

# Novel hole transporting materials with a linear $\pi$ -conjugated structure for highly efficient perovskite solar cells†

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Junjie Wang,<sup>ab</sup> Shirong Wang,<sup>ab</sup> Xianggao Li,<sup>ab</sup> Lifeng Zhu,<sup>c</sup> Qingbo Meng,<sup>c</sup>  
Yin Xiao<sup>\*ab</sup> and Dongmei Li<sup>\*c</sup>

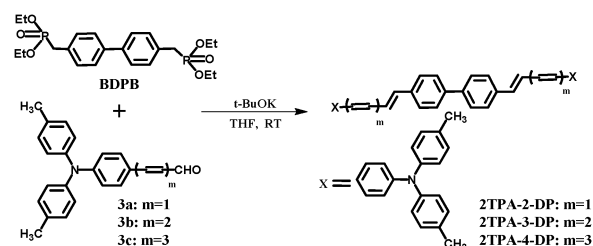
**Novel small-molecule hole transporting materials (HTMs) with a linear  $\pi$ -conjugated structure have been synthesized. The perovskite solar cell based on 2TPA-2-DP as the HTM exhibits an encouraging power conversion efficiency of 9.1% under AM 1.5 G (100 mW cm<sup>-2</sup>) illumination, which is the first demonstration of an effective perovskite solar cell using a linear structured HTM.**

In recent years, there have been considerable interests in the development of amorphous small-molecule hole transporting materials (HTMs). These small-molecule HTMs exhibit many outstanding advantages over polymers, such as structural versatility and identical molecular weight as well as relatively easy purification by chromatography, crystallization or vacuum sublimation.<sup>1</sup> They have been widely used in various electronic devices like emitting diodes, photovoltaic cells, photodiodes and field effect transistors.<sup>2</sup>

Solar cell is one of the most promising devices which convert sunlight directly into electricity. In order to relieve global warming, tremendous efforts have been devoted to develop low-cost and high-efficiency solar cells. Very recently, hybrid organic-inorganic perovskites (CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, where X corresponds to halogens) have been introduced as light harvesters in low cost solar cells.<sup>3</sup> Power conversion efficiencies (PCEs) of up to 15% have been reported using CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> as the light absorber and 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) as the HTM.<sup>4</sup> Although it has been demonstrated that spiro-OMeTAD is the most effective small-molecule HTM for perovskite solar cells, the spiro-bifluorene core in the spiro-OMeTAD molecule is relatively expensive due to its tedious synthetic methodology. To develop a cheaper alternative to spiro-OMeTAD,

Jeon and co-workers have developed novel pyrene arylamine derivatives as HTMs in fabricating mesoporous TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/HTM/Au solar cells with a PCE of 12.4%, a short-circuit current density ( $J_{sc}$ ) of 20.2 mA cm<sup>-2</sup> and an open-current voltage ( $V_{oc}$ ) of 0.886 V.<sup>5</sup> These pyrene arylamine derivatives also possess a bulky three-dimensional structure and their performance is comparable to the commonly used spiro-OMeTAD. To reveal the structure-property relationships of the HTM for more fundamental chemical aspects behind the structural design and to bring perovskite solar cells one step closer to viable commercial applications, exploration of more cost-effective small-molecule HTMs with a diverse structure is highly desirable.

In this communication, we report the synthesis and characterization of novel small-molecule HTMs with a linear  $\pi$ -conjugated structure, which is based on a diphenyl (DP) unit and a triphenylamine (TPA) unit linked with olefinic bonds (Scheme 1). The small molecular size of the HTMs could permit good pore filling of the TiO<sub>2</sub> layer. The large linear  $\pi$ -conjugated system makes the HTMs solution-processable, which enables fabrication of convenient devices in a wet process such as spin-coating and ink-jet printing. TPA usually serves as building blocks for construction of various HTM molecules with efficient hole mobilities.<sup>6</sup> The propeller-like TPA located at the terminal of the linear conjugated molecule can be expected to prevent close contact between the perovskite and HTMs, which is in favor of reducing the electronic coupling and charge recombination. The perovskite solar cell, based on one of the TPA derivatives as a HTM, shows a PCE of 9.1% under AM 1.5 G (100 mW cm<sup>-2</sup>) illumination without optimization of

Scheme 1 The synthetic route for 2TPA-*n*-DP (*n* = 2, 3, 4).

