Design of cyclopentadithiophene-based small organic molecules as hole selective layer for perovskite solar cells

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Thiophene-based p-type molecules are being extensively investigated and employed in opto-electrical devices due to their intriguing semiconducting characteristics. Herein, we report the synthesis and characterization of 4H-cyclopenta[1,2-b:5,4-b']dithiophene-based core, having methoxy-substituted triphenylamine side arms as donor groups. These rationally designed molecules are obtained through easy cross-coupling reactions using few synthetic and purification steps. The synthesized molecules coded as **CDTh 1** and **CDTh-EtHex 2** showed excellent thermal stability, and the fabricated perovskite solar cells using the **CDTh 1** and **CDTh-EtHex 2** as hole transporting materials (HTMs) exhibited competitive device performance compared to the state-of-the-art Spiro-OMeTAD. Photoluminescence experiments of perovskite layers coated with these novel HTMs, show relatively high quenching suggesting the injection of hole from the valence band of perovskite into the HOMO of HTM. The estimated production cost was calculated to be a fraction of commercially available state-of-the-art Spiro-OMeTAD.

Introduction

In a very short time frame, organic-inorganic perovskites solar cells have outpaced all other third-generation solar technologies in terms of power conversion efficiency (PCE) and developed into highly investigated photovoltaics materials. This research line was upraised from the report by Miyasaka et al.¹ in 2009 using methyl ammonium lead iodide (CH₃NH₃PbI₃) perovskite as a light harvesting material in dye sensitized-solar cells. The intriguing properties of perovskites solar cells (PSCs)², such as simple and customizable devices architecture, versatility in deposition process³, tuneable optical absorption by anion or cation substitution^{4,5} in perovskite structure, designing of the new charge selective contacts⁶, have attracted chemist, physicist, engineers to make substantial progress in this new field^{7,8}.

Organic-inorganic hybrid perovskites show excellent opto-electrical properties such as high absorption coefficient, long electron and hole diffusion lengths, and high charge-carrier mobilities⁹. The overall PCE of the PSCs have improved from 3.8% to 22.7% in less than seven years¹⁰. Among the various device architectures explored, the most

efficient one is n-i-p type structure, in which perovskite layer acts as an intrinsic light absorber, sandwiched by a mesoporous (mp)-TiO₂ scaffold as a n-type selective contact and hole transporting material (HTM) as p-type material. The hole transporting layer plays a significant role in PSCs to achieve both long-term stability and enhanced performance.

To date, the most used and the efficient HTM is 2,2',7,7'-tetrakis (N,N-p-dimethoxyphenylamino)-9,9'-spirobifluorene, abbreviated as Spiro-OMeTAD. Despite its high performance, it suffers from UV instability and high-synthesis cost, which contributes to almost 25% of the whole module price¹¹. Due to its cumbersome multi-step synthetic procedure, demanding purification process, poor hole mobility and conductivity, it is of paramount importance to develop an alternative HTM with minimum number of steps and simple workup procedures to rival Spiro-OMeTAD. Recently, new polymeric, organometallic and small organic materials based HTMs have been explored to substitute Spiro-OMeTAD. As of now, PTAA is the most efficient polymer based HTM yielded high efficiency and suitability for inverted planar structure¹², while metal complex based on phthalocyanines represents the most common structure among organometallic HTMs^{13–15}. PTAA was found to be a material of choice, in terms of efficiency, easy production and purification, however as for Spiro-OMeTAD, its high cost necessarily lead to design of new small organic HTMs¹⁶. Different building blocks have been explored so far, such as triphenylamine¹⁷, indole^{18,19}, carbazole²⁰, triazatruxene^{21–24}, silolothiophene²⁵, thiophene derivatives^{26,27}, most of them suitably substituted with diarylamines, triarylamines and/or carbazole side groups^{28,29}. Thiophene derivatives represent one of the most important core for the development of materials for optoelectronic devices^{30,31}, in particular its application in PSCs is vouched due to their affinity with the perovskite^{32,33}. The sulphur atoms on the thiophene moiety create a strong interaction with

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perovskite's iodine atoms, enhancing the HTM-perovskite contact and improving the hole extraction^{34,3}.

