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A new thermal-stable truxene-based hole-transporting material for perovskite solar cells

Jiang Wang [a], Yu Chen [b, *], Mao Liang [b], Gaoyang Ge [b], Renjie Zhou [b], Zhe Sun [b], Song Xue [b, *]

[a] *Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, PR China*
[b] *Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, PR China*

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ABSTRACT

Developing effective hole-transporting material is critical to achieve high efficiency $CH_3NH_3PbI_3$ perovskite solar cells. A new thermal-stable truxene-based material, 2,7,12-tri(N,N-di(4-methoxyphenyl)amino)-5,5′,10,10′,15,15′-hexapropyltr-uxene, has been synthesized by a facile route. A reference compound, 1,3,5-tris(di-p-anisylamino)benzene, was prepared as well. Their optical, electronic properties, thermal stability and photovoltaic performances were investigated. This new truxene-based material exhibits a high decomposition temperature (432 °C), a high glass transition temperature (134 °C), and a suitable highest occupied molecular orbital level well-matched with the valence band of $CH_3NH_3PbI_3$. The device based on this new material in conjunction with a carbon counter electrode achieves a power conversion efficiency of 3.18% under the illumination of 100 mW cm^{-2}, which is better than that of the reference compound (0.93%). These results indicate truxene core is a promising building block for hole-transporting material.

1. Introduction

Organic–inorganic perovskite solar cells (PSC) have attracted much attention because of their low cost and high performance. Benefiting from the solid-state hole-transporting material (HTM), more than 19% of power conversion efficiency (PCE) has been achieved in a short term [1–4]. The state-of-the-art HTM is spiro-MeOTAD, which was used as a solid hole conductor in dye-sensitized solar cells (DSSCs), and it gave a PCE of 0.74% under full sunlight [5]. Recently, several attempts to develop alternative organic HTMs for sensitized solar cells have been made. Apart from polymer [6–8], and inorganic material [9,10] small molecules containing diarylamine or triarylamine groups have also been investigated due to their facile synthesis and good infiltration [11–15]. These organic small-molecule HTMs have excellent hydrophobic property, which can effectively prevent perovskite materials from being corroded by moisture.

However, the small organic materials tend to dimerize or crystallize, when they are spin-coated at ambient temperature or heated above their glass-transition temperature (T_g) [16–19]. Note that, an amorphous thin film with a low T_g is vulnerable to heat damage, which will in turn cause the degradation of PSC device. In this regard, design and synthesis of new HTMs with high thermal stability is imperative, since an important aspect for HTMs is the ability of the material to be processed in cell and module manufacturing.

Truxene derivatives have attracted a great deal of interest due to their exceptional solubility, high thermal stability and ease with which it may be modified [20–23]. At least twelve topics related to truxene have been identified, such as non-linear optical (NLO) [24], organic photovoltaics (OPVs) [25], organic light-emitting diodes (OLEDs) [26]. In our previous work, truxene dyes have been developed for dye-sensitized solar cells with outstanding charge-transfer performances [27–30]. We strong believe that truxene-based material has a great potential to be used as HTMs for optoelectronic devices. To the best of our knowledge, truxene-based HTMs for PSCs have not been reported yet.

In this paper, we report the synthesis and characterization of a new star-shaped truxene-based HTM, 2,7,12-tri (N,N-di(4-methoxyphenyl)amino)-5,5′,10,10′,15,15′-hexapropyltruxene (**1**). A reference HTM (1,3,5-tris(di-p-anisylamino)benzene), **BzTA** was

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* Corresponding authors. Fax: +86 22 60214252.
E-mail addresses: cy26tj@163.com (Y. Chen), xuesong@ustc.edu.cn (S. Xue).

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prepared for a comparative study. As shown in Fig. 1, both compounds exhibit a starburst structure with an angle close to 120°. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were measured to test the thermal stability of compound **1** and **BzTA**. Spectrum analyses, electrochemical measurements, and theoretical calculations were also carried out to characterize the absorption ability, energy level and optimized geometric structures of the HTMs. PSC devices based on compound **1** and **BzTA** were fabricated and measured to test the corresponding photovoltaic performances. The results indicate that truxene core is a possible candidate for HTM.

2. Experimental

2.1. Synthesis

All reactions were carried out under an argon condition and solvents were distilled from analytical grade reagents. $Pd_2(dba)_3$, *n*-Butyllithium, *t*-BuOK, $(t\text{-Bu})_3P$ were purchased from Energy Chemical (China). 4-tert-Pyridine (TBP) and 0.1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Aldrich. The melting points of the samples were measured with a RY-1 melting point apparatus (Tianfen, China), and temperatures were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer. The reported chemical shifts were referenced against TMS. High resolution mass spectra (HRMS) were obtained with a Micromass GCT-TOF mass spectrometer.

The synthesis route for compound **1** has been shown in Scheme 1. Synthesis of 10,15-dihydro-5H-diindeno[1,2-a; 1′,2′-c]fluorene (**2**) and 5,5′,10,10′,15,15′-hexapropyltruxene (**3**) have been reported in our previous work [31]. **BzTA** was prepared and purified according to a previous reference [32].

