## **Supplementary Information**

# Structure-property correlations of tetraphenylbenzidine-based selfassembled monolayers for perovskite and organic solar cells

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#### **Materials and Synthesis**

All reactions were set up using standard Schlenk techniques and carried out under Argon atmosphere. Commercially available chemicals(1,4-Dibromobenzene, 4-Bromophbenol, 4-Fluoroaniline, Pd(PPh<sub>3</sub>)<sub>4</sub>, Triethyl phosphite, 4-Methoxyaniline, N,N'-Diphenylbenzidine, 1,6-Dibromohexane, Palladium acetate, 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl(X-Phos), Tri-tert-butylphosphine, N4,N4'-bis(4-methoxyphenyl)-[1,1'-biphenyl]-4,4'-diamine) were obtained from Energy Chemical, Bidepharm, TCL and J&K Chemical and used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on silica gel HSGF254 glass plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm and 365 nm).

#### **General Characterizations**

<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectra were measured on a Bruker AV-400 MHz or Bruker AVANCE III 500 MHz spectrometer using tetramethylsilane (TMS) as the internal reference. The multiplicity abbreviations used are as follows: s = singlet; d =doublet; t = triplet; q = quartet; m = multiplet; dd = doublet of doublets; dt = doublet of triplets; td = triplet of doublets. MALDI-TOF-MS spectra were measured on a Bruker BIFLEX III mass spectrometer, with 1,8,9-anthracenetriol as the matrix and sodium trifluoroacetate as the ionizing reagent. TGA measurements were measured on a NETZSCH (TG209F3) apparatus at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. UV-Vis absorption spectra were recorded on a SHIMADZU UV-3600i plus spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 100 mV s<sup>-1</sup> against a saturated calomel electrode reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The potential of saturated calomel electrodes (SCE) was internally calibrated as 0.39 V by using the ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>), which has a known reduction potential of -4.80 eV. DFT calculations for optimization of the ground state geometries

and electronic properties were conducted to investigate the molecular geometry and energy levels at B3LYP/6-31G(d,p) level using the Gaussian 16 package. Tappingmode atomic force microscopy (AFM) images were obtained by using a Bruker Multimode 8 Microscope. The Ultra-High-Vacuum Scanning Kelvin Probe (UHV SKPM) uses a non-contact, non-destructive vibration capacitance device applied to the work function of a conductive material or the surface potential of a semiconductor or insulator material to determine WF (UHV-KP020). Contact angle measurements were performed using a drop shape analysis system (DSA100) with water and ethylene glycol as the test liquid.



Scheme S1. The synthesis of compound 10

**Compound 10.** Compound **10** was synthesized according to the reported literature.<sup>1</sup> 1,4-Dibromobenzene (10.0 g, 42.4 mmol) was added to a three-neck flask and purged with nitrogen for 10 min. After adding 30 mL of dry THF and lowering to -78 °C, n-BuLi (2.5 M, 18.65 mL, 46.63 mmol) was added dropwise to the solution while stirring. The solution was stirred for 30 min and then carefully added dropwise to another three-necked flask containing 1,6-dibromohexane (9.76 mL, 63.58 mmol) and THF (5 mL). Stirring was continued at -78 °C for two hours and warmed to room temperature. The reaction flask was quenched with 20 mL of methanol. It was then washed twice with water, extracted, dried and concentrated to give a clear oil. The excess 1,6-dibromohexane was then removed by distillation under vacuum to give the pure product (8.0 g, 62.6%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), ppm:  $\delta = 7.40$  (d, 2H, J = 8.4Hz), 7.05 (d, 2H, J = 8.25Hz), 3.40 (t, 2H, J = 6.8Hz), 2.56 (t, 2H, J = 7.7Hz), 1.85 (m, 2H), 1.61(m, 2H), 1.47(m, 2H), 1.34(m, 2H). HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>12</sub>H<sub>16</sub>Br<sub>2</sub>) m/z = 319.9598, found 320.1297.



