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Economical and Environmentally Friendly Organic hydrazone Derivatives Characterized by a Heteroaromatic Core as Potential Hole Transporting Materials in Perovskite Solar Cells

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Dedicated to Professor Giorgio A. Pagani

A series of organic electron-rich π-bridged symmetric hydrazones, composed of two donor moieties connected through a thiophene- or a pyrrole-based π-spacer, has been synthesized as a suitable alternative to 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (**Spiro-OMeTAD**), considered the benchmark hole transporting material (HTM) in perovskite solar cells (PSCs). The cheap synthetic protocol is suitable for potential large-scale production. All the compounds were characterized, showing good energy levels alignments with the perovskite and very close energy levels to the **Spiro-** **OMeTAD**. Furthermore, computational analysis confirmed the electrochemical trend observed. The costs of synthesis were estimated, as well as the produced waste to synthesise the final HTMs, underlining the low impact of these compounds on the environment with the respect to **Spiro-OMeTAD**. Overall, the relevant electrochemical properties and the low cost of the synthetic approaches allow these compounds to be a greener and easy-to-synthesize alternative to the **Spiro-OMeTAD** for industrial development of PSCs.

Introduction

Photovoltaic devices allow to convert solar radiation into electricity using different materials. The most widely used technology in this field is the silicon-based one, which is already extensively used in our everyday life. However, the increasing energy demand and the pressure for lowering the prices to be competitive with the fossil fuels economy led to the search for new pathways to tread in the field of photovoltaics.[1] Among these, perovskite solar cells (PSCs) found a remarkable role and interest in the scientific community due to their high efficiency and cheap preparation method so that in just five years their efficiency had a sixfold increase.[2] This rapid improvement in efficiency is in part due to the replacement of the liquid electrolyte with a solid-state hole transporting material (HTM).[3] Nevertheless, the most critical issue to further increase the performance of PSCs remains the development of an optimal HTM. Recent research mainly focuses on organic compounds

due to the easy tuning of their properties, their low cost and their simple synthesis, purification and characterization.[4] Currently, the twisted spirobifluorene-based bulky molecule **Spiro-OMeTAD** is the most studied for this purpose because it showed the best performance in terms of efficiency since its introduction about two decades ago.[5] However, the synthetic procedure to prepare it is complicated and expensive. This procedure uses noble metals and it is not suitable for large-scale production. Therefore, the need to develop new HTM systems seems to be a topic of primary relevance for the commercialization of efficient PSCs, at an affordable cost.[6]

In this scenario, series of different HTMs based on electron-rich compounds, such as triphenylamine, thiophene, or thiophene derivatives, characterized by a simple synthetic route and a low production cost, have been published obtaining good power conversion efficiency, almost comparable with the maximum efficiency obtained with the **Spiro-OMeTAD**.[7] However, they need palladium and copper catalysts in multiple steps of their synthetic path and this is a remarkable limitation for an industrial scale-up.[8]

In 2015, Docampo and coworkers published an innovative 3,4-ethylenedioxythiophene (EDOT)-based HTM synthesized through a Schiff base condensation reaction without using any metal catalyst and affording water as the only by-product.[9] This HTM achieved an efficiency comparable to the one of **Spiro-OMeTAD** in 2015 but with an effective cost one order of magnitude lower. The success of this new HTM lies in a simple and inexpensive synthesis. In fact, the reaction can be performed at near ambient conditions with a very straightforward product purification.

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In subsequent years, many research groups followed this low-cost and one- or two-step synthesis purpose.[10] Nazzeruddin and coworkers achieved the cheapest HTM after a two-step condensation synthesis with a total yield around 60% and the final cost of only 1.38 \$/g respect to the 92 \$/g of **Spiro-OMeTAD**.[10d] Moreover, in 2018, Docampo and coworkers proposed and tested a hydrazone-based HTM even cheaper with promising properties.[11]

Inspired by these successful works, we decided to develop and study a new series of heteroaromatic HTMs based on hydrazone moieties[12] characterized by simple synthetic paths and purifications which produce water as the only by-product of the last condensation. Hydrazone-based compounds are widely used in many fields, like medicine,[13] biology,[14] chemistry[15] and materials science.[16]

HTM should be a transparent and amorphous thin film, as crystallization would prevent effective pore filling and thereby reduce its thermal and photochemical stability as well as carrier mobility. Moreover, its energy levels must be properly engineered to match the position of the edge of the valance band (VB) of the perovskite to allow a faster charge transfer process and to limit the detrimental recombination reactions.[3a]

Herein, we present a series of electron-rich donor-π-spacer-donor (D-π-D) hydrazone-based HTMs and we report the synthesis, the complete optical and electrochemical characterization of these compounds and their suitability, in terms of energetics, for use in PSCs as HTMs. Moreover, density functional theory calculations (DFT) were performed to optimize the geometries and to study the electronic properties of the ground state of each compound. Lastly, we carried out a survey on the actual costs for the synthesis of 1 g of the final product, analysing also the environmental impact due to the waste production and the use of halogen-rich solvents.

