

*Supporting Information for*

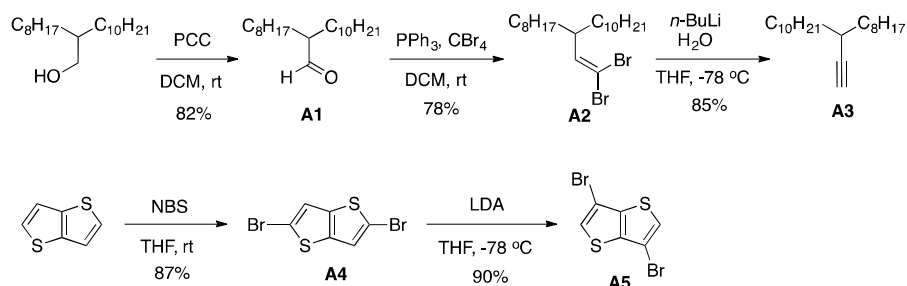
**Regioregular and random difluorobenzothiadiazole electron donor-acceptor  
polymer semiconductors for thin-film transistors and polymer solar cells**

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## 1. Synthesis procedures of intermediates (A1~A5)



**Scheme S1** Synthesis of intermediate **A1~A5**

The intermediates **A1**, **A2** and **A3** were prepared according to the reported procedure<sup>[S1]</sup>. The intermediates **A4**<sup>[S2]</sup> and **A5**<sup>[S3]</sup> were prepared according to the reported procedure with some modification.

**2-Octyldodecanal (A1).** Pyridiniumchlorochromate (20.3 g, 93.8 mmol) was added in small portions to a stirred solution of 2-octyldodecan-1-ol (10 g, 33.5 mmol) in dichloromethane (200 mL), and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was carefully filtered through a short gel column eluting with dichloromethane to afford a colorless oil as the product (8.15 g, 82%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 9.55 (d, J=3.2 Hz, 1H), 2.26-2.18 (m, 1H), 1.62-1.58 (m, 4H), 1.45-1.38 (m, 4H), 1.32-1.23 (m, 28H), 0.88 (t, J=6.8 Hz, 6H).

**9-(2,2-Dibromovinyl)nonadecane (A2).** Triphenylphosphine (34.5 g, 132 mmol) was added slowly to a solution of tetrabromomethane (21.8 g, 65.7 mmol) in dichloromethane (180 mL) at 0 °C. 2-Octyldodecanal (9.75 g, 32.9 mmol) was then added dropwise over a period of 1 h. The reaction mixture was stirred at room temperature for 2 h and was then poured into stirring brine (200 mL), followed by extraction with dichloromethane several times. The combined extract was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give a residue which was purified by flash chromatography on silica gel with hexane as an eluent to afford a colorless oil (11.5 g, 78%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 6.11 (d, J = 9.8 Hz, 1H), 2.36 (s, 1H), 1.38 (m, 2H), 1.26 (m, 30H), 0.88 (t, J = 6.8 Hz, 6H).

**9-(Prop-2-yn-1-yl)nonadecane (A3).** *n*-Butyllithium (13.2 mL, 33.0 mmol) was added dropwise over a period of 1 h to a solution of 9-(2,2-dibromovinyl)nonadecane (15.0 mmol, 6.8 g) in anhydrous

tetrahydrofuran (60 mL) at -78 °C, followed by stirring at -78 °C for 1 h. After the reaction, cold water (60 mL) was carefully added, and the resulting reaction mixture was stirred overnight, allowing the reaction temperature to rise to room temperature. The reaction mixture was extracted with hexane several times, and the combined extract was washed with brine and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel with hexane as an eluent to afford a colourless oil (3.72 g, 85%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 2.30 (m, 1H), 2.03 (d, J=2.4 Hz, 1H), 1.43 (q, J=6.5 Hz, 6H), 1.32-1.24 (m, 26H), 0.88 (t, J=6.9Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 88.33, 68.89, 35.02, 31.95, 31.92, 31.54, 29.74, 29.68, 29.62, 29.58, 29.55, 29.38, 29.34, 27.31, 22.72, 22.67, 14.14.

