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Supporting Information

A lactam building block for efficient polymer solar cells

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1. General characterization

^1H and ^{13}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) were performed on a Waters 1515 series GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was done using a Perkin-Elmer Diamond TG/DTA thermal analyzer under nitrogen. Cyclic voltammetry was conducted 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^+ electrode was used as the reference electrode. Polymers were coated onto glassy carbon electrode and all potentials were corrected against Fc/Fc^+. AFM was performed on a Dimension 3100 microscope (Veeco) using tapping mode. Grazing incidence wide angle X-ray scattering (GIWAXS) was done on a Xeuss SAXS/WAXS instrument. Pure PThBDTP film and PThBDTP/$PC_{71}BM$ blend film were spin-coated onto ZnO/ITO substrate.

2. Synthesis

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. Diethyl 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (**1**),[1] *N*-(2-octyldodecyl)thiophen-3-amine,[2] 2,5-bis(trimethylstannyl)thiophene[3] were prepared according to literatures.

5,5'-Dibromo-[2,2'-bithiophene]-4,4'-dicarboxylic acid (2). A mixture of compound **1** (1.5 g, 3.6 mmol) and sodium hydroxide (0.58 g, 14.4 mmol) in ethanol/THF/water (50 mL/50 mL/10 mL) was refluxed overnight. The solvent was evaporated under vacuum to remove half of it. Water (50 mL) was added to the solution, and the resulting mixture was treated with HCl. The precipitate was filtered and washed with water, and compound **2** as a white solid

(1.2 g, 90%) was obtained. ^{1}H NMR (d_6-DMSO, 400 MHz, δ/ppm): 7.35 (s, 2H), 4.04 (br, 2H).

5,5'-Dibromo-*N*^{4},*N*$^{4'}$-bis(2-octyldodecyl)-*N*^{4},*N*$^{4'}$-di(thiophen-3-yl)-[2,2'-bithiophene]-4,4'-dicarboxamide (3). To a solution of compound **2** (1.9 g, 4.6 mmol) in dry CH_2Cl_2 (40 mL) were added oxalyl chloride (4 mL, 45.6 mmol) and 2 drops of DMF. The mixture was stirred at room temperature overnight. The solvent was removed under vacuum to obtain 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarbonyl dichloride, which was used in next step without purification. To the solution of 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarbonyl dichloride in dry CH_2Cl_2 (40 mL) was added slowly a solution of *N*-(2-octyldodecyl)thiophen-3-amine (4.3 g, 11.5 mmol) and Et_3N (2 mL) in dry CH_2Cl_2 (20 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with $CHCl_3$ three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with CH_2Cl_2 to give compound **3** as a light yellow solid (4.35 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.16 (s, 2H), 6.87 (s, 2H), 6.78 (d, 2H), 6.41 (s, 2H), 3.78 (d, J = 6.6 Hz, 4H), 1.61 (br, 2H), 1.30-1.24 (m, 64H), 0.90-0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 164.33, 140.33, 138.83, 135.76, 125.53, 125.38, 123.69, 120.00, 111.41, 52.57, 36.20, 31.92, 31.91, 31.22, 30.02, 29.66, 29.65, 29.61, 29.57, 29.35, 29.32, 26.31, 22.68, 14.12. MALDI-TOF MS (m/z): 1157.7 (M^+Na).

4,4'-Bis(2-octyldodecyl)-[7,7'-bidithieno[3,2-*b*:2',3'-*d*]pyridine]-5,5'(4*H*,4'*H*)-dione (BDTP). To a solution of compound **3** (2.78 g, 2.45 mmol) in N,N-dimethylacetamide (150 mL) were added $PCy_3 \cdot HBF_4$ (660 mg, 1.8 mmol), Cs_2CO_3 (4.0 g, 12.3 mmol) and $Pd(OAc)_2$ (300 mg, 1.3 mmol) under Ar. The mixture was stirred at 120 °C overnight and then cooled to room temperature. The mixture was poured into water and extracted with $CHCl_3$ three times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified through a silica gel column with petroleum ether/CH_2Cl_2 (1:4) as eluent to give **BDTP** as a yellow solid (1.32 g, 56%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.78 (s, 2H), 7.47 (d, J = 5.4 Hz, 2H), 7.08 (d, J =

5.4 Hz, 2H), 4.22 (d, $J = 4.5$ Hz, 4H), 2.00 (br, 2H), 1.37-1.23 (m, 64H), 0.88-0.85 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 158.48, 141.27, 140.95, 133.49, 129.40, 126.22, 123.25, 117.57, 113.88, 49.39, 37.28, 31.97, 31.87, 31.68, 29.95, 29.61, 29.55, 29.50, 29.31, 29.24, 26.67, 22.65, 22.63, 14.04. MALDI-TOF MS (m/z): 973.8 (M^+).

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). To a solution of **BDTP** (874 mg, 0.90 mmol) in a solvent mixture of $CHCl_3$ (30 mL) and DMF (10 mL) was added NBS (352 mg, 1.98 mmol) under Ar. The mixture was stirred at room temperature for 24 h and then poured into 150 mL methanol. The precipitate was filtered and purified through a silica gel column with petroleum ether/CH_2Cl_2 (1:4) as eluent to give **BDTP-Br** as a yellow solid (632 mg, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.75 (s, 2H), 7.06 (s, 2H), 4.14 (br, 4H), 1.95 (br, 2H), 1.35-1.24 (m, 64H), 0.88-0.85 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 157.98, 140.27, 139.76, 133.57, 129.40, 123.14, 120.55, 115.37, 114.77, 49.31, 37.17, 31.92, 31.89, 31.46, 29.97, 29.64, 29.59, 29.54, 29.35, 29.29, 26.56, 22.69, 22.67, 14.11. MALDI-TOF MS (m/z): 1131.8 (M^+).

