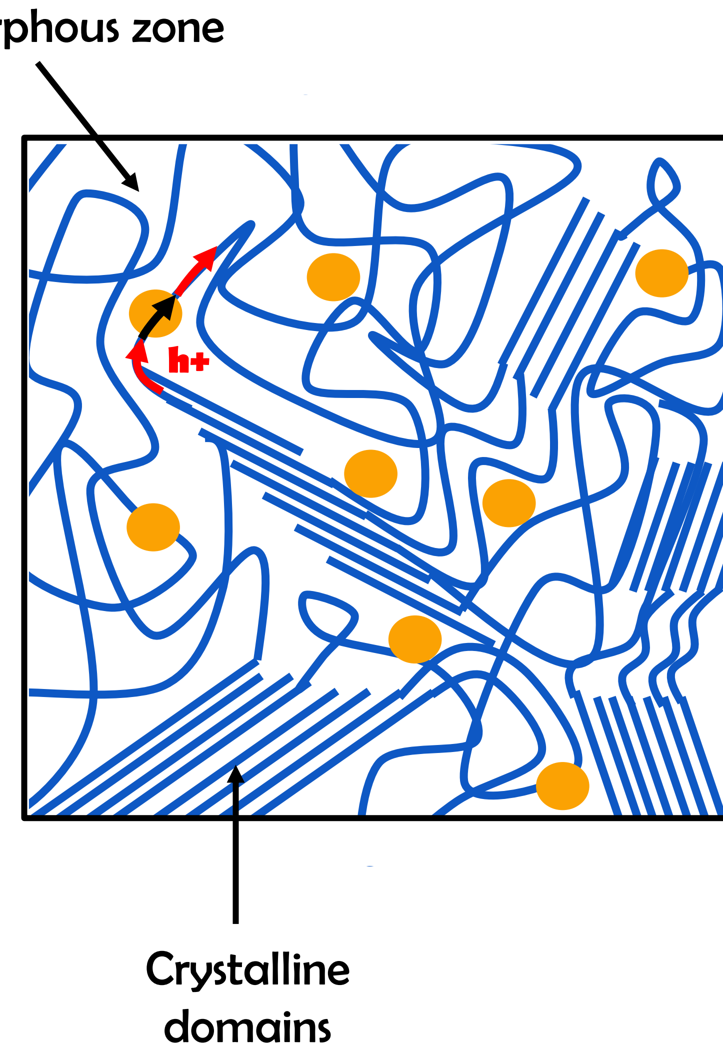
Energy Filtering Effect





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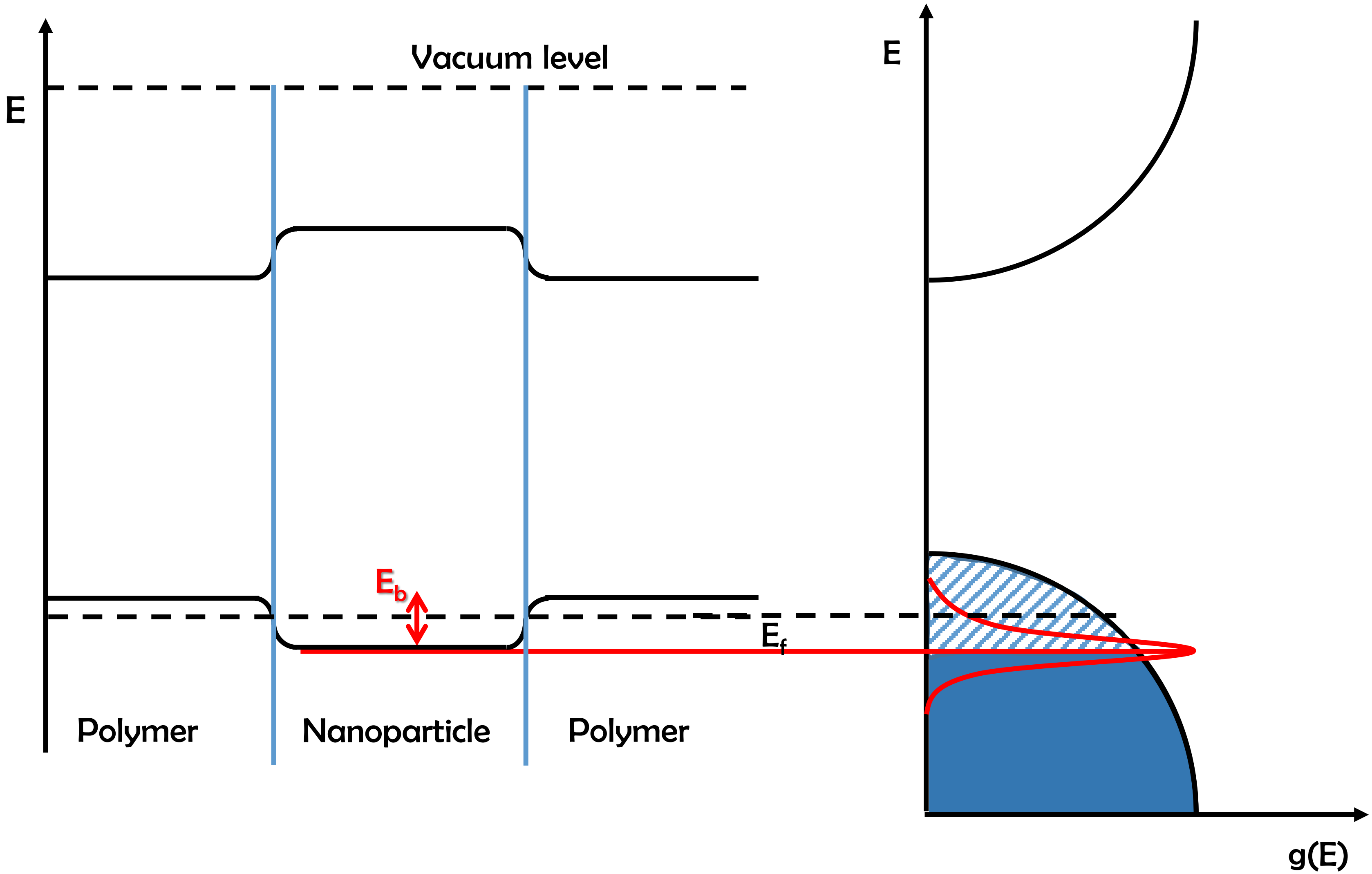
Energy Filtering Effect



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Energy Filtering Effect

CHOOSING CRITERIA

- Intimate contacts between CP and NPs → Chemical interaction between CP and NPs

- Similar work functions of the CP and the NPs
- Interfacial barrier height below 100 meV

→ Choice of CP and NP material

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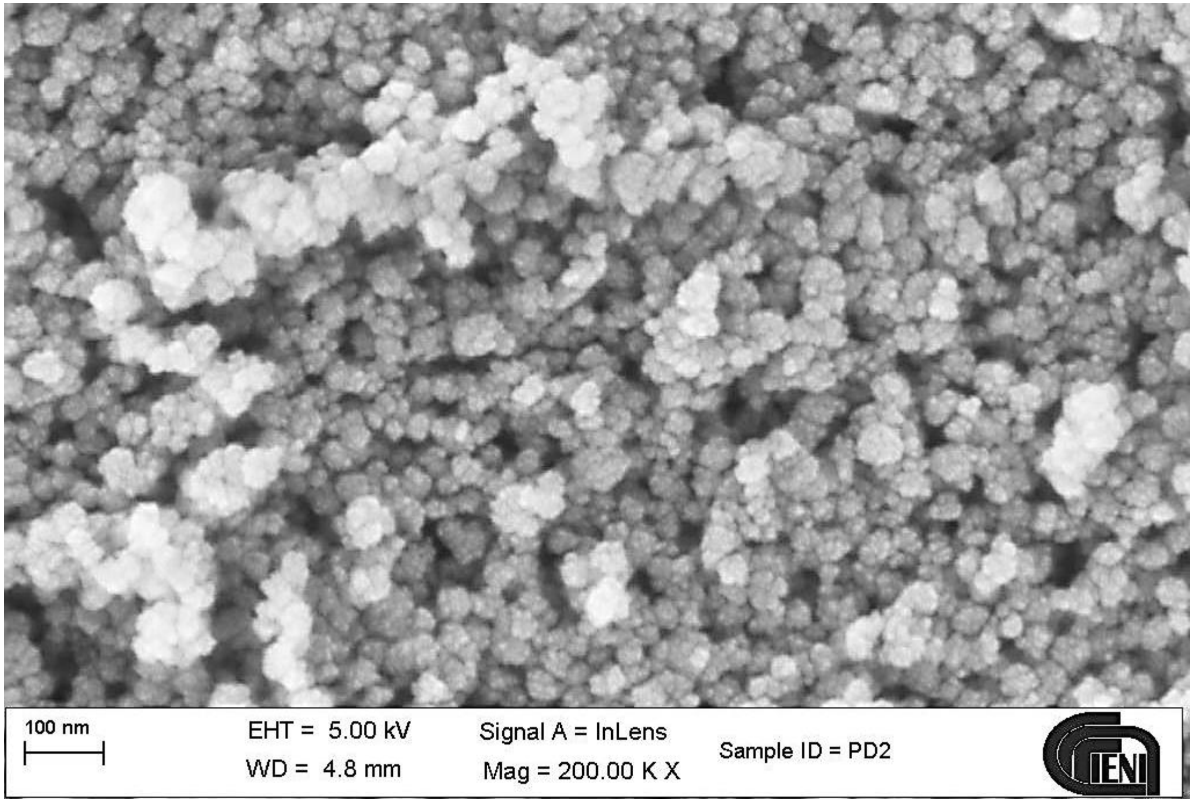
Mn_3O_4 Nanoparticles



