Electronic Supplementary Information

A linear D- π -A based hole transport material for high performance rigid and flexible planar organic-inorganic hybrid perovskite solar cells

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Materials and Methods:

All reagents and chemicals were used without any additional purification unless stated otherwise. Using distillation process over sodium/benzophenone under an inert atmosphere, THF was dried and purified. Each step of the reactions was monitored by thin layer chromatography (TLC). ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in CDCl₃ using tetramethylsilane (TMS) as an internal standard. JASCO V– 570 and Hitachi F–4500 fluorescence spectrophotometers were utilized to measure the UV–Vis absorption and as fluorescence spectra. Also, steady state photoluminescence (PL) spectra and time-resolved transient PL decays of the samples were measured. Thermal analyses were conducted on a Mettler Toledo TGA/SDTA 851e, DSC 822e analyzer under an inert atmosphere at a heating rate of 10 °C min⁻¹. CV studies were carried out with a CHI 600C potentiostat (CH Instruments), which was equipped with a platinum disc as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl as the reference electrode, at a scan rate of 100 mV s⁻¹ in a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte in CH₂Cl₂. The density functional theory (DFT) study was performed with B3LYP functional and 6-311+G** basis sets using a suite of Gaussian 09 programs. To

calculate the mobility, we used the Mott–Gurney law as follows,
$$J = \left(\frac{9}{8}\right)\mu\varepsilon_{0}\varepsilon_{r}\left[\frac{V^{2}}{L^{3}}\right]$$

where μ , ε_{0} , ε_{r} , V, and L are the hole mobility, free space permittivity, dielectric constant, applied voltage, and thickness of the HTM film, respectively. The OSC performance was measured under simulated AM 1.5G illumination with an irradiance of 100 mWcm⁻² (Oriels Sol AAATM Class models 94043A). The irradiance of the sunlight-simulating illumination was calibrated using a standard Si photodiode detector fitted with a KG5 filter. The *J–V* curves

were measured automatically using a Keithley 2400 Source Meter measurement unit. The *J-V* curves were measured by reverse (forward bias (1.2 V) to short circuit (0 V)) or forward (short circuit (0 V) to forward bias (1.2 V)) scans. For the measurement hysteresis of J - V curves, the forward and reverse scan rate was set to 200 ms/10 mV as a standard condition and was varied from 100 ms/10 mV to 1000 ms/10 mV. *J-V* curves for all devices were measured by masking the active area with a 0.11 cm² metal mask. The stability tested PSCs and IOSCs were not encapsulated and were stored in atmosphere with humidity of 28±2.2% and at room temperature without light illumination.

Experimental Section

Synthesis:

Synthesis of 4''-bromo-N,N-bis(4-methoxyphenyl)-[1,1':4',1, ''-terphenyl]-4-amine (1). A mixture of (4-(bis(4-methoxyphenyl)amino)phenyl)boronic acid (1 g, 2.86 mmol) and 4,4'-dibromo-1,1'-biphenyl (1.07 g, 3.44 mmol) were dissolved in 40 mL dry toluene and add 2M Na₂CO₃ solution and purge 15 min. After purging, added Pd(PPh₃)₄ (0.33 g, 0.029 mmol) and stirred under N₂ atmosphere at 110 °C for 24 h. After the reaction, the mixture was cooled to RT, the reaction mixture was poured into water and extracted with CH₂Cl₂. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by column chromatography using hexane: EtOAc (4:1) as eluent. (yield: 52.18%). ¹H NMR (300 MHz, CDCl₃): δ 7.70-7.57 (m, 6H), 7.52-7.43 (m, 4H), 7.11-7.02 (m, 4H), 6.87 (d, J = 8.1 Hz, 2H), 6.84 (d, 4H), 3.82 (s, 6H).

Synthesis of N,N-bis(4-methoxyphenyl)-4"-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)-[1,1':4',1"-terphenyl]-4-amine (2). A mixture of the compound (1) (1 g,

1.86 mmol) and bis(pinacolato)diboron (0.71 g, 2.80 mmol) were dissolved in 30 mL 1,4dioxane and added CH₃COOK (0.27 g, 2.80 mmol) and purged 15 min. Then, added Pd(dppf)Cl₂ (0.014 g, 0.019 mmol) and stirred under N₂ atmosphere at 85 °C for 3 days. After the reaction the mixture was cooled to RT, the reaction mixture was poured into water and extracted with CH₂Cl₂. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by column chromatography using hexane: EtOAc. (yield: 49.72 %). ¹H NMR (300 MHz, CDCl₃): δ 7.90 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.1 Hz, 6H), 7.44 (d, J = 8.2 Hz, 2H), 7.09-7.0 (m, 6H), 6.85 (d, J = 7.5 Hz, 4H), 3.80 (s, 6H), 1.36 (s, 12H).

