# **Supporting Information**

# Comparative study of o, p-dimethoxyphenyl-based hole transport materials by altering $\pi$ -linker units for highly efficient and stable perovskite solar cells

Xing Li, <sup>a,b</sup> Molang Cai, <sup>b</sup> Zhongmin Zhou, <sup>b</sup> Kang Yun, <sup>a</sup> Fengxian Xie, <sup>b</sup> Zhang Lan, <sup>b</sup> Jianli Hua \*<sup>a</sup> and Liyuan Han \*<sup>b</sup>

a. Key Laboratory for Advanced Materials, Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 200237 Shanghai, P.R. China. jlhua@ecust.edu.cn b. Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS). HAN.Liyuan@nims.go.jp

### **Device Fabrication**

Fluorine-doped tin oxide (FTO) glass was washed in a detergent solution for 20 min with sonication, which was followed by consecutive rising with water, ethanol, and acetone. A dense blocking layer of TiO<sub>2</sub> (30 nm, bl-TiO<sub>2</sub>) was deposited onto the FTO by spray pyrolysis, using a 20 mM titanium diisopropoxide bis(acetylacetonate) solution (Aldrich) at 500 °C. To prepare the mp- TiO<sub>2</sub> layer, the TiO<sub>2</sub> nanoparticle (30-NRT, Dyesol) paste diluted in ethanol (1:6, weight ratio) was spin coated onto the substrate at 4000 rpm for 20 s and annealed at 500 °C for 30 min, which lead to an around 170 nm thick mp- TiO<sub>2</sub> mesoporous film. The mixed perovskite precursor solution was prepared by dissolving FAI (1 M), PbI<sub>2</sub> (1.1 M), MABr (0.2 M) and PbBr<sub>2</sub> (0.2 M) in anhydrous mixed solvent DMF: DMSO (4:1) volume ratio. A (FAPbI<sub>3</sub>)<sub>0.45</sub> (MAPbBr<sub>3</sub>)<sub>0.15</sub> layer was formed on TiO<sub>2</sub> layer through spin-coating of the mixed perovskite precursor solution and 6000 rpm for 10 and 30 s respectively. During the second step, 110  $\mu$ L of chlorobenzene was poured at 15s prior to the end of the program. The substrates were then annealed at 100 °C for 60 min. The HTMs was deposited by spin-coating at 4000 rpm for 30 s. The device fabrication was finally completed by the thermal evaporation under high vacuum (< 4 ×10<sup>-5</sup> Pa) of 80 nm thick film of Au.<sup>1</sup>

# Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured at 400 and 100 MHz, respectively. Chemical shifts  $\delta$ , were calibrated against TMS as an internal standard. HRMS measurements were performed by using a Waters LCT Premier XE spectrometer. The absorption spectra of the HTMs were measured with a Varian Cary 500 spectrophotometer. Fluorescence spectra were measured with a Horiba Fluoromax-4 fluorescence spectrometer. SEM images were obtained by using a SU8200 field-emission scanning electron microscope. The UV photoelectron emission spectroscopies were measured using an AC-3 spectrometer (Riken Keiki), with using an Au sample as reference.

The cyclic voltammograms were determined by using a CHI660E electrochemical workstation (Chenhua Co. Ltd, Shanghai, China) in a three-electrode cell. The working electrode was a glassy carbon

electrode, used in conjunction with a Pt auxiliary electrode and an Ag/AgCl wire reference electrode. The electrolyte consisted of 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) solution in dichloromethane containing  $10^{-3}$  M of the dye. The Fc/Fc<sup>+</sup> redox couple was used as an external potential reference. The scan rate was 50 mV/s.