Mn_3O_4

p-type material

work function: 4,4 eV

Thanks to Dr. Simone Battiston
IENI-CNR, Padova

Starting salt	Size control agent	Reagent	T (°C)	Size SEM determined (nm)
$MnCl_2 \cdot 4H_2O$	Ethanolamine	H_2O	25	25±6

S. Lei, K. Tang, Z. Fang, and H. Zheng, *Cryst. Growth Des.* 6, 1757 (**2006**)

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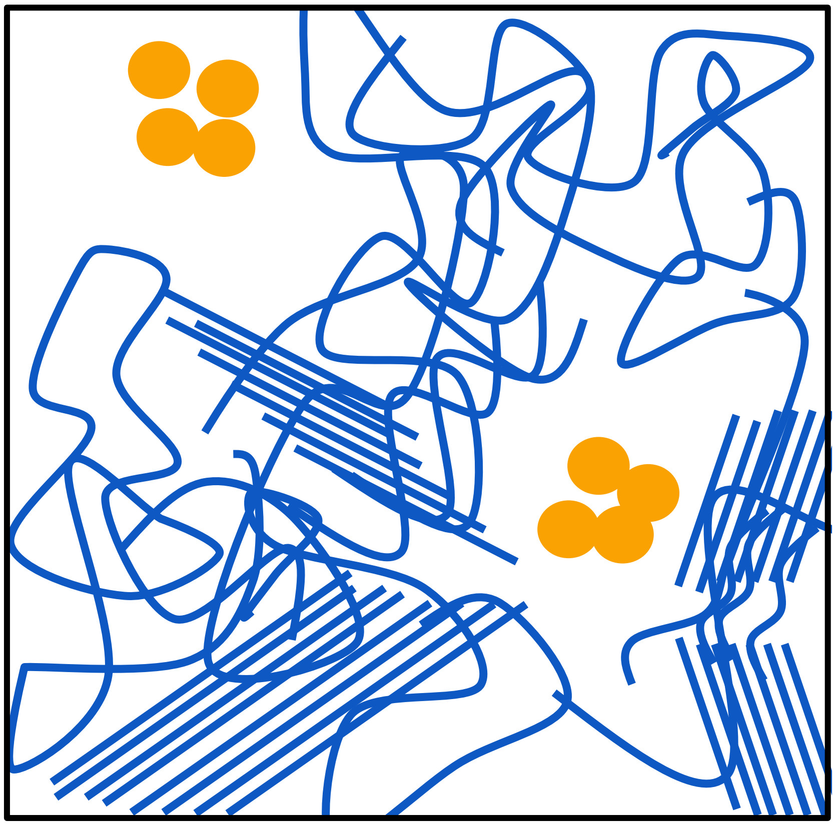
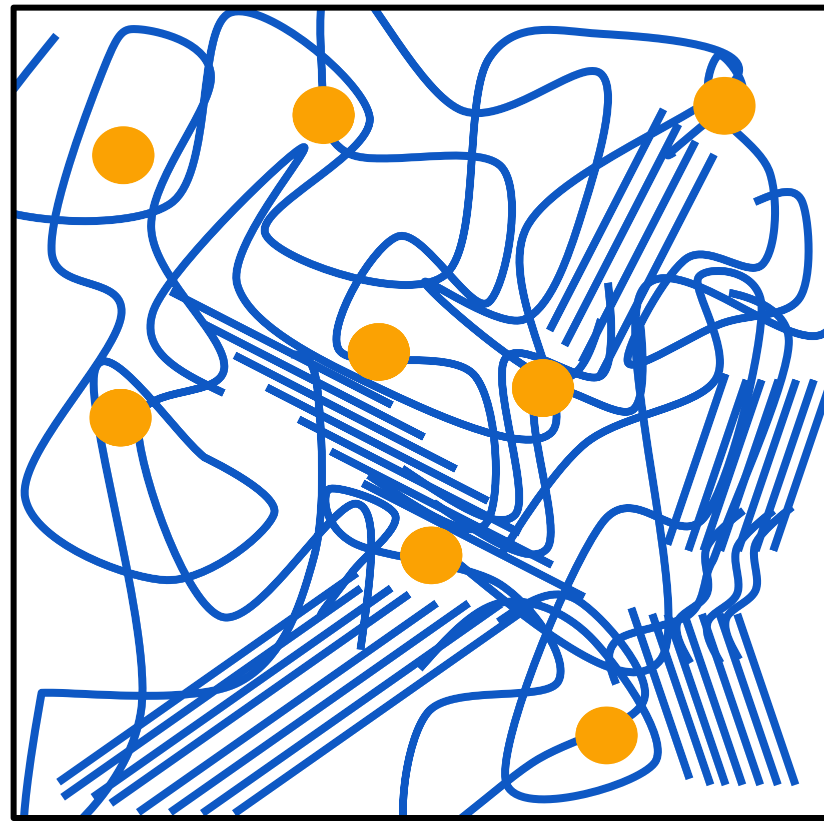
Nanoparticle Functionalization





✗ Phase separation

✓ Homogeneous dispersion

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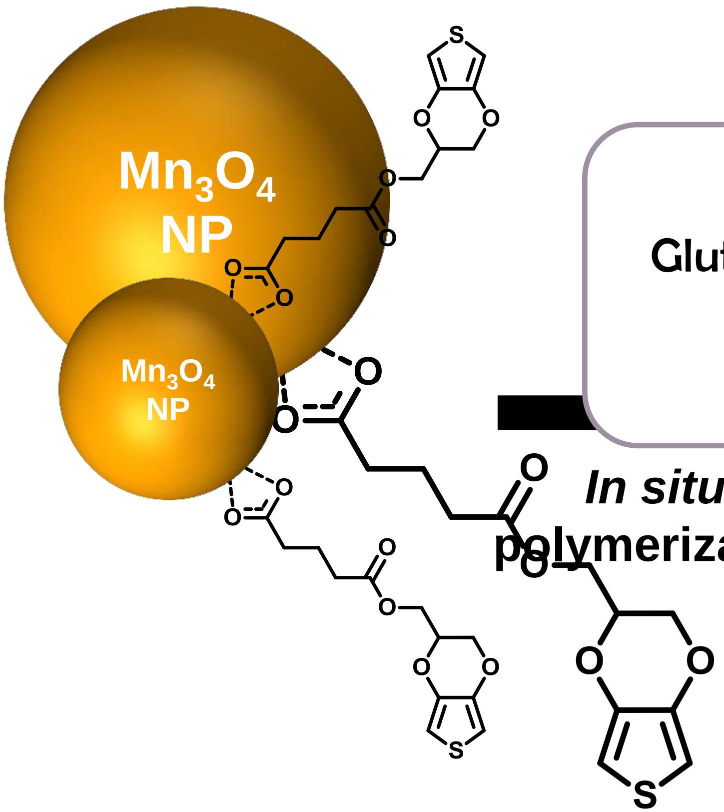
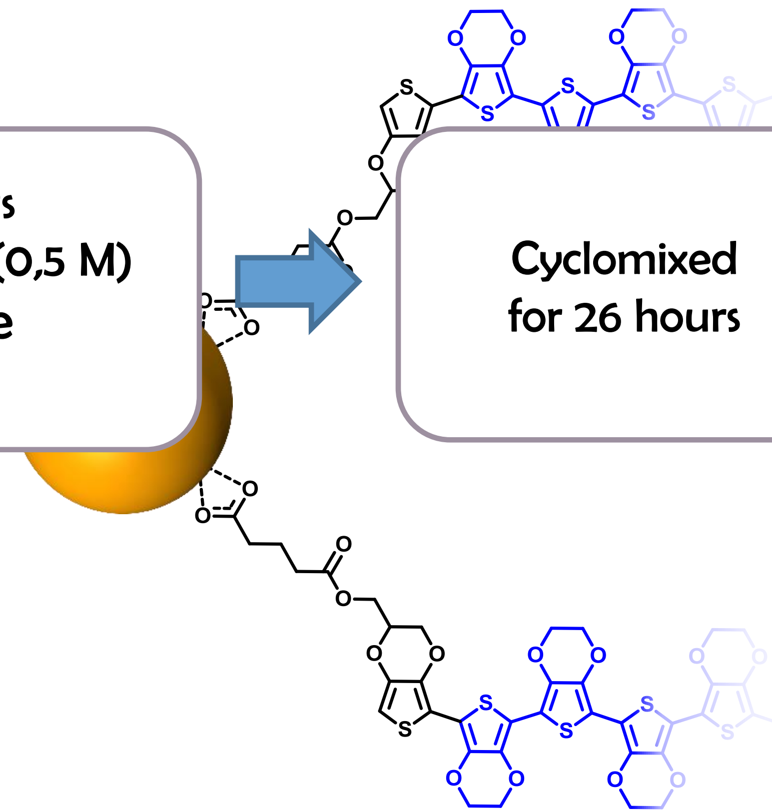
Nanoparticle Functionalization