4.1.1 Synthesis of 4-bromo-N'-(4-(hexyloxy)benzoyl)benzohydrazide (bh). A mixture of 4-(hexyloxy)benzoyl chloride (1.85 mL, 8.30 mmol) and NMP (50 mL) was stirred at 0 °C, and a solution of 4-bromobenzhydrazide (1.78 g, 8.30 mmol) in 20 mL pyridine was added. The reaction mixture was stirred at 40 °C for 4 h, after which the reaction mixture was poured into 200 mL distilled water. The precipitated product of 4-bromo-N'-(4-(hexyloxy)benzoyl)benzohydrazide was collected by filtration. (yield: 89.08%). ¹H NMR (300 MHz, CDCl₃): δ 10.50 (s, 1H), 10.36 (s, 1H), 7.88-7.83 (m, 4H), 7.72 (d, J = 9 Hz, 2H), 7.02 (d, J = 9 Hz, 2H), 4.01 (t, J = 6 Hz, 2H), 1.69 (d, J = 6 Hz, 2H), 1.37-1.28 (m, 6H), 0.85 (m, 3H). ¹³C NMR (75 MHz, CDCl₃, δ): 165.72, 165.45, 161.94, 132.03, 129.96, 129.79, 126.07, 124.81, 114.57, 68.14, 31.42, 28.97, 25.59, 22.52, 14.37.

Synthesis of 2-(4-bromophenyl)-5-(4-hexyloxy)phenyl)-1,3,4-oxadiazole(3). A mixture of 4bromo-*N'*-(4-hexyloxy)benzoyl)benzohydrazide (1 g, 2.38 mmol) in 20 mL POCl₃ was stirred at 120 °C for 7 h. After cooling to room temperature, the mixture was poured into ice water. The precipitate was collected by filtration and washed twice with de-ionized water to afford a white powder of 2-(4-bromophenyl)-5-(4-(hexyloxy)phenyl)-1,3,4-oxadiazole. (yield: 90.90%). ¹H NMR (300 MHz, CDCl₃): δ 8.04-7.96 (m, 4H), 7.65 (d, J = 6 Hz, 2H), 7.00 (d, J = 6 Hz, 2H), 4.01 (t, J = 6 Hz, 2H), 1.80 (t, J = 6 Hz, 2H), 1.4 (m, 2H), 1.34 (m, 4H), 0.90 (m, 3H). ¹³C NMR (75 MHz, CDCl₃, δ):164.75, 163.33, 162.06, 132.34, 128.69, 128.17, 126.11, 122.97, 115.83, 114.97, 68.27, 31.54, 29.06, 25.66, 22.59, 14.04.

Synthesis of 4"'-(5-(4-(hexyloxy)phenyl)-1,3,4-oxadiazol-2-yl)-N,N-bis(4-

methoxyphenyl)-[1,1':4',1":4",1"'-quaterphenyl]-4-amine (*TPA-BP-OXD*). A mixture of the compound (6) (0.35 g, 0.60 mmol) and (4) (0.3 g, 0.72 mmol) were dissolved in 40 mL dry toluene and add 2M Na₂CO₃ solution and purged for 15 min, then added Pd(PPh₃)₄ (0.007 g, 0.006 mmol) and stirred under N₂ atmosphere at 110 °C for 24 h. After the reaction, the mixture was cooled to RT, the reaction mixture was poured into water and extracted with CH₂Cl₂. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by column chromatography using hexane: EtOAc as eluent. (yield: 55.0%). ¹H NMR (300 MHz, CDCl₃): δ 8.21 (d, J= 9 Hz, 2H), 8.08 (d, J=9 Hz, 2H), 7.81 (d, J= 9 Hz, 2H), 7.75 (s, 4H), 7.71-7.64 (m, 4H), 7.48 (d, J= 9Hz, 2H), 7.09 (m, 4H), 7.03 (d, J= 9 Hz, 4H), 6.86 (d, J = 9Hz, 4H), 4.04 (t, J= 6 Hz, 2H), 3.81 (s, 6H), 1.85-1.78 (m, 2H), 1.49 (m, 2H), 1.37 (m, 4H), 0.92 (m, 3H). ¹³C NMR (75 MHz, CDCl₃, δ):164.60, 163.98, 161.97, 143.67, 140.54, 138.52, 128.68, 127.51, 127.46, 127.43, 127.30, 126.84, 116.13, 114.97, 114.69, 68.28, 55.49, 31.55, 29.09, 25.67, 22.59, 14.04. MS (FAB+): *m/z* (100%): calcd for C₅₂H₄₇N₃O₄, 778.3567; found, 778.3642. Anal. calcd for C₅₂H₄₇N₃O₄: C, 80.28; H, 6.09; N, 5.40; O, 8.23; found: C 80.21; H, 6.14; N, 5.38; O, 8.29.

