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Phenanthrenone-based hole transport material for efficient dopant-free perovskite solar cells

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Abstract

Spiro-OMeTAD is the most popular hole transport material (HTM) for perovskite solar cells. The insertion of one carbonyl group into the spirobifluorene framework in spiro-OMeTAD gave a novel phenanthrenone-based hole transport material (spiro-PT-OMeTAD). It is found that the introduction of one carbonyl group into spiro-PT-OMeTAD led to a big difference in the absorption behaviors, frontier molecular orbital energy levels hole mobilities. The steady-state and photoluminescence characterization and the space-charge-limited-current measurement indicate that this phenanthrenone-based material plays an important role in hole collection and transportation in perovskite solar cells. As a result, the dopant-free perovskite solar cells based on spiro-PT-OMeTAD showed highly improved performance by exhibiting a short-circuit current density of 22.36 mA/cm², an open-circuit voltage of 0.99 V, and a fill factor of 0.62% under 1 sun illumination, which gave an overall power conversion efficiency (PCE) of 13.83%, compared to 10.5% for the spiro-OMeTAD based devices.

1. Introduction

Solar energy is a clean, sustainable and renewable energy sources with less negative impacts on the environment. Although currently the silicon solar cell is the mainstream commercial solar cell, new photovoltaic technologies including organometal halid perovskites [1-9] have been developed to achieve low-cost and high efficiency solar cells. Since Miyasaka et al. reported the application of CH₃NH₃PbX₃ (X = Br, I) perovskite as a sensitizer in dye-sensitized solar cells with the efficiency of 3.8% in 2009 [10], a rapid progress in the development of perovskite solar cells (pero-SC) has led to a PCE booming over 22% [11-12] via interfacial engineering [13-21] and composition modulation [22-27]. So pero-SC showed the great potential for efficient solar energy conversion due to its long exciton diffusion length and exciton lifetime [28-29], high absorption coefficient in the visible range and low loss in charge recombination [30-31]. So far it has attracted extensive research interest.

Hole transport materials (HTM) play an important role in charge carrier collection and transportation, which was produced on the perovskite photoactive layer. In pero-SC, organic molecular compounds [32-35], polymeric materials [36-38] and inorganic species [39-41] have been used as HTM. 2,2',7,7'-tetrakis(*N*,*N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene

(spiro-MeOTAD) was the most widely used HTM due to its high thermal stability, high-quality film formation capability and suitable frontier molecular orbital energy levels for charge transport [42-43]. In order to achieve high efficiency of pero-SC, many spiro-MeOTAD derivatives to date have been developed [44-47]. For example, Seok et al. applied the ortho-substituted derivative of spiro-OMeTAD as HTM and obtained better performance than the para- and meta-substituted derivatives [48]. Seo and coworkers used a fluorene-terminated HTM with a fine-tuned energy level and a high glass transition temperature to ensure highly efficient pero-SC with a steady-state efficiency of 22.85% [12]. Although high efficiency was achieved with a dopant via improving the conductivity of HTM, the doping method generally results in a complicated device fabrication procedure, and also leads to the mismatched energy levels [49]. In addition, the dopant such as Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI) can speed up degradation of device performance due to the deliquescent behavior [35].

In order to simplify the device fabrication process and reduce the overall device cost, efficient dopant-free HTM with good charge-carrier transport characteristics was highly desirable. So far the dopant-free HTM has demonstrated the great potential in achieving high efficiency pero-SC [50-56]. Jang et al. used novel conjugated small-molecule based on di(1-benzothieno)[3,2-b:2',3'-d]pyrrole framework as an HTM in pero-SC and reported a PCE of 18.09 % [57]. A polythiophene-based copolymer (PDVT-10) with excellent hole mobility was also used as dopant-free HTM for a pero-SC, which exhibited a high PCE of 13.4% under 100 mW cm⁻² illumination [58].