Herein, we report the synthesis of simple triphenylamine-based HTMs with cyclopentadithiophene as core and study the influence of methoxy group inserted on triphenylamine and the alkyl group substituted on the cyclopentadithiophene moiety on their opto-electrical, thermal properties, and their performances in PSC devices.

Figure 1 a) Band alignment of the materials studied for the perovskite solar cells, along with the newly synthesized HTMs and Spiro-OMeTAD, and b) chemical structure of the CDTh 1, CDTh-EtHex 2 and Spiro-OMeTAD.

Results and discussion

Design and synthesis of new HTMs

The proposed molecules represented as 4,4'-(4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(N,N-bis(4-ethoxyphenyl)aniline) **CDTh 1** and 4,4'-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) **CDTh-EtHex 2** were rationally designed after optimization of our initial molecule 4,4'-(4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl) bis (N,N-diphenylaniline) **CDTh 0** (structure and synthetic route illustrated in Scheme 1).

Scheme 1 Synthetic route of **CDTh 0**

Initially, **CDTh 0** was employed as HTM in perovskite solar cells to evaluate its performance. The usage of **CDTh 0** as HTM in pure MAPbI₃ and mixed (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} PSCs gave encouraging PV results, with a PCE value of 8.57% and 3.72% respectively (PV parameters are summarized in Table S1).

Scheme 2: Synthetic route of **CDTh 1** and **CDTh-EtHex 2**. (i) Suzuki coupling: Pd(PPh₃)₄, K₂CO₃, reflux in THF.

The obtained results points towards unfavourable match between the highest occupied molecular orbitals (HOMO) of the **CDTh 0** and the perovskite valence band (Fig S1 and Table S2).

The data suggest that the mixed perovskite valence band is favourably aligned with the HOMO of **CDTh 0** HTM compared to the pure methyl ammonium lead triiodide (MAPbI₃).

HOMO level of **CDTh 0** was further tuned by insertion of methoxy group on triphenylamine moieties, which decreased the oxidation potential and assure a better hole extraction³⁵ and the desired molecule was named as **CDTh 1**. Further by molecular engineering, branched alkyl chains were inserted on the core to increase the solubility and named as **CDTh-EtHex 2**.

These two proposed HTMs (**CDTh 1**, **CDTh-EtHex 2**) based on 4H-cyclopenta[1,2-b:5,4-b']dithiophene core were synthesized by a facile Pd-mediated Suzuki coupling reaction for PSC application and their chemical structure are depicted in Fig.1 with their energy level diagram, while the synthetic route is illustrated in Scheme 2.

4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (compound 1 in Scheme 1) was synthesized as reported elsewhere^{36,37}, while the final compounds were synthesized through Suzuki-Miyaura cross coupling reaction, as illustrated below. The detailed synthesis of the intermediates, 4-Methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1), 4H-Cyclopenta[1,2-b:5,4-b']dithiophene (2) and 4,4-Bis(2-ethylhexyl)-

4H-cyclopenta[1,2-b:5,4-b']dithiophene (**3**) of the final compound is reported in Supporting Information, along with an estimation of the chemical cost of each intermediate and the final products.

The presence of alkyl substituents (2-ethylhexyl) on the cyclopentadithiophene core in **CDTh-EtHex 2** enhances the solubility in organic solvents such as dichloromethane, chlorobenzene and toluene, and their influence on the opto-electrical and photovoltaic properties was studied. It is important to note that the laboratory level rough cost estimation of these two new HTMs, **CDTh 1** (167.26 €/g) and **CDTh-EtHex 2** (179.05 €/g), were found to be more than three times lower than that of Spiro-OMeTAD (~600 €/g).³⁸ Table 1 shows the summary of the optical, electrochemical and thermal properties of these synthesized molecules.