<sup>a</sup> Department of Applied Chemistry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. E-mail: xiaoyin@tju.edu.cn

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

<sup>c</sup> Key Laboratory for Renewable Energy, Chinese Academy of Sciences, Beijing 100190, China

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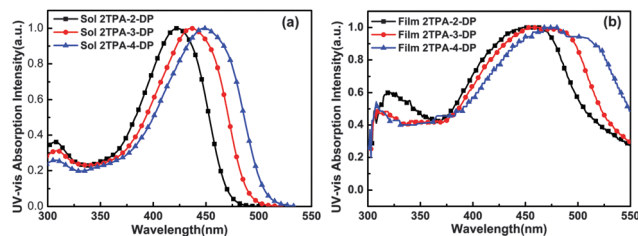


Fig. 1 UV spectra of **2TPA-*n*-DP** (*n* = 2, 3, 4): (a) in THF solutions (*c* = 10<sup>−5</sup> mol L<sup>−1</sup>); (b) in thin films.

the fabrication process and solar cell configuration. To the best of our knowledge, this is the first case for the adoption of small-molecule HTMs with a linear  $\pi$ -conjugated structure in fabricating perovskite solar cells with an impressive performance. The synthetic route for the HTMs is depicted in Scheme 1, and experimental details are given in the ESI†

The HTMs were obtained by a simple process based on Horner–Wadsworth–Emmons (HWE) condensation with high yields. **2TPA-2-DP** was successfully purified by recrystallization. Pure **2TPA-3-DP** and **2TPA-4-DP** were afforded by column chromatography. The synthesized HTMs were fully characterized by <sup>1</sup>H NMR spectrometry, mass spectrometry, IR spectrometry and elemental analysis (ESI†). The proton signals of the formyl group at  $\delta$  = 9.62–9.66 ppm, which are present in the <sup>1</sup>H NMR of aldehydes **3a–3c**, disappeared in the spectra of **2TPA-2-DP**, **2TPA-3-DP** and **2TPA-4-DP** (see Fig. S1, ESI†). In addition, the signals at  $\delta$  = 7.38–7.55 ppm assigned to the diphenyl moiety of the Horner reagent (BDPB) shift to 7.46–7.65 ppm after conjugation with triphenylamine units. The structures of **2TPA-*n*-DP** (*n* = 2, 3, 4) were further identified by mass spectrometry and their molecular ion (*[M]<sup>+</sup>*) peaks were found to be: 801.42 for **2TPA-2-DP** (calculated: 800.41); 853.45 for **2TPA-3-DP** (calculated: 852.44); and 905.48 for **2TPA-4-DP** (calculated: 904.47). After HWE condensation, the absorption bands of aldehydes (**3a–3c**) at 2832–2720 cm<sup>−1</sup> and 1689 cm<sup>−1</sup> disappear and absorptions at 968–997 cm<sup>−1</sup> (*trans* double bond) are noticeable in the FTIR spectrum of **2TPA-*n*-DP** (*n* = 2, 3, 4) (see Fig. S2, ESI†), indicating that the DP and TPA moiety has been successfully linked with an olefinic bridge. All the analytical data are consistent with the proposed structures. The three HTMs have good solubility in commonly used solvents, such as dichloromethane, chloroform, tetrahydrofuran, toluene, *etc.*

The UV-vis absorption spectra of **2TPA-*n*-DP** (*n* = 2, 3, 4) in dilute THF solutions and thin films are depicted in Fig. 1. In dilute THF solution, all HTMs show absorption bands in the visible region, and the absorption maxima are located at 423, 436 and 451 nm for **2TPA-2-DP**, **2TPA-3-DP** and **2TPA-4-DP**, respectively. This is due to inter-band transition between delocalized states, which can be derived from  $\pi$ -orbitals interaction of triphenylamine and olefinic bonds.<sup>7</sup> The UV-vis spectra of the thin films display a similar pattern as those of the solutions, which indicates that no significant aggregation or crystallization occurs in solid films.<sup>8</sup> The absorption maximum present a bathochromic shift (33, 22 and 26 nm for **2TPA-2-DP**, **2TPA-3-DP** and **2TPA-4-DP**, respectively) and

Table 1 Electrochemical characteristics of the TPA derivatives

	2TPA-2-DP	2TPA-3-DP	2TPA-4-DP
$E^{1/2}/\text{eV}$	0.45	0.40	0.39/0.60
$E_{\text{onset}}^{\text{ox}}/\text{eV}$	0.16	0.12	0.10
$E_{\text{HOMO}}^{\text{b}}/\text{eV}$	−4.96	−4.92	−4.90
$E_{\text{g}}^{\text{opt c}}/\text{eV}$	2.62	2.58	2.45
$E_{\text{LUMO}}^{\text{d}}/\text{eV}$	−2.34	−2.34	−2.45