Herein, we introduced one carbonyl group into spiro-OMeTAD to yield 2,2',7,7'-tetrakis(bis(4-methoxyphenyl)amino)-10'H-spiro[fluorene-9,9'-phenanthren]-10'-one (spiro-PT-OMeTAD). The introduction of one carbonyl group could increase the stiffness of the backbone which led to the increase of glass-transition temperature for Spiro-PT-OMeTAD. Furthermore, the attachment of one carbonyl group to aryl group could increase conjugation length, which could tune the electronic structure of the resulting compound. The carbonyl group enhances the hole mobility of spiro-PT-OMeTAD over the spiro-OMeTAD, and the HOMO energy levels of spiro-PT-OMeTAD is higher than that of spiro-OMeTAD. When applied as dopant-free HTM in planar structure photovoltaic device, spiro-PT-OMeTAD-based perovskite ($FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$) [4, 59-62] solar cell demonstrated power conversion efficiency of 13.83%, much higher than that for the spiro-OMeTAD-based device (10.5%).

2. Experimental

General information

All chemicals were purchased from J&K Scientific, Titan, Acros, and Strem chemicals. Anhydrous solvents were obtained from an Innovative Technology solvent purification system. ¹H NMR spectra were recorded on a Bruker 400 MHz NMR instrument. Thermogravimetric analysis (TGA) was recorded on a TA SDT 2960 instrument at a heating rate of 10 °C/min under nitrogen. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a BRUKER ultrafleXtreme MALDI-TOF spectrometer. UV–vis absorption spectra were measured on Cary 60 spectrometer (Agilent Technologies). PL spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Cyclic

voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. The cyclic voltammograms were obtained at a scan rate of 100 mV/s. Degassed DCM was used as solvent for oxidation scan with tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) as the supporting electrolyte.

Devices Fabrication Process

The FTO substrate was thoroughly cleaned with a sequential sonication treatment in acetone, ethanol and distilled water, then was dried under nitrogen, and followed by ultraviolet/ozone treatment for 15 min prior to device fabrication. In this article, the conventional device structure (FTO/c-TiOx/Perovskite/HTM/Ag electrode) was applied. Compact TiO_x and mixed halide perovskites were prepared according to related literature [5]. The TiO_x precursor was spin coated on top of the FTO substrates at 4000 rpm for 30 s and then annealed at 450 °C for 45 min. The perovskite precursor solution (1.2 mol/L, \sim 50 µL) was spin coated on the top of TiO_x firstly at 1000 rpm for 10 s and secondly at 5500 rpm for 35 s. Then chlorobenzene (100 µL) was added on the perovskite film. The substrates were annealed at 100 °C for 10 min in glove box. The hole-transporting materials (70 mmol/L in chlorobenzene, ~50 µL) were spin-coated on the top of perovskite films. Finally, Ag electrode (~100 nm) was evaporated on the hole transport layer to complete the device manufacturing process. We performed the J-V measurement of our unencapsulated devices in an ambient environment with 40±3% relative humidity. The J-V curves were obtained under reverse/forward scan, which run at a voltage range from -1.2 to 1.2 V with a scan speed of 400 mV/s.

Hysteresis indices

The hysteresis indices (HI) of the spiro-OMeTAD and spiro-PT-OMeTAD were calculated, respectively, with the following formula [63].

$$HI = \frac{J_{RS}(0.8V_{OC}) - J_{FS}(0.8V_{OC})}{J_{RS}(0.8V_{OC})}$$

SCLC measurement

Space charge limited current (SCLC) was measured by Mott-Gurney

equation [64,65]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where *J* is the current density, ε_r is the relative dielectric constant of HTM usually 2-4 for organic semiconductor, herein we use a relative dielectric constant of 3, ε_0 is the permittivity of empty space, μ is the mobility of the HTM, *d* is the thickness of the HTM, and *V* is the internal voltage in the device.

Materials synthesis

2,7-bis(bis(4-methoxyphenyl)amino)-9H-fluoren-9-one

This fluorenone was prepared according literature procedure [66].