2.1.1. Synthesis of 2,7,12-tribromo-5,5′,10,10′,15,15′-hexapropyltruxene (*4*)

The similar synthesis procedure has been shown in a previous report [33]. Compound **3** (1.74 g, 3 mmol) was dissolved in 20 mL dichloromethane, then bromine (0.5 mL) was added into the solution at room temperature free from light. After 12 h, the reaction solution was washed with sodium bicarbonate solution three times and dried over anhydrous sodium sulphate. The solvent was removed by rotary evaporation. The residue was purified by column chromatography with silica gel to give pure compound **4** (2.24 g, 90%) as a green solid. M.p. 225–227 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, 3H, $J = 8.5$ Hz), 7.60 (s, 3H), 7.54 (d, 3H, $J = 8.5$ Hz), 2.88–2.73 (m, 6H), 2.10–2.05 (m, 6H), 0.63–0.43 (m, 30H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.06, 145.15, 138.91, 137.69, 129.58, 126.07, 125.76, 121.21, 56.17, 39.34, 17.40, 14.51. HRMS (ESI) calcd. for $C_{45}H_{51}Br_3$ $(M + H^+)$: 828.1551, found: 828.1543.

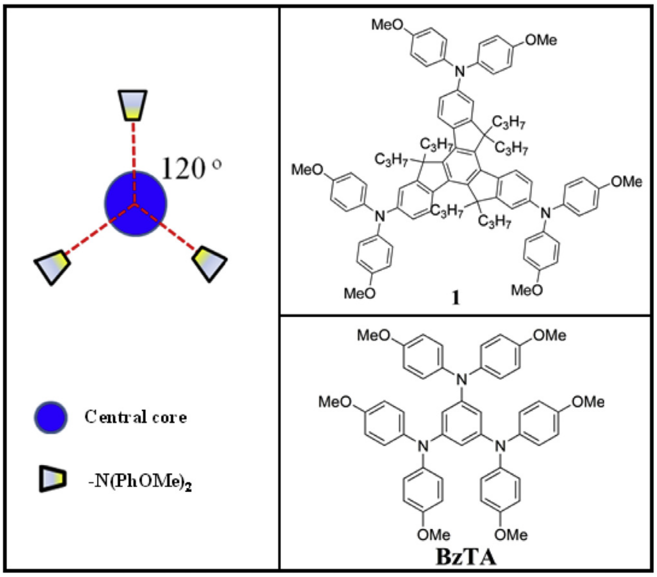

Fig. 1. The schematic structures of compound **1** and **BzTA**.

2.1.2. Synthesis of 2,7,12-tri(N,N-di(4-methoxyphenyl)amino)-5,5′,10,10′,15,15′-hexapropyltruxene (*1*)

To a 100 mL two neck round-bottom flask were added compound **4** (1.25 g, 1.50 mmol), bis(4-methoxyphenyl)amine (1.55 g, 6.75 mmol), $Pd_2(dba)_3$ (0.14 g), *t*-BuOK (1.01 g), $P(t\text{-Bu})_3$ (0.21 mL) and 30 mL anhydrous toluene. The reaction mixture was refluxed overnight under argon. After cooling down to room temperature, the mixture was exacted with ethyl acetate and washed by brine (3 × 15 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and concentrated in vacuum to give the crude product, which was purified by column chromatograph packed with silica gel to afford pure compound **1** (1.11 g, 58%) as a white crystal. M.p. 170–172 °C. ^1H NMR (DMSO, 400 MHz): δ 7.99 (3H, d, $J = 8.4$ Hz), 7.06 (12H, d, $J = 8.8$ Hz), 6.97 (3H, s), 6.93 (12H, d, $J = 8.8$ Hz), 6.75 (3H, d, $J = 8.4$ Hz), 3.75 (18H, s), 2.74–2.61 (6H, m), 1.81–1.66 (6H, m), 0.62–0.38 (30H, m). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.67, 155.06, 147.06, 142.59, 141.61, 137.96, 133.91, 126.31, 125.13, 119.13, 115.13, 114.72, 55.66, 55.44, 39.31, 17.51, 14.77. HRMS (ESI) calcd. for $C_{87}H_{93}N_3O_6$ $(M + H^+)$: 1276.7082, found: 1276.7064.

The ^1H NMR and ^{13}C NMR of compounds **4** and **1** are given in the supplementary materials.

2.2. Spectral, electrochemical and thermal stability measurements

The absorption spectra of compound **1** and **BzTA** in solution and coated on mesoporous TiO_2 and $TiO_2/CH_3NH_3PbI_3$ films were measured by SHIMADZU UV-2600 spectrophotometer. Fluorescence measurements were carried out with a HITACHI F-4500 fluorescence spectrophotometer. The morphology and structural properties of the films were analyzed using a ULTRA plus ZEISS field emission scanning electron microscope (FESEM) and a Bruker AXS-D8 Advance X-ray diffractometer (XRD) using Cu Ka radiation.

Cyclic voltammetry (CV) measurements for compound **1** and **BzTA** were performed on a Zennium electrochemical workstation (ZAHNER, Germany) using a three-electrode system. Tetrabutylammonium hexafluorophosphate ($n\text{-}Bu_4NPF_6$) of 0.1 M was added into a dichloromethane solution (DCM) as electrolyte. An Ag/0.01 M $AgNO_3$ electrode (acetonitrile as solvent) was used as the reference electrode. In three-electrode system of compound **1**, a FTO conductive glass was used as the working electrode, and a glass carbon electrode was used as the counter electrode. In three-electrode system of **BzTA**, platinum net was used as the working electrode, and a FTO conductive glass was used as the counter electrode. The scan rates were 50 mV/s. The measurements were calibrated using ferrocene as standard. The redox potential of ferrocene internal reference is taken as 0.63 V versus NHE.

The thermal stability was determined by thermogravimetry (TG) and differential scanning calorimetry (DSC). TG analyses were performed on TG 209 F3 Tarsus (NETZSCH, Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere. DSC analyses were conducted on DSC 200 F3 Maia (NETZSCH, Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere.