

## Supplementary Information

### Clarifying the effects of sidechain substitution direction on the optoelectronic properties of isomeric diketopyrrolopyrrole-based conjugated polymers for near-infrared organic phototransistors

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#### 1. Instruments and Measurements

All commercially available solvents, reagents, and chemicals were purchased from Aldrich, TCI and several other reagent companies and used as received without further purification unless otherwise specified. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns were designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). Deuterated chloroform was used as the solvent. The NMR chemical shifts were reported in ppm (parts per million) relative to the residual solvent peak at 7.26 ppm (chloroform) for the  $^1\text{H}$  NMR spectroscopy and

77.6 ppm (chloroform) for the  $^{13}\text{C}$  NMR spectroscopy. The MALDI-TOF mass spectra were measured by a Bruker autoflex maX MALDI-TOF mass spectrometer. Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra were acquired from PerkinElmer Lambda 750 spectrophotometer. Polymer molecular weights were characterized on Polymer Laboratories GPC-PL220 high temperature GPC/SEC system (Agilent Technologies) at 150 °C vs polystyrene standards using 1,2,4-trichlorobenzene as the eluent. Thermogravimetric analysis (TGA) curves were collected on Mettler STAR<sup>e</sup> (TA Instrument), with a heating ramp of 10 °C min<sup>-1</sup>. Cyclic voltammetry (CV) measurements of polymer films were performed under argon atmosphere using a CHI760E voltammetric analyzer with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode were employed. The scanning rate was 0.1 V s<sup>-1</sup>. Polymer films were drop-casted from chloroform solutions on a Pt working electrode (2 mm in diameter). The supporting electrolyte solution was thoroughly purged with argon before all CV measurements. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured under the same conditions, and it was located at 0.34 V vs. the Ag/AgCl electrode. It was assumed that the redox potential of Fc/Fc<sup>+</sup> has an absolute energy level of -4.80 eV to a vacuum. The HOMO and LUMO energy levels were then calculated according to the following equations:

$$E_{\text{HOMO}} = -(\varphi_{\text{ox}} + 4.46) \text{ (eV)} \quad (\text{Eq. 1})$$

$$E_{\text{LUMO}} = -(\varphi_{\text{re}} + 4.46) \text{ (eV)} \quad (\text{Eq. 2})$$

where  $\varphi_{\text{ox}}$  is the onset oxidation potential vs. Ag/AgCl and  $\varphi_{\text{re}}$  is the onset reduction potential vs. Ag/AgCl.

## 2. Fabrication and Characterization of Organic Transistors

The OFETs with a bottom-gate top-contact configuration were prepared to characterize the electrical performance of solution-processed polymer films. A highly *n*-doped Si wafer with a thermally grown SiO<sub>2</sub> (300 nm, Ci = 10 nF cm<sup>2</sup>) was utilized

as the substrate and gate dielectrics. The SiO<sub>2</sub> surface was modified with a self-assembled monolayer (SAM) of octadecyltrimethoxysilane (OTS). The cleaned substrates were transferred into a N<sub>2</sub>-filled glove box (O<sub>2</sub>, H<sub>2</sub>O concentration < 0.1 ppm) for the deposition of the active layers on top. The semiconductor layer was spin-coated from chlorobenzene solution (5 mg mL<sup>-1</sup>), then annealed at 160°C for 30 min followed by cooling down process. Finally, source and drain electrode was thermally evaporated on top under high vacuum (< 10<sup>-6</sup> Torr) to complete OTFT fabrication.

The field-effect transistor devices were measured in a N<sub>2</sub>-filled glove box with Keithley S4200 SCS semiconductor characterization system. The saturation field effect mobility ( $\mu$ ) was calculated from the average slope of the  $|I_{SD}|^{1/2}$  vs  $V_g$  plot according to the following equation:

$$I_{SD} = (W/2L)C_i\mu(V_g - V_{th})^2$$

where  $I_{SD}$  is the drain current in the saturated regime, W (4200 $\mu$ m) and L (50 $\mu$ m) are the semiconductor channel width and length, respectively.

### 3. Additional Synthetic Details

**Synthetic Details of the monomers:** All chemicals were purchased from Tokyo Chemical Industry (TCI), Kanto, and Sigma-Aldrich and used as received unless otherwise stated.

*Synthesis of 2,5-bis(2-octyldodecyl)-3,6-bis(5'-(2-(2-octyldodecyl)-6-((2-octyldodecyl)oxy)-3-oxo-4-(thiophen-2-yl)-2,3-dihydropyrrolo[3,4-c]pyrrol-1-yl)-[2,2'-bithiophen]-5-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (ODO):* 2,5-bis(2-octyldodecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl)-2,5-

dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.5g, 0.45 mmol), PPO-Br (1.27g, 1.35 mmol), Pd<sub>2</sub>dba<sub>3</sub> (5%, 20 mg), P(*o*-tol)<sub>3</sub> (20%, 30 mg), Aliquat 336 (three drops) were successively added into a Schlenk tube. Then, 10 mL anhydrous toluene and 2 ml potassium carbonate solution (2M) was added via syringe. The reaction solution was rigorously stirred at 110 °C for 12 h under argon atmosphere. Removal of the toluene by rotary evaporator afforded the crude product, which was then purified by chromatograph column (CC) on silica gel using a mixture of petroleum ether and dichloromethane as eluent. The title compound was obtained as a purple solid (42% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 9.01 (d, *J* = 4.0 Hz, 2H), 8.39 (br s, 2H), 8.23 (br s, 2H), 7.68 (br s, 2H), 7.38(m, 4H), 7.22 (t, *J* = 4.0 Hz, 2H), 4.51 (br s, 4H), 4.06 (d, *J* = 8.0 Hz, 4H), 3.93 (d, *J* = 4.0 Hz, 4H), 1.99 (br s, 2H), 1.83 (br s, 4H), 1.28-1.21 (m, 254H), 0.87-0.84 (m, 48H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 165.83, 161.50, 161.33, 148.00, 142.67, 142.19, 140.44, 139.30, 138.85, 137.80, 135.39, 132.89, 131.67, 130.26, 128.08, 126.74, 125.51, 124.69, 124.18, 114.41, 112.28, 108.91, 73.07, 46.58, 46.12, 38.45, 38.14, 32.19, 31.64, 31.46, 30.40, 29.95, 29.68, 27.44, 26.72, 26.49, 22.95, 14.36. MALDI-TOF MS (*M*<sub>w</sub> = 2580.26): found *m/z* = 2580.76[M<sup>+</sup>].

*Synthesis of* 2,5-bis(2-octyldodecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**OBO**): 4,7-bis(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)benzo[*c*][1,2,5]thiadiazole (0.5g, 1.29 mmol), PPO-Br (3.6g, 3.83 mmol), Pd<sub>2</sub>dba<sub>3</sub> (5%, 60 mg), P(*o*-tol)<sub>3</sub> (20%, 90 mg), Aliquat 336 (three

drops) were successively added into a Schlenk tube. Then, 30 mL anhydrous toluene and 6 ml potassium carbonate solution (2M) was added via syringe. The reaction solution was rigorously stirred at 110 °C for 12 h under argon atmosphere. Removal of the toluene by rotary evaporator afforded the crude product, which was then purified by chromatograph column (CC) on silica gel using a mixture of petroleum ether and dichloromethane as eluent. The title compound was obtained as a purple solid (48% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.48 (d, *J* = 4.0 Hz, 2H), 8.25 (m, 4H), 7.93 (br s, 2H), 7.66 (d, *J* = 4.0 Hz, 2H), 7.21 (t, *J* = 4.0 Hz, 2H), 4.54 (d, *J* = 4.0 Hz, 4H), 3.93 (d, *J* = 4.0 Hz, 4H), 1.85 (br s, 4H), 1.42-1.22 (m, 152H), 0.87-0.85 (m, 28H).  
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 165.81, 161.28, 152.50, 148.67, 144.22, 141.82, 139.75, 135.31, 130.27, 129.12, 128.57, 128.05, 125.90, 125.78, 114.31, 111.94, 73.05, 46.01, 38.13, 38.03, 32.16, 31.85, 29.99, 29.72, 29.62, 27.31, 26.49, 22.97, 22.95, 14.37. MALDI-TOF MS (*M*<sub>w</sub> = 1855.00): found *m/z* = 1854.93 [*M*<sup>+</sup>].

#### ***Direct arylation polymerization of P3BT-B***

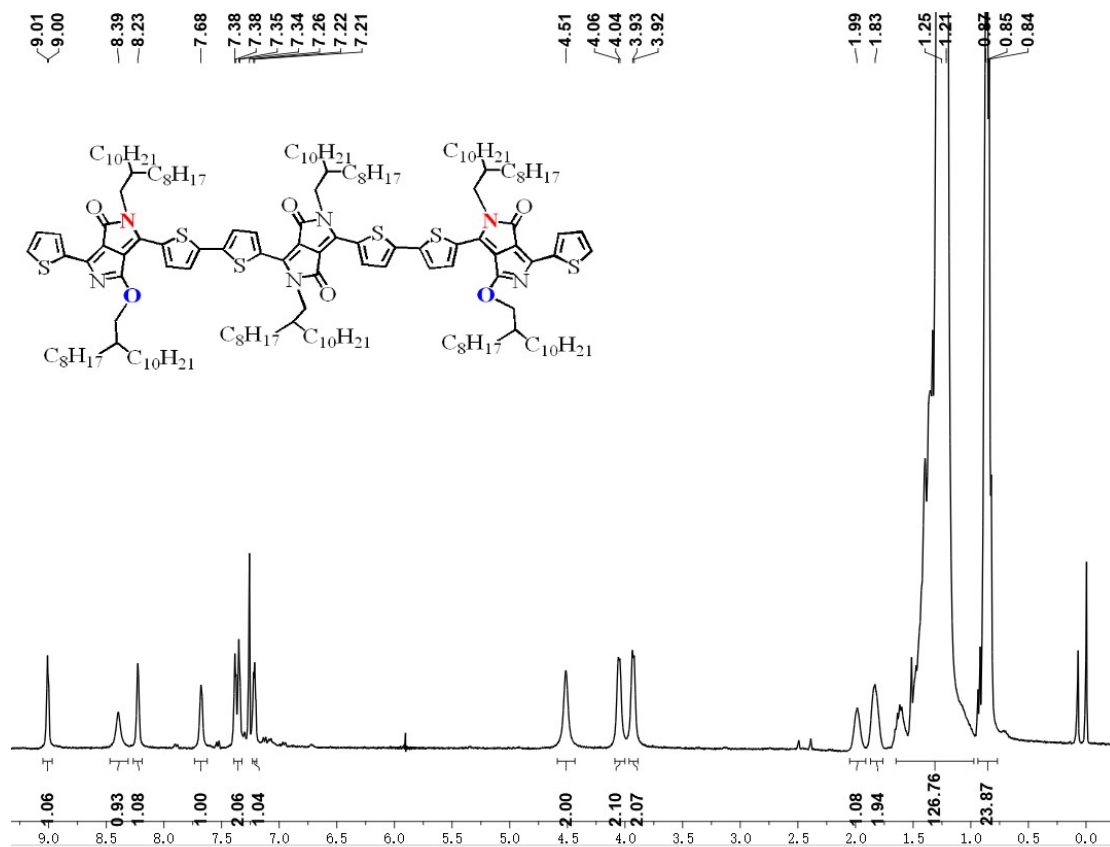
ODO (258 mg, 0.1 mmol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (29 mg, 0.1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5 mg, 5%), P(*o*-anisyl)<sub>3</sub> (15 mg, 10%), PivOH (10 mg, 0.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (90 mg, 0.25 mmol) were added into a well-dried Schlenk flask. This flask was subjected to pump and purge cycles with N<sub>2</sub> for three times, followed by the addition of 1.5 mL of toluene. After stirring for 1 hours at 110°C, the mixture was dropped into 100 mL of methanol. The crude product was filtered and then purified via

