

Supporting Information

## **D-A copolymers containing lactam moieties for polymer solar cells**

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## 1. General characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was done on a Perkin-Elmer Diamond TG/DTA thermal analyzer under nitrogen. Cyclic voltammetry was measured on a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag<sup>+</sup> electrode was used as the reference electrode. All potentials were corrected against Fc/Fc<sup>+</sup>. AFM was performed on a Dimension 3100 microscope (Veeco). X-ray diffraction (XRD) was performed in the reflection mode using Cu K $\alpha$  radiation (40 kV, 200 mA) on a 2 kW Rigaku D/max 2500 X-ray diffractometer.

## 2. Synthetic procedures

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co. and other suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 2,2'-Dibromo-4,4'-bis(2-octyldodecyl)-[7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'(4*H*,4'*H*)-dione (**BDTP-Br**) was prepared according to our previous report.<sup>1</sup>

**Poly{2,6-(4,8-bis(2-ethylhexyloxy))benzo[1,2-*b*:4,5-*b'*]dithiophene-*alt*-2,2'-(4,4'-bis(2-octyldodecyl))-[7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'(4*H*,4'*H*)-dione} (P1).** **BDTP-Br** (80.8 mg, 0.07 mmol) and 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (**BDT**) (54.13 mg, 0.07 mmol) were dissolved in 30 mL toluene, and the solution was flushed with argon for 15 min, then 8 mg Pd(PPh<sub>3</sub>)<sub>4</sub> was added into the solution. The mixture was flushed again with argon for 20 min. The reaction solution was heated to reflux for 24 h. Then the solution was cooled to room temperature and added dropwise to 150 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. Subsequently, the precipitate was collected and dried under vacuum overnight to give **P1** as a purple-red solid (93 mg, 92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 7.64-6.21 (br, 6H), 4.96 (br, 4H), 4.40-3.75 (br, 4H), 1.57-0.84 (br, 108H). Elemental analysis (%) calcd for C<sub>84</sub>H<sub>122</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>: C, 71.24; H, 8.68;

N, 1.98. Found: C, 70.61; H, 8.46; N, 2.10.

**Poly{2,5-selenophene-*alt*-2,2'-(4,4'-bis(2-octyldodecyl))-[7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'(4*H*,4'*H*)-dione} (P2).** P2 was synthesized by following the same procedures for P1. BDTP-Br (81.0 mg, 0.07 mmol) and 2,5-bis(trimethylstannyl) selenophene (32.5 mg, 0.07 mmol) were used as starting materials. P2 was obtained as a purple solid (72 mg, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.66-6.76 (br, 6H), 4.85 (br, 4H), 1.63-0.84 (br, 78H). Elemental analysis (%) calcd for C<sub>62</sub>H<sub>88</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>Se: C, 67.66; H, 8.06; N, 2.55. Found: C, 67.81; H, 8.10; N, 2.59.