*2,5-Dibromothieno[3,2-*b*]thiophene (A4)*. *N*-Bromosuccinimide (374 mg, 21 mmol) was added to a solution of thieno[3,4-*b*]thiophene (1.403 g, 10 mmol) in tetrahydrofuran (20 mL) at room temperature and the mixture was stirred for 20 h. After addition of water, the reaction mixture was extracted with chloroform. The combined extracts were dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give a residue which was purified by recrystallization from ethanol to afford a white solid (2.59 g, 87%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 7.17 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 138.27, 121.76, 113.62.

*3,6-Dibromothieno[3,2-*b*]thiophene (A5)*. Lithium diisopropylamide (4.2 mL, 8.4 mmol) was added dropwise to a solution of 2,5-dibromothieno[3,2-*b*]thiophene (1.0 g, 3.4 mmol) in anhydrous tetrahydrofuran (25 mL) at -78 °C, and the resulting reaction mixture was stirred at -78 °C for 1 h, and then allowed to slowly warm up to room temperature, and then stirred at room temperature for another 10 h. After slow addition of cold brine (30 mL), the reaction mixture was extracted with diethyl ether and the combined extract was dried with anhydrous sodium sulfate. Removal of solvent under reduced pressure gave a residue which was purified by recrystallization from ethanol to afford a white solid (913 mg, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.34 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ ppm 139.81, 125.15, 103.03.

## References:

- [S1] Lafleur-Lambert, A.; Giguère, J. B.; Morin, J. F. *Polym. Chem.* **2015**, *6*, 4859-4863
- [S2] Zhong, H.; Li, Z.; Deledalle, F.; Fregoso, E. C.; Shahid, M.; Fei, Z.; Nielsen, C. B.; Yaacobi-Gross, N.; Rossbauer, S.; Anthopoulos, T. D.; Durrant, J. R.; Heeney, M. J. *Am. Chem. Soc.* **2013**, *135*, 2040-2043.
- [S3] Miguel, L. S.; Porter III, W. W.; Matzger, A. J. *Org. Lett.* **2007**, *9*, 1005-1008.

## 2. Fabrication and characterization of OTFTs

A top-contact, bottom-gate device configuration was utilized in our OTFT characterization of D-A polymer semiconductors. A heavily *p*-doped Si wafer substrate with a top SiO<sub>2</sub> layer (350 nm; specific capacitance  $\sim 10$  nF cm<sup>-2</sup>) was used as a gate electrode/gate dielectric layer. The SiO<sub>2</sub> surface of the substrate was pretreated with octadecyltrichlorosilane (OTS-18). The polymer semiconductor thin films were deposited on the substrate surface by spin casting from their chlorobenzene solutions (2mg/mL for **reg-P3** and 3 mg/mL for other samples) in ambient conditions. Gold source/drain electrodes were then thermally evaporated onto the polymer semiconductor films through a shadow mask under high vacuum ( $\sim 10^{-4}$  Pa), thus creating a series of OTFT devices with channel length of 80  $\mu$ m and channel width of 1500  $\mu$ m. All of the devices were evaluated in ambient conditions using a Keithley2636B with two channel SourceMeters. The field-effect mobility ( $\mu_h$ ) in the saturation regime was calculated according to the expression:

$$I_{DS} = (W/2L) \mu C_i (V_G - V_{TH})^2.$$

Where  $I_{DS}$  is the drain current,  $\mu$  is the field-effect mobility,  $C_i$  (10 nF cm<sup>-2</sup>) is the capacitance per unit area of gate dielectric, and  $V_G$  and  $V_{TH}$  are gate voltage and threshold voltage, respectively.  $L$  and  $W$  are respectively channel length and width of the transistor.