Soxhlet extraction with methanol, acetone, hexane, and chloroform. The collected chloroform fraction was concentrated, and then precipitated into methanol to obtain a dark solid (90%). GPC (1,2,4-trichlorobenzene, 150 °C):  $M_n = 27.1 \text{ kg mol}^{-1}$ , PDI = 2.1.

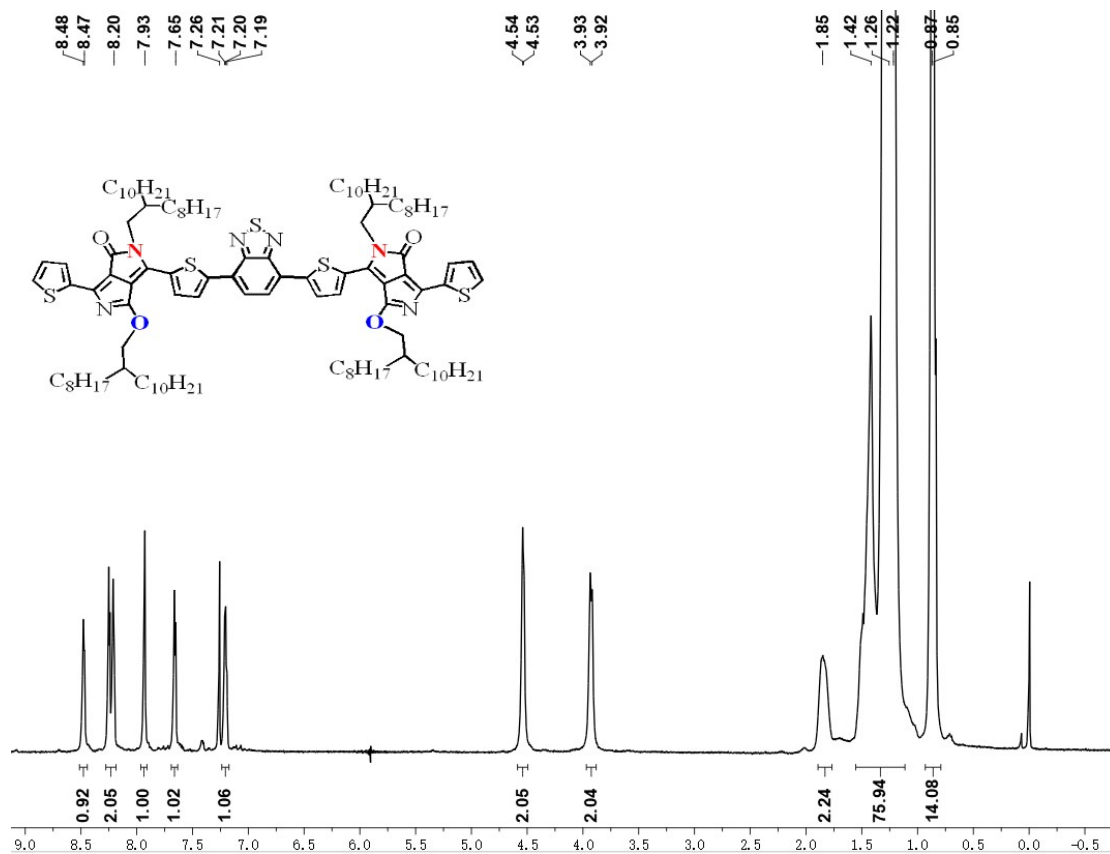
#### ***Direct arylation polymerization of P3BT-C***

OBO (186 mg, 0.1 mmol), 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (102 mg, 0.1 mmol),  $\text{Pd}_2(\text{dba})_3$  (5 mg, 5%),  $\text{P}(o\text{-anisyl})_3$  (4 mg, 10%), PivOH (10 mg, 0.1 mmol),  $\text{Cs}_2\text{CO}_3$  (80 mg, 0.25 mmol) were added into a well-dried Schlenk flask. This flask was subjected to pump and purge cycles with  $\text{N}_2$  for three times, followed by the addition of 2 mL of toluene. After stirring for 12 hours at 110°C, the mixture was dropped into 100 mL of methanol. The crude product was filtered and then purified via Soxhlet extraction with methanol, acetone, hexane, and chloroform. The collected chloroform fraction was concentrated, and then precipitated into methanol to obtain a dark solid (92%). GPC (1,2,4-trichlorobenzene, 150 °C):  $M_n = 20.8 \text{ kg mol}^{-1}$ , PDI = 2.3.