HTM property evaluation

Figure 2a shows the UV-visible absorption spectra of **CDTh 1** and **CDTh-EtHex 2** dissolved in dichloromethane and their optical parameters are listed in Table 1. **CDTh 1** and **CDTh-EtHex 2** exhibit main absorption peaks in the visible region at 442 and 446 nm respectively, which is due to the π - π^* transition of the conjugated system, along with a hyperchromic shift for **CDTh-EtHex 2**. A side shoulder peak appears at 370 nm in both HTMs showing a minute absorption in UV-region. It can be deduced from the absorption spectra that the synthesized molecules show minimal absorption in the visible spectrum, which is an advantage to avoid reabsorption of the transmitted light and suggests its suitability for inverted configuration, as they will not compete with perovskite absorption in PSCs for light harvesting. **CDTh-EtHex 2** shows high extinction coefficient than **CDTh 1**. The λ_{max} of both **CDTh 1** and **CDTh-EtHex 2** is slightly red shifted compared to the absorption peak of Spiro-OMeTAD (Fig.2a), due to cyclopentadithiophene core. Furthermore, **CDTh-EtHex 2** shows an additional red shift with respect of **CDTh 1**, due to the presence of alkyl substituent on the thiophene-based core. The optical band gap (E_g) of HTMs estimated from the λ_{onset} of the absorption are 2.47 eV and 2.45 eV, respectively. The electrochemical properties of **CDTh 1** and **CDTh-EtHex 2** were investigated using cyclic voltammetry experiments were made (Fig.S3a) in dichloromethane at room temperature [$c \sim 1 \cdot 10^{-3}$ M] with TBAPF [0.1 M] as supporting electrolyte.

The HOMO energy level of **CDTh 1** and **CDTh-EtHex 2** was estimated from the first oxidation potential using the equation $E_{\text{HOMO}} = -4.4 - (E_{\text{ox}} - E^{1/2}(\text{Fc}/\text{Fc}^+))$, where E_{ox} is the onset oxidation potential (vs. Fc/Fc^+)³⁹. Therefore, the HOMO levels of **CDTh 1** and **CDTh-EtHex 2** were estimated to be -5.32 and -5.25 eV, respectively, which are a little deeper than the HOMO level of Spiro-OMeTAD (-5.22 eV), leading to a better match with the valence band of both $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ and MAPbI_3 perovskite, and a relatively higher V_{oc} (open circuit voltage) in PSCs than Spiro-OMeTAD. The lowest unoccupied molecular orbital (LUMO) level calculated using the expression, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$, are -2.86 and -2.81 eV (Table 1) for **CDTh 1** and **CDTh-EtHex 2**, respectively, which are slightly lower than LUMO of Spiro-OMeTAD (-2.20 eV) however, they still could effectively block electron transfer from perovskite to the Au electrode.

The **CDTh-EtHex 2** shows the lowest oxidation potential, due to the presence of electron donating ethyl-hexyl substituent on the cyclopentadithiophene core, which might result in a faster hole extraction from perovskite to the **CDTh-EtHex 2** HTM. While the relatively higher oxidation potential for **CDTh 1** will be advantageous for obtaining a high V_{oc} .⁴⁰

Figure 2 a) UV-vis absorption of **CDTh 1** and **CDTh-EtHex 2** and Spiro-OMeTAD b) Thermogravimetric analysis (TGA) curves recorded for **CDTh 1** and **CDTh-EtHex 2** under N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

The conductivity of these two HTMs was measured on substrates having interdigitating gold electrodes with a channel length of 2.5 μm . The HTMs were spin-coated onto the substrates from their corresponding solutions in chlorobenzene as described in the device preparation. The cobalt complex FK209 was added (6 mol%) to the solution to partially oxidize the HTM. The corresponding current voltage (I - V) curves are shown in Figure 3. The conductivity was calculated using Ohms law. The calculated conductivity for undoped **CDTh 1** and **CDTh-EtHex 2** were $1.2 \times 10^{-6} \text{ Scm}^{-1}$ and $5.5 \times 10^{-8} \text{ Scm}^{-1}$ respectively. After doping with cobalt complex FK209, the conductivity increased to $4.2 \times 10^{-4} \text{ Scm}^{-1}$ and $1 \times 10^{-5} \text{ Scm}^{-1}$ for **CDTh 1** and **CDTh-EtHex 2** respectively, which are 2-3 orders of magnitude higher than the undoped HTMs. In fact, the conductivity values of **CDTh 1** are very close to the ones observed with doped Spiro-OMeTAD ($\sigma = 4.06 \times 10^{-4} \text{ Scm}^{-1}$).

Even if the cobalt complex FK209 was not added as dopant in the PSCs devices, it was added in the HTL for conductivity measurements in order to have a better understanding on the differences between Spiro-OMeTAD and the novel HTMs and their compatibility with FK209 dopant. Since Spiro-OMeTAD is performing better with the addition of the cobalt complex, the same amount has been added to the newly synthesized molecules in order to allow a more accurate comparison.