Scheme S2. The synthesis of compound 5

**Compound 5.** X-Phos (0.117 g, 0.246 mmol) and palladium (II) acetate (0.022 g, 0.098 mmol) were dissolved in anhydrous dioxane (13 mL, 6.5 mL per gram of 4,4'-dibromobiphenyl) and stirred under argon atmosphere at 80°C for 10min. 4,4'-Diiodobiphenyl (2 g, 4.93 mmol), 4-Fluoroaniline (1.15 g, 10.34 mmol) and sodium tert-butoxide (1.04 g, 10.84 mmol) were added and the mixture was heated at reflux for 24 hours. After termination of reaction the mixture was diluted with THF and filtered through Celite passivated with 2% triethylamine solution in THF. Solvent was removed, residue dissolved in hot THF and ethyl acetate was added. Mixture was left to cool down and formed solid was filtered and washed with n- hexane to give greyish white powder (93 %, 1.73 g). The product was used in the next step without further purification. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.46 (d, *J* = 8.5 Hz, 4H), 7.11 – 7.05 (m, 4H), 7.05-6.87 (m, 8H), 5.63 (s, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  159.3, 156.9, 142.7, 138.9, 133.3, 127.4, 120.6, 120.5, 117.2, 116.1, 115.9. HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>24</sub>H<sub>18</sub>F<sub>2</sub>N<sub>2</sub>) m/z = 372.1438, found 372.0660.



Scheme S3. The synthesis route of compound 6PA-TPD.

**Compound 1.** Tri-tert-butylphosphine (0.06 g, 0.297 mmol) and palladium (II) acetate (0.017 g, 0.074 mmol) were dissolved in anhydrous toluene (40 mL) and stirred under argon atmosphere at 80°C for 10min. N<sup>4</sup>,N<sup>4'</sup>-diphenyl-[1,1'-biphenyl]-4,4'- diamine (0.5 g, 1.49 mmol), **10** (1.15 g, 10.34 mmol) and sodium tert-butoxide (0.314 g, 3.27 mmol) were added and the mixture was heated at reflux for 24 hours. After

being cooled to room temperature, the mixture was filtered through Celite and washed with toluene and water. The organic layer was extracted with ethyl acetate (50 mL × 3) and dried over MgSO<sub>4</sub>. The solvent was evaporated on a rotary evaporator, and the dark brown mixture was purified by column chromatography on silica gel using methylene chloride/n-hexane (1:4) as eluent to give a colorless oily **1**. Yield: 1.21 g (35%). <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.43 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 7.9 Hz, 4H), 7.07 (dt, *J* = 34.8, 17.4 Hz, 18H), 3.41 (t, *J* = 6.8 Hz, 4H), 2.58 (s, 4H), 1.92 – 1.83 (m, 4H), 1.64 (m, 4H), 1.52 – 1.44 (m, 4H), 1.42 – 1.35 (m, 4H). HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>48</sub>H<sub>50</sub>Br<sub>2</sub>N<sub>2</sub>) m/z = 814.2320, found 813.9135.

**Compound 2.** Compound **1** (0.254 g, 0.31 mmol) was dissolved in triethylphosphite (5 mL) and the reaction mixture was heated at reflux for 24 h. After reaction completion (TLC, THF : n-hexane, 1:2, v:v) the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography using THF : n-hexane, 1:1, v:v as eluent to give a colorless oily **2**. Yield: 0.275 g (94%).<sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$  7.51 (d, *J* = 8.3 Hz, 4H), 7.29 (t, *J* = 7.8 Hz, 4H), 7.14 (d, *J* = 8.1 Hz, 4H), 7.04-6.96 (m, 14H), 3.95 (m, 8H), 2.54 (d, *J* = 7.4 Hz, 4H), 1.68 (dt, *J* = 17.8, 7.7 Hz, 4H), 1.55 (m, 4H), 1.46 (m, 4H), 1.34 (m, 8H), 1.21 (t, *J* = 7.0 Hz, 12H). HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>56</sub>H<sub>70</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>) m/z=928.4709, found 928.0941.