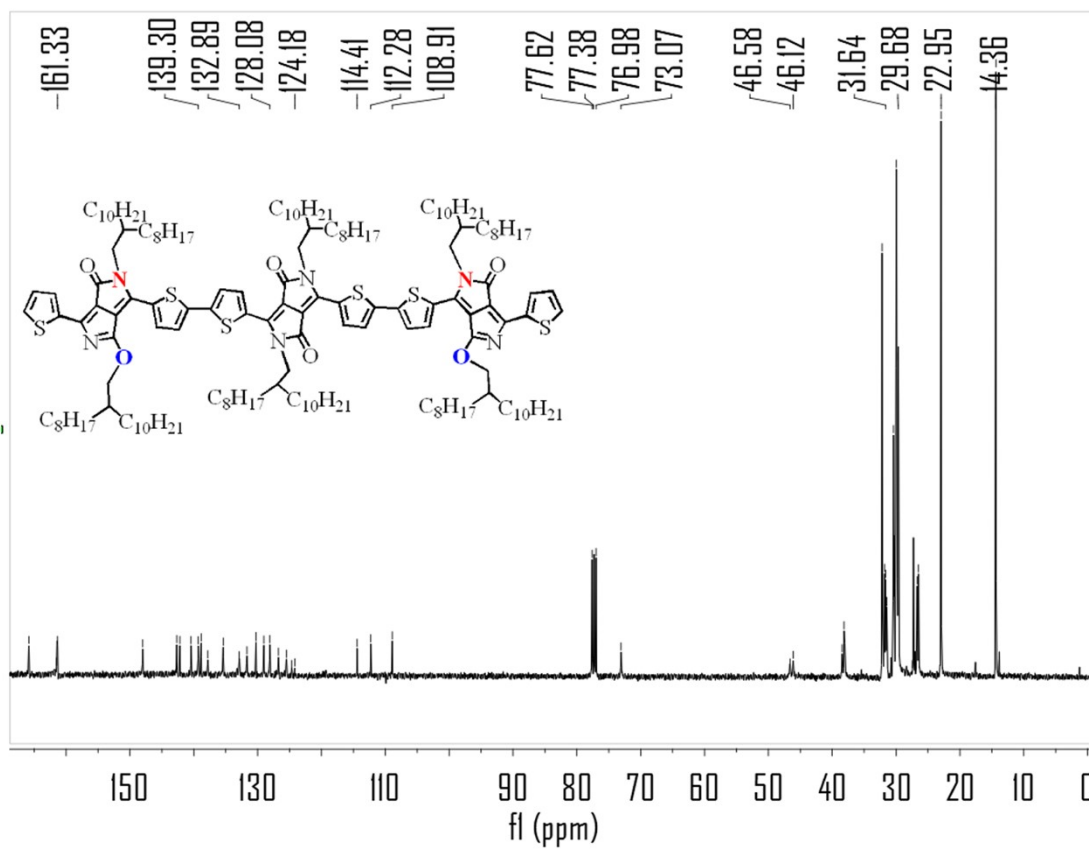
#### **4. Supplementary Tables and Figures**