Glutaryl-EDOT

Mn_3O_4 NPs
Glutaryl-EDOT (0,5 M)
Imidazole
Ethanol

***In situ* polymerization**



Cyclomixed for 26 hours

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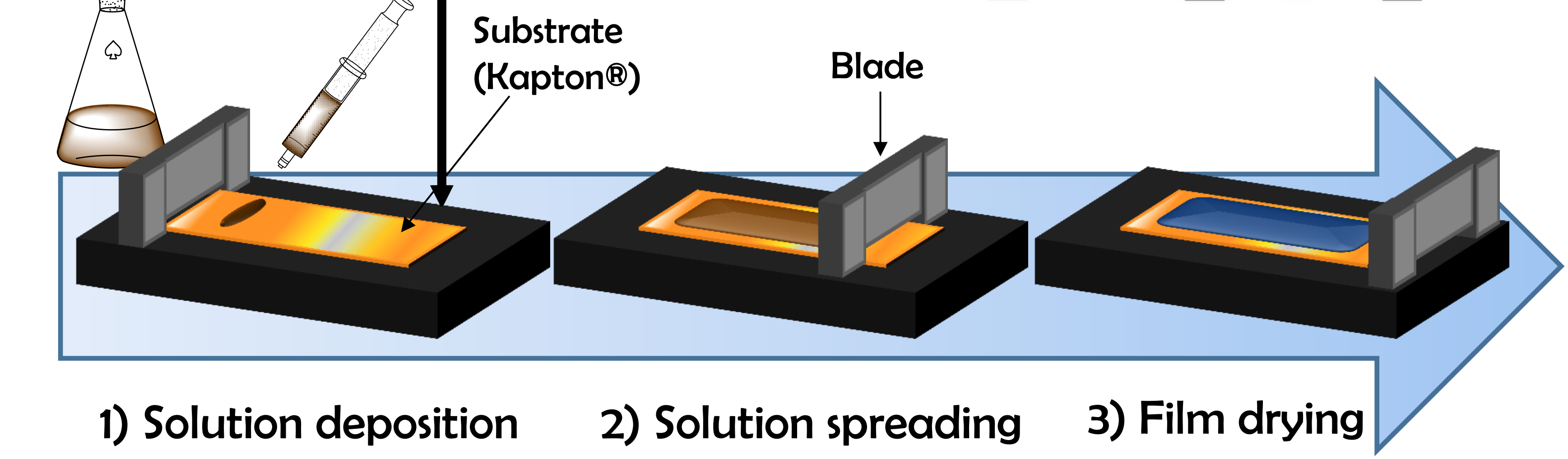
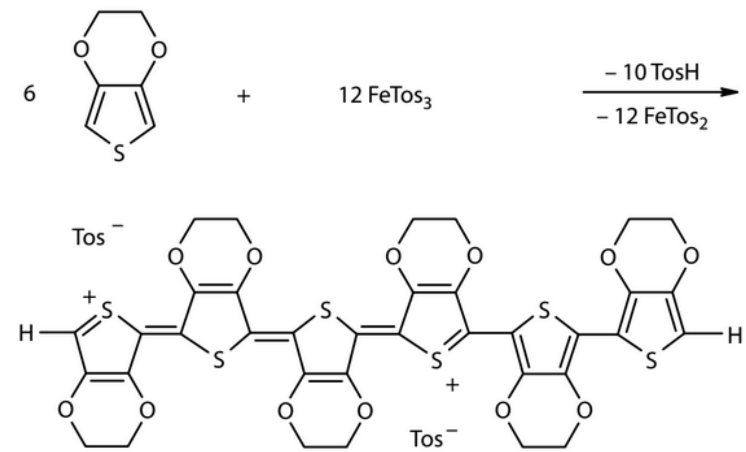
Hybrid Film Making
Blade Coating





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Thermoelectric Characterization

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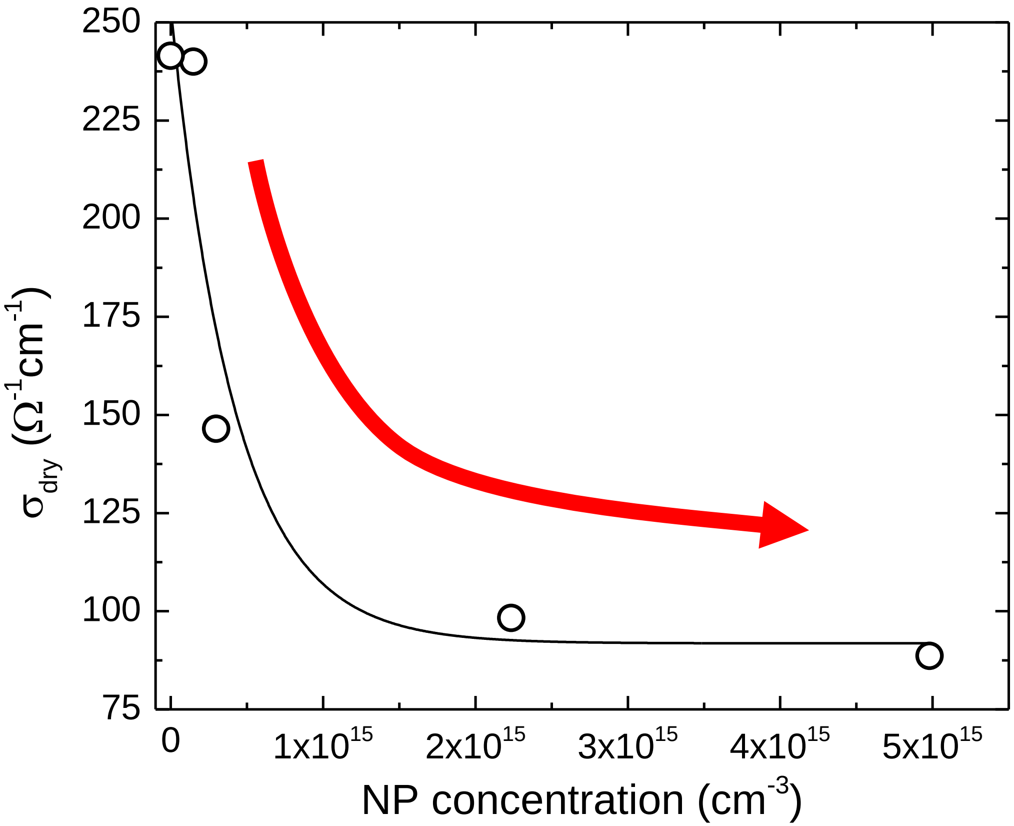
	[NP] (cm^{-3})	σ_{dry} ($\Omega^{-1}cm^{-1}$)	α_{dry} (μVK^{-1})
PEDOT:Tos	0	242±9	15.8±0.9
HF1	$1.5 \cdot 10^{14}$	240±9	14.8±0.5
HF2	$3.0 \cdot 10^{14}$	147±6	15.5±0.7
HF3	$2.2 \cdot 10^{15}$	98±4	15.0±0.2
HF4	$3.0 \cdot 10^{15}$	89±3	15.5±0.8

$$\sigma = ep\mu$$

$$\sigma = ep\left(\mu_0 + \mu_1 e^{-[NP]/N_0}\right)$$



[NP]: NP density

σ: electrical conductivity

α: Seebeck coefficient

e: electronic charge (1.6×10^{-19} C)

p: charge carrier density (holes) [cm^{-3}]