### 3. NMR

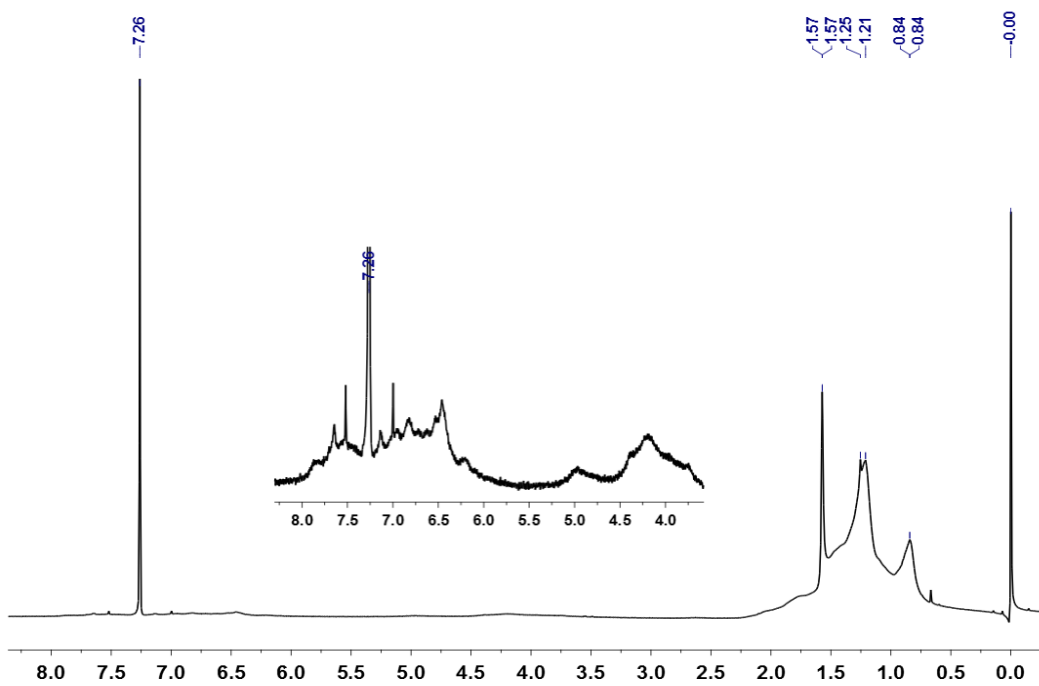


Figure S1  $^1\text{H}$  NMR spectrum of P1.

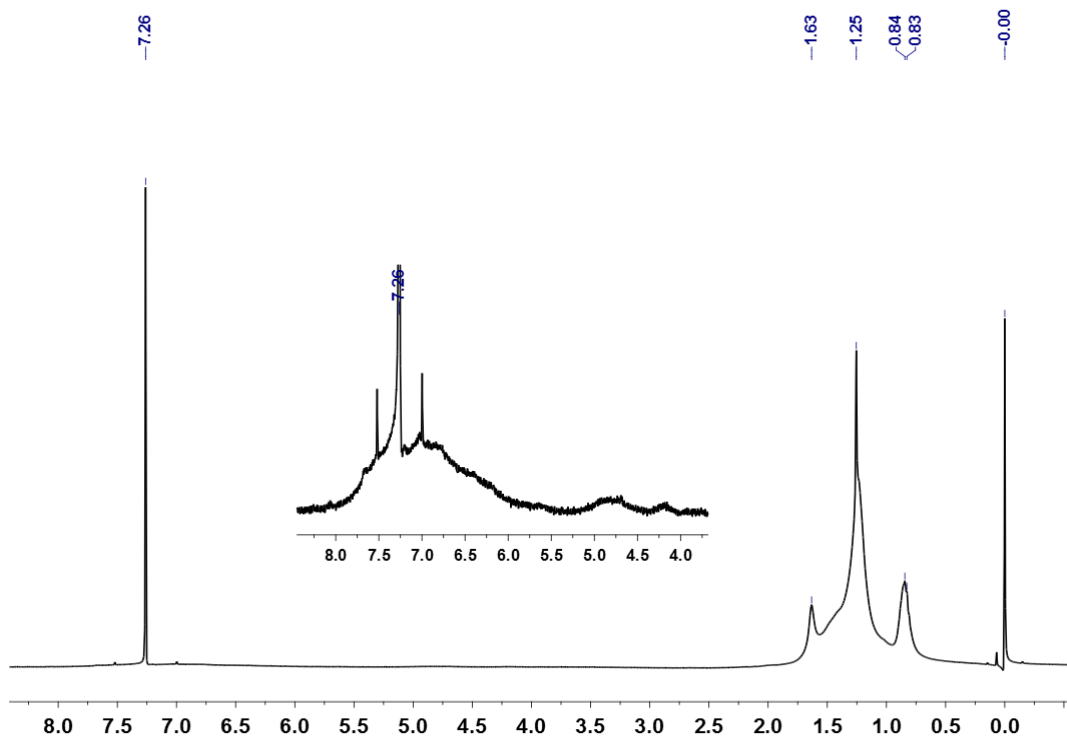


Figure S2  $^1\text{H}$  NMR spectrum of P2.