Results and Discussion

Design and synthesis

The investigated symmetric D-π-D HTMs are listed in Figure 1.

On the basis of an our unpublished study, we knew that D-π-D derivatives of 1,2-di(2-pyrrolyl)ethenes-based hydrazones showed a nicely reversible oxidation behaviour and can be easily prepared on a large scale in almost ambient conditions with straightforward purification. They also presented a proper energetic alignment to be used as HTM in PI-PSC devices. Furthermore, a similar class of hydrazone-based compounds has been successfully used as active material in both perovskite and bulk heterojunction solar cells.[11,16c]

Based on that, we designed and investigated a system based on a 1,2-di(2-pyrrolyl)ethene functionalized with two 2-ethylhexyl chains on the nitrogen atoms (**Ph₂-P-Ph₂**) and three systems based on a 3,4-dibutoxythiophene-based π-spacer (**Ph₂-T-Ph₂**, **Me₂-T-Me₂**, **Ph-T-Ph**). From these cores, two hydrazone symmetrical donor arms started. As donor moieties, we selected three different substituents on the hydrazones group, namely diphenyl, dimethyl and phenyl. The presence of the alkyl chains in all these compounds is crucial to give an amorphous character to the films, to avoid an undesirable crystallization of the film and to improve the solubility of these molecules in organic solvents, which is an important feature to better deposit a homogeneous HTM layer.[4a]

The synthetic pathways are reported in Scheme 1.

Cristina Decavoli was born in Reggio Emilia, Italy. She received her PhD in Material Science and Nanotechnologies (2022) at the University of Milano-Bicocca under the lead of Prof. Abbotto, with a thesis about organic dye-based photosystems for the production of solar fuels. She is currently a postdoctoral associate in the Energy Sciences Institute at Yale University under the lead of Prof. Brudvig. Her research is now focused on molecular iridium catalysts and molecular photosensitizers for water oxidation.

Chiara Liliana Boldrini was born in Milan, Italy. She got her PhD in Materials Science and Nanotechnology at the University of Milano-Bicocca under the lead of Prof. Abbotto, with a thesis on materials and devices for solar generation of electricity and fuels (2018). She has then worked as a Postdoc fellow in the same research group, focusing on photo-electrodes for dye-sensitized water splitting and novel electrolyte solvents for dye-sensitized solar cells (2019–2022). She is currently working as a research technologist in Milano-Bicocca Solar Energy Research Center (MIB-SOLAR) with a wide interest on all PV devices.

Alessandro Abbotto is full professor of organic chemistry and organic materials for renewable energy. He is currently President of the Division of Organic Chemistry of Società Chimica Italiana (Italian Chemical Society) and National Coordinator of Italian Chemistry Olympiad, excellence program for secondary school students. His main research interests are in materials and devices for solar energy and artificial photosynthesis, including dye-sensitized solar cells, green hydrogen photo-generation from water, and artificial nitrogen fixation.

Norberto Manfredi is an associate professor in organic chemistry at the University of Milano-Bicocca. His main research interests are in the synthesis and development of organic materials and devices for emerging photovoltaic technologies and solar fuels production. Moreover, in the last year, he started investigating molecular conductive materials for application in bioelectronics. He is currently involved in the Milano-Bicocca Solar Energy Research Center (MIB-SOLAR).
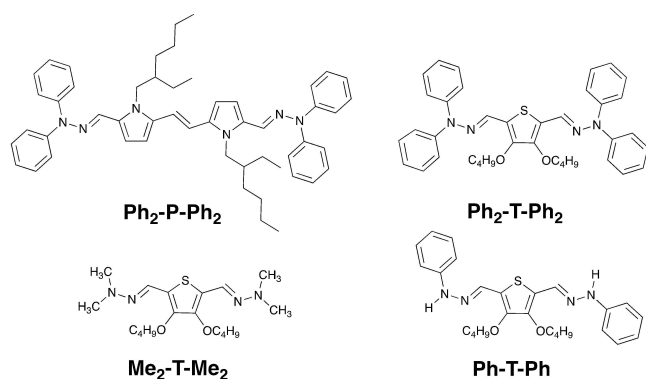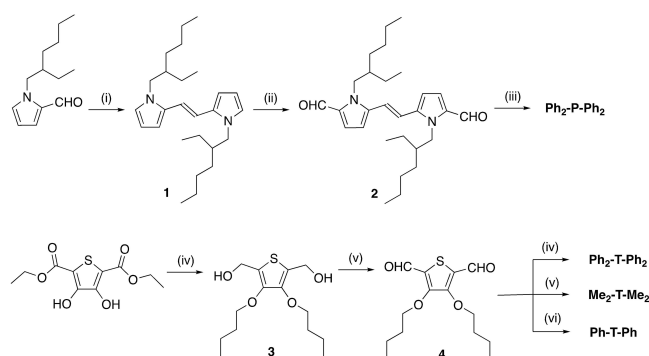
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Figure 1. Electron rich symmetric hydrazone investigated in this work.