**Compound 6PA-TPD.** Compound **2** (0.105 g, 0.113 mmol) was dissolved in dry DMF (20 mL) under argon. Afterwards, bromotrimethylsilane (0.173 g, 1.13 mmol) was added dropwise. Reaction was kept for 2 h at 40°C under argon atmosphere. After being cooled to room temperature and dropwise add distilled water to quench the reaction and get white flocculent, continue to stir for 2h, filter, dry to get white powder **6PA-TPD**. Yield: 0.085 g (92%).<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.52 (d, *J* = 8.4 Hz, 4H), 7.29 (t, *J* = 7.9 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 7.00 (dt, *J* = 12.2, 6.8 Hz, 12H), 2.54 (d, *J* = 9.5 Hz, 4H), 1.55 (t, *J* = 7.2 Hz, 4H), 1.47 (d, *J* = 10.4 Hz, 8H), 1.38-1.19 (m, 8H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  147.7, 146.8, 145.1, 138.1, 133.9, 130.0,

129.9, 127.5, 125.1, 124.0, 123.4, 123.2, 35.0, 31.2, 30.2, 28.8, 28.7, 27.4, 23.2, 2.5, 2.3. <sup>31</sup>P NMR (162 MHz, DMSO)  $\delta$  26.90. HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>48</sub>H<sub>54</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>) m/z=816.3457, found 816.2137.



Scheme S4. The synthesis route of compound 6PA-TPDO.

**Compound 3.** Compound **3** was synthesized in the same way as described for the synthesis of Compound **1**. Yield: 0.875 g (57%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.38 (s, 6H), 6.85 (s, 18H), 3.81 (s, 6H), 3.41 (s, 4H), 2.57 (s, 4H), 1.87 (s, 4H), 1.62 (s, 4H), 1.52 – 1.44 (m, 4H), 1.38 (qd, J = 8.1, 5.4 Hz, 4H). HR-MS (MALDI-TOF):  $[M + H]^+$  (C<sub>50</sub>H<sub>54</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>) m/z=874.2532, found 873.9067.

**Compound 4.** Compound **4** was synthesized in the same way as described for the synthesis of Compound **2**. Yield: 0.480 g (95%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.49 – 7.40 (m, 4H), 7.10 (d, J = 8.4 Hz, 4H), 7.06 – 7.00 (m, 4H), 6.92 (dd, J = 8.7, 1.6 Hz, 8H), 6.90 – 6.84 (m, 4H), 4.01 – 3.89 (m, 8H), 3.74 (s, 6H), 2.51 (d, J = 2.1 Hz, 6H), 1.74 – 1.62 (m, 4H), 1.59 – 1.50 (m, 4H), 1.49 – 1.41 (m, 4H), 1.41 – 1.34 (m, 4H), 1.30 (q, J = 7.3, 6.2 Hz, 5H), 1.21 (t, J = 7.0 Hz, 13H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  140.4, 129.7, 127.6, 127.2, 123.8, 121.8, 115.5, 61.5, 61.5, 55.7, 34.8, 31.1, 30.0, 29.8, 28.5, 25.4, 24.0, 22.3, 22.2, 16.7, 16.6. HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>58</sub>H<sub>74</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>) m/z=988.4920, found 988.0899.

**Compound 6PA-TPDO.** Compound **6PA-TPDO** was synthesized in the same way as described for the synthesis of Compound **6PA-TPD**. Yield: 0.038 g (86%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.42 (d, J = 8.3 Hz, 4H), 7.08 (d, J = 7.9 Hz, 4H), 7.01 (d, J = 8.3 Hz, 4H), 6.96 – 6.79 (m, 12H), 3.76 (s, 6H), 2.52 (d, J = 8.3 Hz, 4H), 1.64 –

1.43 (m, 12H), 1.43 – 1.09 (m, 12H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  156.4, 147.2, 145.5, 140.4, 137.1, 132.9, 129.7, 127.6, 127.2, 123.8, 121.8, 115.5, 55.7, 35.0, 31.3, 30.9, 30.4, 30.3, 28.8, 28.7, 27.3, 23.2, 23.1, 2.5, 2.3. <sup>31</sup>P NMR (162 MHz, DMSO)  $\delta$  27.11. HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>50</sub>H<sub>58</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>) m/z=876.3668, found 876.2253.



Scheme S5. The synthesis route of compound 6PA-TPDF.

**Compound 6.** Compound **6** was synthesized in the same way as described for the synthesis of Compound **1**. Yield: 0.351 g (21%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.40 (s, 4H), 7.06 (s, 13H), 7.03 – 6.95 (m, 9H), 3.41 (s, 2H), 2.57 (s, 4H), 1.87 (s, 4H), 1.63 (s, 4H), 1.51 – 1.43 (m, 4H), 1.38 (s, 4H). HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>48</sub>H<sub>48</sub>Br<sub>2</sub>F<sub>2</sub>N<sub>2</sub>) m/z=850.2132, found 849.9027.

