

Supporting Information

Incorporation of Fluorine onto Different Positions of Phenyl Substituted Benzo[1,2-b:4,5-b']dithiophene Unit: Influence on Photovoltaic Properties

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Materials.

Lithium diisopropylamide (LDA), n-butyllithium (n-BuLi), $\text{Sn}(\text{CH}_3)_3\text{Cl}$ and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) were obtained from Acros Organics, and they were used as received. Toluene was dried over P_2O_5 and freshly distilled prior to use. 4-Bromo-2-fluorophenol, 5-bromo-2-fluorophenol and other solvents were purchased from Aldrich and TCI Chemical Co. respectively. The new monomers 2,6-bis(trimethyltin)-4,8-bis(4-ethylhexyloxy-1-*meta*-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (M2) and 2,6-bis(trimethyltin)-4,8-bis(3-ethylhexyloxy-1-*para*-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (M3) can be easily synthesized *via* a Grignard reaction. 4,7-Di(5-bromothiophen-2-yl)-5,6-dioctyloxy benzo[c][1,2,5]oxadiazole (M1) monomer was prepared according to the reported procedures.¹⁻³

Synthetic Procedures

4-Bromo-1-(2'-ethylhexyloxy)-2-fluorobenzene (2a)

In a 250 mL three-neck round-bottom flask equipped with magnetic stirrer, 4-bromo-2-fluorophenol (1a) (5 g, 26.2 mmol), K_2CO_3 (4.4 g, 31.4 mmol) and dry DMF (50 mL) were combined and purged with argon (Ar) for 0.5 h at 60 °C. 1-Bromo-2-ethylhexane (5 g, 26.2 mmol) was added and the reaction mixture was stirred for 10 h at 150 °C. And then cooled to room temperature, the reaction mixture was poured into 100 mL water and was extracted three times with chloroform. The organic extraction was washed successively with saturated potassium hydroxide and water for twice, respectively. The combined organic phases were dried over magnesium sulfate. After filtration, the solvents were evaporated under vacuum and the crude product was purified on a silica gel column eluting with petroleum ether. Colorless oil was obtained (6.5 g, 82% yield). ^1H NMR (500 MHz, CDCl_3 , ppm): δ : 7.24 (dd, 1H), 7.19 (dd, 1H), 6.86 (t, 1H), 3.91 (d, 2H), 1.78 (m, 1H), 1.59 – 1.32 (m, 8H), 0.95 (m, 6H). MS: $m/z=302$ (M^+).

4,8-Bis (4-ethylhexyloxy-1-*mata*-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (4a)

Under vigorous stirring, 4-bromo-1-(2'-ethylhexyloxy)-2-fluorobenzene (5.56 g, 18.4 mmol) was added drop wisely to magnesium turnings (0.538 g, 22.1 mmol) in anhydrous THF (22 mL) which was protected by Ar. During the process, I₂ (10 mg) was added as catalyst in the reaction. The solution was refluxed for 5 h until the magnesium was consumed. The mixture was refluxed for one more hour and then was cooled down. The solution system was added slowly to benzo[1,2-b:4,5-b']dithiophene-4,8-dione (1.35 g, 6.15 mmol) dispersed in 10 mL THF. SnCl₂·2H₂O (8.9 g) was dissolved in 10% aqueous HCl (12.4 mL) and then added dropwisely into the above reaction mixture. The solution was stirred for another 1 h at 50 °C. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice, the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (1.2 g, 31% yield). ¹H NMR (500 MHz, CDCl₃, ppm): δ: 7.47–7.43 (d, 2H), 7.45 (m, 4H), 7.36 (d, 2H), 7.17 (t, 2H), 4.05 (d, 4H), 1.88 (m, 2H), 1.68–1.38 (m, 16H), 0.96 (m, 12H). MS: m/z= 634 (M⁺).

2,6-Bis(trimethyltin)-4,8-bis(4-ethylhexyloxy-1-*mata*-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (M2)

A solution of compound 4 (0.76 g 1.2 mmol) in dry THF (30 mL) was deoxygenated with argon for 30 min, and then 2 M LDA solution in n-hexane (1.8 mL, 3.6 mmol) was added dropwisely at -78 °C. Then the solution was allowed to warm up to 50 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (4.8 mL, 4.8 mmol) was added under -78 °C. Then the mixture was poured into water and extracted with dichloromethane. The organic phase was evaporated, and the residue was recrystallized from 20 mL acetone to afford the pale yellow solid (0.93g, 85%). ¹H NMR (500 MHz, CDCl₃, ppm): δ: 7.49 – 7.43 (dd, 2H), 7.46 (s, 2H),