Scheme 1. Synthetic protocol for the preparation of **Ph₂-P-Ph₂, Ph₂-T-Ph₂, Me₂-T-Me₂, Ph-T-Ph**. Reagents and conditions. (i) TiCl₄, Zn, pyridine, THF anhyd., N₂, reflux, 2.5 h; (ii) POCl₃, DMF, CH₃CN dry, rt, 20 h; (iii) N,N-diphenyl-hydrazine hydrochloride, THF, rt, 20 h; (iv) 1. Butyl bromide, K₂CO₃, DMF, 60 °C, 2 days, 2. LiAlH₄, THF, from −78 °C to rt, overnight; (v) MnO₂, CHCl₃, rt, 1.5 h; (vi) N,N-diphenyl hydrazine hydrochloride, THF, rt, 20 h; (vii) N,N-dimethyl hydrazine, PTSA, THF, rt, 20 h; (viii) N-phenyl hydrazine, PTSA, THF, rt, 20 h.

We chose simple synthetic protocols in order to realize HTMs that could be effectively transferred to a large-scale production. The synthesis of **Ph₂-P-Ph₂** is a four-step pathway. Starting from the 1-(2-ethylhexyl)-1H-pyrrole-2-carbaldehyde, synthesized following the alkylation reaction with 2-ethylhexyl iodide reported in literature,[17] the dipyrrolylethene core has been obtained via McMurry reaction in presence of Zn and TiCl₄. Pyridine was added to remove acid evolved during the reaction from the solution and prevent degradation of product **1**. The following Vilsmeier formylation inserted the dialdehyde functionalities to give **2** with high yield. In the end, the dialdehyde intermediate, as well as the dialdehyde of the 3-4-dibutoxythiophene, was submitted with the stoichiometric amount of acid to the final condensation with the proper hydrazine in THF at room temperature to give the corresponding product. Although the synthesis of 3-4-dibutoxythiophene-2,5-bisaldehyde was reported in literature by Ono et al.,[18] we decided to develop a new synthetic protocol to reduce the cost of the final compounds that will be discussed later. In fact, using as starting material for the initial nucleophilic substitution reaction the 3,4-dihydroxythiophene-2,5-dicarboxylic acid dieth-

yl ester, instead of the dimethyl ester, the final cost had a 6-fold reduction. Therefore, the first step, mentioned above as nucleophilic substitution reaction on the two hydroxyl groups of the thienyl ring, was performed with butyl bromide as nucleophile and potassium carbonate as base. The crude product was immediately subdued to a reduction reaction performed with lithium aluminium hydride to obtain the corresponding alcohol. In the end, the dialdehyde intermediate was obtained after a mild oxidation of the dialcohol derivative performed with manganese (IV) oxide in chloroform, adapted from a literature procedure,[19] instead of the more expensive and complicated oxidation with tetrapropylammonium per-ruthenate (VII) and N-methylmorpholine N-oxide proposed by Ono et al.[18] The final yields of the three-step synthetic protocols were around 55% for the disubstituted hydrazones and around 40% for the monosubstituted one. On the contrary, the overall yield achieved for the synthesis of **Ph₂-P-Ph₂** was around 30% at the end of the four-step protocol, mainly due to the low yield of the initial alkylation reaction.

Optical properties

The optical properties of the investigated compounds both as thin film prepared via spin coating (5×10^{-5} M in chlorobenzene, 2000 rpm, 30 s) and in solution (THF) are depicted in Figures 2 and S1 (Supporting Information). The main optical parameters are collected in Table 1. Optical bandgaps were calculated by means of the Tauc plots[20] and listed in the same table.

