

## Photochemistry

# Efficient Hole Transporting Materials with Two or Four N,N-Di(4methoxyphenyl)aminophenyl Arms on an Ethene Unit for Perovskite Solar Cells

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**Abstract:** Novel steric bulky hole transporting materials (HTMs) with two or four *N*,*N*-di(4-methoxyphenyl)aminophenyl units have been synthesized. When the **EtheneTT-PA** was used as a hole transporting material in perovskite solar cell, the power conversion efficiency afforded 12.77% under AM 1.5 G illumination, which is comparable to the widely used **spiro-OMeTAD** based solar cell (13.28%).

Organic-inorganic hybrid perovskite solar cells have attracted great attention due to their high efficiency and low cost.<sup>[1]</sup> The organometal halide perovskites (CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, X=Cl, Br, I) have been introduced as light harvesters due to their direct band gap, large optical absorption and high mobility.<sup>[2]</sup> An impressive photovoltaic performance around 15% power conversion efficiency was achieved using perovskites as a light harvester and 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) as a hole transporting material (HTM).<sup>[3]</sup> The most effective HTM for the hybrid solar cells is spiro-OMeTAD in terms of the efficiency and stability. However, the high synthetic cost of spiro-OMeTAD may be a major obstacle for the general utilization of the perovskite solar cells. Therefore, it is highly desirable to develop low cost HTM material or alternative cell architectures. The development of HTMfree solar cells has already demonstrated impressive power conversion efficiency with 9-10%.<sup>[4]</sup> For the benefit of low cost and good stability, the p-type conducting polymers have been employed.<sup>[5]</sup> Also, some small molecule HTMs remain a promising target because they are quite cheap and synthetically easy compared to the spiro-OMeTAD. Recently, impressive photovoltaic performance has been achieved using small molecule HTMs such as bathocuproine,<sup>[6]</sup> azomethine-,<sup>[7]</sup> 3,4-ethylenedioxythiophene-,<sup>[8]</sup> pyrene-,<sup>[9]</sup> linear  $\pi$ -conjugated-,<sup>[10]</sup> butadiene-,<sup>[11]</sup> **spiro-OMeTAD** derivative-,<sup>[12]</sup> carbazole derivative-,<sup>[13]</sup> tetrathiafulvalene-,<sup>[14]</sup> tetraphenyl-benzidine-,<sup>[15]</sup> oligothiophene derivative-,<sup>[16]</sup> and spiro-thiophene<sup>[17]</sup> derivative-based materials, which show efficiencies in the range of 10–15%. Recently, we<sup>[18]</sup> reported quinolizino acridine-, star-shaped triphenylamino-, and triazine-based HTMs, exhibiting high conversion efficiencies with approximately 14%. Nevertheless, most small molecule HTMs are still expensive, together with low conversion efficiency and low stability compared to **spiro-OMeTAD**. Therefore, the development of cheap HTMs with operation stability is still very important.

Herein, we report new types of hole transporting materials by incorporating an ethylene unit into tetraphenyl benzidine or substituting four triphenylamines into the ethylene unit. The molecular structure of the two HTMs is shown into Figure 1.

The synthetic outline for the preparation of bis[(4-methoxy-phenyl)aminophenyl]ethene (EtheneDTPA) and tetrakis[(4-me-



Figure 1. Chemical structures of: a) EtheneDTPA, and b) EtheneTTPA.

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Scheme 1. Outline for the synthesis of EtheneDTPA and EtheneTTPA.

thoxyphenyl)aminophenyl]ethene (**EtheneTTPA**) is shown in Scheme 1. The key step for their syntheses is the N-arylation<sup>[19]</sup> of bis(4-fluorophenyl)methanone and 4,4'-dimethoxydiphenylamine. The final HTM **EtheneTTPA** was synthesized by McMurry coupling<sup>[20]</sup> of bis(4,4'-(dimethoxydiphenylamino)phenyl)methanone in the presence of Zn and TiCl<sub>4</sub>. The target HTM **EtheneTTPA** was obtained in 75% yield.