μ: charge carrier mobility [$cm^2/(V \cdot s)$]

μ_0, μ_1, N_0: constants

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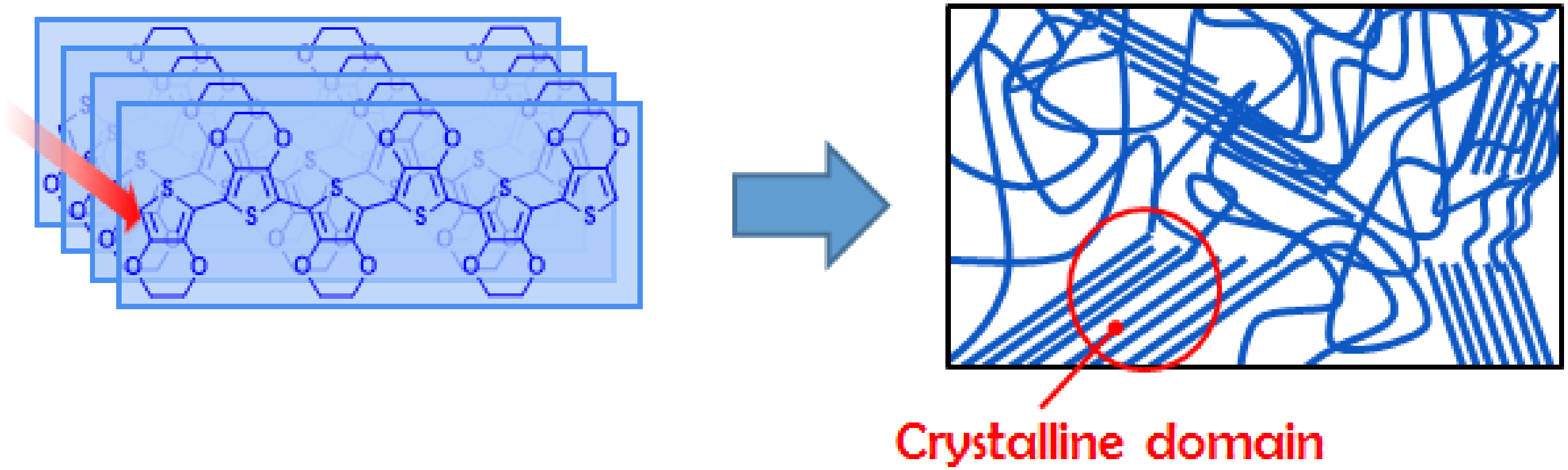
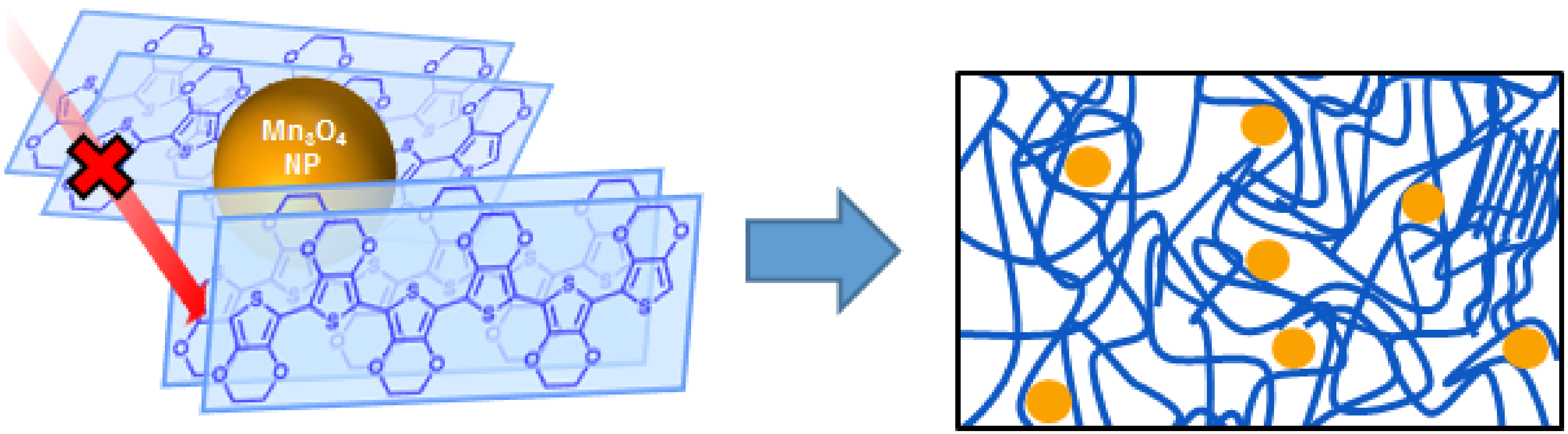
Results

Nanoparticle Influence on Polymer Morphology





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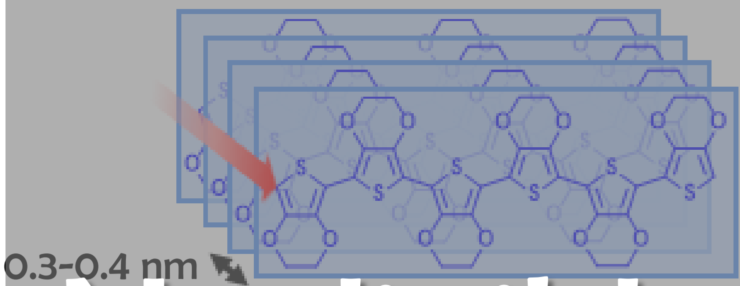
Humidity Effect

Detrimental effect on σ:

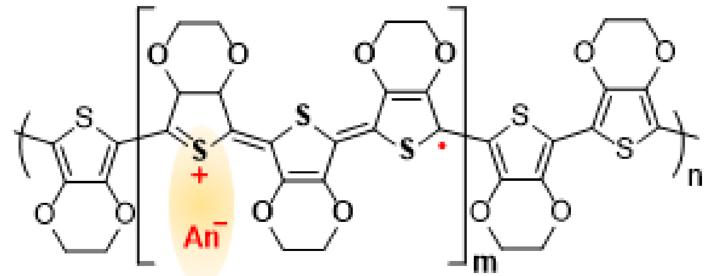
Water interposition between polymer chains



Negligible in NP presence

Beneficial effect on σ:

Counterion solvatation



H. Wang et al., *Adv. Energy Mater.* 5, 1 (2015).

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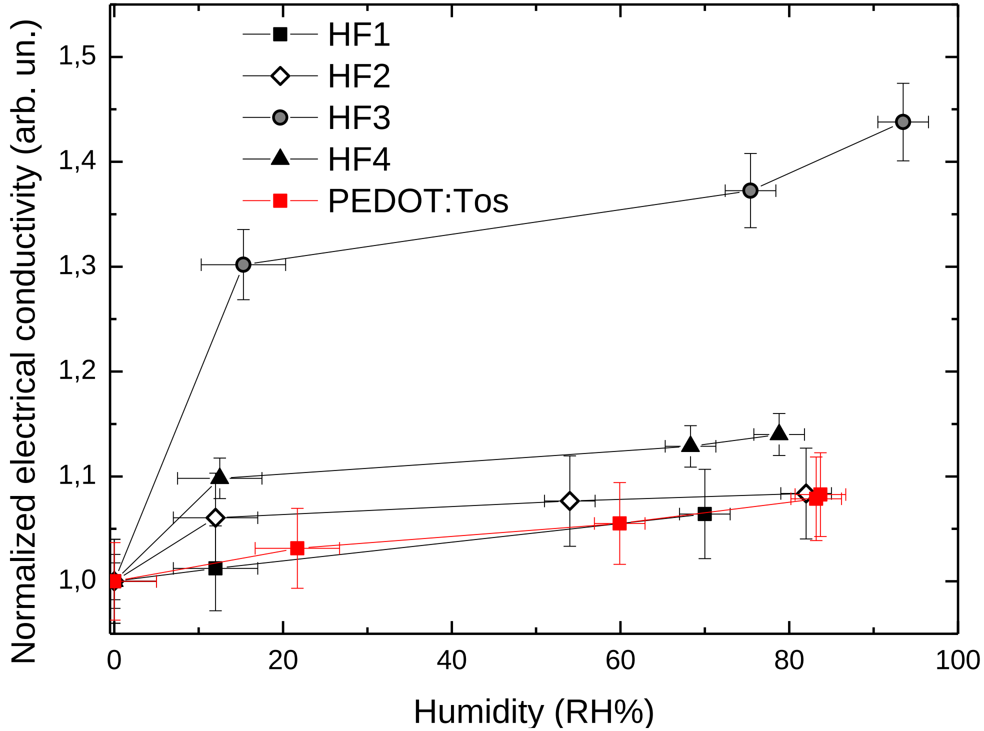
Humidity Effect