#### 4. TGA

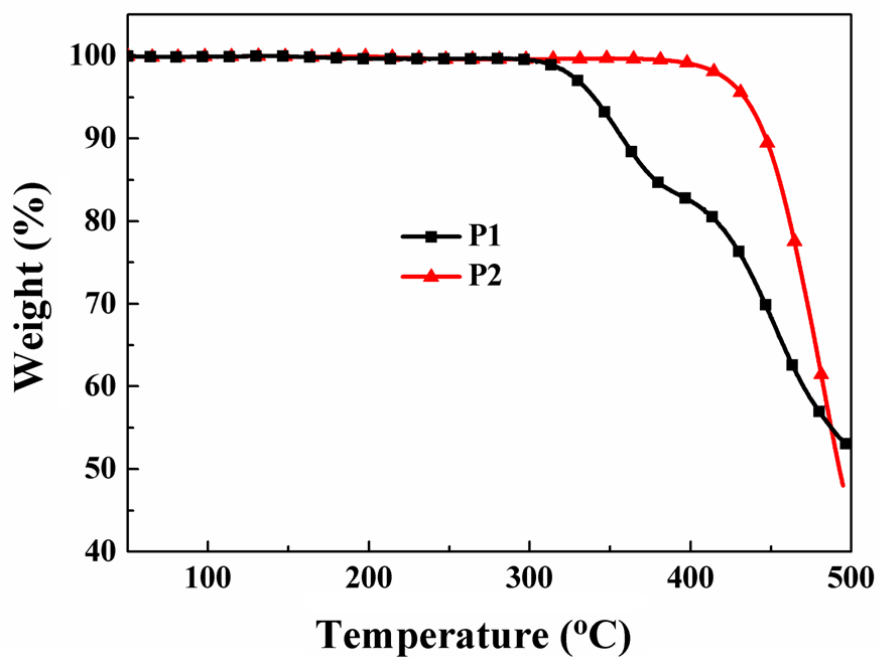


Figure S3 TGA curves for P1 and P2.

#### 5. CV

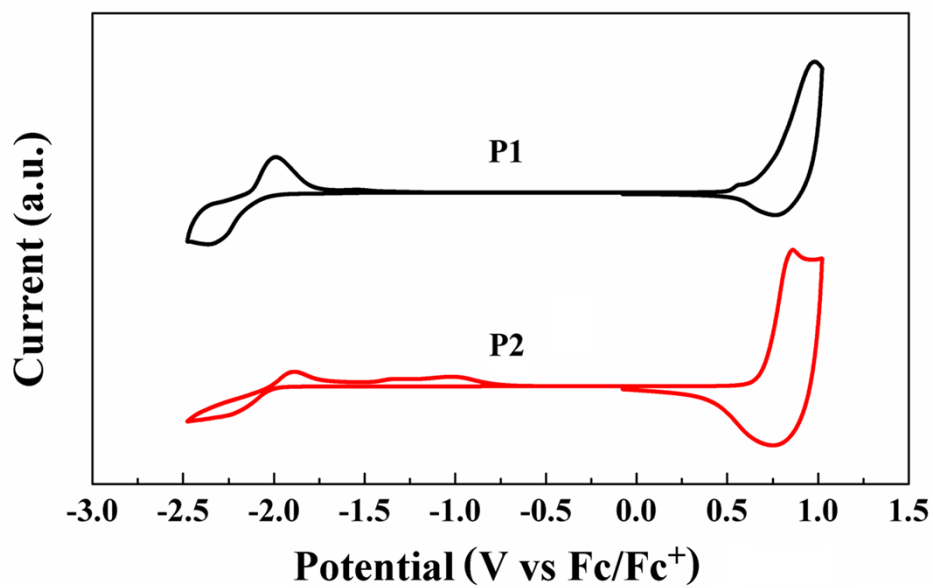


Figure S4 Cyclic voltammograms for P1 and P2.