The absorption spectra of the compounds showed an intense absorption peak related to the π-π* transition of the molecules at between 430–450 nm for the diphenyl- and phenyl-derivatives, and at about 380 nm for the dimethyl hydrazone. The molar extinction coefficients were similar in the homologous class of compounds due to the same π-spacer. In fact, the thienyl-based compounds presented a molar extinction

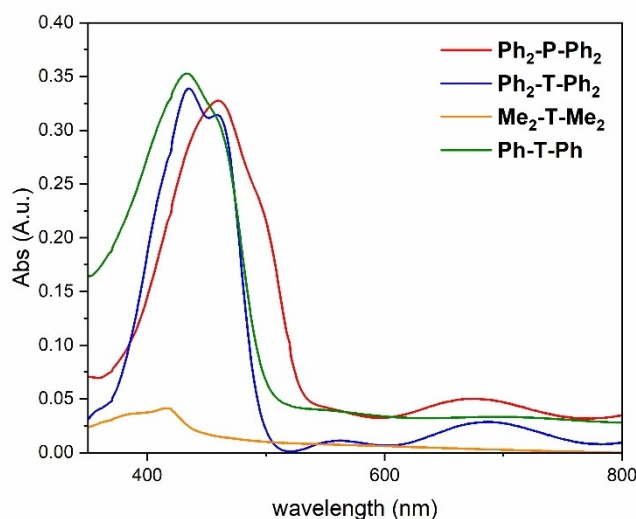**Figure 2.** Absorption spectra of hydrazone based HTMs as thin film.

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Table 1. Optical characterization of hydrazone-based HTMs.

Compound	λ_{max} sol[1] [nm]	ε [M^{-1} cm^{-1}]	λ_{max} film [nm]	E_{gap}^{opt} [eV]
Spiro-OMeTAD	387	57300 $\pm$ 300	–	–
Ph$_2$-P-Ph$_2$	452	50400 $\pm$ 800	460	2.46
Ph$_2$-T-Ph$_2$	431	29900 $\pm$ 900	435	2.61
Me$_2$-T-Me$_2$	379	27900 $\pm$ 500	389	2.99
Ph-T-Ph	432	21800 $\pm$ 800	434	2.60

[1] in 10^{-5} THF solution.

coefficient close to 29000 M^{-1}cm^{-1}, a little lower for the phenyl-hydrazone around 21000 M^{-1}cm^{-1}, whereas the **Ph$_2$-P-Ph$_2$** showed a much higher value around 50000 M^{-1}cm^{-1} and it could be attributed to the longer conjugation of its π-spacer. It is important to highlight that **Me$_2$-T-Me$_2$**, as **Spiro-OMeTAD**, presented an optical transparency in the visible reason, which is highly desirable for application in tandem cells.[3a] Moreover, it exhibited a molar extinction coefficient less than half of that of **Spiro-OMeTAD**. These are significant characteristics for an HTM because it must not affect the light-harvesting of the perovskite ensuring that most of the photons can reach the active layer of the PSC, thus avoiding lowering the efficiency of the device. On thin film, the absorption maxima are slightly red-shifted (less than 10 nm) compared to the analogous in solution, as expected, indicating poor π-π intermolecular interactions in the thin film. Indeed, the absence of any important change in absorption spectra for these thin films indicates the amorphous structure of the spin-coated films.[21]

Electrochemical properties

CV and DPV performed on the studied compounds to determine the redox characteristics and calculate HOMO/LUMO energy levels are shown in Figure 3 and Figure S2 (Supporting Information), respectively. All the experimental electrochemical parameters are collected in Table 2 and pictorially represented in Figure 4.

In the CV investigation, every compound exhibited a reversible oxidation peak, while the reduction processes, when present, were always irreversible. The oxidation waves showed two unresolved current signals (a peak and its shoulder) except in the case of **Ph-T-Ph**, which made somewhat complicated the energy level calculation. The first wave corresponds to the formation of a delocalized radical cation, whereas the second is associated with the formation of the dication. Both the position and the potential separation between the two peaks can be used to probe the electronic coupling between the end-capping units and the electron-accepting core. For these reasons, DPV was employed. DPV allowed isolating the different electrochemical processes with the exception of the **Ph-T-Ph** where the two oxidation processes appear as a single broad peak. In this case, the HOMO energy level has been determined from the current onset rather than the current peak.