The UV/Vis spectra of EtheneDTPA and EtheneTTPA measured in chlorobenzene are shown in the insert of Figure 2a. As summarized in Table S1 in the Supporting Information, the UV/Vis absorption peaks of EtheneDTPA and EtheneTTPA were observed at 403 and 370 nm, respectively. The  $\lambda_{abs}$  of EtheneDTPA was shown to be red-shifted by 33 nm compared with that of EtheneTTPA. This large bathochromic shift was attributed to the more planar configuration of EtheneDTPA. The dihedral angle between the ethylene and the phenyl unit in EtheneDPTA is 4.3°. On the other hand, the dihedral angle between the ethylene and the phenyl unit in EtheneTTPA is 22.3°, which is more twisted due to the steric hindrance of peripheral substituents. The fluorescence spectrum of EtheneDT-PA exhibits an emission at 463 nm with a small Stoke's shift of 60 nm compared with a large Stoke's shift of 192 nm in EtheneTTPA, demonstrating that a small structural change in the excited state occurs in EtheneDTPA. Figure 2a shows the absorption spectra of the perovskite-coated mesoporous TiO<sub>2</sub> films with the two HTMs. Two HTMs-coated films exhibit an enhanced absorption band from 360 to 560 nm.

Figure 2 b shows the energy level diagram of the corresponding components in the device. The energy level of HTMs was determined by cyclic voltammetry. The HOMO levels of **EtheneDTPA** and **EtheneTTPA** were measured to be -5.19 and -5.02 eV, respectively, which have a suitable energy level with the CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> (~5.43 eV). Figure 2 c shows the cross-sectional scanning electron microscopy (SEM) images. It shows

the formation of a well-defined hybrid structure with clear interfaces. The thickness of  $TiO_2$  film incorporated with perovskite and HTM layer is 620 nm, respectively.

We prepared PSCs using the new molecules and spiro-OMeTAD by doping with additives such as 4-tert-butylpyridine (tBp) and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI)<sup>[21]</sup> into the HTM as detailed in the Supporting Information. Figure 3 a shows photocurrent density-voltage (J-V) curves of three devices. For reference, the device with spiro-OMeTAD as HTM was fabricated. In Table 1, we summarize the device performance parameters, as extracted from fitting of the J-V curves in Figure 3a. The **EtheneDTPA**-based device gave  $J_{sc} =$ 16.99 mA cm<sup>-2</sup>,  $V_{oc} = 0.99$  V, and ff = 0.64, affording PCE = 10.26%. Under similar condition, the EtheneTTPA- and spiro-**OMeTAD**-based cells gave a  $J_{sc} = 21.29$  and 21.27 mA cm<sup>-2</sup>, a  $V_{\rm oc}$  of 0.91 and 0.94 V and ff of 0.65 and 0.66, corresponding to a  $\eta$  of 12.59 and 13.20%, respectively. Figure 3b shows the incident photon-to-current conversion efficiency for three perovskite cells. Generation of  $J_{sc}$  starts at approximately 800 nm and reaches peak values of over 78% over the entire visible region. The integrated photocurrent density of EtheneDTPA and EtheneTTPA is 16.12 and 20.22 mA cm<sup>-2</sup>, respectively, which is in good agreement with the measured photocurrent density of 16.99 and 21.29 mA cm<sup>-2</sup>. The EtheneDTPA-based cell showed a high open circuit voltage ( $V_{oc}$ ), which was about 80 mV higher than that of EtheneTTPA-based cell. This can be rationalized considering that the  $E_{\text{HOMO}}$  for **EtheneDTPA** was about 170 meV lower than the value for EtheneTTPA. The high J<sub>sc</sub> of the EtheneTTPA-based cell compared to the EtheneDT-PA-based one is attributable to the broad and red-shifted absorption and its low series resistance (R<sub>s</sub>) of the mp-TiO<sub>2</sub>/ CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub>/EtheneTTPA device. From the slope of J-V curve around  $V_{or}$ , the  $R_s$  values of **EtheneDTPA**- and **EtheneTTPA**based cells are calculated to be 31.8 and 19.3  $\Omega$  cm<sup>-2</sup>, respec-