The conductivity of **CDTh 1** is one order of magnitude higher than for the **CDTh-EtHex 2** ($\sigma = 1.06 \times 10^{-5} \text{ Scm}^{-1}$). The higher conductivity of **CDTh 1** might be explained by a better packing of the molecules in

the film as the presence of bulky alkyl chains in **CDTh-EtHex 2** may have an isolating effect and hinder intermolecular interactions.

Figure 3 Semi-logarithmic current-voltage plot of **CDTh 1**, **CDTh-EtHex 2** and Spiro-OMeTAD spin coated onto interdigitating gold electrodes.

Table 1: Summary of the optical, electrochemical and thermal properties of new compounds

HTM	$\lambda_{\max}(\text{nm})$	$\epsilon (10^4 \text{ M}^{-1}\text{cm}^{-1})$	$\lambda_{\text{onset}}(\text{nm})$	$E_g(\text{eV})$	HOMO (eV)	LUMO (eV)	$T_d(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
CDTh 1	442	6.08	502	2.47	-5.32	-2.86	325	200
CDTh-EtHex2	446	7.42	507	2.45	-5.25	-2.81	305	200

Steady state PL measurement at perovskite-HTM interface

In order to investigate the charge extraction capability of these HTMs at the perovskite/HTM interface, steady-state photoluminescence (PL) was measured and illustrated in Fig.4. Theoretically, the quenching of steady-state PL indicates the efficient charge extraction. It was found that both HTMs, **CDTh 1** and **CDTh-EtHex 2**, when deposited on perovskite layers, showed a higher PL quenching than perovskite/Spiro-OMeTAD film. This phenomenon suggests that these molecules can effectively extract holes from the perovskite at the perovskite/HTM interface.⁴¹ Moreover, **CDTh-EtHex 2** showed relatively higher quenching efficiency than **CDTh 1**, which is in agreement with its lower oxidation potential due to its electron donating alkyl side group and therefore leads to a faster hole transfer from perovskite to the HTM.³⁹

Figure 4. Photoluminescence (PL) emission spectra recorded for bilayer of mixed perovskite (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}/HTMs upon excitation at 532 nm.

Fabrication and characterization of perovskite solar cells

To exploit the practical utility of these newly developed **CDTh 1** and **CDTh-EtHex 2** HTMs, they were integrated in perovskite solar cell fabrication using two different types of perovskite, {MAPbI₃ and (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}}, since **CDTh 1** and **CDTh-EtHex 2** showed energetic level alignment with both perovskites. So, the devices were fabricated in a mesoscopic configuration using the mixed cation-anion (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} or pure MAPbI₃ perovskite, with the structure FTO/compact-TiO₂ (30nm)/mesoporous-TiO₂ (80nm) / (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} (750 nm) / HTM (65 nm) / Au (80 nm) and FTO/compact-TiO₂(30 nm)/mesoporous-TiO₂ (80 nm) / MAPbI₃ (300 nm) / HTM (75 nm)/ Au (80 nm) respectively. Both types of perovskite were deposited using one step method followed by solvent engineering. The details of the synthesis and device fabrication is given in supporting information. The most noticeable difference between these perovskite is the thickness of the capping layer, which resulted to be 750 nm and 300 nm respectively for (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} or pure MAPbI₃ perovskite. Fig.5. Furthermore, HTL thickness was estimated to be 65-70 nm in (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}-based devices and 75-80 nm for MAPbI₃-based devices, while for both perovskite, the HTM's concentration and spin-coating conditions were kept exactly the same for both HTMs. Moreover, these two HTMs present similar viscosity, which leads to the same thickness of the deposited layers. The reason of the difference in the thickness of HTM for both perovskites might be due to the difference in perovskite composition which may have dissimilar affinity towards HTM structure.

For the hole transporting layer deposition, the newly developed HTMs were dissolved in chlorobenzene solvent and only lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 4-*tert*-butylpyridine (*t*-BP) additives were used without any cobalt complex dopant.