Hole mobilities were measured using the space-charge-limited-current (SCLC) model with holeonly device utilizing the configuration of ITO/PEDOT:PSS/HTM/Au. According the Mott-Gurney law, hole mobilities were extrated by using the dark current under forward bias. The thicknesses of the coated films were measured by a cross-sectional SEM image. The solution concentration of hole transport materials was identical to those used to fabricate the optimized perovskite solar cell devices. HL-1: 30mg in 1 mL mixed solvent of chlorobenzene/chloroform (V/V: 2/8), an additive of 49 μL Libis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (170 mg/mL) and 28.5 μl 2-amylpyridine (2-Py). HL-2 and Spiro-OMeTAD: 30mg in 1 mL chlorobenzene, and the additives are the same as HL-1 solution. The current-voltage curve for the SCLC measurement was obtained using a CHI660E electrochemical workstation.<sup>2</sup>

The current-voltage (*J-V*) characteristics were measured using a solar simulator with standard air mass 1.5 sunlight (100 mW cm<sup>-2</sup>, WXS-155S-10: Wacom Denso Co., Japan) under ambient conditions. The *J-V* curves were measured by forward (-0.2V to 1.2V forward bias) or reverse (1.2V to -0.2V) scans. The step voltage was fixed at 5-10 mV and the delay time was set at 200 ms. J-V curves for all devices were measured by masking the cells with a metal mask 0.09 cm<sup>2</sup> in area. Monochromatic incident photon-to-current conversion efficiency (IPCE) spectra were measured with a monochromatic incident light of  $1 \times 10^{16}$  photons cm<sup>-2</sup> in director current mode (CEP-2000BX, Bunko-Keiki). The light intensity of the solar simulator was calibrated by a standard silicon solar cell provided by PV Measurements Inc.



Fig. S1. The normalized absorption and emission spectra of HL-1 and HL-2 in CH<sub>2</sub>Cl<sub>2</sub>.



**Fig. S2** The highest occupied molecular orbital (HOMO) energy levels of HTMs and valence band (VB) of perovskite were measured by photoelectron yield spectroscopy using an AC-3 spectrometer.



Fig. S3 Optimized structures and the dihedral angles ( $\alpha$  and  $\beta$ ) of HL-1 and HL-2 at the B3LYP/6-31G <sup>3</sup>.



Fig. S4 SEM images of cross-sectional structure of the HL-2 based device.



Fig. S5 (a) Photovoltaic performance of best devices based on the Spiro-OMeTAD; (b) the devices were sealed with epoxy resin by a transparent glass stored under dark and dry condition.



Fig. S6 The histogram of efficiency fabricated with HL-1, HL-2 and Sprio-OMeTAD as HTM, respectively.

## **Synthesis**

Compound 4b was synthesized according to published procedures.<sup>4</sup> All chemicals and solvents were purchased from commercial sources and were used without further purification.

Synthesis of **3**. Under an argon atmosphere, compound **1** (327 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (5 mL, 2M aqueous solution), and Pd(PPh<sub>3</sub>)<sub>4</sub> (42 mg, 0.036 mmol) were dissolved in THF (20 mL). After the mixture was stirred for 30 min and heated to 50°C, a solution of compound 2 (400 mg, 2.2 mmol) in THF (10 mL) was added slowly, and the mixture was heated at reflux for a further 12 h. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with brine and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (5:1–1:1, v/v) as the eluent to give compound 3 (410 mg, 93 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 8.24 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 4H), 6.64 (d, *J* = 2.4 Hz, 2H), 6.59 (dd, *J* = 2.4 Hz, *J* = 2.4 Hz, 2H), 3.78 (d, *J* = 1.2 Hz, 12H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 159.45, 157.01, 141.80, 130.35, 129.80, 129.28, 122.51, 116.18, 105.15, 98.91, 55.44, 55.19. HRMS (m/z): [M+H<sup>+</sup>] calcd for C<sub>28</sub>H<sub>28</sub>N<sub>1</sub>O<sub>4</sub>, 442.2018; found: 442.2012.

Synthesis of **HL-1**. Under an argon atmosphere, compound **3** (363 mg, 0.82 mmol), compound **4a** (162 mg, 0.4 mmol), PdCl<sub>2</sub> (18 mg, 0.1 mmol) and NaOtBu (115 mg, 1.2 mmol) were dissolved in 30 mL of toluene, then 0.5 mL PhP<sub>3</sub> was added slowly. The mixture was refluxed for 12 h before cooling to room temperature, adding 1 mL saturated NH<sub>4</sub>Cl solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers

were washed with brine water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with PE/CH<sub>2</sub>Cl<sub>2</sub> (3/1–2/1, v/v) as eluent to give white compound **HL-1** (360 mg, 87 % yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 7.59 (d, *J* = 8.8 Hz, 4H), 7.42 (d, *J* = 8.8 Hz, 8H), 7.24 (d, *J* = 8.4 Hz, 4H), 7.24 (t, *J* = 8.4 Hz, 12H), 6.66 (d, *J* = 2.4 Hz, 4H), 6.60 (dd, *J* = 2.4 Hz, *J* = 2.4 Hz, 4H), 3.79 (d, *J* = 8.0 Hz, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.05, 157.45, 146.69, 146.03, 134.81, 132.62, 131.06, 130.13, 127.29, 124.40, 123.71, 123.14, 104.63, 99.02, 55.54, 55.43. HRMS (m/z): [M+H<sup>+</sup>] calcd for C<sub>68</sub>H<sub>61</sub>N<sub>2</sub>O<sub>8</sub>, 1033.4428; found: 1033.4431.

Synthesis of **HL-2**. Compound **HL-2** was obtained by using a similar procedure to that of compound **HL-1** (390 mg, 86 % yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 7.90 (d, *J* = 8.4 Hz, 2H ), 7.33 (d, *J* = 8.4 Hz, 8H), 7.21(s, 2H), 7.16 (d, *J* = 8.4 Hz, 4H), 7.03 (d, *J* = 8.4 Hz, 8H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 2.4 Hz, 4H), 6.54 (dd, *J* = 2.4 Hz, 4H), 3.99 (s, 2H), 3.76 (s, 12H), 3.73(s, 12H), 1.50-1.47 (m, 2H), 0.85-0.82 (m, 6H), 0.62-0.64 (m, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 159.73, 157.03, 145.87, 144.81, 141.53, 131.94, 130.52, 129.84, 122.51, 121.88, 120.66, 118.50, 117.18, 105.49, 105.15, 98.85, 55.36, 55.13, 34.15, 30.93, 30.82, 28.44, 26.02, 24.74, 22.03, 21.79, 13.91, 13.61, 11.19. HRMS (m/z): [M+H<sup>+</sup>] calcd for C<sub>74</sub>H<sub>72</sub>N<sub>3</sub>O<sub>8</sub>, 1130.5335; found: 1130.5339.



Fig. S7 <sup>1</sup>H NRM (DMSO-*d*<sub>6</sub>) spectrum of compound **3**.















**Fig. S10** <sup>1</sup>H NRM (DMSO-*d*<sub>6</sub>) spectrum of compound **HL-1**.



Number of isotope peaks used for i-FII = 3 Monoisotopic Mass, Even Electron Ions 13 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass) Elements Used: C: 0-68 H: 0-61 N: 0-2 O: 0-8 JL-HUA ECUST institute of Fine Chem

19-Jun-2016 20:06:02 1: TOF MS ES+ 1.10e+003 HL-YF-702 54 (0.422) Cm (52:56) 1033,4431 100<sub>-</sub> 1032.4341 1034.4413 %-1035.4552 
 1
 849.6385
 863.4996
 893.6544
 937.6761
 1133.4426

 2

Minimum: Maximum:  $^{-1.5}_{100.0}$ 300.0 50.0 Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula 1033.4431 1033.4428 0.3 0.3 39.5 16.8 0.0 C68 H61 N2 O8

Fig. S12 HR-MS spectrum of compound HL-1.





Fig. S15 HR-MS spectrum of compound HL-2.

## **Reference:**

- 1. Y. Yue, N. T. Salim, Y. Wu, X. Yang, A. Islam, W. Chen, J. Liu, E. Bi, F. Xie, M. Cai and L. Han, *Adv. Mater.*, 2016, 28, 10738-10743.
- I. Cho, N. J. Jeon, O. K. Kwon, D. W. Kim, E. H. Jung, J. H. Noh, J. Seo, S. I. Seok and S. Y. Park, *Chem. Sci.*, 2017, 8, 734-741.
- 3. A. D. Becke, J. Chem. Phys., 1993, 98, 1372-1377.
- 4. M. Y. Wong, G. J. Hedley, G. Xie, L. S. Kölln, I. D. W. Samuel, A. Pertegas, H. J. Bolink and E. Zysman-Colman, *Chem. Mater.*, 2015, 27, 6535–6542.