## 6. Device fabrication and measurements

### Conventional solar cells

Patterned ITO glass with a sheet resistance of  $15 \Omega \text{ sq}^{-1}$  was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially and then given UV-ozone treatment. A 30 nm thick poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate (PEDOT:PSS, Clevios™ P VP Al 4083) layer was formed by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT substrates were dried at 150 °C for 10 min. A polymer:PC<sub>71</sub>BM blend solution was spin-coated onto PEDOT layer. Finally, Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca.  $10^{-4}$  Pa). The effective area for the cells is 4 mm<sup>2</sup>. The thicknesses for the active layers were measured by KLA Tencor D-120 profilometer. *J-V* curves were measured using a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a solar simulator (Oriel 91159A, 150 W, AM 1.5G, 100 mW/cm<sup>2</sup>). The illumination intensity of solar simulator was determined using a monocrystalline silicon solar cell (Oriel 91150) calibrated by NREL. The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Tech).

### Inverted solar cells

ZnO precursor solution<sup>2</sup> was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C for 20 min in air. The thickness for ZnO film is ~30 nm. A polymer:PC<sub>71</sub>BM blend solution was spin-coated onto ZnO layer. MoO<sub>3</sub> (~6 nm) and Ag (~80 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca.  $10^{-4}$  Pa).

### Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Al. A polymer:PC<sub>71</sub>BM blend solution was spin-coated onto PEDOT layer. MoO<sub>3</sub> (~6 nm) and Al (~100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca.  $10^{-4}$  Pa). *J-V* curves were measured using a computerized Keithley 2420 SourceMeter in the dark.

## 7. Device optimization

**Table S1** Optimization of the D/A ratio for **P1:PC<sub>71</sub>BM** conventional solar cells.<sup>a</sup>

D:A	$V_{oc}$	$J_{sc}$	FF	PCE
[w/w]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
1:0.8	0.94	4.38	35.1	1.45 (1.41) <sup>b</sup>
1:1.0	0.94	5.76	39.0	2.11 (1.75)
1:1.2	0.92	5.10	37.3	1.78 (1.45)
1:1.4	0.89	4.96	37.2	1.66 (1.22)

<sup>a</sup>Blend solution: 20 mg/mL in a mixed solvent (CB:CF=3:1) with 3 vol% DIO; spin-coating: 800 rpm for 60 s. <sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

**Table S2** Optimization of the active layer thickness for **P1:PC<sub>71</sub>BM** conventional solar cells.<sup>a</sup>

Thickness	$V_{oc}$	$J_{sc}$	FF	PCE
[nm]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
187	0.88	7.13	36.8	2.30 (2.17) <sup>b</sup>
198	0.89	7.72	37.6	2.58 (2.39)
207	0.89	7.35	38.4	2.51 (2.33)
222	0.89	7.24	35.8	2.30 (2.15)

<sup>a</sup>D/A ratio: 1:1, w/w; blend solution: 20 mg/mL in a mixed solvent (CB:CF=3:1) with 3 vol% DIO. <sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

**Table S3** Optimization of the additive content for **P1:PC<sub>71</sub>BM** conventional solar cells.<sup>a</sup>

DIO	$V_{oc}$	$J_{sc}$	FF	PCE
[v/v, %]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
0	0.90	4.69	31.1	1.31 (1.19) <sup>b</sup>
1	0.89	8.50	38.8	2.94 (2.81)
2	0.92	6.00	39.6	2.19 (2.04)
3	0.94	5.66	39.0	2.07 (1.79)

<sup>a</sup>D/A ratio: 1:1, w/w; blend solution: 20 mg/mL in a mixed solvent (CB:CF=3:1); spin-coating: 1200 rpm for 60 s. <sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

**Table S4** Optimization of solvent for **P1:PC<sub>71</sub>BM** conventional solar cells.<sup>a</sup>

Solvent	$V_{oc}$	$J_{sc}$	FF	PCE
	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
CB:CHCl <sub>3</sub> (1:1)	0.87	8.25	37.2	2.67 (2.55) <sup>b</sup>
CB:CHCl <sub>3</sub> (2:1)	0.87	8.80	41.1	3.14 (2.99)
CB:CHCl <sub>3</sub> (3:1)	0.89	8.50	38.8	2.94 (2.81)
ODCB	0.97	1.62	26.6	0.38 (0.30)

<sup>a</sup>D/A ratio: 1:1, w/w; blend solution: 20 mg/mL with 1 vol% DIO; spin-coating: 1200 rpm for 60 s. <sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.