However, it should be noted that Spiro-OMeTAD was used in the standard condition i.e. cobalt complex (FK209) dopant with LiTFSI and *t*-BP additives. Fig. S5 shows the cross-sectional SEM images of mixed perovskite and MAPbI₃ using Spiro-OMeTAD as HTM for comparison. The use of cobalt dopant induces instability in perovskite solar cells and the new HTMs **CDTh 1** and **CDTh-EtHex 2** without the use of FK209 as a dopant yielded comparable performance to Spiro-OMeTAD.

Figure 5 Cross-sectional SEM images of (a) mixed perovskite/CDTh 1; (b) mixed perovskite/CDTh-EtHex 2; (c) MAPbI₃/CDTh 1; (d) MAPbI₃/CDTh-EtHex 2.

Fig. 6a shows the current density–voltage (*J*–*V*) curves of the fabricated devices using **CDTh 1** and **CDTh-EtHex 2** as HTM and for comparison, Spiro-OMeTAD was used as reference device. The PV parameters for each configuration are summarized in Table 2, while the statistical data are listed in Table S3 (Supporting Information).

The devices based on MAPbI₃ perovskite and **CDTh 1** as HTM with a configuration of FTO/compact-TiO₂/mesoporous-TiO₂/perovskite/HTM/Au showed a *J*_{sc} 20.5 mA/cm², *V*_{oc} of 1030 mV, a FF of 70.8%, a series resistance (*R*_s) of 6.08 Ω cm² and a shunt resistance (*R*_{sh}) of 2788.95 Ω cm², yielding a PCE of 15%, while devices with **CDTh-EtHex 2** HTM showed improved photovoltaic behaviour in terms of efficiency value and, *J*_{sc} of 19.55 mA/cm², *V*_{oc} of 1020 mV, FF of 77.7%, *R*_s of 4.1 Ω cm² and a *R*_{sh} of 5228.89 Ω cm² leading to a PCE of 15.5%. A minute decrease in *J*_{sc} and *V*_{oc} was found while FF significantly enhanced to 77.7% compare to **CDTh 1**. The higher efficiency of **CDTh-EtHex 2** can be attributed to the high FF. It is reported the high FF is a result of low series resistance and high shunt resistance⁴², which is consistent with our results. The value of series resistance and shunt resistance for all type of devices is reported in Table 2. For the **CDTh-EtHex 2**, the *R*_s is very low and *R*_{sh} is very high compared to **CDTh 1** for the same thickness and at same doping level. Therefore, the improved performance of **CDTh-EtHex 2** in MAPbI₃ based perovskite solar cells can be ascribed to the low series and high shunt resistance. As the *R*_{sh} strongly relates with the leakage current due to the presence of pin holes or charge recombination^{43,44}, therefore, a large value of the *R*_{sh} in case of **CDTh-EtHex 2** in MAPbI₃ based perovskite solar cells indicates lower leakage current in **CDTh-EtHex 2** than **CDTh 1**, therefore, the enhanced fill factor is also assumed to originate from the reduced interfacial charge recombination.

The reference cell with Spiro-OMeTAD as HTM exhibited 16.2% efficiency. It is notable that these newly synthesized HTMs works well also with mixed perovskite, However, the PCE was lower comparatively to the MAPbI₃ based perovskite.

Figure 6 a) Current density–voltage curves for devices based on **CDTh 1**, **CDTh-EtHex 2** and Spiro-OMeTAD, b) Incident photon-to-current conversion efficiency (IPCE) spectra of the devices.

The devices based on mixed perovskite and **CDTh 1** as HTM showed improved performance compare to **CDTh-EtHex 2** and a *J*_{sc} 20.81 mA/cm², *V*_{oc} of 980 mV, a FF of 70.63 %, a series resistance (*R*_s) of 5.87 Ω cm² and a shunt resistance (*R*_{sh}) of 4004.16 Ω cm², yielding a PCE of 14.35%, while devices with **CDTh-EtHex 2** HTM showed poor performance and PCE of 13.77% was achieved. The higher efficiency of **CDTh 1** can be ascribed to the high value of FF.