[NP]: NP density
σ: electrical conductivity
e: electronic charge (1.6×10^{-19} C)
x_w: water molar fraction
β: dimensionless function ($\beta>0$)

$$\sigma-\sigma_{dry}=\beta([NP])x_w\left(\sigma_0+\sigma_1 e^{-[NP]/N_0}\right)$$

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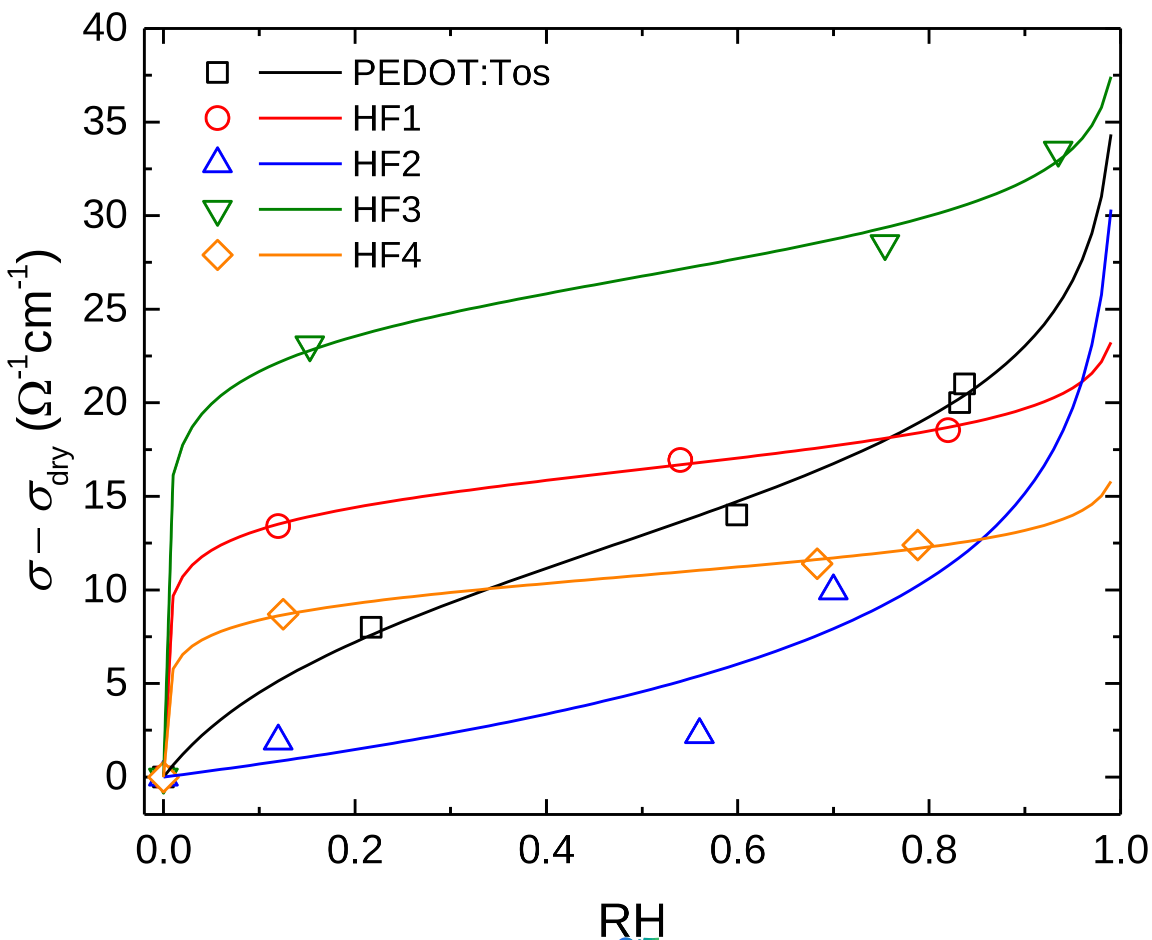
Humidity Effect

$$\sigma - \sigma_{\rm dry} = \beta\xi(\mathrm{RH};\delta_x, x_0)\left(\sigma_0 + \sigma_1 e^{-[NP]/N_0}\right)$$



[NP]: NP density
σ: electrical conductivity
β, δ_x, x_0: model parameters
RH: relative humidity

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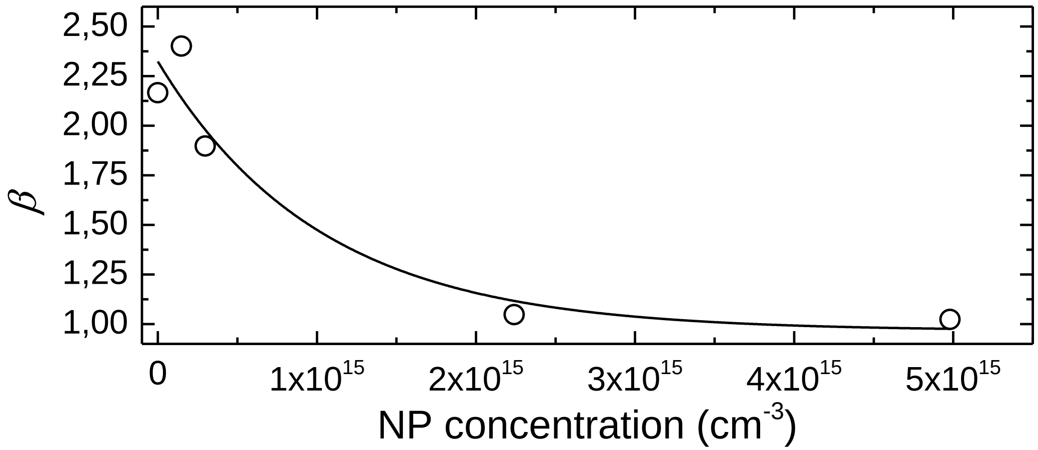
Humidity Effect
Understanding parameters

$$\sigma - \sigma_{\text{dry}} = \beta\xi(\text{RH}; \delta_x, x_0)\left(\sigma_0 + \sigma_1 e^{-[NP]/N_0}\right)$$



Parameter β (variation of p due to x_w) exponential decay vs [NP]

Water molecules sequestration by NPs

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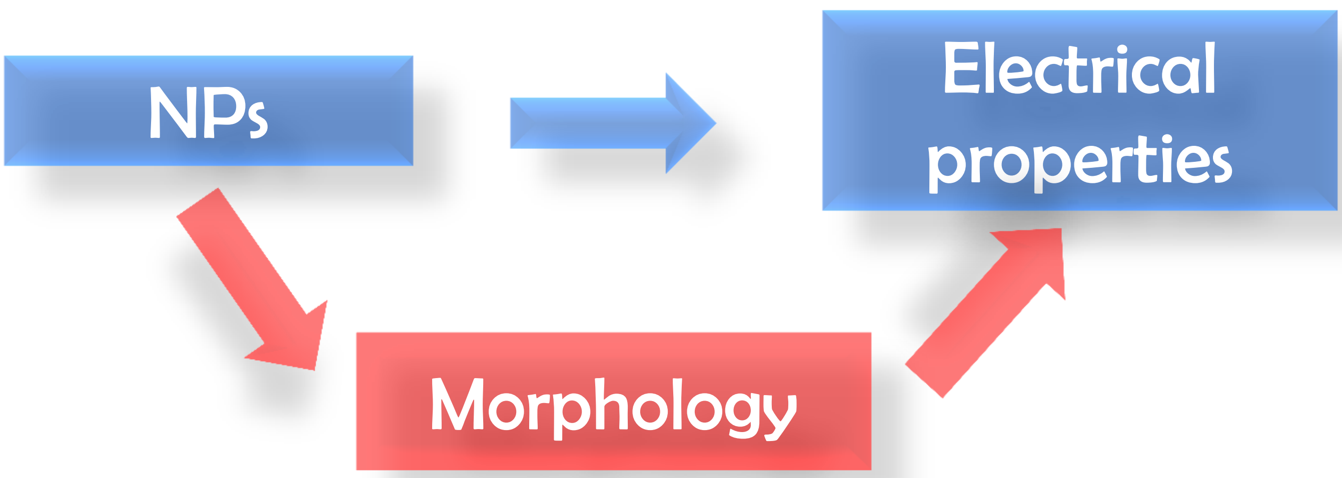
Conclusions and Further Developments

Results obtained:

- A novel protocol to obtain hybrid material CP/INPs has been developed
- Understanding of morphology related aspects of the developed system