7.38 (bs, 2H), 7.19 (t, 2H), 4.05 (d, 4H), 1.87 (dq, 2H), 1.67 – 1.31 (m, 16H), 1.00 (m, 12H), 0.39 (t, 18H). MS: $m/z=961$ (M^+)

Synthesis of PBO-*m*-FPO

M1 (0.14 g, 0.2 mmol), M2 (0.19 g, 0.2 mmol) and 15 mL of dry toluene were put into a two-necked flask. The solution was flushed with Ar for 20 min, then $\text{Pd(PPh}_3)_4$ (15 mg) was added into the flask. The solution was flushed with Ar again for 20 min. The oil bath was heated to 110 °C carefully, and the reactant was stirred for 24 h at this temperature under argon atmosphere. Then the reaction mixture was cooled to room temperature and then poured into methanol (100 mL) slowly. The resulting precipitate was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexane and chloroform. Finally the polymer was recovered as a solid from the chloroform fraction by rotary evaporation. Finally, the violet-black solid was obtained (0.21 g, yield: 89%). ^1H NMR (500 MHz, CDCl_3 , ppm) δ 8.38 (s, 2H), 7.54 (s, 2H), 7.02 (s, 2H), 8.51-6.79 (br, 6H), 4.70-3.91 (br, 8H) 1.98– 1.85 (m, 2H), 1.54-0.89 (m, 58H). Anal. calcd for $(\text{C}_{68}\text{H}_{80}\text{N}_2\text{O}_5\text{S}_4\text{F}_2)_n$ (%): C, 69.74; H, 6.83; N, 2.39. Found (%): C, 69.58; H, 7.12; N, 2.43.

4-Bromo-2-(2'-ethylhexyloxy)-1-fluorobenzene (2b)

2b was synthesized similarly as described above for 2a (6g, 76%). ^1H NMR (500 MHz, CDCl_3 , ppm): δ : 7.24 (dd, 1H), 7.22-7.16 (m, 1H), 6.86 (t, 1H), 3.92 (d, 2H), 1.80 (m, 1H), 1.57-1.30 (m, 8H), 1.02-0.88 (m, 6H). MS: $m/z=302$ (M^+).

4,8-Bis (3-ethylhexyloxy-1-*para*-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (4b)

4b was synthesized similarly as described above for 4a (1.3g, 34%). ^1H NMR (500 MHz, CDCl_3 , ppm): δ : 7.46 (d, 2H), 7.36 (d, 2H), 7.34 (dd, 2H), 7.30–7.25 (d, 2H), 7.23 (m, 2H), 3.96 (d, 2H), 1.83 (dq, 2H), 1.61–1.23 (m, 12H), 0.94 (m, 12H). MS: $m/z= 633$ (M^+).

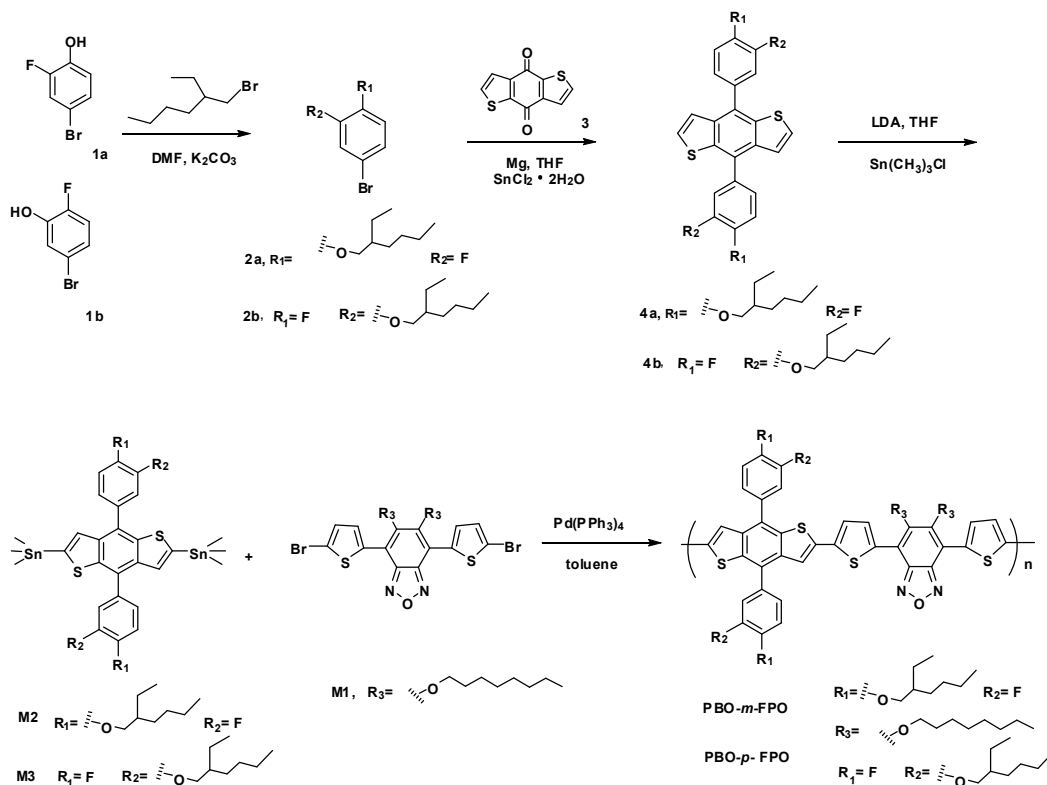
2,6-Bis(trimethyltin)-4,8-bis(3-ethylhexyloxy-1- *para* -fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (M3)

