Electronic Supplementary Information for:

# Effects of alkoxylation position on fused-ring electron acceptors

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## Materials

Unless stated otherwise, all the chemical reagents and solvents were obtained commercially and used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone under nitrogen. 2FIC,<sup>S1</sup> compound 1,<sup>S2</sup> compound 5,<sup>S3</sup> IOIC2,<sup>S2</sup> and IOIC3<sup>S3</sup> were synthesized according to our reported procedures. PM6 was purchased from Solarmer Materials (Beijing) Inc.

### Synthesis

**Compound 2.** A Grignard reagent was prepared as follows: to a suspension of magnesium turnings (144 mg, 6 mmol) and 2-3 drops of 1,2-dibromoethane in dry THF (6 mL) was added 1-bromo-4-hexyloxybenzene (1.68 g, 6 mmol) dropwise, and the mixture was stirred at 65 °C for 1.5 h. To a solution of compound 1 (430 mg, 0.6 mmol) in dry THF (10 mL) under nitrogen was added the prepared Grignard reagent dropwise at room temperature. The mixture was refluxed for 12 h and then cooled to room temperature. A saturated NH<sub>4</sub>Cl aqueous solution (10 mL) was added and the mixture was extracted with dichloromethane (2 × 50 mL). The combined organic layer was dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, a brown solid was obtained and directly used for next step reaction without further purification.

**Compound 3.** To a solution of compound **2** in octane (50 mL) was added acetic acid (10 mL) and sulfuric acid (0.05 mL) slowly. The resulting solution was stirred at 65 °C for 12 h. After removal of the octane under reduced pressure, the residue was washed by sodium carbonate aqueous solution (50 mL × 3) and extracted with dichloromethane (50 mL × 2). Then, the crude products were purified by column chromatography on silica gel using petroleum ether/dichloromethane (6: 1) to give a yellow solid (320 mg, 2 steps overall yield 41%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.12 (s, 2H), 7.30 (d, *J* = 8.1 Hz, 8H), 7.13 (d, *J* = 4.8 Hz, 2H), 6.96 (d, *J* = 4.8 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 8H), 3.88 (m, 8H), 2.55 (m, 4H), 1.73 (m, 4H), 1.54 (m, 8H), 1.29 (m, 32H), 0.94 (m, 18H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>): δ 162.59, 156.95, 152.66, 139.31, 136.66, 135.67, 133.19, 133.06, 130.50, 128.89, 125.70, 123.93, 121.69, 118.84, 113.37, 112.97, 66.88, 61.75, 33.37, 30.80, 30.56, 29.75, 28.68, 28.23, 28.18, 24.71, 21.65, 21.56, 13.11, 12.99. MS (MALDI-TOF): *m/z* 1301.1 (M<sup>+</sup>).

**Compound 4.** In a dry three-necked round-bottomed flask, compound **3** (261 mg, 0.2 mmol) was dissolved in anhydrous THF (20 mL). The mixture was deoxygenated with argon for 20 min. At -78 °C, a solution of *n*-butyllithium (1.6 M in hexane, 1.27 mL, 2.0 mmol) was added dropwise. After 1 h of stirring at -78 °C, anhydrous DMF (0.8 mL) was added to this solution. The mixture was warmed to room temperature and stirred overnight. Brine (30 mL) was added and the mixture was extracted with dichloromethane (2 × 50 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub> and filtered. After the solvent was removed from the filtrate, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1: 2) as eluent, yielding a yellow solid (209 mg, 77%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.74 (s, 2H), 7.78 (s, 2H),7.60 (s, 2H), 7.31 (d, *J* = 8.1 Hz, 8H), 6.79 (d, *J* = 8.1 Hz, 8H), 3.90 (m, 8H), 2.58 (m, 4H), 1.73 (m, 12H), 1.31 (m, 36H), 0.94 (m, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  181.83, 163.31, 158.07, 157.29, 144.88, 143.62, 142.20, 137.06, 136.60, 133.74, 130.44, 129.41, 125.02, 120.03, 113.83, 67.65, 62.75, 33.92, 31.33, 30.27, 29.24, 28.77, 25.23, 22.22, 22.13, 13.43, 13.30. MS (MALDI-TOF): *m/z* 1357.2 (M<sup>+</sup>).