**Figure S1.** <sup>1</sup>H NMR of ODO.

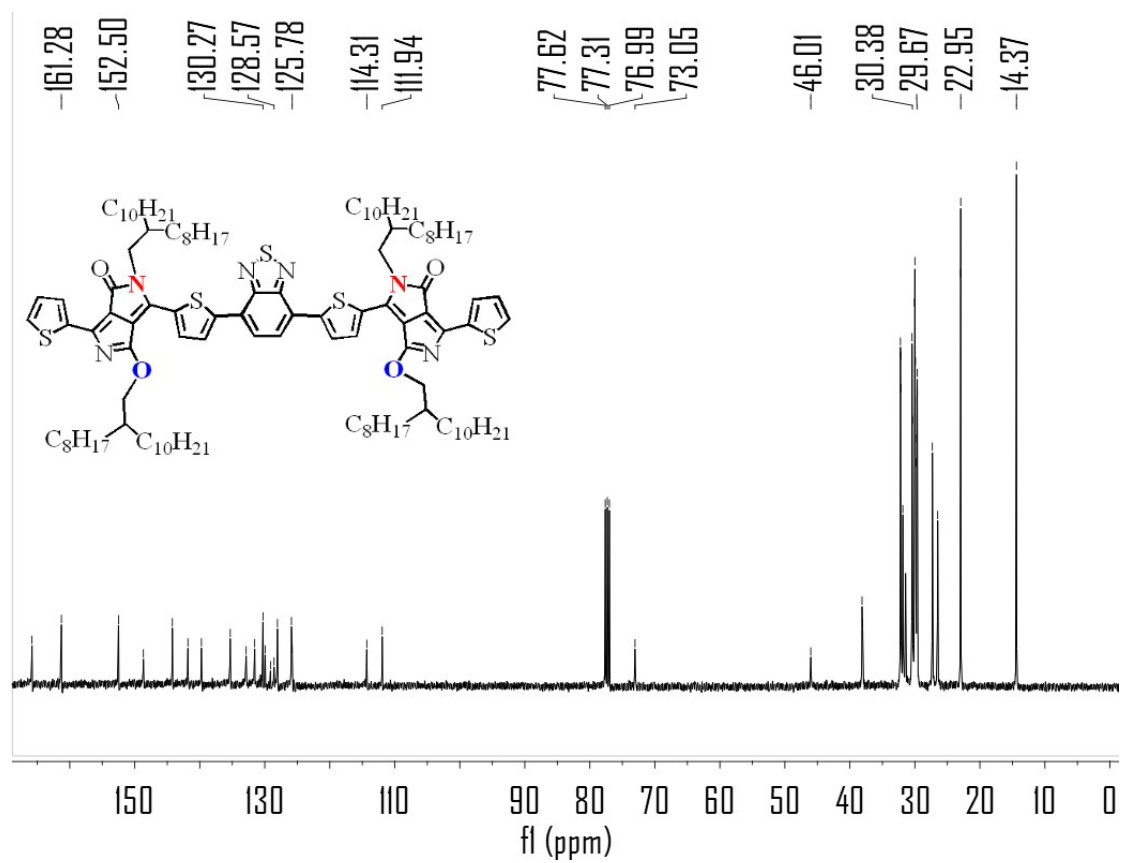


**Figure S2.**  $^1\text{H}$  NMR of OBO.

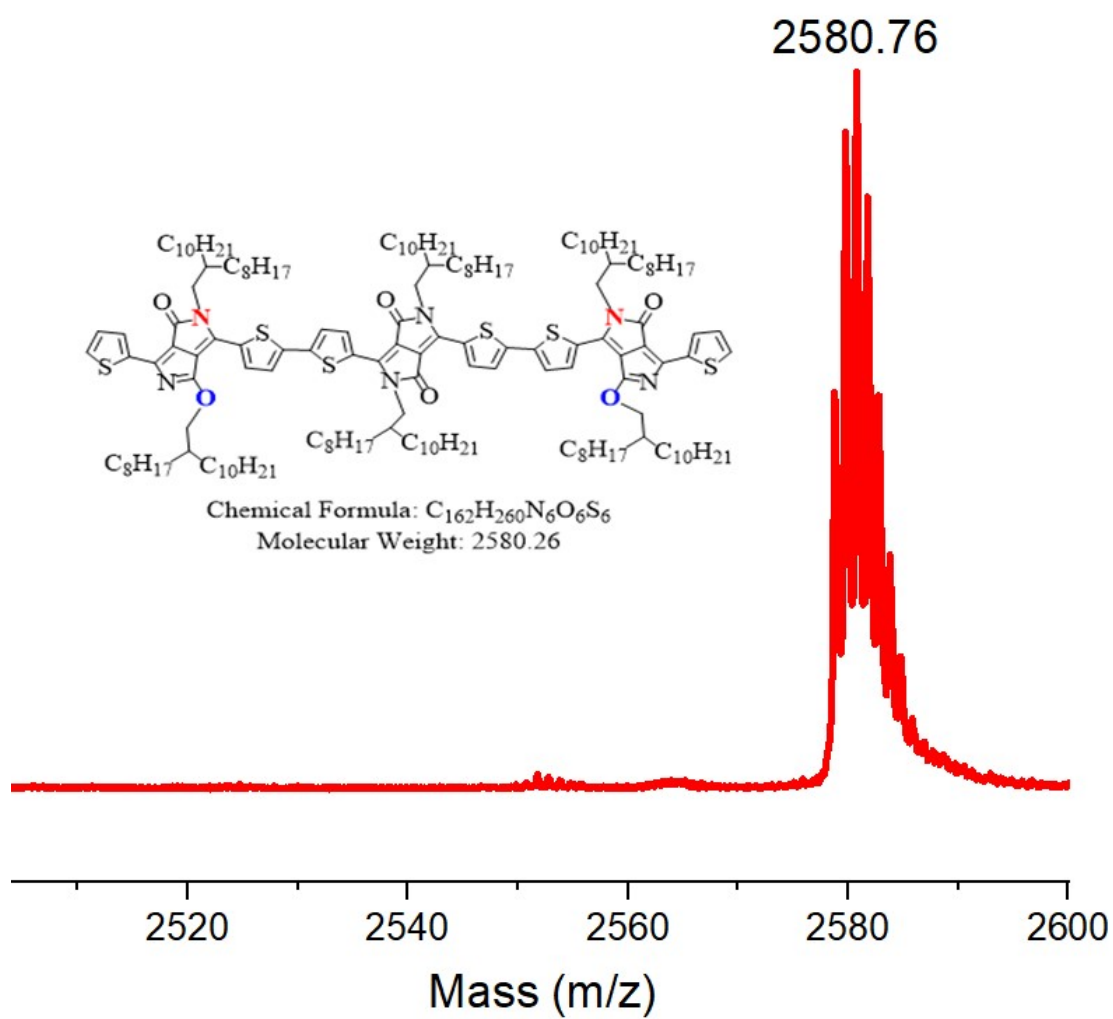