These new hydrazone-based HTMs presented a higher energy HOMO with respect to the edge of the perovskite VB, as
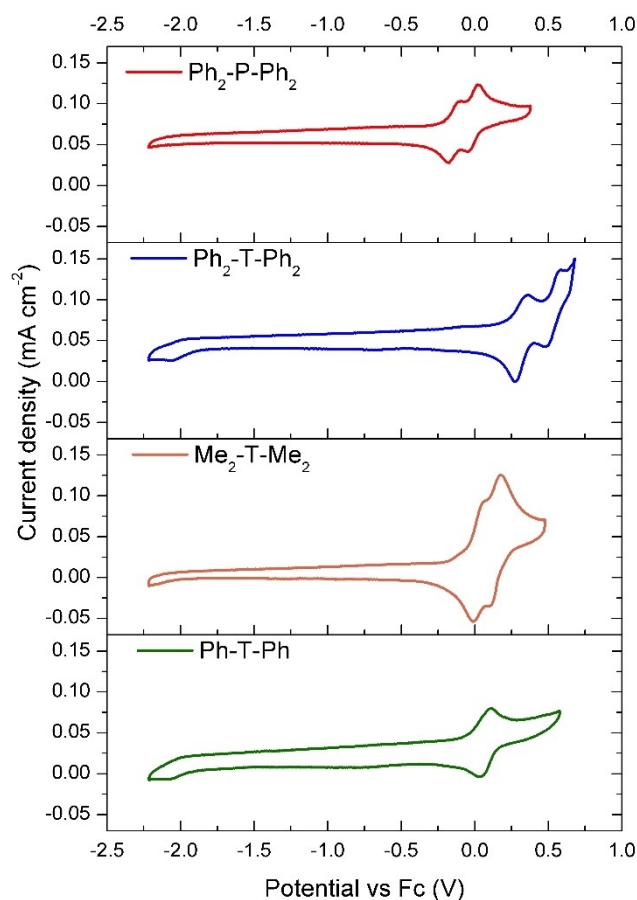

Figure 3. CV plots of a 5×10^{-4} solution of hydrazone-based HTMs in 0.1 M TBAClO$_4$ as supporting electrolyte in THF. The working electrode is a glassy carbon disk, the counter electrode is a Pt flag, and the reference electrode is Ag/AgCl (scan rate of 50 mV/s).

Table 2. Electrochemical parameters of the studied compounds.

Compound	V_{ox} [V vs Fc] $\pm$ 10 mV	HOMO[1] [eV] $\pm$ 0.1 eV	E_{gap}^{opt} [eV]	LUMO[1,2] [eV] $\pm$ 0.1 eV
Spiro-OMeTAD[3]	–	−5.13	–	−2.10
Ph$_2$-P-Ph$_2$	−0.15	−4.98	2.46	−2.52
Ph$_2$-T-Ph$_2$	0.30	−5.43	2.61	−2.82
Me$_2$-T-Me$_2$	−0.015	−5.15	2.99	−2.16
Ph-T-Ph	−0.07	−5.19	2.60	−2.59

[1] Vacuum potential = Fc/Fc$^+$ − 5.1 V,[22] [2] Calculated using optical band gap, [3] Values from Ref. [9]

required for a smooth hole transfer and electron blocking. However, the HOMO level of **Ph$_2$-T-Ph$_2$** showed a value of −5.41 eV, close to the perovskite VB maximum. Considering that a minimal offset of 0.2–0.3 eV is generally required to ensure efficient electron injection,[23] it is reasonable that electron donation is hampered and the whole mechanism is negatively affected with this HTM. Anyway, all others demonstrated very close energy level alignments with the **Spiro-OMeTAD**, particularly **Me$_2$-T-Me$_2$**, which featured roughly the same HOMO and LUMO positions.

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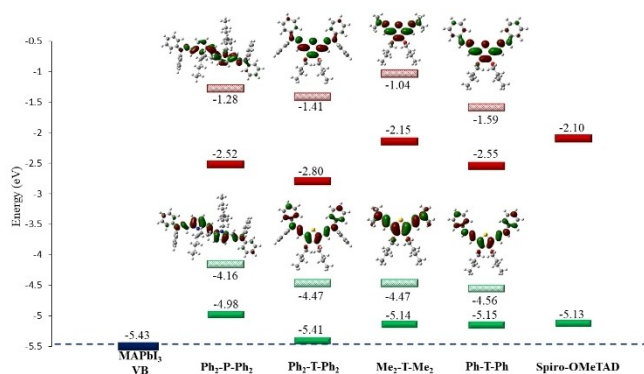European Chemical
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Figure 4. Pictorial representation of the energy levels of the investigated compounds compared to a representative perovskite photoactive compound and **Spiro-OMeTAD**,[9] and distribution of HOMO and LUMO levels calculated by DFT computation using B3LYP/6-31G* as a basis set. The experimentally determined frontier orbital energy levels are shown as solid colours, while the computed values are coloured in stripes.

Thermal Stability

The thermal stability of the unprecedented investigated compounds has been evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the corresponding plots are shown in Figures 5 and S4 (Supporting Information), respectively.

The investigated compounds showed good thermal stability and, except for **Ph-T-Ph**, a decomposition temperature in the air between 180 and 240 °C. In the investigated range of temperature, the DSC analysis showed only the melting transition of the compounds. No other phase transitions have been recorded.
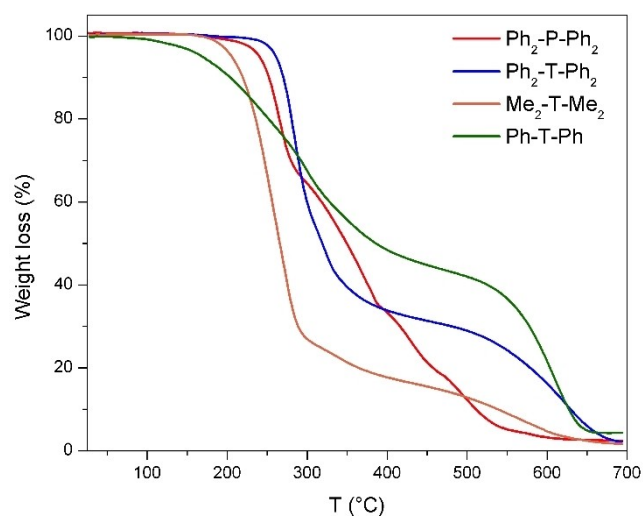
DFT molecular orbital calculation

The optimized geometries and the electronic structures of the compounds were mimicked through molecular modelling with the GAUSSIAN 16 package using the DFT program on the B3LYP/6-31G* level. The calculated frontier orbitals are reported in Table 3 and visualized in Figure 4, while the optimized geometries at ground state are shown in Figure S29–32 and the most important bonds, angles and torsions are reported in Table S5. All the π-spacers of the thienyl HTMs presented a planar conformation, whereas **Ph2-P-Ph2** showed a 30°-torsion between the central double bond and one pyrrole ring. In **Ph2-T-Ph2**, one phenyl ring lies on the plane of the heteroaromatic core and the other lies on a plane perpendicular to it, while the phenyl rings in **Ph2-P-Ph2** are slightly rotated from the perfect planarity and perpendicularity showing a dihedral angle of 4° and 94°, respectively. Also, the phenyl ring in **Ph-T-Ph** lies on the planar plane of the molecule. This is evident also in the electronic isosurfaces where the HOMO of **Ph2-P-Ph2** is only partially localized on its phenyl rings, whereas both in **Ph2-T-Ph2** and in **Ph-T-Ph** a high contribution is given by the phenyl rings placed on the planar plane. This will reflect on the life time of generated cation that would be longer thanks to the delocalization on a larger conjugated planar structure.[24] As shown in Figure 4, the HOMO of thienyl compounds is evenly distributed on the entire molecule, whereas, as expected, the LUMO is more localized on the π-spacer portions. The good overlap between HOMO and LUMO levels, especially for **Me2-T-Me2**, will lead to a strong Coulomb interaction, which is beneficial for the formation of neutral excitons and hole transport.[25] The alkyl chains in all the compounds present no electronic contribution to the π-system. The bandgaps well agree with the trend determined experimentally by means of Tauc plot of the UV-vis spectra.

Cost estimates and waste and environmental impact

Table 4 shows the produced waste, the used halogen-rich solvents, and the cost estimates for the synthesis of 1 g of desirable HTM.

Since these HTMs were designed for large-scale application, we estimated the cost for the synthesis of 1 g of the final product using a method reported in literature (Table S1–4, Supporting Information).[9] However, the price indicated in the Supporting Information should be considered as an upper limit,

Figure 5. Thermogravimetric analysis of investigated hydrazone-based HTMs (heating rate of 10 °C/min).

Table 3. Electrochemical parameters calculated with DFT and compared with optical bandgap.

Compound	HOMO [eV]	HOMO exp [eV]	LUMO [eV]	LUMO exp [eV]	E_{gap}[1] [eV]	E_{gap}^{opt} [eV]
Ph2-P-Ph2	−4.16	−4.98	−1.28	−2.52	2.88	2.46
Ph2-T-Ph2	−4.47	−5.43	−1.41	−2.82	3.06	2.61
Me2-T-Me2	−4.47	−5.15	−1.04	−2.16	3.43	2.99
Ph-T-Ph	−4.56	−5.19	−1.59	−2.59	2.97	2.60

[1] Calculated as $E_{gap} = LUMO - HOMO$.

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Table 4. Estimated materials cost, waste and halogen-rich solvents used for the synthesis of the investigated HTMs.