**Figure 2.** a) Absorption and emission spectra of the HTMs in chlorobenzene. Inset: UV/Vis absorption spectra of HTMs coated on mp-TiO<sub>2</sub>/MAPbI<sub>3</sub> films. b) Cross-sectional field-emission scanning electron microscopy (FE-SEM) image of mp-TiO<sub>2</sub>/MAPbI<sub>3</sub>/HTMs/Au. c) Energy level diagram of each component.

tively, in which the lower value of  $R_s$  in the latter cell results in the enhanced photocurrent density. The high fill factors in the **EtheneTTPA**- and **spiro-OMeTAD**-based cells followed a trend identical to those found among the conductivities and mobilities. To check the effect of hole mobility on the fill factor, we measured the hole mobility of HTMs form the space charge limitation of current (SCLC) *J–V* characteristics. The hole mobility values of **EtheneDTPA** and **EtheneTTPA** evaluated using the Mott–Gurney law<sup>[22]</sup> are calculated to be  $2.24 \times 10^{-5}$  and  $4.45 \times 10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. The high hole mobility of **EtheneTTPA**- compared with that of the **EtheneDTPA**-based cell led to an improved fill factor.

Figure 4 shows the photovoltaic performance during the long-term aging test of two devices. After 200 h of aging, the

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HTM		J <sub>sc</sub> [mA cm <sup>-2</sup> ]	V <sub>oc</sub> [V]	ff	η [%] <sup>[a]</sup>
EtheneDTPA	best	18.17	1.03	0.61	11.42
	average	16.99	0.99	0.61	10.26
EtheneTTPA	best	21.24	0.92	0.67	13.0
	average	21.29	0.91	0.65	12.5
Spiro-OMeTAD	best	21.66	0.97	0.66	13.82
	average	21.27	0.94	0.66	13.20

Communication



Figure 3. a) Photocurrent–voltage (J-V) curves of the solar cells with EtheneTTPA (**a**), EtheneDTPA (**b**) and spiro-OMeTAD (**a**) as the HTMs, respectively. b) Corresponding IPCE spectra.

initial efficiency of 12.64% of the **EtheneTTPA**-based cell decreased to 8.04%, giving a 36.4% reduction. On the other hand, the initial efficiency of 10.22% of the **EtheneDTPA**-based cell sharply decreased to 5.82%, giving a 43.1% reduction. The stability of the **EtheneTTPA**-based cell compared with the **EtheneDTPA**-based one may be attributable to an interfacial tight packing due to a planar and sterically bulky configuration.

In summary, we have designed and synthesized two novel ethylene based HTMs with two or four triphenylamine units. Although the photophysical property of the two HTMs is simi-



Figure 4. Time-course changes in the performance parameters of the solar cells with EtheneDTPA ( $\bullet$ ) and EtheneTTPA ( $\bullet$ ) as the HTMs, respectively.

lar, the photovoltaic performance is quite different depending on the number of peripheral substituents. The **EtheneTTPA**based cell affords an overall conversion efficiency of 13.09%, showing a comparable photovoltaic performance to the **spiro**-**OMeTAD**-based cell (13.87%). We believe that the development of highly efficient hole transporting materials comparable to the **spiro-OMeTAD** is possible through meticulous molecular design, and studies directed to this goal are now in progress.

## **Experimental Section**

#### Synthesis and characterization of materials

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled as appropriate. All reagents were purchased from Sigma–Aldrich and TCI. 4-(Bis(4-methoxyphenyl)amino)benzal-dehyde  $(1)^{[23]}$  and 4,4'-dimethoxydiphenylamine  $(2)^{[24]}$  were synthesized using procedures from the literature.