**IOIC4.** To a three-necked round bottom flask were added compound **4** (136 mg, 0.1 mmol), 2FIC (83 mg, 0.36 mmol), pyridine (0.5 mL) and chloroform (30 mL). The mixture was deoxygenated with nitrogen for 20 min and then stirred at reflux for 15 h. After cooling to room temperature, the mixture was poured into methanol (200 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1: 2) as eluent yielding a purple solid (135 mg, 76%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.78 (s, 2H), 8.50 (m, 2H), 7.76 (s, 2H), 7.62 (m, 4H), 7.35 (d, *J* = 7.8 Hz, 8H), 7.21 (d, *J* = 7.8 Hz, 8H), 3.91 (m, 8H), 2.56 (m, 4H), 1.75 (m, 12H), 1.39 (m, 36H), 0.94 (m, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  184.96, 164.47, 163.88, 159.56, 157.51, 156.81,

154.07, 151.63, 151.47, 143.76, 139.15, 137.73, 137.29, 137.07, 136.90, 133.33, 128.79, 128.51, 124.92, 120.08, 119.11, 113.39, 67.00, 61.97, 33.35, 30.73, 30.54, 29.74, 28.17, 24.70, 21.67, 21.56, 13.13, 13.01. MS (MALDI-TOF): *m/z* 1781.8 (M<sup>+</sup>). Anal. Calcd for C<sub>110</sub>H<sub>104</sub>F<sub>4</sub>N<sub>4</sub>O<sub>6</sub>S<sub>4</sub>: C, 74.13; H, 5.88; N, 3.14. Found: C, 74.02; H, 5.96; N, 3.09.

**Compound 6.** A Grignard reagent was prepared as follows: to a suspension of magnesium turnings (144 mg, 6 mmol) and 2-3 drops of 1,2-dibromoethane in dry THF (6 mL) was added 1-bromo-4-hexyloxybenzene (1.68 g, 6 mmol) dropwise, and the mixture was stirred at 65 °C for 1.5 h. To a solution of compound **5** (449 mg, 0.6 mmol) in dry THF (10 mL) under nitrogen was added the prepared Grignard reagent dropwise at room temperature. The mixture was refluxed for 12 h and then cooled to room temperature. A saturated NH<sub>4</sub>Cl aqueous solution (10 mL) was added and the mixture was extracted with dichloromethane (2 × 50 mL). The combined organic layer was dried over MgSO<sub>4</sub>. After removal of the solvent under reduced pressure, a brown solid was obtained and directly used for next step reaction without further purification.

**Compound 7.** To a solution of compound **6** in octane (50 mL) was added acetic acid (10 mL) and sulfuric acid (0.05 mL) slowly. The resulting solution was stirred at 65 °C for 12 h. After removal of the octane under reduced pressure, the residue was washed by sodium carbonate aqueous solution (50 mL × 3) and extracted with dichloromethane (50 mL × 2). Then, the crude products were purified by column chromatography on silica gel using petroleum ether/dichloromethane (5: 1) to give a yellow solid (336 mg, 2 steps overall yield 42 %). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.27 (d, *J* = 8.4 Hz, 8H), 7.22 (d, *J* = 4.8 Hz, 2H), 6.95 (d, *J* = 4.8 Hz, 2H), 6.90 (s, 2H), 6.73 (d, *J* = 8.4 Hz, 8H), 3.89 (m, 12H), 1.73 (m,12H), 1.22 (m, 36H), 0.91 (m, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.73, 156.73, 152.35, 150.67, 139.74, 133.78, 131.94, 128.89, 126.63, 125.98, 125.46, 122.00, 121.42, 113.72, 112.44, 97.91, 66.84, 61.86, 30.70, 30.57, 28.68, 28.28, 27.26, 24.73, 24.55, 21.57, 21.46, 13.12, 12.99. MS (MALDI-TOF): *m/z* 1333.3 (M<sup>+</sup>).