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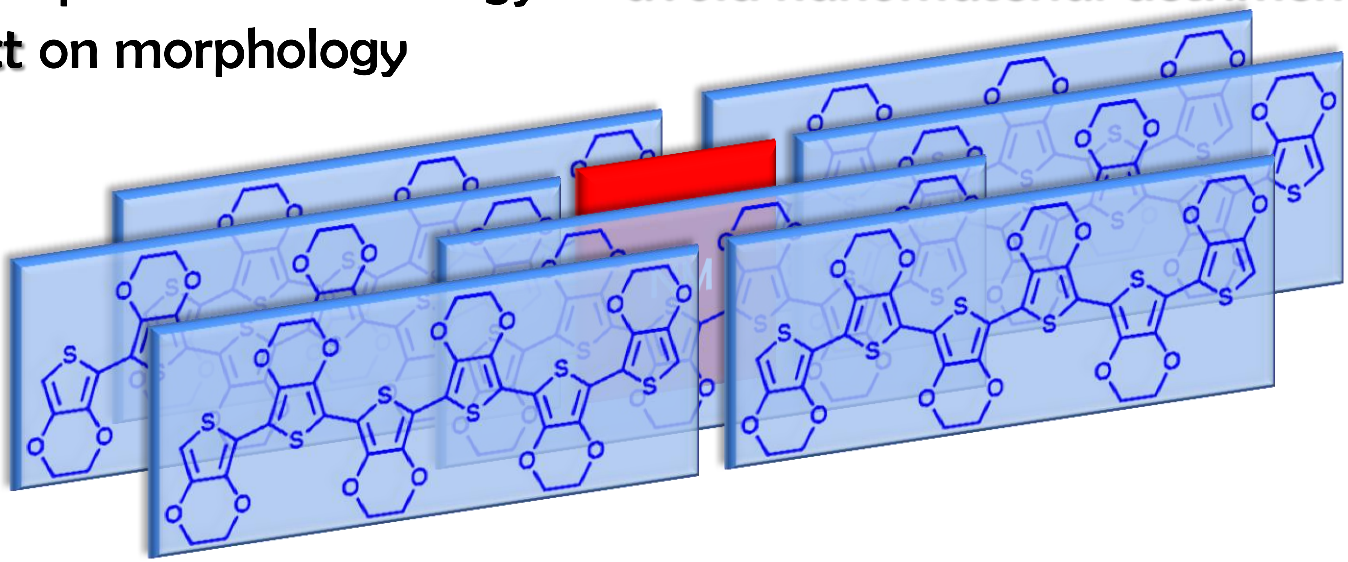
Conclusions and Further Developments

Further Developments:

- Development of a strategy to avoid nanomaterial detrimental effect on morphology



1. Implement polymerization and post-polymerization treatments to favor the rearrangements of NPs (head-to-tail)
2. Using 1D nanomaterial

Thank you for your kind attention!

Aknowledgments

University of Milano-Bicocca

Thermoelectrics Group:

Professor Dario Narducci, Dr. Bruno Lorenzi, Dr. Laura Zulian

LaSMO Group (Organic Synthesis):

Professor Luca Beverina, Dr. Mauro Sassi

Electrochemistry Group:

Professor Riccardo Ruffo

AFM Characterization:

Dr. Silvia Trabattoni

Co-Supervisor:

Dr. Luca Bertini

IENI-CNR Padova

SEM Characterization:

Dr. Simone Battiston

University of Pavia

Co-Supervisor:

Professor Umberto Anselmi-Tamburini

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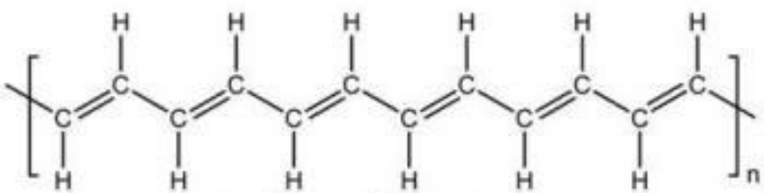
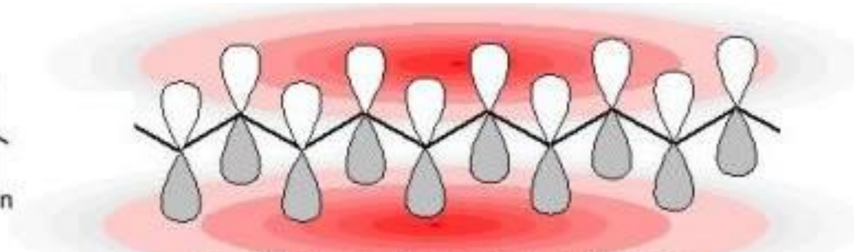
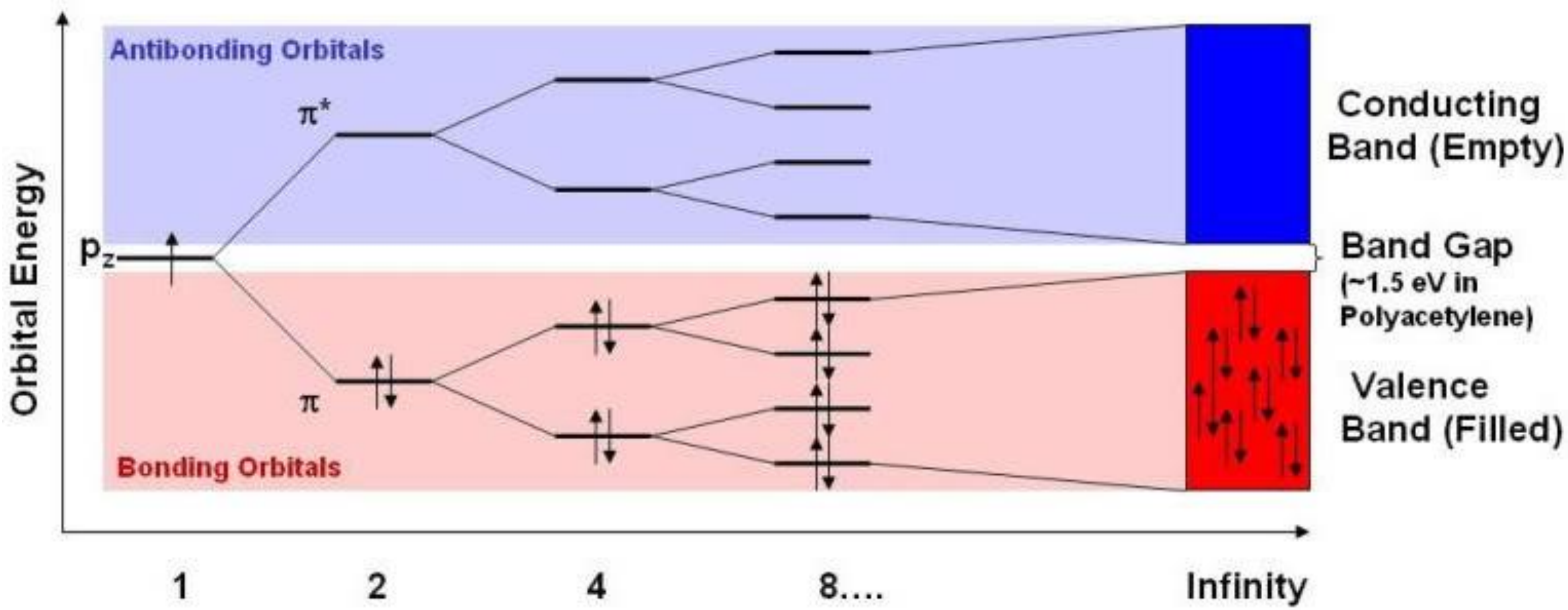
Further explanations