2,2',7,7'-tetrakis(bis(4-methoxyphenyl)amino)-10'H-spiro[fluorene-9,9'-phenanthren]-10'-one (spiro-PT-OMeTAD)

2,7-bis(bis(4-methoxyphenyl)amino)-9H-fluoren-9-one (2.0 g, 3.15 mmol) and P(OEt)₃ (10 mL, 58 mmol) were mixed in a flask (250 mL), then the reaction mixture was heated to reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (eluent: ethyl acetate/petroleum ether/dichloromethane 1:1:4) to afford the target material (30%, 1.0 g). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.9 Hz, 2H), 7.34 (d, J = 2.5 Hz, 2H), 7.03 (d, J = 8.8 Hz, 9H), 6.90 (d, J = 8.8 Hz, 8H), 6.81 (d, J = 8.8 Hz, 8H), 6.74 (d, J = 8.8 Hz, 8H), 6.70 (dd, J = 8.6, 1.9 Hz, 3H), 6.47 (d, J = 1.9 Hz, 2H), 3.77 (s, 14H), 3.71 (s, 10H). MS (MALDI-TOF) m/z: 1253.465. Anal. calcd for: C82H68N4O9 (%): C 78.59, H 5.43, N 4.47; found: 78.11, H 5.83, N 4.34.

3. Results and discussion

The synthetic route of spiro-PT-OMeTAD was depicted in Scheme 1. The intermediate 2,7-bis(bis(4-methoxyphenyl)amino)-9H-fluoren-9-one was prepared via Buchwald-Hartwig cross coupling reaction between 2,7-dibromo-fluoren-9-one and bis(4-methoxy-phenyl)amine. Then the amino functionalized fluorenone reacted with triethyl phosphite (TEP) to give 2:1 adducts of pentaoxyphosphoranes [67], which underwent rearrangement to afford the target compound, which was fully characterized with ¹H NMR spectroscopy (Figure S1), MALDI-TOF-MS and elemental analysis. All the analytical data supports the proposed structure. The

thermal properties of spiro-PT-OMeTAD were investigated with TGA and DSC measurement (Figure 1), and it demonstrated good thermal stabilities with the decomposition temperatures (corresponding to 5% weight loss) of 411°C and glass transition temperature (T_g) of 188 °C. The T_g of spiro-PT-OMeTAD is much higher than that of spiro-OMeTAD (124 °C) [68], resulting in better morphological stability. The UV–vis absorption spectra of spiro-PT-OMeTAD and spiro-OMeTAD were illustrated in Figure 2. These two compounds both show strong absorption around 380 nm. It's notable that spiro-PT-OMeTAD exhibits a weak absorption in the range of 400-500 nm, which would be attributed to intramolecular charge transfer from the substituted fluorene fragment to phenanthrenone unit. So spiro-PT-OMeTAD will not obstruct sunlight from efficiently reaching the active layer in the solar cells, and spiro-PT-OMeTAD has a narrower bandgap of 2.24 eV in comparison with that of spiro-OMeTAD (2.96 eV), which are determined by their absorption onset.

The electrochemical properties of spiro-PT-OMeTAD were studied with cyclic voltammetry (CV) measurement to determine its frontier molecular orbital energy levels (Figure S2). The first oxidation potential is slightly lower for spiro-PT-OMeTAD than for spiro-OMeTAD, indicating that spiro-PT-OMeTAD has higher HOMO energy level, which is due to the spatial π -orbital overlap between fluorene and carbonyl group in spiro-PT-OMeTAD [69]. The HOMO levels of spiro-PT-OMeTAD and spiro-OMeTAD are determined to be -4.70 eV and -4.84 eV, respectively, with the reference ferrocene/ferrocenium couple at -4.8 eV vs vacuum. The LUMO energy levels are estimated with the difference between the HOMOs and the optical bandgap (Table 1). Considering that spiro-PT-OMeTAD contains one additional C=O group, it's reasonable that spiro-PT-OMeTAD (-2.46 eV) has lower LUMO than spiro-OMeTAD (-1.90 eV). Nevertheless, it is sufficiently high to prevent electron back-transfer from the cathodic electrode to the perovskite.