**Table S5** Optimization of the active layer thickness for **P1:PC<sub>71</sub>BM** inverted solar cells.<sup>a</sup>

Thickness	$V_{oc}$	$J_{sc}$	FF	PCE
[nm]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
212	0.88	9.81	38.1	3.29 (3.04) <sup>b</sup>
203	0.89	10.23	47.2	4.29 (3.96)
195	0.89	10.37	54.7	5.05 (4.53)
189	0.90	10.07	48.3	4.37 (4.18)

<sup>a</sup>D/A ratio: 1:1, w/w; blend solution: 20 mg/mL in a mixed solvent (CB:CF=2:1) with 1 vol% DIO. <sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

**Table S6** Optimization of the D/A ratio for **P2:PC<sub>71</sub>BM** conventional solar cells.<sup>a</sup>

D:A	$V_{oc}$	$J_{sc}$	FF	PCE
[w/w]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
1:0.6	0.86	7.26	52.3	3.26 (3.05) <sup>b</sup>
1:0.8	0.89	7.58	52.7	3.55 (3.30)
1:1.0	0.92	7.91	59.1	4.30 (4.20)
1:1.2	0.91	7.95	61.8	4.47 (4.31)
1:1.4	0.87	7.52	52.4	3.43 (3.25)

<sup>a</sup>Blend solution: 20 mg/mL in ODCB with 3 vol% DIO; spin-coating: 800 rpm for 60 s. <sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

**Table S7** Optimization of the active layer thickness for **P2:PC<sub>71</sub>BM** conventional solar cells.<sup>a</sup>

Thickness [nm]	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF [%]	PCE [%]
127	0.82	8.01	54.5	3.58 (3.40) <sup>b</sup>
135	0.85	7.83	55.7	3.70 (3.43)
146	0.92	7.91	59.1	4.30 (4.17)
167	0.90	7.62	60.5	4.14 (3.95)
180	0.90	6.44	59.8	3.46 (3.22)

<sup>a</sup>D/A ratio: 1:1.2, w/w; blend solution: 20 mg/mL in ODCB with 3 vol% DIO.

<sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

**Table S8** Optimization of the additive content for **P2:PC<sub>71</sub>BM** conventional solar cells.<sup>a</sup>

DIO [v/v, %]	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF [%]	PCE [%]
0	0.90	8.37	65.6	4.94 (4.74) <sup>b</sup>
1	0.89	8.60	66.4	5.08 (4.98)
2	0.91	8.27	67.0	5.04 (4.92)
3	0.91	8.22	65.6	4.91 (4.82)
4	0.90	8.14	66.4	4.86 (4.60)

<sup>a</sup>D/A ratio: 1:1.2, w/w; blend solution: 20 mg/mL in ODCB; spin-coating: 800 rpm for 60 s. <sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

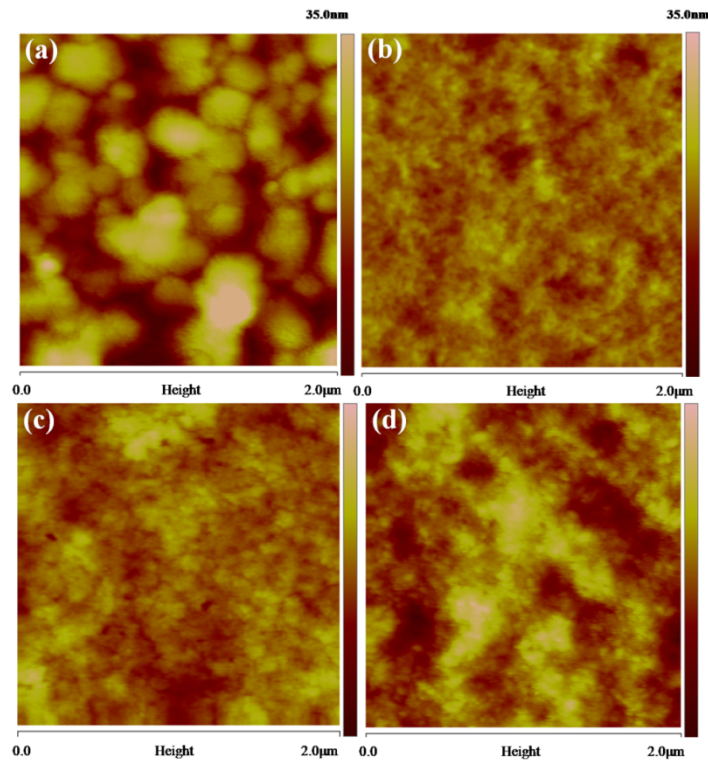
**Table S9** Optimization of the active layer thickness for **P2:PC<sub>71</sub>BM** inverted solar cells.<sup>a</sup>