Conductivity in CP







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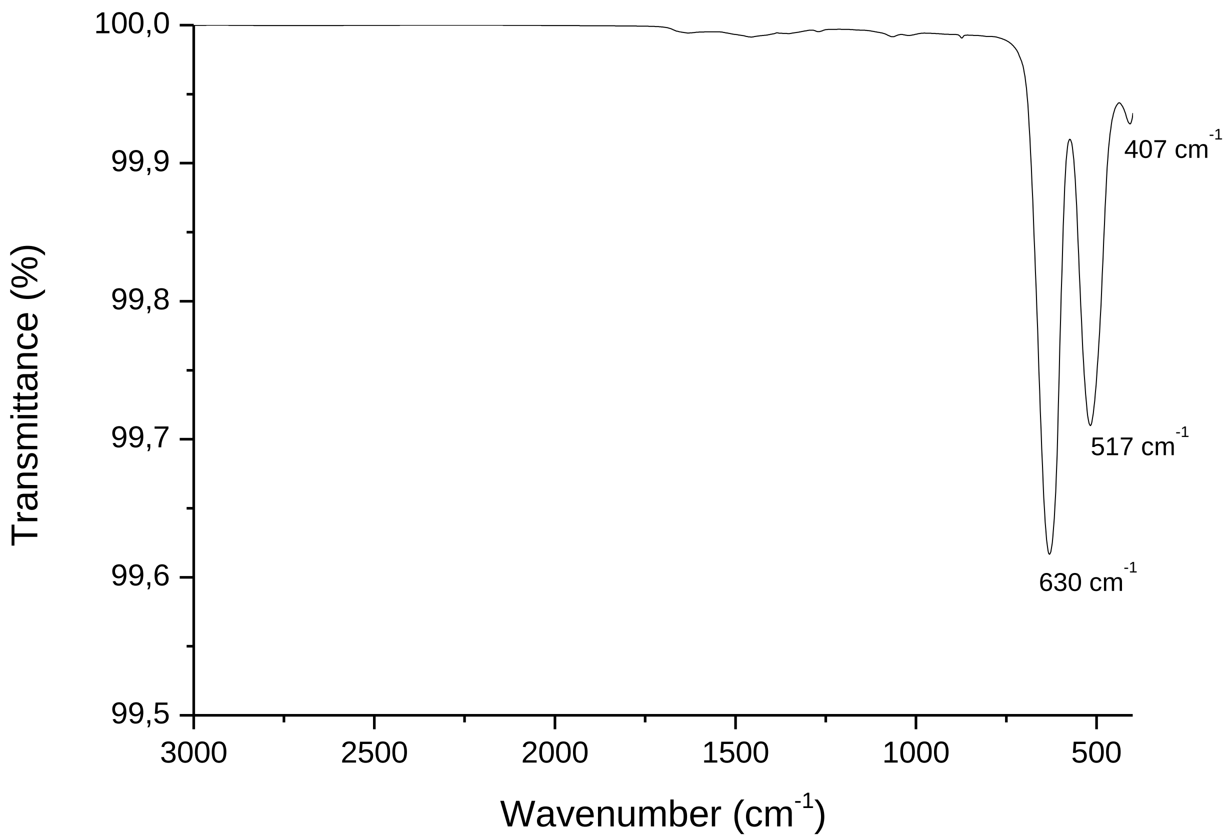
Further explanations

NP IR Characterization



- **630 cm^{-1}**

  Mn-O stretching modes in tetrahedral sites
- **517 cm^{-1}**

  Mn-O stretching modes in octaedral sites
- **407 cm^{-1}**

  Mn^{3+}-O vibrational modes in octahedral sites

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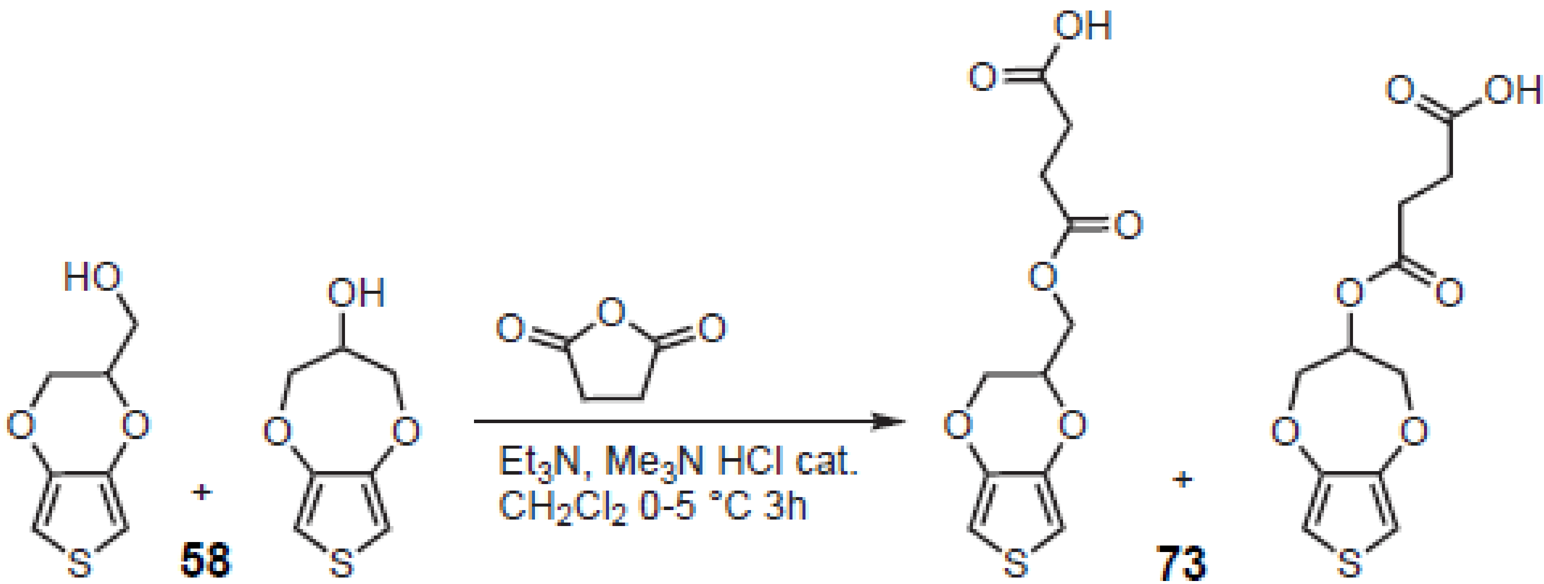
Further explanations

Synthesis of glutaryl-EDOT



58 isomers mix 95:5

73 isomers mix 95:5

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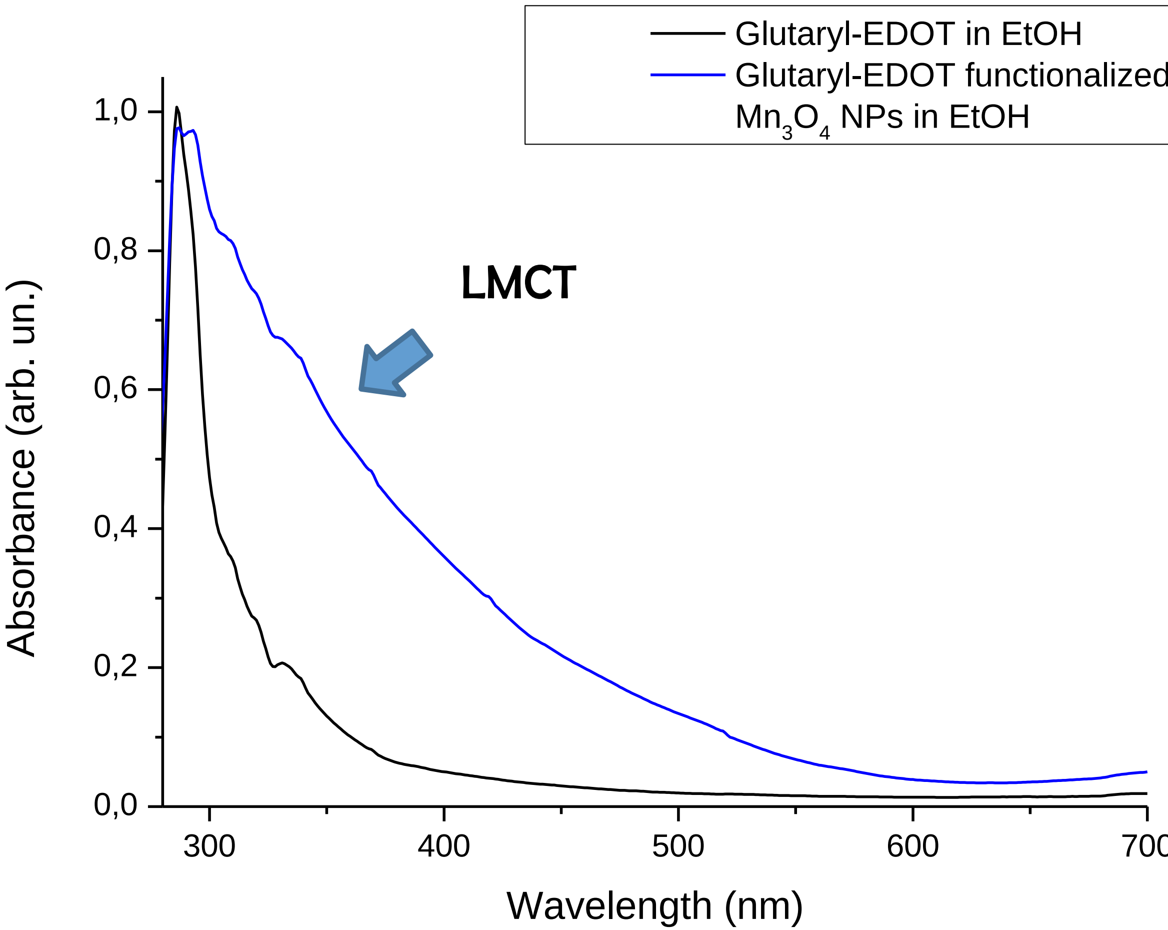
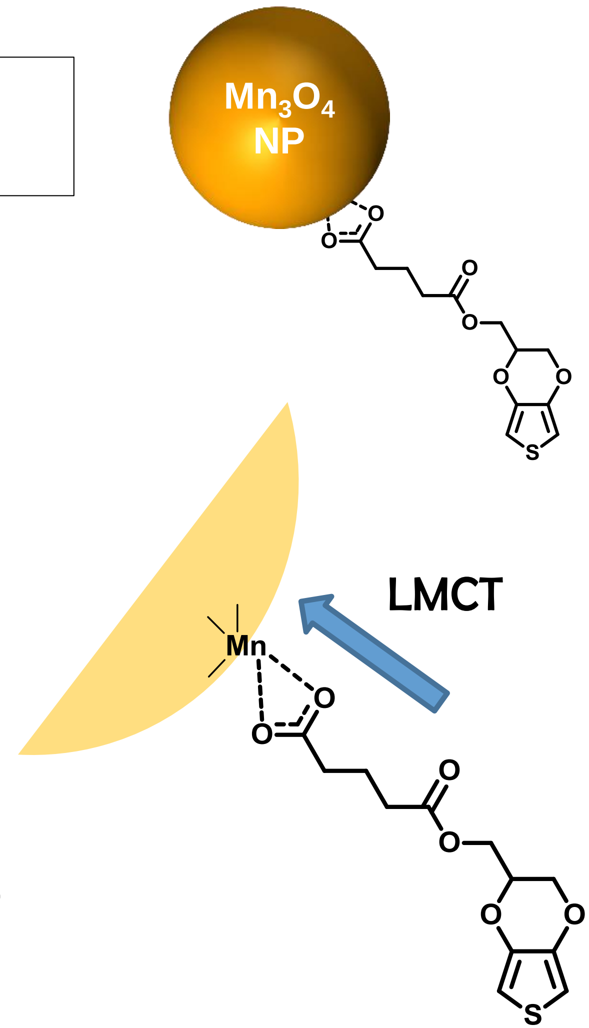
Further explanations