**Compound 7.** Compound 7 was synthesized in the same way as described for the synthesis of Compound 2. Yield: 0.155 g (39%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.50 (dd, *J* = 8.5, 1.6 Hz, 4H), 7.15 (td, *J* = 8.6, 1.6 Hz, 8H), 7.06 (m, 4H), 7.00 – 6.89 (m, 8H), 3.96 (s, 8H), 2.54 (d, *J* = 8.0 Hz, 4H), 1.69 (dd, *J* = 17.1, 8.1 Hz, 5H), 1.54 (q, *J* = 7.5 Hz, 4H), 1.46 (q, *J* = 8.1, 5.7 Hz, 4H), 1.35 (dt, *J* = 21.6, 7.6 Hz, 9H), 1.21 (td, *J* = 7.1, 1.6 Hz, 13H). HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>56</sub>H<sub>68</sub>F<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>) m/z=964.4521, found 964.0720.

**Compound 6PA-TPDF.** Compound **6PA-TPDF** was synthesized in the same way as described for the synthesis of Compound **6PA-TPD**. Yield: 0.065 g (94%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.49 (d, J = 8.3 Hz, 4H), 7.14 (t, J = 8.4 Hz, 8H), 7.05 (t, J = 6.5 Hz, 4H), 6.94 (t, J = 7.5 Hz, 8H), 1.63 – 1.42 (m, 12H), 1.41 – 1.13 (m, 12H). <sup>13</sup>C

NMR (101 MHz, DMSO- $d_6$ )  $\delta$  146.9, 145.2, 144.0, 138.0, 133.7, 129.9, 127.5, 126.7, 126.6, 124.6, 122.8, 116.9, 116.7, 35.0, 31.2, 30.4, 30.2, 28.8, 28.7, 23.2, 2.5, 2.3. <sup>31</sup>P NMR (162 MHz, DMSO)  $\delta$  26.67. HR-MS (MALDI-TOF): [M + H]<sup>+</sup> (C<sub>48</sub>H<sub>52</sub>F<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>) m/z=852.3269, found 852.1885.

#### **Device Fabrication and Characterizations**

**Materials**: Ammonium formamide iodide (FAI) was procured by Greatcell Solar. Lead iodide (PbI<sub>2</sub>), Cesium iodide (CsI), [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were procured by Xi'an Sunbath Photovoltaic Technology Co. 1-Allyl-3-methylimidazolium dicyanamide (AMI) and Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) nanoparticle dispersion (20 wt% in IPA) was purchased from Sigma-Aldrich. PEAI, N, N-Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), NMP, chlorobenzene (CB) and isopropanol (IPA) were purchased from Aladdin. PM6, Y6 were purchased from Solarmer Materials Inc. PNDIT-F3N was purchased from Dongguan Volt Ampere Photoelectric Technology Co., LTD. All solvents and materials were commercially available and used without further purification.

**Device fabrication:** The ITO glass substrates were ultrasonically cleaned successively in detergent solution, deionized water (twice), and isopropanol (twice), each lasting 30 minutes. Following the thorough cleansing, the substrates were left to reside overnight in a drying oven. Before preparing the device, the dried ITO glass substrates were cleaned with plasma for 5 min to remove organic residues, and all subsequent preparation processes were done in a nitrogen glove box.

PSC devices were fabricated with structure of ITO/SAM/Al<sub>2</sub>O<sub>3</sub>/Cs<sub>0.05</sub>FA<sub>0.95</sub>PbI<sub>3</sub>/PEAI/PCBM/BCP/Ag. Firstly, SAMs solution (0.33 mg mL<sup>-1</sup> in IPA) was spin-coated onto the ITO glass at a rotation speed of 3000 rpm for 30 seconds, followed by a thermal annealing step at 130 °C for 10 minutes. An isopropanol-diluted dispersion of Al<sub>2</sub>O<sub>3</sub> NPs (Al<sub>2</sub>O<sub>3</sub>: IPA = 1:50) was then spin-coated