**Compound 8.** In a dry three-necked round-bottomed flask, compound 7 (267 mg, 0.2 mmol) was dissolved in anhydrous THF (20 mL). The mixture was deoxygenated with argon for 20 min. At -78 °C, a solution of *n*-butyllithium (1.6 M in hexane, 1.27 mL, 2.0 mmol) was added dropwise. After 1 h of stirring at -78 °C, anhydrous DMF (0.8 mL) was added to this solution. The mixture was warmed to room temperature and stirred overnight. Brine (30 mL) was added and the mixture was extracted with dichloromethane (2 × 50 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub> and filtered. After the solvent was removed from the filtrate, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1: 2) as eluent, yielding a yellow solid (208 mg, 75%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.77 (s, 2H), 7.59 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 8H), 6.81 (d, *J* = 8.0 Hz, 8H), 6.56 (s, 2H), 3.93 (m, 8H), 3.73 (m, 4H), 1.74 (m, 12H), 1.23 (m, 36H), 0.85 (m, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  182.38, 163.09, 158.55, 157.60, 151.94, 145.29, 144.89, 143.30, 135.30, 131.32, 130.06, 126.95, 122.95, 113.91, 99.23, 68.22, 63.50, 32.07, 31.82, 30.22, 30.16, 29.83, 29.49, 28.50, 27.20, 26.84, 25.64, 22.82, 13.10. MS (MALDI-TOF): *m/z* 1389.6 (M<sup>+</sup>).

**IOIC5.** To a three-necked round bottom flask were added compound **8** (139 mg, 0.1 mmol), 2FIC (83 mg, 0.36 mmol), pyridine (0.5 mL) and chloroform (30 mL). The mixture was deoxygenated with nitrogen for 20 min and then stirred at reflux for 15 h. After cooling to room temperature, the mixture was poured into methanol (200 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1: 2) as eluent yielding a purple solid (145 mg, 80%). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.81 (s, 2H), 8.39 (m, 2H), 7.62 (m, 4H), 7.35 (d, *J* = 8.1 Hz, 8H), 6.83 (d, *J* = 8.1 Hz, 8H), 6.55 (s, 2H), 3.93 (m, 8H), 3.68 (m, 4H), 1.73 (m, 8H), 1.53 (m, 4H), 1.41 (m, 28H), 1.06 (m, 8H), 0.88 (m, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  185.98, 164.35, 161.63, 160.44, 158.71, 155.77, 152.28, 144.97, 140.38, 138.67, 138.25, 136.58, 134.60, 131.41, 130.15, 129.42, 127.40, 123.33, 121.04, 115.01, 114.71, 114.51, 114.10, 99.92, 99.81, 69.09,

68.27, 63.55, 62.37, 31.93, 31.73, 29.41, 28.48, 25.84, 22.72, 22.65, 14.06, 13.89. MS (MALDI-TOF): *m/z* 1813.8 (M<sup>+</sup>). Anal. Calcd for C<sub>110</sub>H<sub>104</sub>F<sub>4</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>: C, 72.82; H, 5.78; N, 3.09. Found: C, 72.66; H, 5.87; N, 3.13.