M3 was synthesized similarly as described above for M2 (1.7g, 90%). ^1H NMR (500 MHz, CDCl_3) δ 7.44 – 7.37 (m, 2H), 7.35 (d, 2H), 7.31 (d, 2H), 7.29 – 7.25 (m, 2H), 3.97 (d, 4H), 1.87 (dq, 2H), 1.63 – 1.28 (m, 16H), 0.96 (m, 12H), 0.40 (t, 18H). MS: $m/z=960$ (M^+).

Synthesis of PBO-*p*-FPO

PBO-*p*-FPO was obtained by the similar procedure with the synthesis of PBO-*m*-FPO, starting from M1 (0.103 g, 0.15 mmol) and M3 (0.144 g, 0.15 mmol). Finally, the violet-dark solid was obtained (0.14 g, yield: 80%). ^1H NMR (500 MHz, CDCl_3) δ 8.22 (s, 2H), 7.49 (s, 2H), 7.07 (s, 2H), 8.46-6.71 (br, 6H), 4.35-3.78 (br, 8H) 1.97-1.87 (m, 2H), 1.52 – 0.88 (m, 58H). Anal. calcd for $(\text{C}_{68}\text{H}_{80}\text{N}_2\text{O}_5\text{S}_4\text{F}_2)_n$ (%): C, 69.74; H, 6.83; N, 2.39. Found (%): C, 69.58; H, 7.12; N, 2.41.

Scheme S1. Synthetic routes of the monomers and the corresponding polymers.



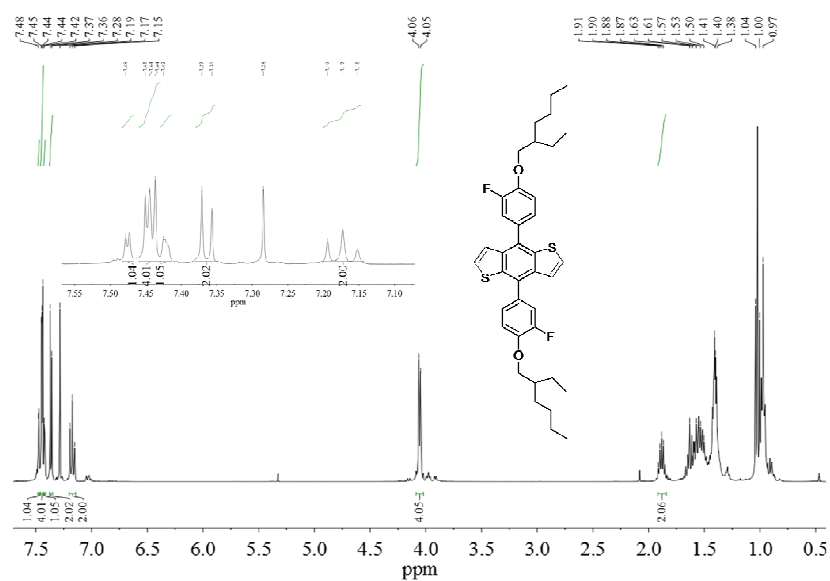


Figure S1. ¹H NMR spectrum of 4,8-bis(4-ethylhexyloxy-1-mata-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (4a).