## 3. Fabrication and characterization of BHJ-PSCs

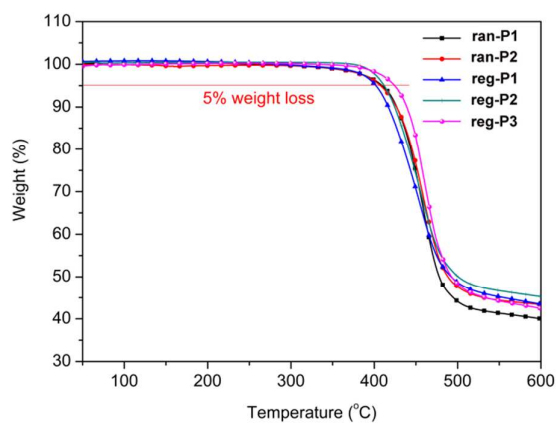
The configuration of BHJ-PSC devices used in the evaluation was ITO/ZnO/active layer/MoO<sub>3</sub>/Ag. The solution for the active layer was prepared by dissolving appropriate amounts of D-A polymer and PC<sub>71</sub>BM in hot chlorobenzene (90 °C) with or without 1~5 vol % of 1,8-diiodooctane (DIO). The solution was spin coated on ZnO-coated ITO glass and dried in vacuum oven. After the active layer was completely dried, MoO<sub>3</sub> (2 nm) and Ag (100 nm) were thermally deposited as the cathode under  $10^{-6}$  Torr. The active area of the device was about 9 mm<sup>2</sup>. The devices for PCE and EQE measurements were encapsulated in the glove box and measure in ambient conditions. A SAN-EI XEC-301S solar simulator equipped with a 300 W xenon lamp and an air mass (AM) 1.5G filter was used to generate a simulated AM 1.5G solar spectrum irradiation source. The irradiation intensity was 100 mW cm<sup>-2</sup> calibrated by a standard silicon solar cell VS 0831. A monochromator WDG30 and Bentham DH-Si silicon detector were used in external quantum efficiency (EQE) measurements.

The hole mobility of donor polymers in the PC<sub>71</sub>BM:Donor polymer blended films was also measured by space-charge-limited current (SCLC) method using a device configuration of

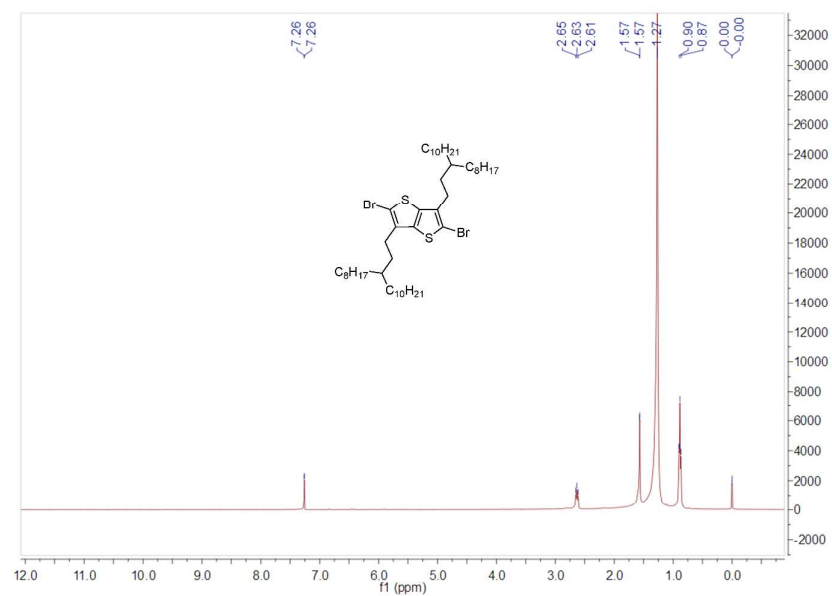
ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/Ag. The hole mobility values for the donor polymers as obtained from the measurements are provided in the following Table.