## Characterization

The NMR spectra were measured using Bruker AVANCE 300 or 400 MHz spectrometer. Mass spectra were measured on a Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. The UPS data were recorded on the Kratos AXIS ULTRA DLD. The gas discharge lamp was used for UPS, with helium gas admitted and the HeI (21.22 eV) emission line employed. UPS samples were prepared on silicon substrate by spin coating. UV-vis absorption spectra were recorded using a JASCO V-570 spectrophotometer. The atomic force microscope (AFM) measurements were performed on a MFP-2D-BIO, Asylum Research in AC mode. The transmission electron microscopy (TEM) characterization was carried out on a JEM-2100 transmission electron microscope operated at 200 kV. The samples for the TEM measurements were prepared as follows: The active layer films were spin-casted on indium tin oxide (ITO)/poly(3, 4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS) substrates, and the substrates with the active layers were submerged in deionized water to make the active layers float onto the air-water interface. Then, the floated films were picked up on unsupported 200 mesh copper grids for the TEM measurements. The grazing-incidence wide-angle X-ray scattering (GIWAXS) and small-angle X-ray scattering (GISAXS) measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°. Both GIWAXS and GISAXS samples were prepared on silicon substrate by spin coating.

### Fabrication and characterization of OSCs

OSCs were fabricated with the structure of ITO/ZnO/PM6: acceptor/MoO<sub>3</sub>/Ag. The patterned ITO glass (sheet resistance = 10  $\Omega$ ) was pre-cleaned in an ultrasonic bath with

acetone and isopropanol. ZnO electron transport layer was prepared onto the ITO glass through spin coating at 4000 rpm from a ZnO precursor solution, then the ZnO substrates were immediately baked in air at 200 °C for 30 min. A CHCl<sub>3</sub> solution (totally 13.5 mg mL<sup>-1</sup>) of PM6: acceptor was spin-coated (2500 rpm) on the ZnO layer to form a photoactive layer (ca. 100 nm). The thickness of the photoactive layer was measured using Bruker Dektak-XT. The MoO<sub>3</sub> layer (ca. 5 nm) and Ag (ca. 80 nm) were successively evaporated onto the surface of the photoactive layer under vacuum (ca.  $10^{-5}$  Pa). The active area of the device was *ca*. 4 mm<sup>2</sup>. An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70 × 70 mm<sup>2</sup> photobeam size) coupled with AM 1.5G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm<sup>-2</sup>. A  $2 \times 2$  cm<sup>2</sup> monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The currentvoltage (J-V) measurement of the devices was conducted using a computer-controlled Agilent B2912A Precision Source/Measure Unit (Agilent Technologies). The external quantum efficiency (EQE) spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

### **Mobility measurements**

Hole-only or electron-only devices were fabricated using the architectures: ITO/PEDOT: PSS/PM6: acceptor/Au for holes and Al/PM6: acceptor/Al or Al/acceptor/Al for electrons. A chloroform solution (totally 13.5 mg mL<sup>-1</sup>) of acceptor or PM6: acceptor was spin-coated (2500 rpm). Mobilities were extracted by fitting the current density-voltage curves using space charge limited current (SCLC).<sup>S4</sup> The *J*–*V* curves of the devices were plotted as  $\ln[Jd^3/V^2]$  versus  $[V/d]^{0.5}$  using Eq.  $J = 9\varepsilon_0\varepsilon_r\mu_h(\mu_e)V^2/8d^3$  for holes and electrons, where *J* is current density, *d* is film thickness of active layer,  $\mu_h$  is hole mobility,  $\mu_e$  is electron mobility,  $\varepsilon_r$  is relative dielectric constant of the transport medium, and  $\varepsilon_0$  is permittivity of free space (8.85 × 10<sup>-12</sup> F m<sup>-1</sup>).  $V = V_{appl} - V_{bi}$ ,  $V_{appl}$  is the applied voltage,  $V_{bi}$  is the offset voltage.



Scheme S1 Synthetic routes to IOIC4 and IOIC5.



Fig. S1 UV-Vis absorption spectra of the IOIC series in chloroform solution ( $10^{-6}$  M).



Fig. S2 UPS (He I: 21.22 eV) data of the (a) PM6, (b) IOIC2, (c) IOIC3, (d) IOIC4 and (e) IOIC5 neat films.