One of the reason for this decrease in efficiency might be due to the high energy barrier (*E*_b) of 0.3–0.4 eV between the valence band of the (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} perovskite and HOMO of these two novel HTMs. While with MAPbI₃, the energy difference is 0.11–0.18 eV. Hence, we may conclude that for a favourable energy level matching, the energy difference (eV) should be in between 0.4 > Δ*E* ≥ 0.10. The other reason might be the morphological difference between these two perovskites with these new HTMs. A thin layer of HTM (65–70 nm) is deposited on large grains of mixed perovskite, as demonstrated by cross sectional SEM images (Fig. 5a & b). This thin layer might not be sufficiently thick to cover uniformly the rough surface of perovskite film and leads to pinhole defects. Therefore, due to these pinhole defects in HTM layer, perovskite could directly come in contact with Au cathode, and degrades perovskite as well as cathode contact due to the chemical reaction between the iodide ions in perovskite and metal cathode. Another possibility is the diffusion of metal cathode into perovskite results in short-circuit of device, which is further proved by a low value of *R*_{sh} with mixed perovskite using **CDTh-EtHex 2** HTM, which indicates

increased interfacial charge recombination and therefore it showed low fill factor. Hence further optimization of perovskite and HTM layer thickness, dopant concentration is required to achieve the higher efficiency in case of mixed perovskite based solar cells.

The PV parameters extracted from the *J-V* curves recorded in the backward and forward scans are summarized in Table S3, while the *J-V* curves along with the HI values are depicted in Figure S3. In case of MAPbI₃ based perovskite, the least hysteresis can be seen with **CDTh-EtHex 2** HTM based devices. While in (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} mixed perovskite, the least hysteresis was calculated for the **CDTh1** based devices. Fig. 6b illustrates the incident photon-to-electron conversion efficiency (IPCE) spectra of the fabricated devices for each configuration. The IPCE spectra represent the percentage of extracted electron per incident photon for each wavelength, and the integrated current for the devices are in agreement with the short circuit current density measured under 1 sun (Fig.S4 Supplementary information). The devices with mixed perovskite-based configurations, showed a lower IPCE response in the range from 550 - 800 nm, compared to Spiro-OMeTAD based devices. This lower response could be due to the presence of traps and recombination

sites at the perovskite/HTM interface,⁴⁵ which is further supported by the thin layer of HTM covered over the mixed perovskite causing pin hole defects and create sites for recombination which is further proved by lower value of shunt resistance. Additionally, a further possible reason for low IPCE at longer wavelength could be due to the self-absorption of reflected light from gold.

Table 1. The current–voltage (*J-V*) characteristics of MAPbI₃ and (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}-based devices with **CDTh 1** and **CDTh-EtHex 2** and Spiro-OMeTAD, measured under simulated AM 1.5G irradiation

Perovskite	HTM	$R_s (\Omega \text{ cm}^2)$	$R_{sh} (\Omega \text{ cm}^2)$	$V_{oc}(\text{mV})$	$J_{sc}(\text{mA}/\text{cm}^2)$	FF (%)	PCE(%)
(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15}	CDTh 1	5.87	4004.16	980	20.81	70.63	14.35
MAPbI ₃		6.08	2788.95	1030	20.53	70.84	15.01
(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15}	CDTh-EtHex 2	6.84	1486.07	1000	20.51	66.86	13.77
MAPbI ₃		4.19	5228.89	1020	19.55	77.69	15.51
(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15}	Spiro	5.18	10256.24	1000	21.41	75.54	16.30
MAPbI ₃		2.90	6074.17	980	21.16	78.08	16.19

The additives used for the deposition of hole transporting layer are as follows: For CDTh 1 and CDTh-EtHex 2, only LiTFSI, t-BP were used while for Spiro-OMeTAD LiTFSI, t-BP and FK209 dopant were used.

Experimental

Device fabrication

All chemicals and reagent were purchased from Sigma-Aldrich and TCI, and used without further purification. 2,2',7,7'-tetrakis (*N,N*-di-*p*-methoxy phenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Merck KGaA. Perovskite solar cells (PSC) devices were fabricated on laser etched FTO-coated glass (TEC, Pilkington). The substrates were cleaned by ultrasonication bath in Hellmanex, rinsed with deionized water, then ultrasonicated in acetone and in 2-propanol and finally dried by compressed air. A TiO₂ compact layer was deposited by spray pyrolysis at 450°C using 1mL of titanium diisopropoxide