Donor Polymer	Active Layer Thickness (nm)	Hole mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
ran-P1	185	3.49×10 <sup>-4</sup>
ran-P2	189	4.80×10 <sup>-4</sup>
reg-P1	160	5.80×10 <sup>-4</sup>
reg-P2	165	9.01×10 <sup>-4</sup>

#### 4. Figures in Supporting Information

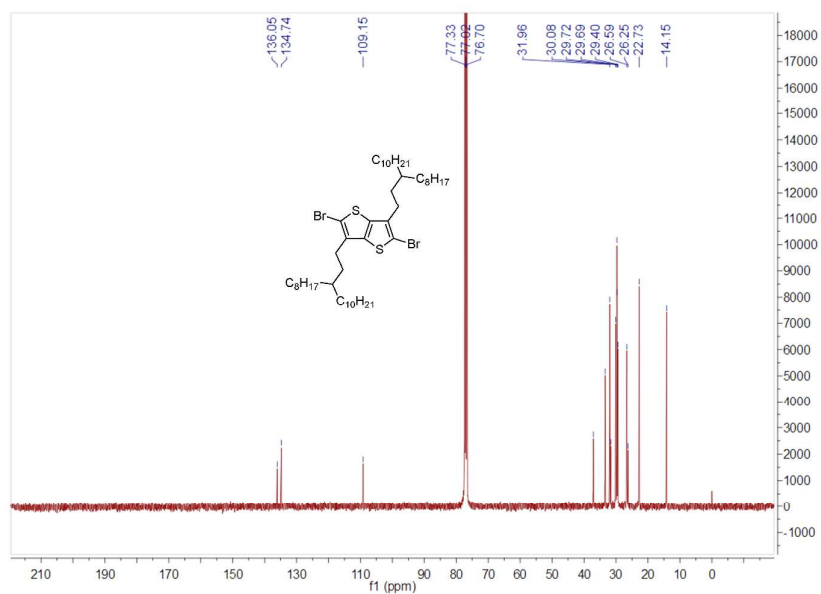


**Figure S1.** TGA plots of D-A polymers at a heating rate of  $10\text{ }^{\circ}\text{Cmin}^{-1}$  under  $\text{N}_2$  atmosphere.