Fig. S3 J-V characteristics in the dark for electron-only devices based on IOIC4 and IOIC5.



**Fig. S4** *J-V* characteristics in the dark for (a) hole-only and (b) electron-only devices based on PM6: acceptor blended films.



**Fig. S5** AFM height images of (a) PM6: IOIC2, (b) PM6: IOIC3, (c) PM6: IOIC4, and (d) PM6: IOIC5 blended films.



**Fig. S6** TEM images of (a) PM6: IOIC2, (b) PM6: IOIC3, (c) PM6: IOIC4, and (d) PM6: IOIC5 blended films.



**Fig. S7** (a) 2D GIWAXS patterns of the pure acceptors. (b) The corresponding intensity profiles along the (b) in-plane and (c) out-of-plane directions.



Fig. S8 2D GISAXS patterns of the blend films.

active layer	D/A (w/w)	$V_{\rm OC}({ m V})$	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF (%)	PCE (%)
PM6: IOIC2	1:1	0.969	15.5	63.7	9.57
PM6: IOIC2	1:1.2	0.973	15.3	63.5	9.45
PM6: IOIC2	1:1.5	0.970	14.8	62.8	9.02
PM6: IOIC3	1:1	0.922	18.4	66.1	11.2
PM6: IOIC3	1:1.2	0.922	18.2	65.6	11.0
PM6: IOIC3	1:1.5	0.921	17.8	64.7	10.6
PM6: IOIC4	1:1	0.966	16.1	62.2	9.67
PM6: IOIC4	1:1.2	0.964	16.6	62.7	10.0
PM6: IOIC4	1:1.5	0.961	15.4	63.1	9.34
PM6: IOIC5	1:1	0.921	18.7	66.5	11.5
PM6: IOIC5	1:1.2	0.920	19.6	68.1	12.3
PM6: IOIC5	1:1.5	0.917	18.3	67.2	11.2

**Table S1** Photovoltaic parameters of the OSCs based on PM6: acceptors with differentdonor/acceptor (D/A) weight ratios in chloroform and thermal annealing at 100 °C for 5 min.

active layer	DIO content (vol%)	$V_{\rm OC}\left({ m V} ight)$	$J_{\mathrm{SC}} (\mathrm{mA} \mathrm{cm}^{-2})$	FF (%)	PCE (%)
PM6: IOIC2	0.1	0.963	15.8	64.8	9.86
PM6: IOIC2	0.2	0.972	15.9	66.0	10.2
PM6: IOIC2	0.3	0.970	16.3	66.1	10.5
PM6: IOIC3	0.1	0.921	19.7	68.8	12.5
PM6: IOIC3	0.2	0.920	20.0	69.7	12.8
PM6: IOIC3	0.3	0.916	19.3	68.3	12.1
PM6: IOIC4	0.1	0.964	17.3	66.7	11.1
PM6: IOIC4	0.2	0.965	16.7	65.2	10.5
PM6: IOIC4	0.3	0.956	17.2	63.6	10.4
PM6: IOIC5	0.1	0.921	20.6	70.7	13.4
PM6: IOIC5	0.2	0.920	20.9	71.5	13.8
PM6: IOIC5	0.3	0.918	20.3	68.9	12.9

 Table S2 DIO content optimization of the OSC devices based on the optimal D/A ratios and

 thermal annealing at 100 °C for 5 min.

 Table S3 Hole and electron mobilities of blended films.

active layer	$\mu_{\rm h} (10^{-4}  {\rm cm}^2  { m V}^{-1}  { m s}^{-1})$	$\mu_{\rm e} (10^{-4}{\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	$\mu_{ m h}/\mu_{ m e}$
PM6: IOIC2	2.3	0.5	4.6
PM6: IOIC3	2.4	0.6	4.0
PM6: IOIC4	1.6	0.4	4.0
PM6: IOIC5	4.5	1.4	3.2

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