Thickness [nm]	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF [%]	PCE [%]
115	0.90	9.71	71.4	6.23 (6.15) <sup>b</sup>
131	0.91	9.96	74.5	6.76 (6.64)
149	0.90	10.23	72.8	6.70 (6.48)
164	0.89	10.49	71.8	6.70 (6.55)

<sup>a</sup>D/A ratio: 1:1.2, w/w; blend solution: 20 mg/mL in ODCB with 1 vol% DIO.

<sup>b</sup>Data in parentheses stand for the average PCEs for 10 cells.

## 8. AFM



**Figure S5** AFM height images for **P1:PC<sub>71</sub>BM** blend films without (a) and with (b) 1% DIO; **P2:PC<sub>71</sub>BM** blend films without (c) and with (d) 1% DIO.

## 9. Space charge limited current (SCLC) measurements

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

where  $J$  is the current density,  $\mu$  is the zero-field mobility of holes ( $\mu_h$ ),  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon_r$  is the relative permittivity of the material,  $d$  is the thickness of the blend film, and  $V$  is the effective voltage,  $V = V_{\text{appl}} - V_{\text{bi}}$ , where  $V_{\text{appl}}$  is the applied voltage, and  $V_{\text{bi}}$  is the built-in potential determined by electrode workfunction difference. The mobility was calculated from the slope of  $J^{1/2}$ - $V$  plots.

## 10. XRD

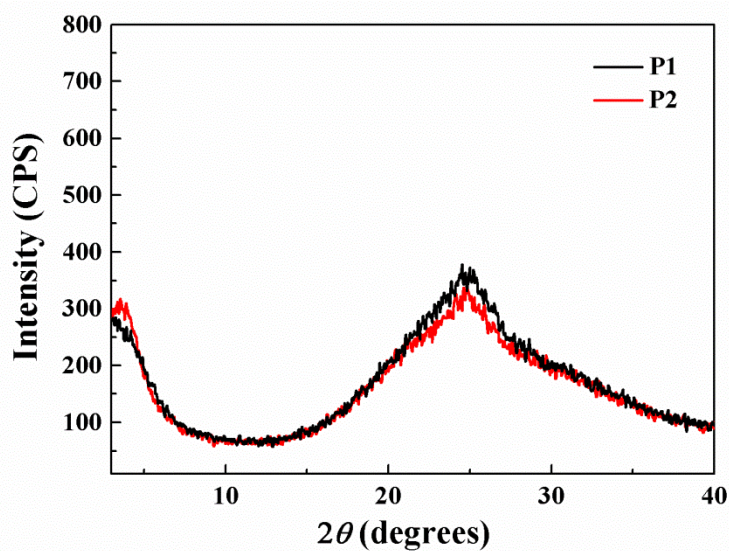


Figure S6 XRD patterns for as-cast P1 and P2 films.

## References

- [1] J. Cao, L. Qian, F. Lu, J. Zhang, Y. Feng, X. Qiu, H.-L. Yip and L. Ding, *Chem. Commun.*, 2015, **51**, 11830.
- [2] Y. Sun, J. H. Seo, C. J. Takacs, J. Seifert and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679.