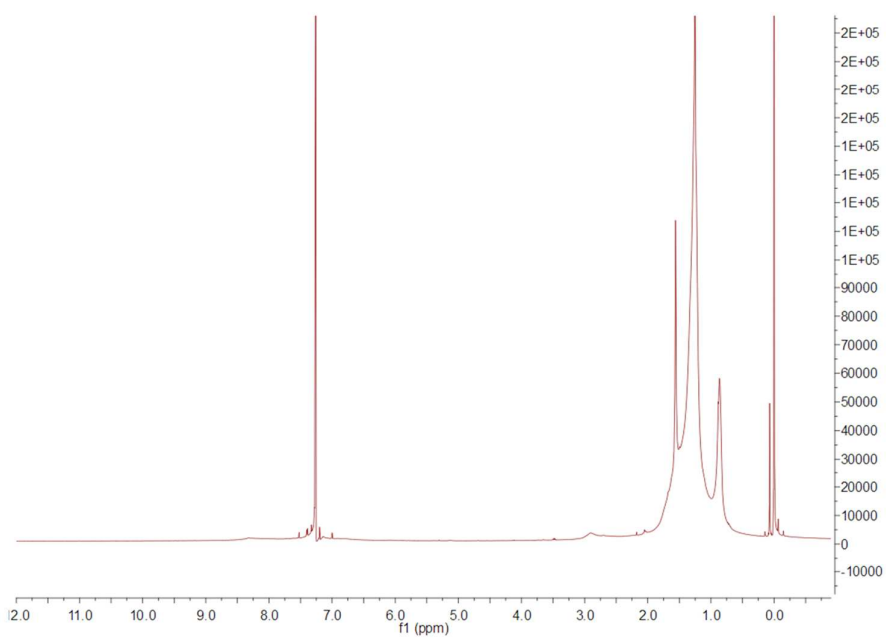


**Figure S2.**  $^1\text{H}$  NMR spectrum of new monomer

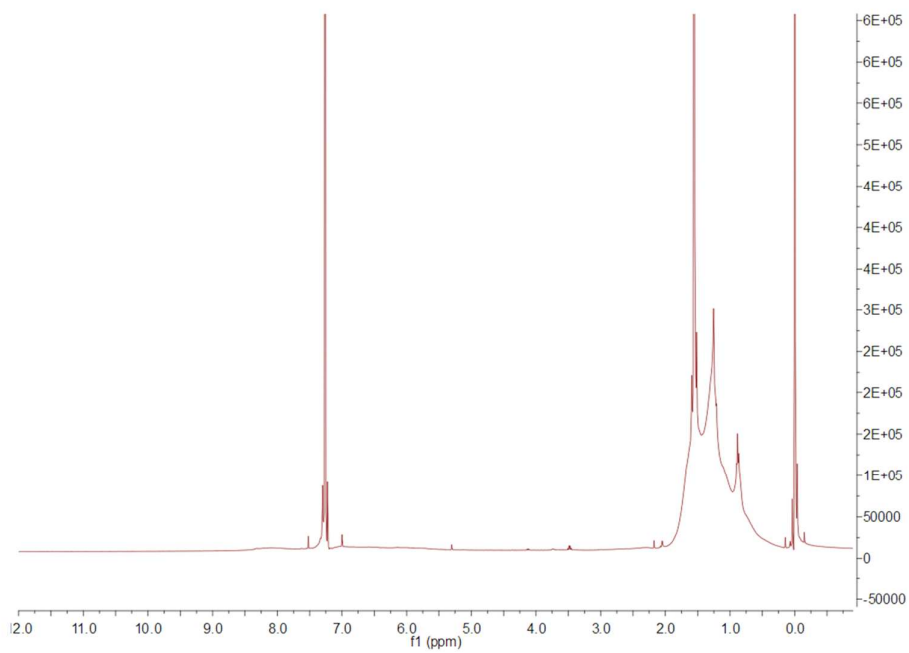
2,5-dibromo-3,6-bis(3-octyltridecyl)-thieno[3,2-*b*]thiophene (**3**) in  $\text{CDCl}_3$ .



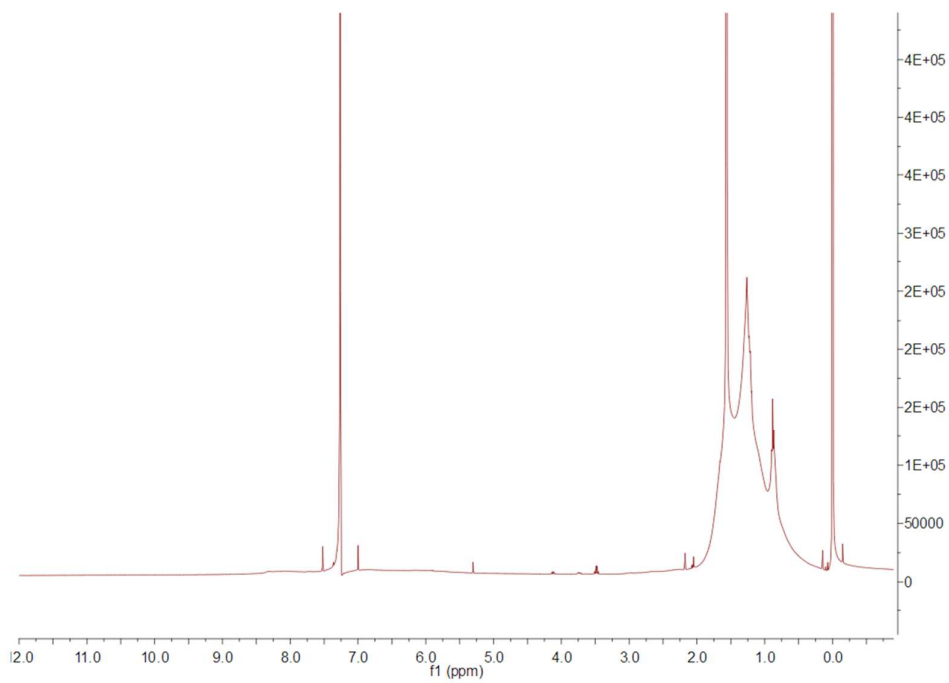
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of new monomer  
2,5-dibromo-3,6-bis(3-octyltridecyl)-thieno[3,2-*b*]thiophene (**3**) in  $\text{CDCl}_3$ .