<sup>a</sup> First onset oxidation potentials calibrated with Fc/Fc<sup>+</sup>. <sup>b</sup>  $E_{\text{HOMO}} = -4.8 - E_{\text{onset}}^{\text{ox}}$ . <sup>c</sup>  $E_{\text{g}}$  was determined from the intersection of the absorption and emission spectra.  $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$ . <sup>d</sup>  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$ .

slight broadening as a solid film, indicating enhanced inter-molecular interactions in the solid state.<sup>9</sup>

The energy levels of the compounds were characterized by cyclic voltammetry (CV, ESI†) and related data are summarized in Table 1. Energy levels are estimated by using the ferrocene (Fc) ionization potential value (4.8 eV) as the standard and calibrated with  $E^{1/2}(\text{Fc}/\text{Fc}^+) = 0.22$  V. Typical reversible oxidation ascribed to TPA derivatives is observed (Fig. S3, ESI†) for all compounds. **2TPA-2-DP** and **2TPA-3-DP** exhibit the one reversible oxidation process at 0.45 and 0.40 V (*vs.* Ag/Ag<sup>+</sup>) respectively, which could be attributed to the removal of electrons from the TPA moiety.<sup>10</sup> However, **2TPA-4-DP** shows the two reversible oxidation process at 0.39 and 0.60 V (*vs.* Ag/Ag<sup>+</sup>). The first oxidation can be assigned to the multi-electron oxidation process of the triphenylamine groups and the second oxidation corresponds to the removal of electrons from the interior moieties.<sup>11</sup> The **2TPA-2-DP**, **2TPA-3-DP**, and **2TPA-4-DP** have onset oxidation potentials of approximately 0.16, 0.12 and 0.10 V respectively *versus* Fc/Fc<sup>+</sup>, which is very close to that of spiro-OMeTAD (0.15 V *versus* Fc/Fc<sup>+</sup>).<sup>12</sup> This probably indicates that **2TPA-*n*-DP** could be potential alternatives to spiro-OMeTAD with good performance in solar cells. The HOMO values determined from the oxidation onset potential values of **2TPA-2-DP**, **2TPA-3-DP** and **2TPA-4-DP** with respect to Fc/Fc<sup>+</sup> are −4.96, −4.92 and −4.90 eV, respectively, which could match with the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (−5.44 eV) and result in the sufficient driving force for hole injection from CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> to the HTM.

The thermal properties of **2TPA-*n*-DP** (*n* = 2, 3, 4) were determined by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. S4, ESI†) and key thermal data are listed in Table 2. The high decomposition temperatures (*T<sub>d</sub>*, in the range of 367–409 °C) and glass transition temperature (*T<sub>g</sub>*, 102, 164 and 158 °C for **2TPA-2-DP**, **2TPA-3-DP**, **2TPA-4-DP**, respectively) suggest excellent thermal stability of these compounds, which is beneficial to their practical application in solar cells.

To understand the charge-carrier transport properties of **2TPA-*n*-DP**, their hole transporting mobilities were evaluated

Table 2 Thermal characteristics of the TPA derivatives

	2TPA-2-DP	2TPA-3-DP	2TPA-4-DP
$T_{\text{g}}/\text{°C}$	102	164	158
$T_{\text{m}}/\text{°C}$	214	225	279
$T_{\text{d}5}/\text{°C}$	343	320	295
$T_{\text{d}}/\text{°C}$	409	367	396

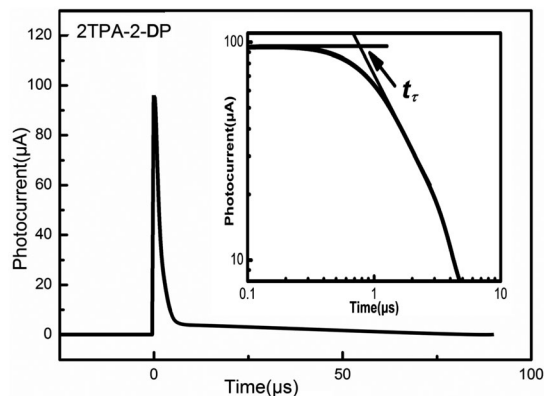


Fig. 2 Representative TOF transients for **2TPA-2-DP** at room temperature.