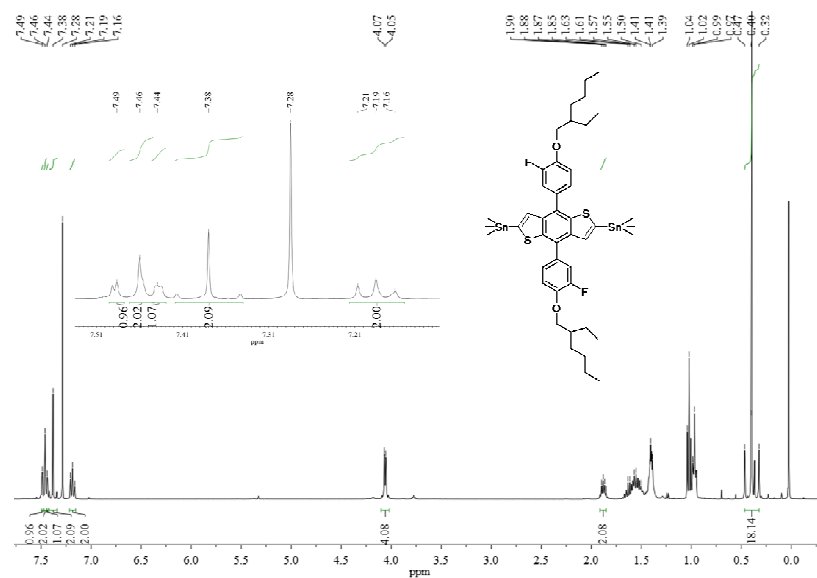


Figure S2. ¹H NMR spectrum of 2,6-bis(trimethyltin)-4,8-bis(4-ethylhexyloxy-1-mata-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (M2).

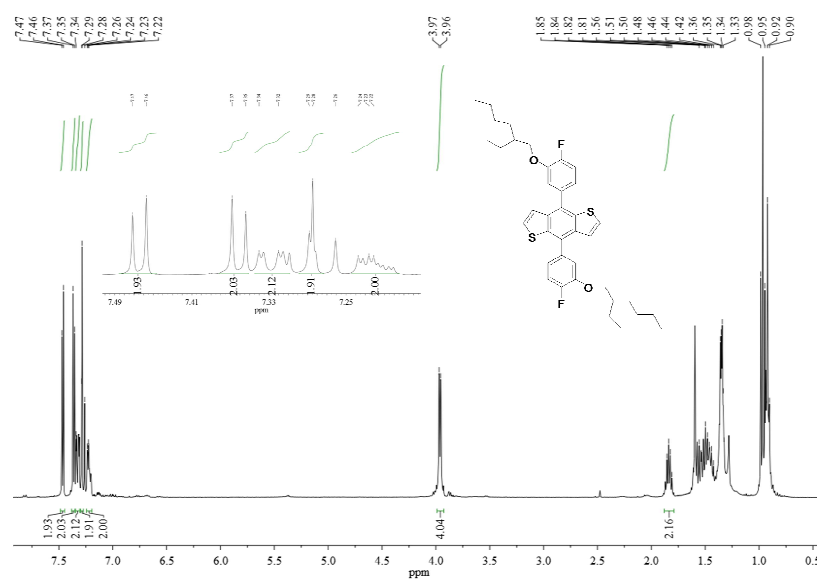


Figure S3. ¹H NMR spectrum of 4,8-bis(3-ethylhexyloxy-1-*para*-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (4b).

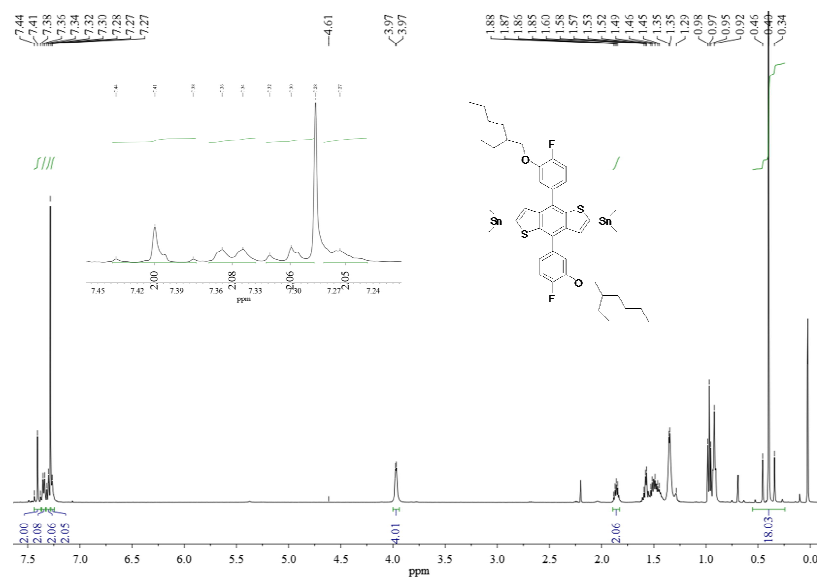


Figure S4. ¹H NMR spectrum of 2,6-bis(trimethyltin)-4,8-bis(3-ethylhexyloxy-1-*para*-fluorophenyl)-benzo[1,2-b:4,5-b']-dithiophene (M3).