#### (E)-4,4'-(Ethene-1,2-diyl)bis(N,N-bis(4-methoxyphenyl)aniline)

[EthyleneDTPA]: A 500 mL three-neck round-bottom flask equipped with a reflux condenser, magnetic stir bar, nitrogen inlet and rubber septum was charged with anhydrous tetrahydrofuran (150 mL). The flask was cooled to  $0^{\circ}$ C and titanium tetrachloride (7.36 mL, 38.8 mmol) was added dropwise by syringe. Zinc (5.07 g, 77.6 mmol) was then added in small portions to the emulsion, and the resulting mixture was refluxed for 45 min. The reaction mixture was cooled to 0°C and a solution of 4-formyltriphenylamine (5.3 g, 19.4 mmol) in anhydrous THF and pyridine (5 mL) was added dropwise from an addition funnel. The mixture was then refluxed, and the progress of the reaction was monitored by TLC (dichloromethane) until completion. The mixture was then cooled and poured into water (80 mL). The resulting emulsion was stirred for 20 min and then partitioned in a separatory funnel. The aqueous layer was extracted with dichloromethane (100 mL), and the combined organic layers were washed with water  $(3 \times 80 \text{ mL})$ . The solution was then dried with MgSO<sub>4</sub> and the solvent was removed by rotary evaporator. The resulting solid was recrystallized from ethanol to yield a yellow solid (4.45 g, 90%). <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 7.51 (d, 2 H, J = 8.4 Hz), 7.42 (d, 2 H, J = 8.4 Hz), 7.07 (d, 10 H, J = 8.7 Hz), 7.00 (d, 2 H, J=9.0 Hz), 6.92 (d, 6 H, J=9.0 Hz), 6.84 (d, 4 H,  $J=9.3 \text{ Hz}), 3.79 \text{ ppm (s, 12H);} {}^{13}\text{C NMR (75 MHz, [D_6]acetone):} \delta=122.7, 123.3, 123.6, 124.1, 124.8, 126.9, 127.5, 129.6, 130.2, 132.3, 147.4, 147.9 \text{ ppm; MS: } m/z 634.28 [M^+]; elemental analysis calcd for C_{42}H_{38}N_2O_4: C 79.47, H 6.03; found: C 79.08, H 5.91.$ 

**Bis(4-bis(4-methoxyphenyl)amino)phenyl)methanone (3)**:<sup>[16]</sup> In a three-neck flask compound **2** (2 g, 8.72 mmol) and sodium *tert*-butoxide (1.2 g, 12.49 mmol) are dissolved in 25 mL anhydrous dimethylformamide. Then bis(4-fluorophenyl)methanone (0.86 g, 3.94 mmol) in 15 mL anhydrous dimethylformamide solution was slowly added dropwise over 1 h under N<sub>2</sub> atmosphere. The reaction mixture was refluxed for 10 h. Upon cooling, the mixture was poured into 100 mL ice water, then a deep yellow solid precipitate was washed with ethanol and filtered to yield a solid (67%). <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 7.58 (d, *J* = 9.0 Hz, 4H), 7.16 (d, *J* = 6.9 Hz, 8H), 6.95(d, *J* = 6.9 Hz, 8H), 6.76 (d, *J* = 9.0 Hz, 4H), 3.80 ppm (S, 12H); <sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 193.0, 158.2, 153.0, 140.1, 132.1, 129.6, 128.0, 116.9, 115.8, 55.7 ppm; MS: *m/z* 636.26 ppm [*M*<sup>+</sup>]; elemental analysis calcd for C<sub>41</sub>H<sub>36</sub>N<sub>2</sub>O<sub>5</sub>: C 77.34, H 5.70; found: C 77.02, H 5.59.

4,4',4'',4'''-(Ethene-1,1,2,2-tetrayl)tetrakis(N,N-bis(4-methoxyphenyl)aniline) [EtheneTTPA]:<sup>[17]</sup> A suspension of zinc (0.3 g, 1.28 mmol) in dry tetrahydrofuran (8 mL) was stirred under nitrogen at 0°C for 10 min. Titanium(IV) chloride (0.07 mL, 0.64 mmol) was injected slowly over a period of 30 min, the ice-salt-water bath was removed and the reaction mixture was heated under reflux for about 2 h. After, a solution of compound 3 (0.2 g, 0.31 mmol) in dry tetrahydrofuran (2 mL) was added slowly using a needle/syringe and the reaction was refluxed, overnight. The reaction mixture was guenched with a 5% aqueous solution of ammonium chloride. The organic extracts were combined, washed with water, dried over MgSO<sub>4</sub>, filtered and the solvent was removed using a rotary evaporator. The crude product was washed with ethanol and filtered to yield a solid (75%). <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta = 6.98$  (d, J = 8.4 Hz, 8H), 6.86 (d, J = 8.4 Hz, 8H), 6.82 (d, J =9.0 Hz, 4 H), 6.66 (d,  $J\!=\!8.4$  Hz, 4 H), 3.75 ppm (S, 12 H);  $^{13}\mathrm{C}$  NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta = 156.7$ , 147.5, 141.5, 137.4, 132.9, 127.1, 126.6, 120.4, 115.4, 55.7 ppm; MS: *m/z* 1240.54 [*M*<sup>+</sup>]; elemental analysis calcd for C<sub>82</sub>H<sub>72</sub>N<sub>4</sub>O<sub>8</sub>: C 79.33, H 5.85; found: C 79.01, H 5.67.