**Figure S3.**  $^{13}\text{C}$  NMR of ODO.

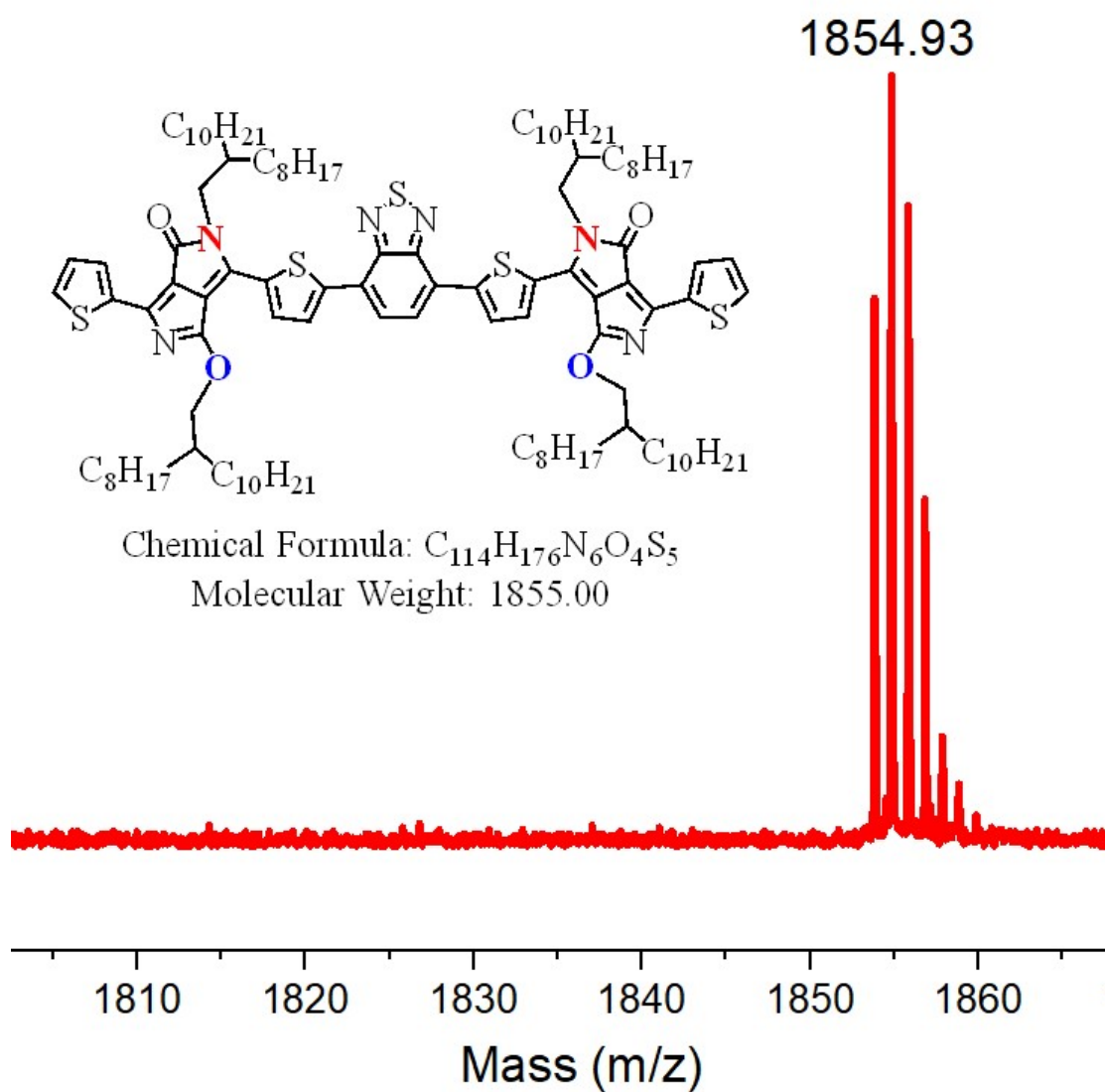




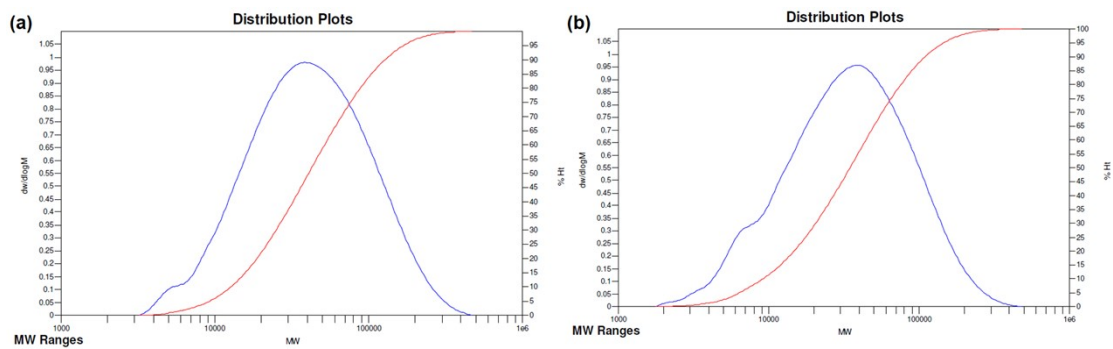
**Figure S4.** <sup>13</sup>C NMR of OBO.