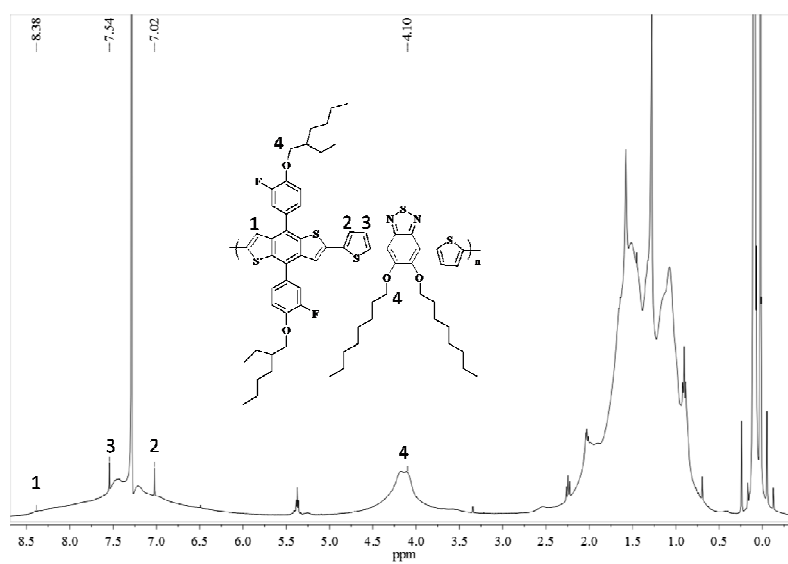


Figure S5. ^1H NMR spectrum of PBO-*m*-FPO.

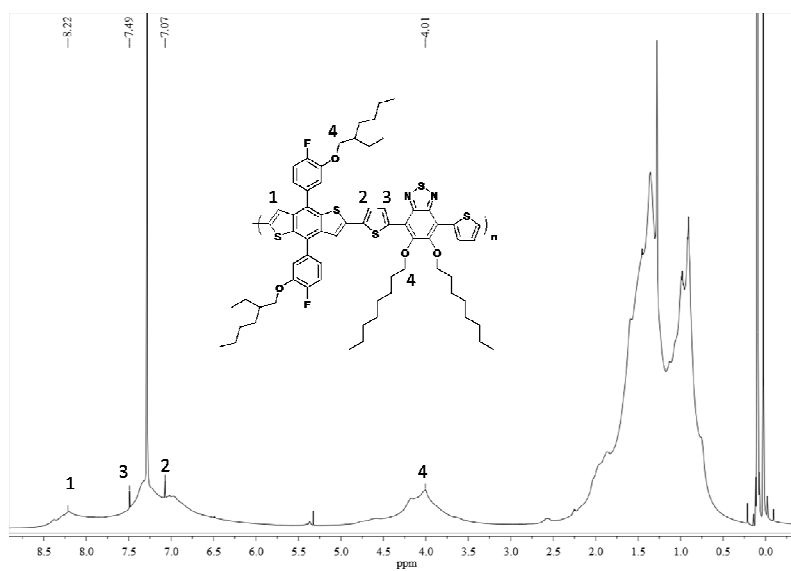


Figure S6. ^1H NMR spectrum of PBO-*p*-FPO.

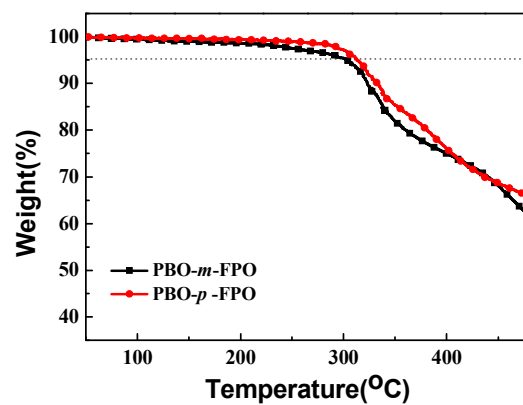
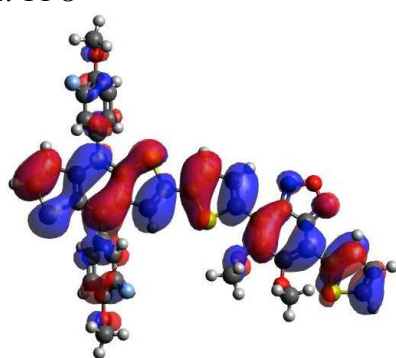
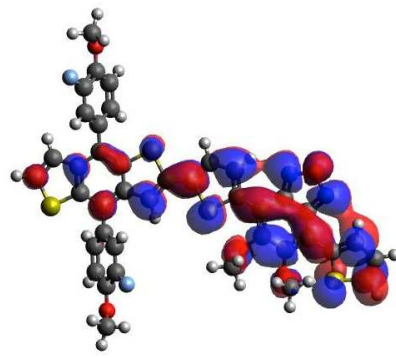