#### Measurements and instruments

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts,  $\delta$ , were calibrated against TMS as an internal standard. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. The absorption and photoluminescence spectrometer were recorded on a PerkinElmer Lambda 2S UV-visible spectrometer and Perkin LS fluorescence, respectively. Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.). Redox potential of materials was measured in dichloromethane solution with  $0.1 \text{ M} (nC_4 H_9)_4 \text{NPF}_6$  as the supporting salt. The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of 0.785 mm<sup>2</sup>, which was polished down to 0.5 µm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgCl secondary electrode. Solar cell efficiencies were characterized under simulated 100  $\rm mW\,cm^{-2}$  AM 1.5 G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using an NREL certified silicon diode with an integrated KG1 optical filter; spectral mismatch factors were calculated for each device in this report to be less than 5%. Short cir-



cuit currents were also found to be with 5% of values calculated using the integrated external quantum efficiency (EQE) spectra and the solar spectrum. The EQE was measured by under filling the device area using a reflective microscope objective to focus the light output from a 75 W Xe lamp, monochromator, and optical chopper; photocurrent was measured using a lock-in amplifier and the absolute photon flux was determined with a calibrated silicon photodiode.

#### **Device fabrication**

F-doped tin oxide (FTO) glass plates (Pilkington, TEC-8) were cleaned in a detergent solution using an ultrasonic bath for 30 min, rinsed with water and ethanol. The compact TiO<sub>2</sub> layer was deposited on the etched FTO substrate by spray pyrolysis at 450 °C, using titanium diisopropoxide bis(acetylacetonate) solution. The FTO glass plates were immersed in 40 mm TiCl<sub>4</sub> aqueous solution at 70°C for 30 min and then sintered at 500°C for 30 min. Mesoporous  ${\rm TiO}_{\rm 2}$  film was deposited by spin coating of a diluted TiO<sub>2</sub> paste (Dyesol 18NR-T, 1:3.5 w/w diluted with ethanol) at 5000 rpm for 30 s. The films were successively sintered at 500 °C. The PbI<sub>2</sub> in DMF solution (1.0 M) was dropped on the TiO<sub>2</sub>/FTO substrate and then spin-coated at 6500 rpm for 30 s and dried on a hot plate at 70 °C for 30 min. After cooling, the film was dipped into a  $CH_3NH_3I/2$ -propanol solution (8 mg mL<sup>-1</sup>) for 25 s, and dried at 70 °C for 15 min. For a deposition of HTM layers, EtheneDTPA/ chlorobenzene (40 mм) and EtheneTTPA/chlorobenzene (30 mм) solutions were prepared with two additives. Lithium bis(trifluoromethanesulonyl)imide (3.5  $\mu$ L; Li-TFSI)/acetonitrile (520 mg/1 mL) and 8.0 µL (4-tert-butylpyridine) (TBP) were added to the HTM/ chlorobenzene solutions as additives. The HTMs were spin-cast on top of the CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub>/TiO<sub>2</sub>/FTO substrate at 3000 rpm. Finally, the device was pumped to lower than 10<sup>-5</sup> torr and an approximately 60 nm thick Au counter electrode was deposited on top.

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**Keywords:** hole transporting materials • organic–inorganic hybrid composites • perovskite • photochemistry • solar cells

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