Fabrication of flexible and rigid i-PSCs:

The TPA-BP-OXD solution (10 mg/mL CB) was spin-cast on top of the commercial PET/ITO

electrode. The films were annealed at 80 °C for 5 min in glove box. PbI₂ (461 mg), CH₃NH₃I (159 mg) and DMSO (78 mg, molar ratio 1:1:1) was mixed in DMF solution (600 mg) at room temperature with stirring for 1 h in order to prepare a CH₃NH₃I·PbI₂·DMSO adduct solution. The transparent CH₃NH₃I·PbI₂·DMSO adduct film was heated at 65 °C for 1 min and 100 °C for 1 min in order to obtain a dense CH₃NH₃PbI₃ film (~300 nm). The PC₆₁BM (20 mg/1 mL CB, ~100 nm) were spin-coated on MAPbI₃ layer at 1000 rpm for 40 sec. Then ZnO NPs solution was spin-coated onto PC₆₁BM layer at 3000 rpm for 20 sec. Finally, a ~120-nm-thick Ag electrode was deposited by thermal evaporation. The similar conditions were carried out for rigid based i-PSCs. The HTM was spin-coated on rigid ITO substrate. Other layers were deposited according to the above mentioned flexible i-PSCs. The optimized thickness of the HTM for flexible i-PSCs is about 40 nm. The obtained results are summarized in the below Table S1.

Table S1. The photovoltaic performance of flexible i-PSCs based on dopant-free HTM with optimized thickness.

Thickness	J_{sc}	V _{OC}	FF	PCE _{max}
	(mA/cm ²)	(V)	(%)	(%)
30 nm	19.76	1.04	60.09	12.44
40 nm	18.81	1.02	67.14	12.90
50 nm	18.71	1.02	67.15	12.85



Fig. S1. Synthetic route of intermediate 3.



Fig. S2 Temperature dependent UV-vis absorption spectra of TPA-BP-OXD in chlorobenzene solution.



Fig. S3 UV-vis absorption spectra of TPA-BP-OXD in chlorobenzene solution with different concentrations.



Fig. S4. Normalized PL spectra of TPA-BP-OXD.



Fig. S5 Optimized molecular geometry of TPA-BP-OXD.



Fig. S6. (a) Device architecture of a hole-only devices and (b) corresponding J-V plots of the hole-only devices based on TPA-BP-OXD.



Fig. S7. (a) Steady state PL spectra and (b) time-resolved transient PL decays of MAPbI₃-based perovskite film, PEDOT:PSS/MAPbI₃ and TPA-BP-OXD/MAPbI₃.



Fig. S8. AFM topography images (10 μ m × 10 μ m) of HTMs, and corresponding HTMs with perovskite.



Fig. S9. (a) Recombination resistance (R_{rec}). (b) Hole conductivity (σ_{HTM}) of the HTMs extracted from the EIS measurements under dark state.



Fig. S10 1 H NMR spectrum of 1 (300 MHz, CDCl₃).



Fig. S11 ¹H NMR spectrum of 2 (300 MHz, $CDCl_3$).



Fig. S12 ¹H NMR spectrum of bh (300 MHz, CDCl₃).



Fig. S13 ¹³C NMR spectrum of bh (75 MHz, CDCl₃).



Fig. S14 ¹H NMR spectrum of 3 (300 MHz, CDCl₃).



Fig. S15 ¹³C NMR spectrum of 3 (75 MHz, CDCl₃).



Fig. S16 ¹H NMR spectrum of TPA-BP-OXD (300 MHz, CDCl₃).



Fig. S17 ¹³C NMR spectrum of TPA-BP-OXD (75 MHz, CDCl₃).



Fig. S18 HRMS (FAB+) spectrum of TPA-BP-OXD.