Figure S7. TGA curves of the polymers with a heating rate of $20 \text{ K} \cdot \text{min}^{-1}$.

PBO-*m*-FPO

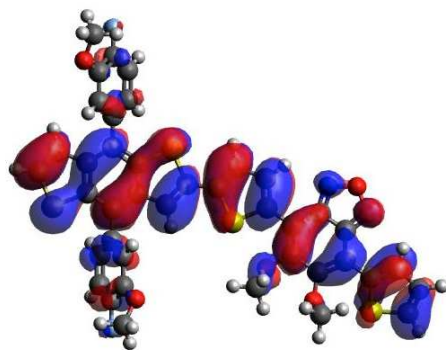


HOMO=-5.02 eV

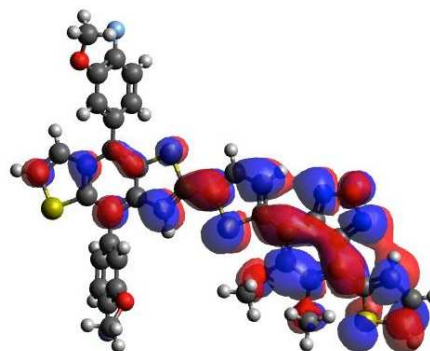


LUMO=-2.60 eV

PBO-*p*-FPO



HOMO=-5.02 eV



LUMO=-2.59 eV

Figure S8. Molecular orbital geometry and energy levels obtained from DFT calculations on the copolymers with chain length $n = 1$ using NWChem6.3 at the B3LYP/6-31G* level.

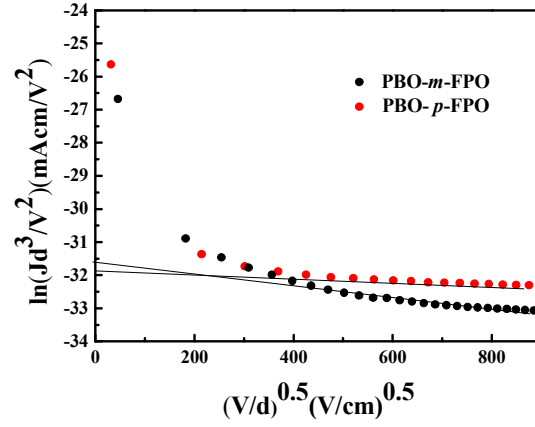


Figure S9. $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$ plots of the blends of PBO-*m*-FPO/PC₇₁BM, PBO-*p*-FPO/PC₇₁BM for electron mobilities measurement by SCLC method.