by time-of-flight (TOF) measurement (ESI†). Fig. 2 displays representative TOF transients for holes of **2TPA-2-DP**. It could be observed that the transient photocurrent exhibits significant current decay, which reveals a typical dispersive charge transport behavior. The hole mobility ( $\mu$ ) is calculated according to the equation  $\mu = d^2/Vt_r$ , where  $d$  is the film thickness and  $V$  is the applied bias voltage.<sup>13</sup> The transit time ( $t_r$ ) is evaluated from the intersection point of two asymptotes in the double logarithmic representations (inset of Fig. 2). At room temperature, hole-drift mobilities of **2TPA-2-DP**, **2TPA-3-DP** and **2TPA-4-DP** are  $1.09 \times 10^{-4}$ ,  $8.39 \times 10^{-5}$  and  $6.79 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively, at an electric field of  $3.1 \times 10^5 \text{ V cm}^{-1}$ . These results indicate that the extension of the conjugated system could retard charge carrier transportation in an efficient manner.<sup>14</sup> The hole mobilities of **2TPA-*n*-DP** are close to that of spiro-OMeTAD ( $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  determined using the same technique<sup>15</sup>), especially for **2TPA-2-DP**, which suggests that these materials could be considered as promising candidates for HTMs in solar cells.

Considering its high hole mobility, **2TPA-2-DP** was employed as the HTM to fabricate a FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/HTM/Au solar cell without any dopant for the HTM. The photovoltaic performance of the perovskite solar cell is evaluated from its photocurrent density–voltage ( $J$ – $V$ ) and IPCE characteristics (Fig. 3). The FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/**2TPA-2-DP**/Au solar cell exhibits an encouraging efficiency ( $\eta$ ) of 9.1%, a remarkably high open-circuit voltage ( $V_{oc}$ ) of 0.94 V and a short-circuit current density ( $J_{sc}$ ) of  $16.3 \text{ mA cm}^{-2}$ , and a fill factor (FF) of 59.7% under AM 1.5 G ( $100 \text{ mW cm}^{-2}$ ) illumination. These factors are comparable to that of the solar cell based on well-studied spiro-OMeTAD fabricated with the same process ( $J_{sc}$  of  $16.8 \text{ mA cm}^{-2}$ ,  $V_{oc}$  of 0.91 V, FF of 67.1%, and  $\eta$  of 10.2%), which evidences that HTMs with linear  $\pi$ -conjugated structures can also be suitable HTMs for high efficient perovskite solar cells. We believe that enhanced performance of the solar cell based on **2TPA-2-DP** as the HTM could be reached after optimization of the device architecture and the fabrication process. A primary study on stability of the perovskite solar cell with **2TPA-2-DP** as the HTM was also carried out. The unsealed cell was kept in dark at an ambient atmosphere and the  $J$ – $V$  characteristics were tested every day during a week. It is

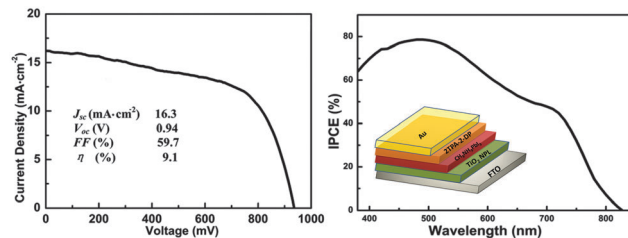


Fig. 3  $J$ – $V$  curve under AM 1.5 G illumination of  $100 \text{ mW cm}^{-2}$  and IPCE spectra of the FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/**2TPA-2-DP**/Au solar cell.

found that the efficiency retained 91% of its initial value after 7 days, while the  $J_{sc}$  remained constant; the  $V_{oc}$  and FF remain 97% and 94%, respectively. Further investigation about stability of the perovskite solar cell under working conditions is in process.

In summary, three novel small-molecule HTMs with a linear  $\pi$ -conjugated structure, namely **2TPA-2-DP**, **2TPA-3-DP** and **2TPA-4-DP**, were synthesized by a simple process with low cost and high yield. The **2TPA-*n*-DP** exhibit good thermal stabilities, high hole-drift mobilities and appropriate HOMO levels, indicating that these materials can be promising HTMs in different types of electronic devices. The perovskite solar cell based on **2TPA-2-DP** as the HTM exhibits an impressive conversion efficiency of 9.1%, which provide compelling evidence that small-molecule HTMs with a linear  $\pi$ -conjugated structure have great potential for the application in perovskite solar cells. To achieve higher efficiency, further optimization of the fabrication process and the device architecture is under investigation and will be reported later.

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