## **Supporting information**

### Novel hole transporting materials with a linear $\pi$ -conjugated

## structure for high efficient perovskite solar cell

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### 1. Chemicals and materials

Starting materials were all commercially available and used as received without further purification if not specially mentioned. 4,4'-Bis-chloromethyl-biphenyl, triethyl phosphite and potassium *t*-butoxide (*t*-BuOK) were purchased from Aladding Institute (Tianjin, China). Methyl triphenyl phosphonium bromide was purchased from Sigma-Aldrich (Saint Louis, Missouri, USA). 4-[*N*,*N*-di(*p*-tolyl)amino]benzaldehyde was purchased from Tianjin Zhongmin Technology Co. LTD, and recrystallized from ethanol before use. Other solvents and materials were provided by JiangTian Institute (Tianjin, China). Tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) and phosphorus oxychloride (POCl<sub>3</sub>) were refreshly distilled before use.

### 2. Instruments and measurement conditions

<sup>1</sup>H NMR (400MHZ) spectra were recorded with a Bruker ACF400 (400MHz) supplied by Bruker Biospin (Fällanden, Switzerland) in CDCl<sub>3</sub> with tetramethylsilane as reference at 298K. High resolution mass spectra (HRMS) were performed on a Bruker micrOTOF-Q II (Bruker, Germany). Elemental analysis was performed on a VarioMICRO CHNOS elemental analyzer (Elementar Analysensysteme, Hanau, Germany). FT-IR spectroscopy measurements were performed on a NICOLET380 (Thermo Nicolet, USA). UV spectra of solutions and of the films were recorded with Thermo Evolution 300 UV-vis spectrometer (Thermo Electron, USA). Thermogravimetrical analyses (TGA) were performed on TA Q500 thermo gravimetric apparatus (TA-Instruments, USA) at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was conducted on TA Q20 Instrument (TA-Instruments, USA) at a heating rate of 10 °C/min under nitrogen atmosphere.

All CV measurements were performed on a Zahner Elektrik IM6e electrochemistry workstation with a three-electrode cell in dry dichloromethane in the presence of tetrabutylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>, 0.1M) as supporting electrolyte with a scanning rate of 50 mV/s at room temperature. A platinum disc and a platinum wire were used as working and counter electrode, respectively, and Ag/AgNO<sub>3</sub> as the reference electrode.

The time-of-flight (TOF) measurements were conducted on TOF401 (Sumitomo Heavy

Industries. Ltd., Japan). Samples were prepared through vacuum deposition using a structure ITO/HTM (about 1  $\mu$ m)/Al (150 nm) having an active area of 3 mm × 10 mm.

Solar cell fabrication: Fluorine doped tin oxide (FTO) glass was etched with zinc powder and diluted HCl solution, the etched substrates were cleaned by ultrasonication using decon-soap solution, deionized water and ethanol, followed by  $O_3/UV$  treatment. The compact TiO<sub>2</sub> underlayer (30 nm) was deposited by aerosol spray pyrolysis on the FTO surface. Mesoporous TiO<sub>2</sub> film was spin-coated onto the compact TiO<sub>2</sub> under-layer and sintered at 500 °C for 30 min. A CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> nanocrystals were deposited on the mesoporous TiO<sub>2</sub> film via spin coating with a mixture of CH<sub>3</sub>NH<sub>3</sub>I and PbI<sub>2</sub> in a  $\gamma$ -butyrolactone solution. Then the nanocrystalline CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer was heated to 100 °C for 30 min. **2TPA-2-DP** was dissolved in chlorobenzene and spin-coated onto the perovskite film at 4000 rpm for 30 s. Finally, an Au cathode layer (100 nm) was deposited by thermal evaporation.

### 3. Synthesis

# Preparation of the small-molecular hole transporting materials with a linear $\pi$ -conjugated structure

The synthetic route for the HTMs is shown in Scheme 1.