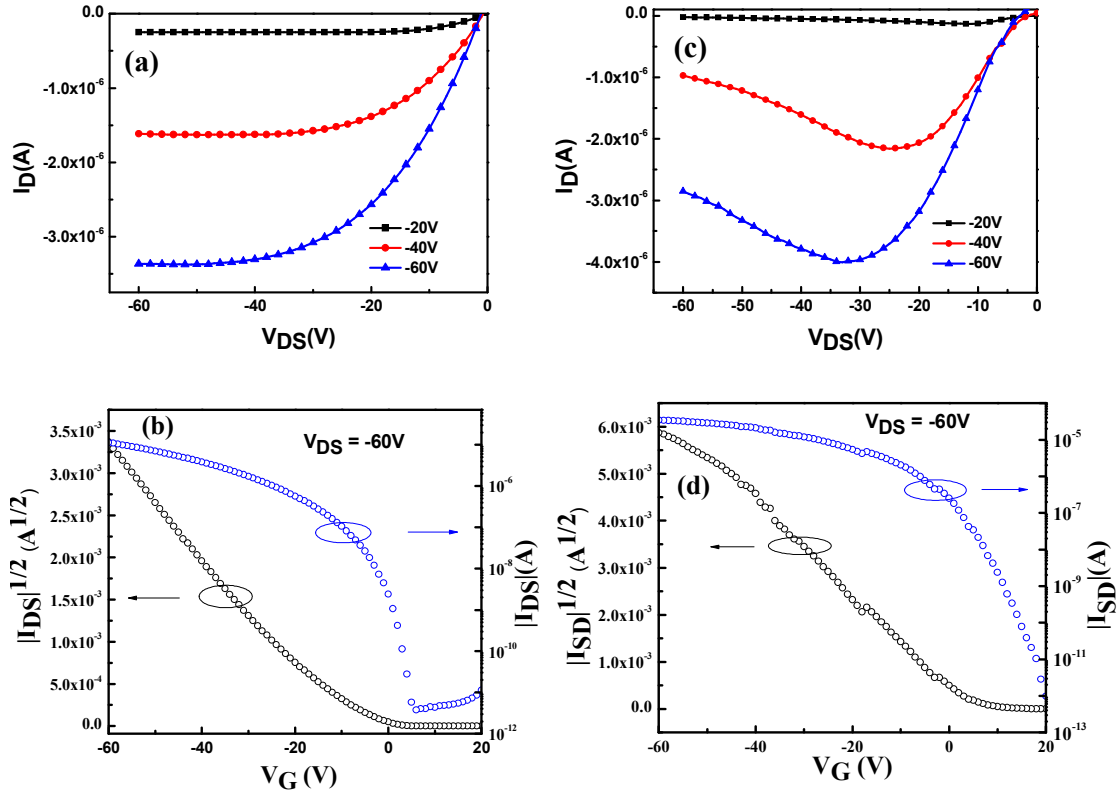
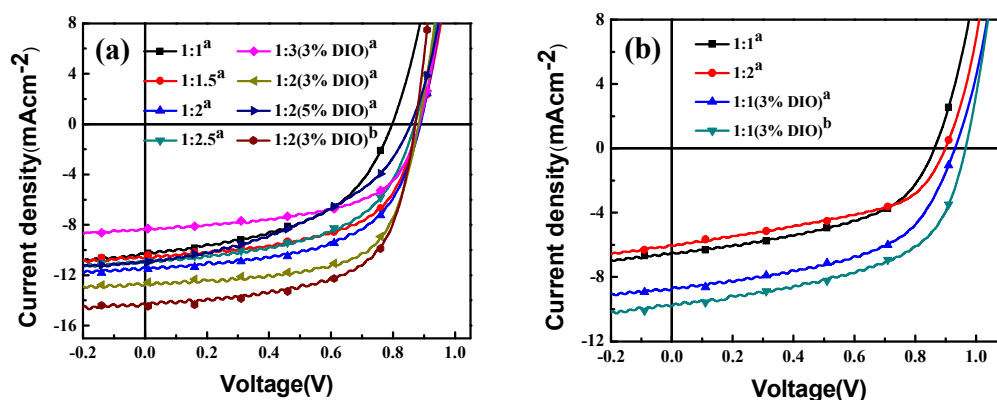


Figure S10. Output (a, c) and transfer (b, d) characteristics of OFETs based on PBO-*m*-FPO (left) and PBO-*p*-FPO (right), under 150 °C annealing.



^aThe cathode interlayer is calcium. ^bThe cathode interlayer is ZrAcac.

Figure S11. *J-V* curves of (a) PBO-*m*-FPO:PC₇₁BM and (b) PBO-*p*-FPO:PC₇₁BM with different cathode and ratio of DIO under illumination of AM 1.5G, 100 mW cm⁻².

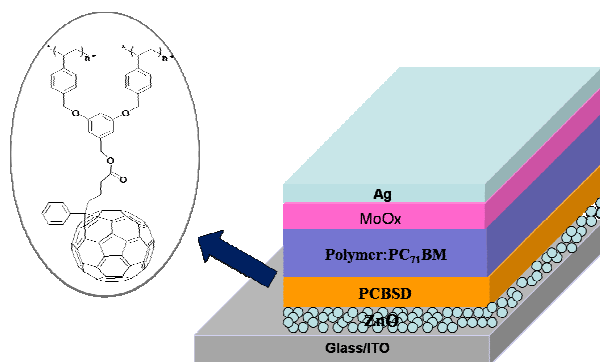


Figure S12. Inverted device geometry of polymers:PC₇₁BM.