onto the SAMs film at 3500 rpm for 30 seconds, with a subsequent annealing step at 120 °C for 10 minutes. The precursor fluid of conventional band-gap PSCs is 1.4 M  $Cs_{0.05}FA_{0.95}PbI_3$  for the PVK precursor solution, AMI was judiciously introduced at varying concentrations into the perovskite precursor solution. The resultant perovskite precursor solution was delicately spin-coated at 4000 rpm for 40 seconds, with a precisely timed addition of 150 µL of CB just 5 seconds before the program's conclusion, succeeded by an annealing process at 100 °C for 30 minutes. Next, the passivation layer PDADI (IPA, 1 mg mL<sup>-1</sup>) was spin-coated onto the perovskite film at 4000 rpm for 30 seconds. The passivation material used in conventional band-gap PSCs is PEAI. Subsequently, PCBM solution (CB, 15 mg mL<sup>-1</sup>) and BCP solution (IPA, 0.5 mg mL<sup>-1</sup>) were coated at 2000 rpm for 30 seconds and 4000 rpm for 30 seconds respectively. Finally, 140 nm-thick Ag were evaporated as the top metal electrode, under a pressure of 9×10<sup>-5</sup> Pa. The active area defined by a shadow mask was 0.078 cm<sup>2</sup>.

The OSC devices were fabricated with structures of ITO/SAM/Active layer/PDINOH/Ag. HTL was spin-coated on the top of ITO at 2500 r/min, and annealed at 100 °C on a hot plate for 15 min. Then, the active layer (PM6:BTP-eC9:L8-F=1:1:0.3, total concentration 7.6 mg mL<sup>-1</sup>) was dissolved in CF. HTL was spin-coated on the top of ITO at 3000 r/min, and annealed at 150 °C on a hot plate for 15 min. Then, the active layer (D:A=1:1.2, wt:wt, total concentration 15.4 mg mL<sup>-1</sup>) was dissolved in chloroform, and stirred at 50 °C for 2 h in glove box. Later, the active layer was spin-coated at 2500 rpm with the suitable thickness onto preheated HTL. Afterward, 10 nm PNDIT-F3N was spin-coated onto the active layers as a cathode interface, and the concentration was 1 mg mL<sup>-1</sup> (with 1% acetic acid in volume). Finally, 100 nm silver was thermally deposited on top of the interface through a shadow mask in a vacuum chamber at a pressure of  $1 \times 10^{-7}$  mbar. The effective area of the device was confined to 0.04 cm<sup>2</sup> by a non-refractive mask to improve the accuracy of measurements.

J-V characteristics were recorded using a Keithley 2400 Source Meter. All photovoltaic parameters for the devices were measured under 1 sun using a solar

simulator testing system from Enlitech Technology Corp., with a light intensity of 100 mW cm<sup>-2</sup> calibrated against a reference monocrystalline silicon cell (Enlitech) certified by the China General Certification Center (CGC). The external quantum efficiency (EQE) was measured using a spectral response system (Enlitech QE-R) with a silicon solar cell as the reference.



Fig. S1 Cyclic voltammetry (CV) curves of 6PA-TPD, 6PA-TPDO and 6PA-TPDF.



**Fig. S2** Dihedral angles between the two benzene rings of the core unit in the SAM molecules (a) 6PA-TPD, (b) 6PA-TPDO, and (c) 6PA-TPDF from DFT simulations.



**Fig. S3** DFT-calculated LUMO distribution of (a) 6PA-TPD, (b) 6PA-TPDO and (c) 6PA-TPDF



Fig. S4 KPFM images of (a) Au and (b) ITO films. (c) AFM height images of bare ITO.



Fig. 5 The SKPM images of ITO/SAMs and bare ITO curves.



Fig. 6 PSD data as a function of spatial frequency.



Fig. S7 Unified fit to the PSD curves of AFM height images of the SAMs.



**Fig. S8** *J-V* curves of PM6:Y6 binary OSCs using 6PA-TPD/6PA-TPDO/6PA-TPDF as the HTL.



Fig. S9 <sup>1</sup>H NMR spectra of Compound 10.



Fig. S10  $^{1}$ H NMR spectra of Compound 5.



Fig. S11 <sup>13</sup>C NMR spectra of Compound 5.



Fig. S12 <sup>1</sup>H NMR spectra of Compound 1.







Fig. S14 <sup>1</sup>H NMR spectra of 6PA-TPD.



Fig. S15 <sup>13</sup>C NMR spectra of 6PA-TPD.



140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 f1 (ppm)

Fig. S16 <sup>31</sup>P NMR spectra of 6PA-TPD.



Fig. S17 <sup>1</sup>H NMR spectra of Compound 3.