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

### Synthesis of Horner regent BDPB

[4'-(diethoxy-phosphorylmethyl)-biphenyl-4-ylmethyl]-phosphonic acid diethyl ester (**BDPB**) was synthesized by Arbuzov-Michale reaction using corresponding aromatic chloride and triethylphosphite.<sup>1</sup> 4,4'-Bis-chloromethyl-diphenyl (5.00 g, 1 mmol) and triethyl phosphite (36.00 mL, 10 mmol) were refluxed for 5h under N<sub>2</sub> atmosphere. After petroleum ether was added to the mixture, the crude compound was precipitated. The crude product was collected by filtration and purification by recrystallization to afford pure Horner regent as white solid. Yield 93.3 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 7.54 (d, *J*=5.9 Hz, 4H), 7.38 (s, 4H), 3.22 (t, *J*=21.7 Hz, 4H), 1.37–1.15 (m, 12H). MS (ESI<sup>-</sup>), found value [M<sup>-</sup>] 453.32, calculated value [M] 454.17. *Synthesis of aromatic alkenes* 2*a*-2*c* 

The aromatic alkenes **2a-2c** were synthesized by the method of Wittig reaction using aldehydes **1a**, **3a**, **3b** and Wittig regent by the following procedure.<sup>2</sup> Methyl triphenyl phosphonium bromide (5.36 g, 15 mmol) and 15 mL of dry THF were added into a round-bottom flask. A solution of *t*-BuOK (2M in THF, 15 mL, 30 mmol) was added drop-wise slowly and the mixture was stirred for 1 h at 0 °C to perform a slightly yellow liquid. A solution of **1a** (1.50 g, 5 mmol) was added and the reaction mixture was stirred at room temperature. Until reaction finished (TLC monitoring), the mixture was extracted with ethyl acetate. The organic layer was washed with distill water and dried over MgSO<sub>4</sub>. After evaporation of solvent, the crude product **2a** was obtained.

**2a** was purified by column chromatography using the mixture of ethyl acetate and petroleum ether in a volume ratio of 1:50 as an eluent. White solid; yield: 86.5 %. <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>),  $\delta$  (ppm): 7.24 (d, *J*=8.1 Hz, 2H), 7.05 (d, *J*=8.1 Hz, 4H), 6.98 (d, *J*=7.9 Hz, 4H), 6.95 (s, 2H), 6.63 (dd, *J*=17.6, 10.9 Hz, 1H), 5.60 (d, *J*=17.6 Hz, 1H), 5.11 (d, *J*=10.9 Hz, 1H), 2.30 (s, 6H). MS (ESI<sup>+</sup>), found value [M] 299.30, calculated value [M] 299.17.

**2b** was purified by column chromatography using the mixture of ethyl acetate and petroleum ether in a volume ratio of 1:240 as an eluent. Light yellow solid; yield: 85.2 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.29 (d, *J*=8.5 Hz, 2H), 7.10 (t, *J*=10.8 Hz, 4H), 7.07–7.03 (m, 4H), 7.01 (d, *J*=8.5 Hz, 2H), 6.72 (dd, *J*=15.5, 10.4 Hz, 1H), 6.56 (dd, *J*=13.8, 6.0 Hz, 1H), 6.52 (dd, *J*=9.8, 7.0 Hz, 1H), 5.32 (d, *J*=17.2 Hz, 1H), 5.15 (d, *J*=9.8 Hz, 1H), 2.37 (s, 6H). MS (APCI<sup>+</sup>), found value [M<sup>+</sup>] 326.45, calculated value [M] 325.18.

**2c** was purified by column chromatography using the mixture of ethyl acetate and petroleum ether in a volume ratio of 1:480 as an eluent. Light yellow solid; yield: 74.6 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.30 (d, *J*=8.2 Hz, 2H), 7.14 (d, *J*=7.5 Hz, 4H), 7.08 (d, *J*=8.1 Hz, 4H), 7.03 (d, *J*=8.4 Hz, 2H), 6.82–6.67 (m, 1H), 6.64–6.31 (m, 4H), 5.30 (d, *J*=16.5 Hz, 1H), 5.17 (d, *J*=9.3 Hz, 1H), 2.31 (d, *J*=63.7 Hz, 6H). MS (APCI<sup>+</sup>), found value [M<sup>+</sup>] 352.22, calculated value [M] 351.20.