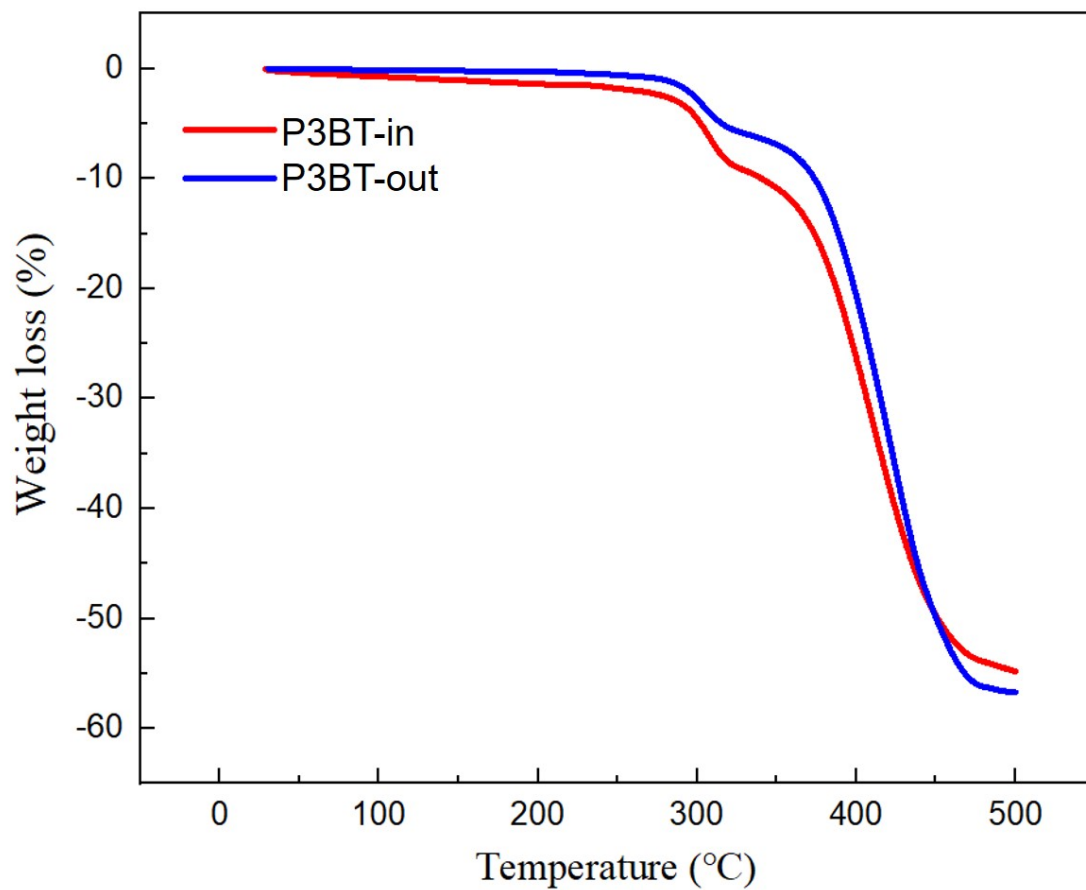
**Figure S5.** The matrix-assisted laser desorption/ionization coupled to time-of-flight (MALDI-TOF) mass spectra of ODO.



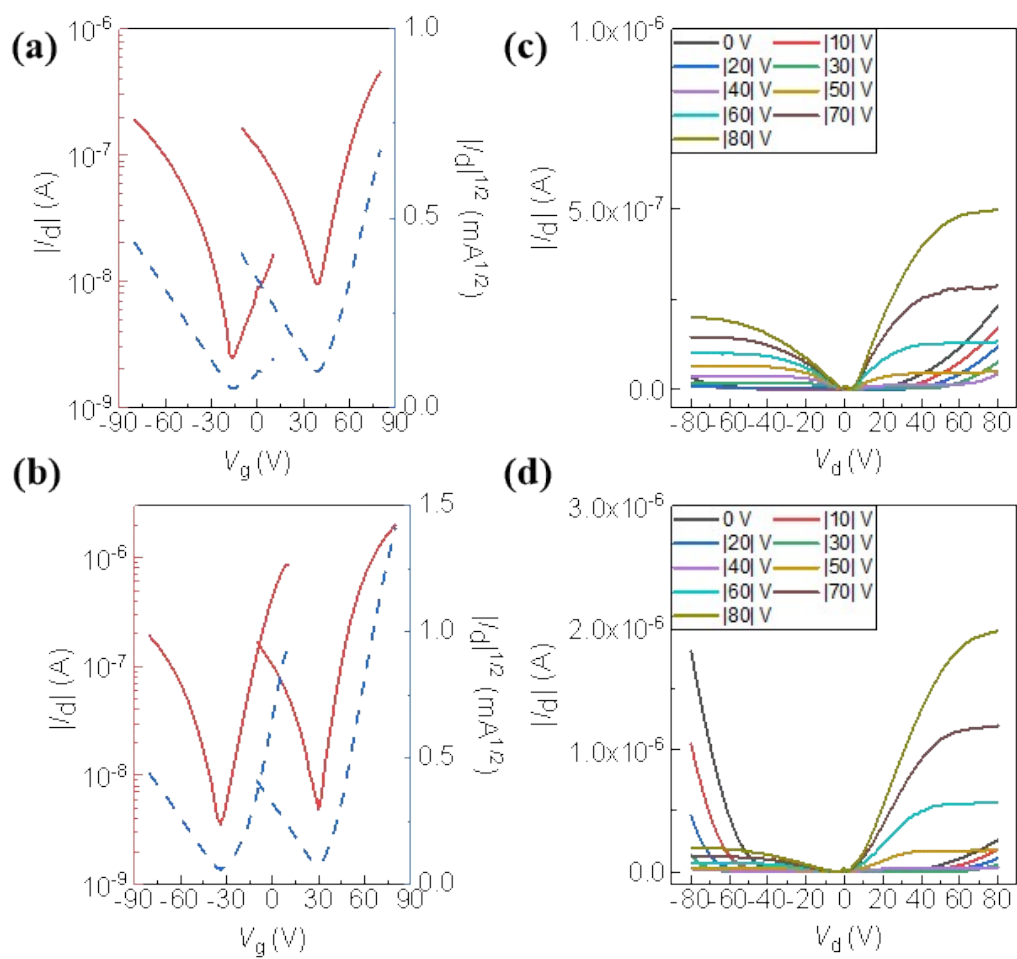
**Figure S6.** The matrix-assisted laser desorption/ionization coupled to time-of-flight (MALDI-TOF) mass spectra of OBO.