Table S1. Optical and electrochemical properties of the synthesized conjugated polymers

Polymer	Absorption spectra				
	Sol		Film		
	λ_{\max}^a (nm)	λ_{\max}^b (nm)	λ_{\max}^c (nm)	λ_{onset} (eV)	$E_g^{\text{opt } d}$
PBO- <i>m</i> -FPO	579	560	610	746	1.66
PBO- <i>p</i> -FPO	577	558	605	751	1.64

^aMeasured at room temperature. ^bMeasured at 90 °C. ^cCast from chloroform solution. ^dBandgap estimated from the onset wavelength of the optical absorption.

Table S2. OFET Characteristics of PBO-*m*-FPO and PBO-*p*-FPO. The OFETs are in bottom-gated, top-contact configuration with and without annealing.

	Mobility [cm ² ·V ⁻¹ s ⁻¹]	V_{th} [V]	I_{on}/I_{off}
PBO- <i>m</i> -FPO	2.37×10^{-3}	- 6.56	7.42×10^2
PBO- <i>m</i> -FPO (annealing)	1.72×10^{-2}	-10.2	4.71×10^3
PBO- <i>p</i> -FPO	2.47×10^{-5}	- 19.6	2.55×10^4
PBO- <i>p</i> -FPO (annealing)	1.32×10^{-2}	3.47	1.37×10^2

Table S3. The device parameters of PSCs based on polymer:PC₇₁BM with different cathode and ratio DIO under illumination of AM 1.5G, 100 mW cm⁻².

Active layer	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
<i>m</i> - : PC ₇₁ BM=1:1 ^a	0.82	10.4	49	4.3
<i>m</i> - : PC ₇₁ BM=1:1.5 ^a	0.89	10.7	58	5.5
<i>m</i> - : PC ₇₁ BM=1:2 ^a	0.89	11.3	58	5.9
<i>m</i> - : PC ₇₁ BM=1:2.5 ^a	0.87	10.9	55	5.2
<i>m</i> - : PC ₇₁ BM=1:3 ^a	0.88	8.5	57	4.3
<i>m</i> - : PC ₇₁ BM=1:2 ^a (3%DIO)	0.88	12.8	65	7.3
<i>m</i> - : PC ₇₁ BM=1:2 ^a (5%DIO)	0.86	10.9	43	4.1
<i>m</i> - : PC ₇₁ BM=1:2 ^b (3%DIO)	0.87	14.3	64	8.0
<i>p</i> - : PC ₇₁ BM=1:1 ^a	0.86	6.4	50	2.8
<i>p</i> - : PC ₇₁ BM=1:2 ^a	0.90	6.1	48	2.6
<i>p</i> - : PC ₇₁ BM=1:1 ^a (3%DIO)	0.93	8.7	53	4.3
<i>p</i> - : PC ₇₁ BM=1:1 ^b (3%DIO)	0.97	9.9	53	5.1

^aThe cathode interlayer is calcium. ^bThe cathode interlayer is ZrAcac.

m- : PBO-*m*-FPO. *p*- : PBO-*p*-FPO

Table S4. Summary of the inverted device parameters based on PBO-*m*-FPO:PC₇₁BM under illumination of AM 1.5G, 100 mW cm⁻².

Active layer	PCBSD	PFN	PFNBr	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
<i>m</i> - : PC ₇₁ BM=1:1.5				0.88	8.6	54	4.1
<i>m</i> - : PC ₇₁ BM=1:2	×			0.88	8.9	55	4.4
<i>m</i> - : PC ₇₁ BM=1:2.5				0.86	8.1	54	3.7
<i>m</i> - : PC ₇₁ BM=1:2 (3% DIO)	×			0.86	9.5	62	5.0
<i>m</i> - : PC ₇₁ BM=1:2 (3% DIO)	✓			0.88	11.8	67	6.3
<i>m</i> - : PC ₇₁ BM=1:2 (3% DIO)		✓		0.84	9.5	64	5.1
<i>m</i> - : PC ₇₁ BM=1:2 (3% DIO)			✓	0.86	9.7	64	5.3
P3HT:PC ₆₀ BM (std)	✓			0.58	9.6	62	3.4

m- : PBO-*m*-FPO

Reference

- (1) Liu, B.; Chen, X.; Zou, Y.; Xiao, L.; Xu, X.; He, Y.; Li, L.; Li, Y. *Macromolecules* **2012**, 45, 6898-6905.
- (2) Ding, P.; Zhong, C.; Zou, Y.; Pan, C.; Wu, H.; Cao, Y. *The Journal of Physical Chemistry C* **2011**, 115, 16211-16219.
- (3) Jiang, J.-M.; Lin, H.-K.; Lin, Y.-C.; Chen, H.-C.; Lan, S.-C.; Chang, C.-K.; Wei, K.-H. *Macromolecules* **2014**, 47, 70-78.