### Synthesis of aromatic aldehydes 3a-3c

The aromatic aldehydes **3a-3c** were prepared *via* Vilsmeier reaction from **2a-2c** by following procedure.<sup>3</sup> POCl<sub>3</sub>(5.06 g, 33 mmol) was added to DMF (2.92 g, 40 mmol) at 0 °C under N<sub>2</sub> atmosphere. The solution of **2a** (1M in DMF, 10 mL, 10 mmol) was added drop-wise to the obtained complex. The reaction mixture was stirred at room temperature. Until the reaction finished (TLC monitoring), the mixture was poured into the ice water and neutralized with sodium hydroxide to pH 7, followed by extraction with dichloromethane. The organic layer was washed with distill water and dried over MgSO<sub>4</sub>. After evaporation of solvent, the crude product **3a** was

obtained.

**3a** was purified by column chromatography using the mixture of ethyl acetate and petroleum ether in a volume ratio of 1:50 as an eluent. Yellow solid; yield: 95.9 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 9.65 (d, *J*=7.8 Hz, 1H), 7.46–7.33 (m, 3H), 7.15 (d, *J*=8.1 Hz, 4H), 7.07 (d, *J*=8.3 Hz, 4H), 6.98 (d, *J*=8.7 Hz, 2H), 6.59 (dd, *J*=15.8, 7.8 Hz, 1H), 2.37 (s, 6H). MS (ESI<sup>+</sup>), found value [M<sup>+</sup>] 328.38, calculated value [M] 327.16. IR (KBr), v/cm<sup>-1</sup>: 3023, 2928, 2856 (Ar, C-H), 2813, 2734 (O=C-H), 1674 (C=O), 1595, 1507 (Ar, C=C), 1310, 1273, 1130 (C-N), 970 (*trans* C=C).

**3b** was purified by column chromatography using the mixture of ethyl acetate and petroleum ether in a volume ratio of 1:40 as an eluent. Orange yellow solid; yield: 88.2 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 9.60 (d, *J*=8.0 Hz, 1H), 7.37–7.25 (m, 1H), 7.13 (d, *J*=8.3 Hz, 1H), 7.05 (d, *J*=8.4 Hz, 1H), 7.01–6.93 (m, 1H), 6.87 (dd, *J*=15.4, 10.5 Hz, 1H), 6.23 (dd, *J*= 15.1, 8.0 Hz, 1H), 2.36 (s, 1H). MS (APCI<sup>+</sup>), found value [M<sup>+</sup>] 354.41, calculated value [M] 353.18. IR (KBr), v/cm<sup>-1</sup>: 3023, 2928, 2856 (Ar, C-H), 2813, 2734 (O=C-H), 1666 (C=O), 1595, 1507 (Ar, C=C), 1310, 1273, 1162, 1115 (C-N), 990 (*trans* C=C).

**3c** was purified by column chromatography using the mixture of ethyl acetate and petroleum ether in a volume ratio of 1:30 as an eluent. Red solid; yield: 84.2 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 9.61 (dd, *J*=35.2, 7.9 Hz, 1H), 7.33–7.12 (m, 3H), 7.08 (d, *J*=8.2 Hz, 4H), 7.01 (d, *J*=8.2 Hz, 4H), 6.94 (d, *J*=8.5 Hz, 2H), 6.87–6.68 (m, 3H), 6.57–6.41 (m, 1H), 6.15 (dd, *J*=15.1, 7.9 Hz, 1H), 2.32 (s, 6H). MS (APCI<sup>+</sup>), found value [M<sup>+</sup>] 380.35, calculated value [M] 379.20. IR (KBr), v/cm<sup>-1</sup>: 3023, 2928, 2856 (Ar, C-H), 2813, 2734 (O=C-H), 1674 (C=O), 1595, 1507 (Ar, C=C), 1310, 1273, 1146, 1115(C-N), 990 (*trans* C=C).

### Synthesis of 2TPA-n-DP

TPA derivatives were synthesized by Horner-Wadsworth-Emmons condensation of **BDPB** and corresponding aldehydes **3a-3c**. A solution of 4.82 g (9.6 mmol) **BDPB** and 3.64 g (19.2 mmol) of aldehyde **3a** in THF (40 mL) was stirred under N<sub>2</sub> condition. A solution of *t*-BuOK (1.92M in THF, 20 mL, 38.4 mmol) was added drop-wise slowly at 0 °C. Then the mixture was stirred at room temperature until the reaction finished (TLC monitoring). After methanol (50 mL) was added to the mixture, the precipitate was filtered and washed with methanol to afford crude product.