Fig. S18 <sup>1</sup>H NMR spectra of Compound 4.



Fig. S19 <sup>13</sup>C NMR spectra of Compound 4.



Fig. S20 <sup>1</sup>H NMR spectra of 6PA-TPDO.



Fig. S21 <sup>13</sup>C NMR spectra of 6PA-TPDO.



140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 f1 (ppm)

Fig. S22 <sup>31</sup>P NMR spectra of 6PA-TPDO.



Fig. S23 <sup>1</sup>H NMR spectra of Compound 6.



Fig. S24 <sup>1</sup>H NMR spectra of Compound 7.



Fig. S25 <sup>1</sup>H NMR spectra of 6PA-TPDF.



Fig. S26 <sup>13</sup>C NMR spectra of 6PA-TPDF.



Fig. S27 <sup>31</sup>P NMR spectra of 6PA-TPDF.

molecule	$T_d^{(a)}$	Solution	Film <sup>c)</sup>			CV <sup>e)</sup>		DFT <sup>f)</sup>		
	[°C]	$\lambda_{\max}^{b)}[nm]$	λ <sub>max</sub> [nm]	λ <sub>edge</sub> [nm]	$E_{\rm gap}^{\rm d)}[{\rm eV}]$	HOI /LUM	MO O[eV]	HO /LUM	MO O[eV]	
6PA-	375	353	359	421	2.95	-5.20	-	-	-	
TPD	575	555	207	.21	2.95	0.20	2.23	5.10	1.39	
6PA-	308	8 356 3	366	433	3 2.86	-5.06	-	-	-	
TPDO			500	155			2.16	4.91	1.28	
6PA-	237	237 34	349	349 307	433	2.86	-5 21	-	-	-
TPDF		519	201	.55	2.00	2.21	2.35	5.11	1.34	

Table S1. The physicochemical properties of 6PA-TPD, 6PA-TPDO and 6PA-TPDF.

a) Decomposition temperature; b) UV-vis spectra in solution; c) UV-vis spectra in thin film; d) Optical bandgap from thin film absorption onset; e) HOMO level measured from cyclic voltammetry:  $E_{HOMO} = -(E_{ox} + 4.41) \text{ eV}$ ;  $E_{LUMO} = (E_{HOMO} + E_{gap}) \text{ eV}$ . f) HOMO and LUMO energy levels calculated by DFT.

Compounds	$WF(eV)^{[a]}$	WF (eV) <sup>[b]</sup>		
Au	5.200			
ITO	4.998	4.700		
ITO/6PA-TPD	4.962	4.709		
ITO/6PA-TPDO	5.019	5.027		
ITO/6PA-TPDF	4.722	4.701		

Table S2. CPD and WF of Au, bare ITO, and SAM-modified ITO.

<sup>*a*</sup> The WF values measured by KPFM.<sup>2</sup> <sup>*b*</sup> The WF values measured by SKPM.

 Table S3. Summary of fitting data of PSD curves.

Sample	G	$R_{g}(Å)$	Р
6PA-TPD	4.95×10 <sup>-10</sup>	1079	0.777
6PA-TPDO	1.79×10 <sup>-8</sup>	1199	1.452
6PA-TPDF	7.91×10 <sup>-8</sup>	385.1	2.19

**Table S4.** The contact angle of water and ethylene glycol and the surface energy of 6PA-TPD, 6PA-TPDO and 6PA-TPDF.

-	ITO/SAMs	$\theta_{\rm water}$ [°]	$ heta_{_{EG}}[^\circ]$	surface energy[mJ/m <sup>2</sup> ]
-	6PA-TPD	82	49	34.7
	6PA-TPDO	90	45	49.9
	6PA-TPDF	80	54	32.3

	$V_{\rm oc}(V)$	$J_{\rm SC} ({\rm mA~cm}^{-2})$	FF (%)	PCE (%)
6PA-TPD	0.820	28.46	71.91	16.95(16.79±0.23)
6PA-TPDO	0.710	28.15	68.70	13.86(13.73±0.11)
6PA-TPDF	0.847	27.48	74.81	17.74(17.41±0.47)

**Table S5.** Performance of PM6:Y6 based OSCs using 6PA-TPD, 6PA-TPDO and 6PA-TPDF as HTLs, measured under AM 1.5 G illumination (100 mW cm<sup>-2</sup>).

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