HTM	Steps	Waste [kg/g]	Halogen Rich solvents [kg/g]	Reagents [€/g]	Solvents [€/g]	Workup materials [€/g]	Cost [€/g]
Spiro-OMeTAD[1]	6	3.6	1	5.05	1.69	68.00	74.74
Ph$_2$-P-Ph$_2$	4	1.17	0.07	6.71	2.97	29.11	38.79
Ph$_2$-T-Ph$_2$	3	0.38	0.12	8.92	1.16	2.93	13.01
Me$_2$-T-Me$_2$	3	0.61	0.17	19.15	2.15	5.09	26.38
Ph-T-Ph	3	0.67	0.17	15	2.35	5.19	22.53

[1] Value from Ref. [9].

because bulk orders would significantly reduce the price. **Ph$_2$-P-Ph$_2$** presented a higher cost with the respect to the other HTMs, not only due to the four-step protocol instead of the three-step one but, mainly for the presence of two chromatographic purifications which required a large amount of workup materials. On the other hand, the other diphenyl derivative, **Ph$_2$-T-Ph$_2$**, presented the lowest cost estimated accordingly with the use of cheaper reagents and high-yield reactions. In the end, the most promising HTMs, **Me$_2$-T-Me$_2$** and **Ph-T-Ph**, presented a cost of only 26.38 €/g and 22.53 €/g, respectively, three times lower than the estimated cost of **Spiro-OMeTAD**. This difference in price is related both to the reduction in the number of synthetic steps and to the elimination of steps that require the use of expensive catalysts. The reduction in the number of synthetic steps not only has a high impact on the costs but also on the production of chemical wastes, mainly due to the purification processes. The total amount of chemicals used per step is nearly one third of that required to perform one step of the **Spiro-OMeTAD** synthesis. Although the synthesis of **Ph$_2$-P-Ph$_2$** is only one-step longer than the other HTMs presented in this work, it produced approximately twice as much waste as the others, mainly due to the presence of two purification steps via column-chromatography. Moreover, many chemicals have a significant impact on the environment, above all the halogen-rich solvents because they are dangerous for human health, being often carcinogenic, and their release into the environment can cause damage to local fauna and flora. The synthesis of these new HTMs required very low amounts of halogen-rich solvents, less than 20% of that required by **Spiro-OMeTAD**. The Scheme S1–4 (Supporting information) graphically present the flowcharts of the synthesis of the investigated HTMs, which indicate the amount of reactants, the necessary solvents and the waste produced for each step of the synthetic route.

Conclusion

In conclusion, four new hydrazone-based HTMs were synthetized with simple and inexpensive reactions and we proposed a cheaper and simpler synthetic route for the production of the already-known 3-4-dibutoxythiophene-2,5-bisaldehyde building block. All the compounds exhibited electrochemical oxidation potentials that allowed to calculate HOMO values in good agreement with the requirements of matching the position of the edge of the VB of the perovskite. In particular, **Me$_2$-T-Me$_2$** is

a promising candidate to replace the **Spiro-OMeTAD** benchmark. In fact, it showed the most similar optical and electrochemical properties to **Spiro-OMeTAD** among the proposed compounds, which were also confirmed by the DFT calculation. Finally, the cost estimates carried out on the synthesis of these new compounds have shown that the cost of the thienyl derivatives is approximately three times lower than the **Spiro-OMeTAD** estimate, and the environmental impact is about five times lower than it.

This preliminary investigation already highlights how the use of simple organic molecules could significantly lower both the cost of production of an HTM, as shown in Table 4, and the impact that these compounds have on the environment. These are important characteristics because the ultimate goal of the PSC technology is to surpass the fossil fuel-based society by introducing a sustainable and renewable energy-based society in order to reduce the impact that our lives have on the environment.

Experimental Section

General Information: NMR spectra were recorded with a Bruker AMX-500 spectrometer operating at 500.13 MHz (^{1}H) and 125.77 MHz (^{13}C) and a Bruker Avance Neo spectrometer operating at 400 MHz (^{1}H) and 100 MHz (^{13}C). Coupling constants are given in Hz. Absorption spectra were recorded with a V-570 Jasco spectrophotometer. Infrared spectra (IR) were recorded with an ATR-FTIR Perkin-Elmer Spectrum100 spectrometer. DSC have been performed on a Mettler Toledo DSC-1 system (25–200 5° min^{-1}, constant N2 flux of 50 mL min^{-1}), and TGA have been recorded on a Mettler Toledo TGA/DSC1 STARe System (30–700 °C, heating rate of 10 °C min^{-1}, constant air flux of 50 mL min^{-1}). Reactions performed under inert atmosphere were done in oven-dried glassware and a nitrogen atmosphere was generated with Schlenk technique. Conversion was monitored by thin-layer chromatography by using UV light (254 and 365 nm) as a visualizing agent. Purification of the compounds with flash chromatography was performed with Merck grade 9385 silica gel 230–400 mesh (60 Å). All reagents and anhydrous solvents were obtained from commercial suppliers at the highest purity grade and used without further purification. After extraction, the organic phases were dried with Na$_2$SO$_4$ and filtered before removal of the solvent by evaporation at reduced pressure. The 1-(2-ethylhexyl)-1H-pyrrole-2-carbaldehyde was prepared according to literature,[17] whereas 3,4-dihydroxythiophene-2,5-dicarboxylic acid diethyl ester and **Spiro-OMeTAD** were purchased by Sigma Aldrich.