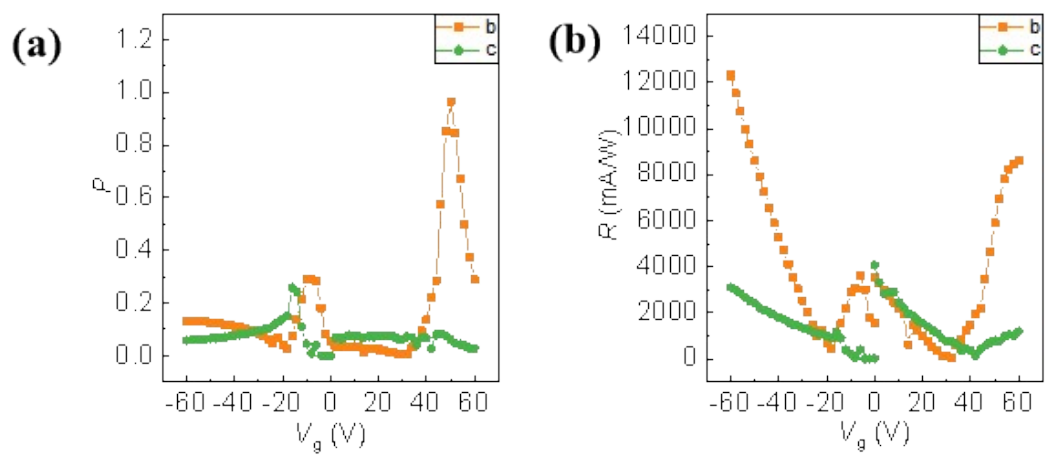
**Figure S7.** High-temperature gel permeation chromatography (HT-GPC) of the two polymers (a) P3BT-in; (b) P3BT-out.



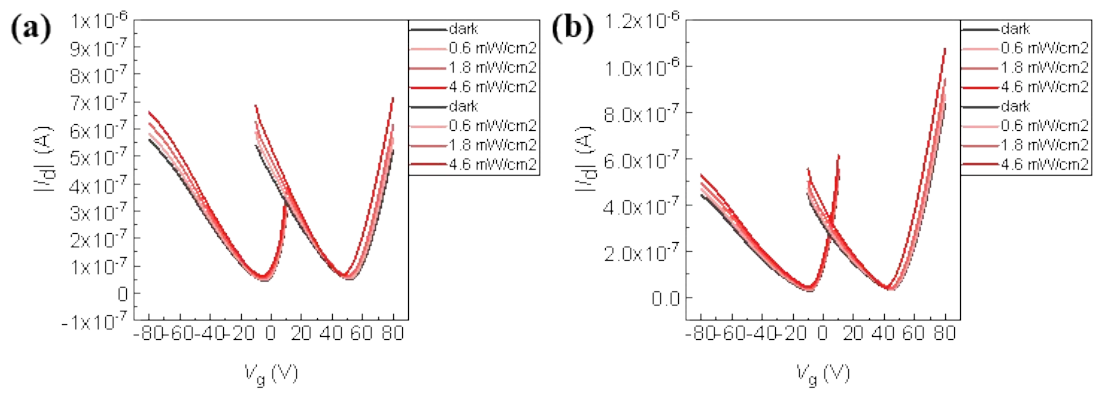
**Figure S8.** Thermogravimetric analysis (TGA) of the polymers under the nitrogen flow at the heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .



**Figure S9.** (a, b) Transfer and (c, d) output curves of OFET based on (a, c) P3BT-in and (b, d) P3BT-out, respectively.



**Figure S10.** (a) The photo/dark current ratio ( $P$ ) and (b) Responsivity ( $R$ ) versus  $V_g$  for the NIR-OPTs. (light intensity =  $4.6 \text{ mW cm}^{-2}$ )



**Figure S11.** The transfer characteristics of the device under different power light irradiation of (a) P3BT-in and (b) P3BT-out, respectively.



**Table S1.** Crystallographic parameters of films measured by GIWAXS.

<b>d-d stacking cell axis (100) in the in-plane direction</b>					<b><math>\pi</math>-<math>\pi</math> stacking cell axis (010) in the out-of-plane direction</b>			
Polymers	$Q$ ( $\text{\AA}^{-1}$ )	$d$ -spacing ( $\text{\AA}$ )	FWHM <sup>a</sup> ( $\text{\AA}^{-1}$ )	CCL <sup>b</sup> ( $\text{\AA}$ )	$Q$ ( $\text{\AA}^{-1}$ )	$d$ -spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	CCL ( $\text{\AA}$ )
P3BT-in	0.289	21.7	0.0324	193.925	1.694	3.7	0.2482	25.315
P3BT-out	0.285	22.0	0.0564	111.404	1.700	3.7	0.4008	15.677

<sup>a</sup> Full width at half maxima, calculated by Gaussian fitting.

<sup>b</sup> Crystalline coherence length.