**2TPA-2-DP** was purified by recrystallization with the solution of methanol/THF. Yellow power; yield: 87.5 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.62–7.52 (m, 4H), 7.48 (d, *J*=8.3 Hz, 4H), 7.31–7.19 (m, 4H), 7.07 (d, *J*=8.3 Hz, 8H), 7.00 (d, *J*=8.4 Hz, 8H), 6.98–6.93 (m, 6H), 6.84 (dd, *J*=15.2, 10.6 Hz, 2H), 6.62 (dd, *J*=15.3, 8.2 Hz, 4H), 2.31 (s, 12H). MS (APCI<sup>+</sup>), found value [M<sup>+</sup>] 801.42, calculated value [M] 800.41. Elemental analysis: calculated for C<sub>60</sub>H<sub>52</sub>N<sub>2</sub>: C, 89.96 %; N, 3.50 %; H, 6.54 %. Found: C, 90.24 %; N, 3.51 %; H, 6.25 %. IR (KBr), v/cm<sup>-1</sup>: 3023, 2928, 2856 (Ar, C-H), 1595, 1507 (Ar, C=C), 1310, 1273 (C-N), 987 (*trans* C=C).

**2TPA-3-DP** was purified by column chromatography using the mixture of dichloromethane and hexane in a volume ratio of 1:5 as an eluent. Orange yellow power; yield:79.2 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.60 (d, *J*=8.1 Hz, 4H), 7.49 (d, *J*=8.1 Hz, 4H), 7.28 (d, *J*=6.6 Hz, 4H), 7.10 (d, *J*=8.2 Hz, 8H), 7.03 (d, *J*=8.2 Hz, 8H), 6.96 (dd, *J*=20.7, 9.0 Hz, 6H), 6.79 (dd, *J*=15.5, 9.3 Hz, 2H), 6.69–6.45 (m, 8H), 2.35 (s, 12H). MS(APCI<sup>+</sup>), found value [M<sup>+</sup>] 853.45, calculated value [M] 852.44. Elemental analysis: calculated for C<sub>64</sub>H<sub>56</sub>N<sub>2</sub>: C, 90.10 %; N, 3.28 %; H, 6.62 %. Found: C, 90.06 %; N, 3.29 %; H, 6.65 %. IR (KBr), v/cm<sup>-1</sup>: 3016, 2921, 2848 (Ar, C- H), 1595, 1507 (Ar, C=C), 1310, 1273 (C-N), 997 (trans C=C).

**2TPA-4-DP** was purified by column chromatography using the mixture of dichloromethane and hexane in a volume ratio of 1:3 as an eluent. Orange red power; yield: 75.2 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.56 (d, *J*=6.7 Hz, 4H), 7.46 (d, *J*=6.5 Hz, 4H), 7.26–7.21 (m, 4H), 7.07 (d, *J*=7.8 Hz, 8H), 6.99 (d, *J*=8.0 Hz, 8H), 6.94 (d, *J*=7.9 Hz, 6H), 6.79–6.34 (m, 14H), 2.35–2.26 (m, 12H). MS (APCI<sup>+</sup>), found value [M<sup>+</sup>] 905.48, calculated value [M] 904.47. Elemental analysis: calculated for C<sub>68</sub>H<sub>60</sub>N<sub>2</sub>: C, 90.22 %; N, 3.09 %; H, 6.68 %. Found: C, 90.53 %; N, 3.10 %; H, 6.37 %. IR (KBr), v/cm<sup>-1</sup>: 3016, 2921, 2848 (Ar, C-H), 1595, 1507 (Ar, C=C), 1310, 1273 (C-N), 997 (*trans* C=C).

### **Figures and tables**





Fig. S2 FTIR of 2TPA-2-DP and 3a







Fig. S4 DSC and TGA thermograms of 2TPA-n-DP (n=2, 3, 4) under  $N_2$  at the heating rate of 10 °C /min.

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