Electrochemical Characterization: Pulsed Voltammetry (DPV) and Cyclic Voltammetry (CV) were carried out at scan rate of 20 and 50 mV/s, respectively, using a PARSTA2273 potentiostat in a two-

compartments, three-electrode electrochemical cell in a glove box filled with N_2 ($[O_2]$ and $[H_2O] \leq 0.1$ ppm). The working, counter, and the pseudo-reference electrodes were a glassy carbon pin, a Pt flag and an Ag/AgCl wire, respectively. The working electrode discs were well polished with alumina 0.1 µm suspension, sonicated for 15 min in deionized water, washed with 2-propanol, and cycled 50 times in 0.5 M H_2SO_4 before use. The Ag/AgCl pseudo-reference electrode was calibrated, by adding ferrocene (10^{-3} M) to the test solution after each measurement. Oxidation potential values were determined using DPV traces by following the reference methods reported in the literature.[26] For mono-electronic well-defined current wave, the potentials were calculated by the peak position. In the presence of overlapping peaks due to molecular additional oxidation, potential values were calculated using the current onsets of the oxidation processes for both the standard (ferrocene) and the molecules.

Density functional theory calculations: The ground-state geometries were optimized using DFT with the B3LYP functional at the basis set level of 6-31G*,[27] which provides a correct description of the neutral states in extended π-conjugated systems. All calculations were carried out using Gaussian16 program.[28] The frontier molecular orbitals were visualized using GaussView 6.0[29] and an isovalue of 0.03 a.u., while the optimized geometries of the ground state are visualized using AVOGADRO software.[30]

Estimations of the synthesis cost of the materials investigated: We roughly estimated the synthetic costs of 1 g of the investigated HTMs following the cost model proposed by Petrus et al.[9] and by Osedach et al.[31] For every synthetic step the required amounts of reactants, catalysts, reagents and solvents were calculated to obtain 1 gram of the final product. Moreover, the required materials for workup and purification were estimated using the procedure as published in literature.[31] These tables do not take into account other several important parameters like the energy consumption, waste treatment and labor, whose estimation results complicated for a simple rough analysis. However, the cost of the compounds of interest was compared with the cost of **Spiro-OMeTAD** reported in literature and estimated with the same method,[9] not taking into account these additional parameters. The cost of **Spiro-OMeTAD** was converted in euros using the current euro-dollar exchange of 1.22 ratio.

The prices of the chemicals and solvents have been obtained from the website of the major chemical suppliers known in Italy (Sigma-Aldrich, Fluorochem, TCI, VWR, Carlo Erba). Large-scale production could significantly affect these estimates by lowering the prices of reagents and solvents due to bulk quantities purchases.

Acknowledgements

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

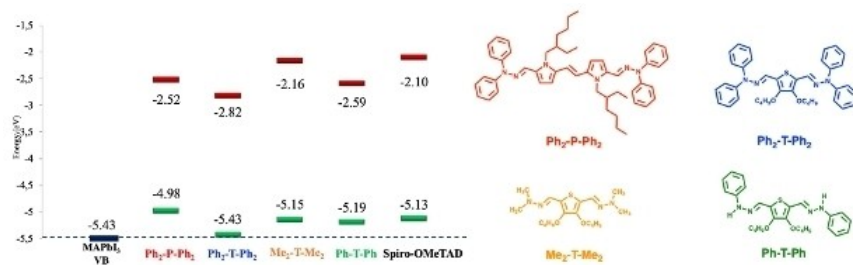The data that support the findings of this study are available from the corresponding author upon reasonable request.

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RESEARCH ARTICLE

Dr. C. Decavoli, Dr. C. L. Boldrini, Prof. A. Abbotto, Prof. N. Manfredi

Economical and Environmentally Friendly Organic hydrazone Derivatives Characterized by a Heteroaromatic Core as Potential Hole Transporting Materials in Perovskite Solar Cells

Electron-rich hydrazone-based molecules centred on thiophene or pyrrole π-bridges have been investigated in their optical and electrochemical properties as potential hole transport material for use in perovskite solar cells. A brief cost analysis has also been carried out to evaluate the sustainability of their synthetic process.