**Figure S4.**  $^1\text{H}$  NMR spectrum of polymer **ran-P1** in  $\text{CDCl}_3$ .

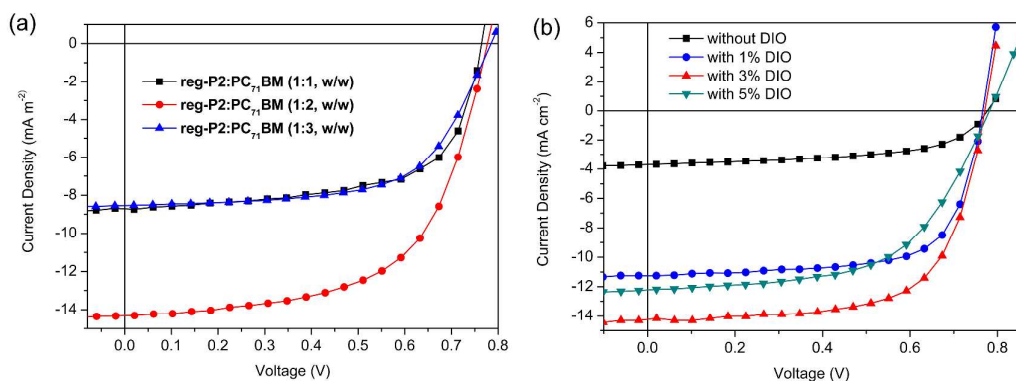


**Figure S5.**  $^1\text{H}$  NMR spectrum of polymer **reg-P1** in  $\text{CDCl}_3$ .

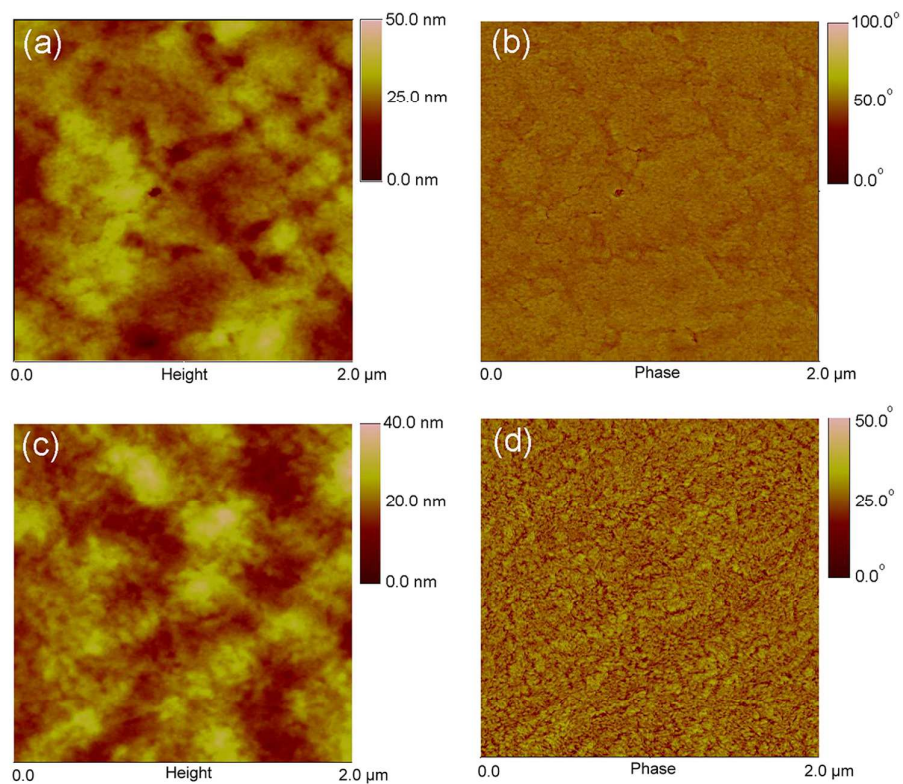


**Figure S6.**  $^1\text{H}$  NMR spectrum of polymer **reg-P2** in  $\text{CDCl}_3$ .

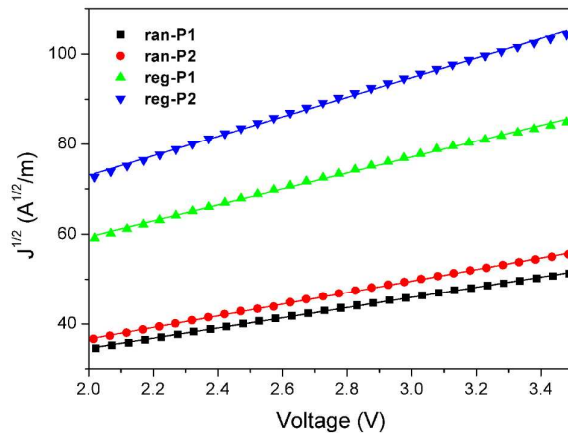




**Figure S7.** (a) Current density-voltage curves of devices with active layers of **reg-P2:PC<sub>71</sub>BM** of different weight ratios; (b) Current density-voltage curves of devices with active layer of **reg-P2:PC<sub>71</sub>BM** (1:2, w/w) with varying amounts of DIO.



**Figure S8.** AFM height and phase images of **ran-P2:PC<sub>71</sub>BM** blends (1:2, w/w) with 3 vol % DIO (a; b) and **reg-P1:PC<sub>71</sub>BM** blends (1:2, w/w) with 3 vol % DIO (c; d).



**Figure S9.**  $J^{1/2}$ - $V$  curves of the hole-only donor polymer/PC<sub>71</sub>BM devices

## 5. Tables

**Table S1.** Performance characteristics of BHJ-PSCs with active layers of **reg-P2**:PC<sub>71</sub>BM of different compositions (with 3 vol % DIO)

<b>reg-P2</b> :PC <sub>71</sub> BM (w/w)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%) <sup>a)</sup>
1:1	0.76	9.53	63.68	4.89 (4.75)
1:2	0.78	14.56	66.45	7.57 (7.11)
1:3	0.78	8.73	61.54	4.41 (4.22)

<sup>a)</sup> Average PCEs given in parentheses.

**Table S2.** Performance characteristics of BHJ-PSCs with active layers of **reg-P2**:PC<sub>71</sub>BM (1:2, w/w) with different amounts of DIO.

DIO (Vol%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%) <sup>a)</sup>
0	0.78	3.70	57.10	1.64 (1.60)
1.0	0.77	11.25	69.21	6.00 (5.87)
3.0	0.78	14.56	66.45	7.57 (7.11)
5.0	0.78	12.22	57.60	5.50 (5.37)

<sup>a)</sup> Average PCEs given in parentheses.