In order to understand the photophysical properties of these two HTMs, density functional theory (DFT) calculations were performed to simulate the frontier molecular orbital spatial distributions at a B3LYP/6-31G(d) level (Figure 3). For spiro-OMeTAD, the HOMO is mainly distributed on the bis(4-methoxyphenyl)amine group and partially on fluorene unit, and its LUMO is distributed on fluorene unit. While the HOMO of spiro-PT-OMeTAD is localized in the substituted fluorene unit, and its LUMO is localized in phenanthrenone group. So these two compounds show similar HOMO energy levels, but different LUMO energy levels. The intrinsic

electron-withdrawing property of phenanthrenone helps us to explain the observation of lower LUMO of spiro-PT-OMeTAD. Thus the DFT calculation results were consistent with their photophysical properties and CV data.

In order to evaluate the performance of spiro-PT-OMeTAD as HTM for perovskite cells, dopant-free devices (Figure 4) with a configuration solar of FTO/TiO_x /perovskite (FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})₃)/HTM/Ag [5] were fabricated, where MA was methylammonium and FA was formamidinium. The devices based on spiro-OMeTAD were also built for comparison purpose. The J-V characteristics under standard 1 sun illumination and external quantum efficiency (EQE) spectra are shown in Figure 5, and the photovoltaic parameters are summarized in Table 2. The device based on spiro-PT-OMeTAD exhibited higher PCE of 13.83% ($V_{OC} = 0.99$ V, $J_{SC} =$ 22.36 mA cm⁻², FF = 0.62) under the reverse scan direction than that based on spiro-OMeTAD (10.5%, $V_{OC} = 1.02$ V, $J_{SC} = 21.78$ mA cm⁻², FF = 0.47) under parallel condition. The current density-voltage curves under forward scan direction were shown in Figure S3 and the device parameters are summarized in Table S1. It's worth noting that the J_{sc} value obtained from integrating the external quantum efficiency (EQE) curves is in good agreement with the measured one (Figure 5b). The overall PCE enhancement is mainly attributed to the improvement in J_{SC} and FF. To elucidate and illustrate the FF enhancement, the hole-transport properties of spiro-PT-OMeTAD and spiro-OMeTAD were investigated by a space-charge-limited-current (SCLC) analysis with device configuration of glass/ITO/PEDOT:PSS/HTL/MoO₃/Ag. The SCLC mobility (Figure 6) was calculated by Mott-Gurney equation. The hole mobility of spiro-PT-OMeTAD and Spiro-OMeTAD is estimated to be 3.84×10^{-4} cm² V⁻¹ s⁻¹ and 1.28×10^{-4} cm² V⁻¹ s⁻¹, respectively. In order to further the understanding of FF enhancement, the film morphology of perovskite, perovskite/Spiro-OMeTAD and perovskite/Spiro-PT-OMeTAD was studied by AFM, and the roughness of these three films was 36.18 nm, 10.06 nm and 9.13 nm, respectively (Figure S4). The uniform morphology usually benefits the charge transfer at the interface and produces less pin-holes and current leakage, thus leading to better device performance. This result indicates that spiro-PT-OMeTAD could efficiently conduct the hole and suppress charge recombination.

To determine the origin of the charge extraction properties of spiro-PT-OMeTAD, the interfacial charge transfer capabilities of the perovskite/spiro-PT-OMeTAD were

investigated by the steady-state photoluminescence (PL) measurement. As shown in Figure 7, when the perovskite film was coated with HTMs, its PL emission was significantly quenched due to electron transfers from the HOMO of HTMs to the excited state of perovskite [70]. Spiro-PT-OMeTAD exhibited a better quenching than spiro-OMeTAD due to its well-matched energy levels and a more efficient hole transfer between the perovskite and the phenanthrenone-based HTMs. In order to more study the hole transfer at the interface, we have measured the photoluminescence lifetime of perovskite with different HTMs on top, and the relevant data are shown in Figure S5. The photoluminescence lifetime of the pure perovskite layer was 22.89 ns. When the HTM was deposited on the perovskite layer, photo-generated electron-hole pairs were separated between perovskite and HTM, and the holes was transferred to the HTL to reduce the electron-hole pair recombination. The lifetimes were reduced to 4.79, and 4.52 ns for spiro-OMeTAD-coated and spiro-PT-OMeTAD-coated perovskite layers, respectively. So there is more efficient charge extraction with spiro-PT-OMeTAD as HTMs. Furthermore, the devices based on spiro-PT-OMeTAD exhibited low hysteresis. The hysteresis indices (HI) of the spiro-OMeTAD and spiro-PT-OMeTAD were estimated to be 0.0850, and 0.0505. The improved J_{SC} and FF values and the negligible hysteresis observed in spiro-PT-OMeTAD-based device indicate the excellent hole transportation and less charge accumulation at the perovskite/spiro-PT-OMeTAD interface [71].