bis(acetyl acetate) precursor solution (75% in 2-propanol, Sigma Aldrich) in 19 mL of pure ethanol using air as carrier gas. After the blocking layer deposition, a TiO₂ mesoporous layer (Dyesol paste, 30NRD) was deposited by spin coating (4000 rpm for 20 s) and then annealed them to 500°C for 30 min. Atop of this, methyl ammonium lead triiodide perovskite (MAPbI₃) or mixed cation halide perovskite ((FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}) was deposited by one step method followed by solvent engineering approach. For mixed cation halide perovskite, a 1.4 M mixture of lead iodide (PbI₂), lead bromide (PbBr₂) and a mixture of formamidinium iodide (FAI) and methyl ammonium bromide (MABr) were dissolved in 4:1 *N,N*-dimethylformamide (DMF) : dimethyl sulfoxide (DMSO) solution. While for the pure methyl ammonium perovskite, a 1.2 M solution of PbI₂ in DMSO was

left to stirring overnight at 80°C to promote the proper dissolution of lead iodide; then, a stoichiometric amount of methyl ammonium iodide was added and properly mixed by stirring for 10 minutes. The perovskite precursor solution was spin-coated on top of the mesoporous layer at 1000 rpm for 10 seconds and then 6000 rpm for 30 seconds. During the second step, chlorobenzene was dripped in the centre of the substrate during the last 10 seconds. After solvent treatment, the films were transferred onto a hotplate and annealed at 100°C for 1 hour. A 60 mM solution of the CDTh 1, CDTh-EtHex 2 and Spiro-OMeTAD was prepared by dissolving the appropriate amount of the HTMs in 1 mL of chlorobenzene, and standard additives 17.5 μ L of a lithium bis (trifluoromethylsulphonyl)imide (LiTFSI) prepared from the stock solution (520 mg of LiTFSI in 1 mL of acetonitrile), 28.8 μ L of 4-tert-butylpyridine (*t*-BP) were added. 21.9 μ L of a FK209 (Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III)Tris(bis(trifluoromethylsulfonyl)imide)) prepared from the stock solution (400 mg in 1 mL of acetonitrile) was added only in the Spiro-OMeTAD solution. Then 35 μ L of each HTM solution were dropped on the perovskite substrates of the solar cell samples described above and the samples were spin coated at 4000 rpm for 20 seconds. After that, 80 nm of gold was thermally evaporated atop of HTM under a vacuum level between 10^{-6} and 10^{-5} torr and used as cathode. All the solutions were prepared inside an argon filled glove box under controlled moisture and oxygen conditions (H_2O level: <1 ppm and O_2 level: <5 ppm).

Conclusions

In summary, by molecular engineering we have designed simple yet effective small-molecule based p-type organic semiconductor. We have shown how a minute alteration in the chemical structure affects opto-electrical properties of HTMs and influences the PV properties significantly. The high thermal stability of these novel HTMs was due to the insertion of functionalized cyclopentadithiophene core. **CDTh 1** and **CDTh-EtHex 2** can be synthesized and purified using short synthetic route with high-yield, using a simple Pd-catalyzed Suzuki coupling. In these molecules, column-chromatography purification grade is sufficient to reach comparable photovoltaic behaviour as of Spiro-OMeTAD, which requires a sublimation grade purification. Facile synthesis and simple purification process of the presented HTMs will also allow to reach low synthetic costs and wide market penetration. Photoluminescence quenching indicates that both HTMs, **CDTh 1** and **CDTh-EtHex 2** can efficiently extract holes from perovskite. The photovoltaic characteristics obtained with the newly designed HTMs, **CDTh 1** and **CDTh-EtHex 2**, were tested in two different types of perovskites and they were found to be at par with Spiro-OMeTAD, even without the addition additives such as Co-complex dopant. Additives help to achieve higher open circuit voltage, but at the cost of device stability. Due to its facile synthesis, purification process and performance in devices, **CDTh 1** and **CDTh-EtHex 2** are potentially attractive candidates to replace the expensive Spiro-OMeTAD.

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Notes and references

Author Contributions

LC made all the experiments and graphs, SK made electro-optical characterization, analysis of data and provide guidance to LC. IZ performed conductivity measurements and MKN supervised it and analysed the data. MS provide support for devices and chemical structure experiments. S.A directed and coordinated the research. All authors contributed to the completion of the final document.

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