UV-vis Characterization of decorated NP





Further explanations

Power Factor Values

	[NP] (cm^{-3})	σ_{dry} ($\Omega^{-1}cm^{-1}$)	α_{dry} (μVK^{-1})	PF_{dry} ($\mu WK^{-1}m^{-1}$)
PEDOT:Tos	0	242±9	15.8±0.9	6.0±0.8
HF1	$1.5 \cdot 10^{14}$	240±9	14.8±0.5	5.5±0.7
HF2	$3.0 \cdot 10^{14}$	147±6	15.5±0.7	3.8±0.5
HF3	$2.2 \cdot 10^{15}$	98±4	15.0±0.2	2.2±0.6
HF4	$3.0 \cdot 10^{15}$	89±3	15.5±0.8	2.0±0.3

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Further explanations

Humidity Effect

Understanding the model

$$\sigma = e\,p(x_w,[NP])\left(\mu_0 + \mu_1 e^{-[NP]/N_0}\right)$$

$$\Rightarrow\; p(x_w,[NP]) = p(0,[NP]) + \left(\frac{\partial p}{\partial x_w}\right)_{x_w=0} x_w \equiv p_0\left(1+\beta([NP])x_w\right)$$

$$\sigma - \sigma_{dry} = \beta([NP])x_w\left(\sigma_0 + \sigma_1 e^{-[NP]/N_0}\right)$$

Rault's equation for non-ideal solution: $P_w^{(0)}/P^0 = \dfrac{P_w/P^0}{a_w(x_w)}$

Water activity approximated as a standard sigmoidal: $a_w(x_w) = \operatorname{csch}\left(\frac{1}{2\delta_x}\right)\sinh\left(\frac{x_w}{2\delta_x}\right)\cosh\left(\frac{x_0-1}{2\delta_x}\right)\operatorname{sech}\left(\frac{x_w-x_0}{2\delta_x}\right)$

Water molar fraction according to the water activity formula: $x_w = 2\delta_x \coth^{-1}\left(\dfrac{(\mathrm{RH}-1)\tanh\left(\frac{x_0}{2\delta_x}\right)+\coth\left(\frac{1}{2\delta_x}\right)}{\mathrm{RH}}\right) \equiv \xi(\mathrm{RH};\delta_x,x_0)$

$$\sigma - \sigma_{dry} = \beta\xi(\mathrm{RH};\delta_x,x_0)\left(\sigma_0 + \sigma_1 e^{-[NP]/N_0}\right)$$

[NP]: NP density
σ: electrical conductivity
e: electronic charge (1.6×10^{-19} C)
x_w: water molar fraction

β: dimensionless function (β>0)
p: charge carrier density (holes) [cm^{-3}]
μ: charge carrier mobility [$cm^2/(V\cdot s)$]
μ_0, μ_1, N_0: constants
P_0: 1 bar

$P_w^{(0)}$: equilibrium water pressure
a_w: water activity
RH: relative humidity $= \dfrac{\text{actual vapor density}}{\text{saturation vapor density}} x100\%$

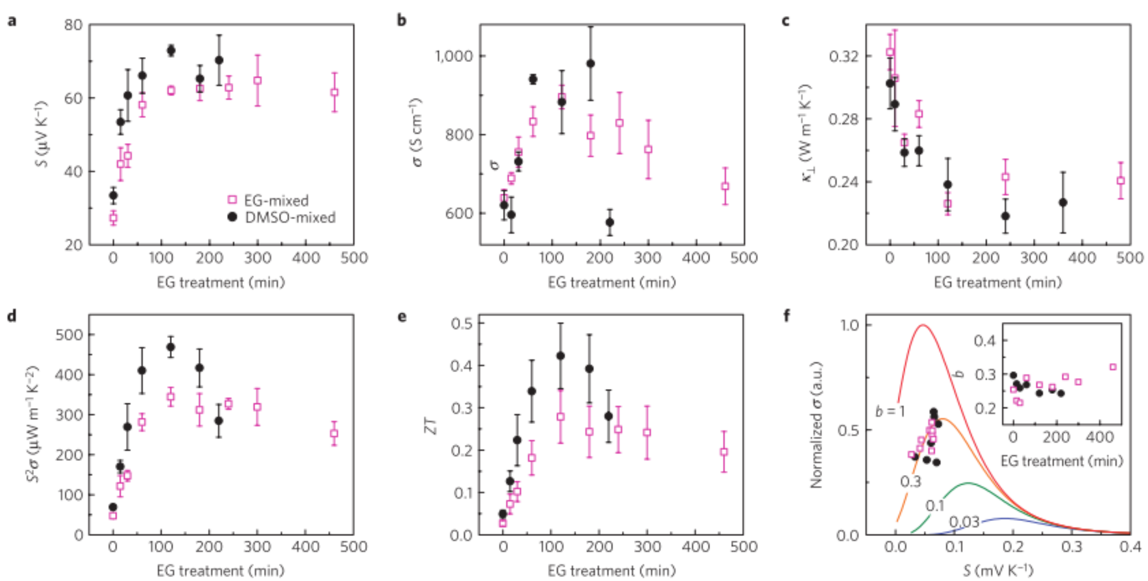
Further explanations

Record ZT value at room temperature

nature materials
LETTERS
PUBLISHED ONLINE: 5 MAY 2013 | DOI: 10.1038/NMAT3635

Engineered doping of organic semiconductors for enhanced thermoelectric efficiency

G-H. Kim[1], L. Shao[1], K. Zhang[1] and K. P. Pipe[1,2]*



Significant improvements to the thermoelectric figure of merit *ZT* have emerged in recent years, primarily due to the engineering of material composition and nanostructure in inorganic semiconductors[1] (ISCs). However, many present high-*ZT* materials are based on low-abundance elements that pose challenges for scale-up, as they entail high material costs in addition to brittleness and difficulty in large-area deposition. Here we demonstrate a strategy to improve *ZT* in conductive polymers and other organic semiconductors (OSCs) for which the base elements are earth-abundant. By minimizing total dopant volume, we show that all three parameters constituting *ZT* vary in a manner so that *ZT* increases; this stands in sharp contrast to ISCs, for which these parameters have trade-offs. Reducing dopant volume is found to be as important as optimizing carrier concentration when maximizing *ZT* in OSCs. Implementing this strategy with the dopant poly(styrenesulphonate) in poly(3,4-ethylenedioxythiophene), we achieve *ZT* = 0.42 at room temperature.