4. Conclusion

In conclusion, a novel HTM (i.e. spiro-PT-OMeTAD) was designed and synthesized by the introduction of one carbonyl group into spiro-OMeTAD. The CV measurement and DFT calculation indicated these two compounds had similar HOMO energy levels but different LUMO energy levels. The SCLC studies revealed that spiro-PT-OMeTAD showed better hole transfer properties than spiro-OMeTAD. The steady-state PL measurement suggested that an efficient charge transfer occurred at the perovskite/spiro-PT-OMeTAD interface. As a result, dopant-free perovskite solar cells based on spiro-PT-OMeTAD exhibited better device performance than spiro-OMeTAD. It was clear that the introduction of one carbonyl group into spiro-PT-OMeTAD led to a great enhancement in device efficiency. The present results and findings may provide new insights for the design of novel and efficient HTMs.

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Fig 1. The TGA curve (left) and DSC curve (right) of Spiro-PT-OMeTAD at a heating rate of 10 $^{\rm o}C$ /min under $N_2.$

Chip Marine



Fig 2. UV–Vis spectra of Spiro-PT-OMeTAD and Spiro-OMeTAD in DCM at room temperature.



Spiro-OMeTAD

Spiro-PT-OMeTAD

Fig 3. Theoretically calculated spatial distributions and energies of the HOMO and LUMO levels of Spiro-OMeTAD and Spiro-PT-OMeTAD as well as their values of E_{g} .

HTM	λ_{max}	$T_{\rm d}$ [°C]	$T_{\rm g}[^{\rm o}{\rm C}]$	HOMO	LUMO	$E_{ m g}$
	[nm]			[eV]	[eV]	[eV]
Spiro-PT-OMeTAD	376.9	411	188	-4.70	-2.46	2.24
Spiro-OMeTAD	386.7	449	124	-4.84	-1.90	2.96

Table 1. Summary of Optical and electrochemical properties of the Spiro-OMeTAD and Spiro-PT-OMeTAD

 $T_{\rm g}$ = glass-transition temperature.

 $T_{\rm d}$ = temperature for 5% weight loss.

 $E_{\rm g}$ = energy gap calculated from the onset absorption wavelength.

HOMO is estimated by cyclic voltammetry, and LUMO is deduced from E_g and HOMO.





Fig 5. a) Current density–voltage characteristics pristine Spiro-OMeTAD and pristine Spiro-PT-OMeTAD. b) EQE spectra for the devices with pristine Spiro-OMeTAD and pristine (dopant free) Spiro-PT-OMeTAD as HTMs.

Table	2.	Summary	of	photovoltaic	parameters	of	dopant-free	devices	based	on
Spiro-	PT-	OMeTAD a	and	Spiro-OMeTA	AD					

HTM	$V_{\rm oc}$ [V]	$J_{\rm sc} [{\rm mA/cm}^2]$	FF	PCE [%]
Spiro-PT-OMeTAD	0.99	22.36	0.62	13.83
Spiro-OMeTAD	1.02	21.78	0.47	10.5



Fig 6. The hole mobility measurement of HTMs from the SCLC J-V characteristics obtained in the dark for hole-only devices.



Fig 7. Steady-state PL spectra of perovskite films, and perovskite films coated with spiro-OMeTAD and with spiro-PT-OMeTAD

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The introduction of one carbonyl group into HTM led to a great improvement in dopant-free device performance with PCE enhanced from 10.50% to 13.83%.

Highlights

The insert of carbonyl group increased structural rigidity and glass-transition temperature.

The introduction of carbonyl group into Spiro-PT-OMeTAD gave an increase in hole mobility.

The small roughness of perovskite/Spiro-PT-OMeTAD film led to improved device performance.