Poly{2,5-thiophene-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} (PThBDTP). **BDTP-Br** (116 mg, 0.10 mmol) and 2,5-bis(trimethylstannyl)thiophene (42 mg, 0.10 mmol) were dissolved in 30 mL toluene, and the solution was flushed with argon for 15 min, then 8 mg $Pd(PPh_3)_4$ 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 **PThBDTP** as a purple solid (90 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.76-6.66 (br, 6H), 4.21 (br, 4H), 1.58-0.85 (br, 78H). Elemental analysis (%) calcd for $C_{62}H_{88}N_2O_2S_5$: C, 70.67; H, 8.42; N, 2.66. Found: C, 70.56; H, 8.58; N, 2.79.

3. NMR

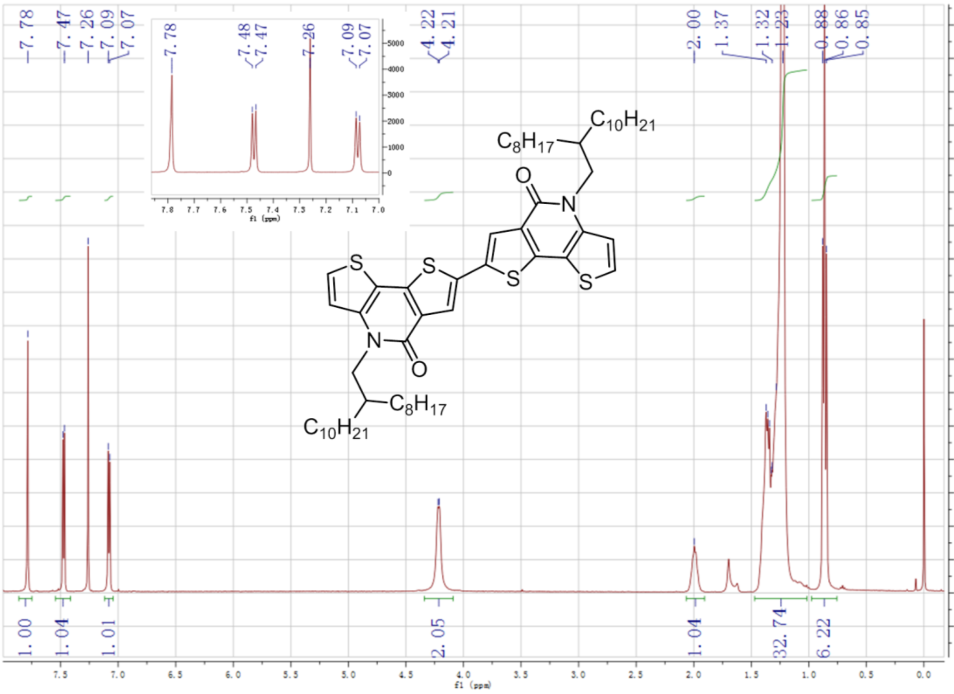

Figure S1 ^{1}H NMR spectrum for **BDTP**.

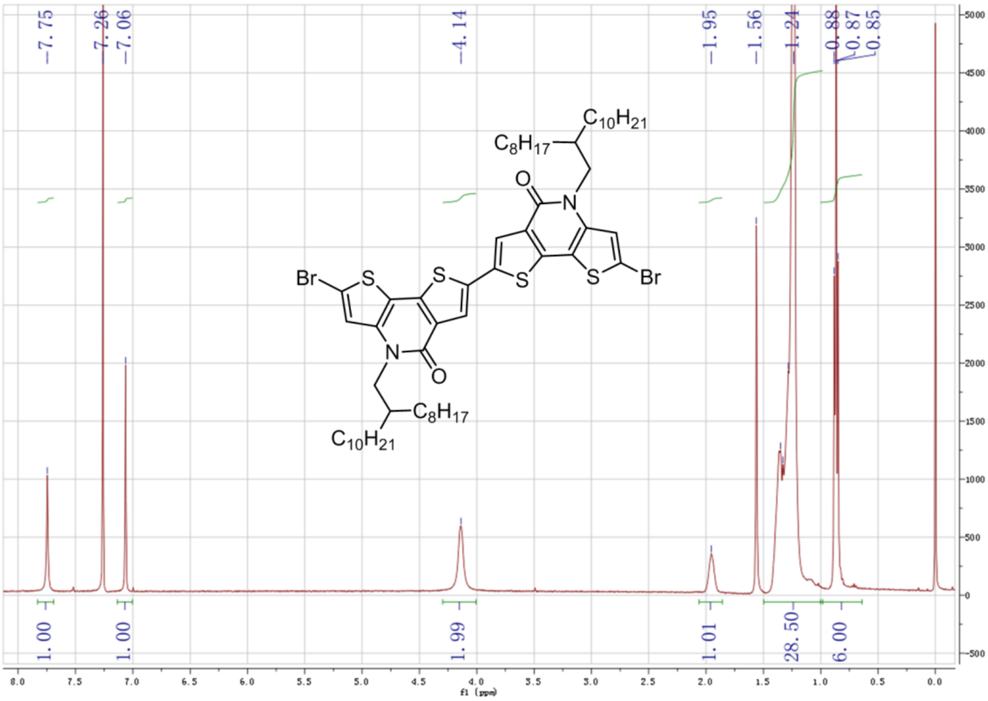

Figure S2 ^{1}H NMR spectrum for **BDTP-Br**.

4. TGA

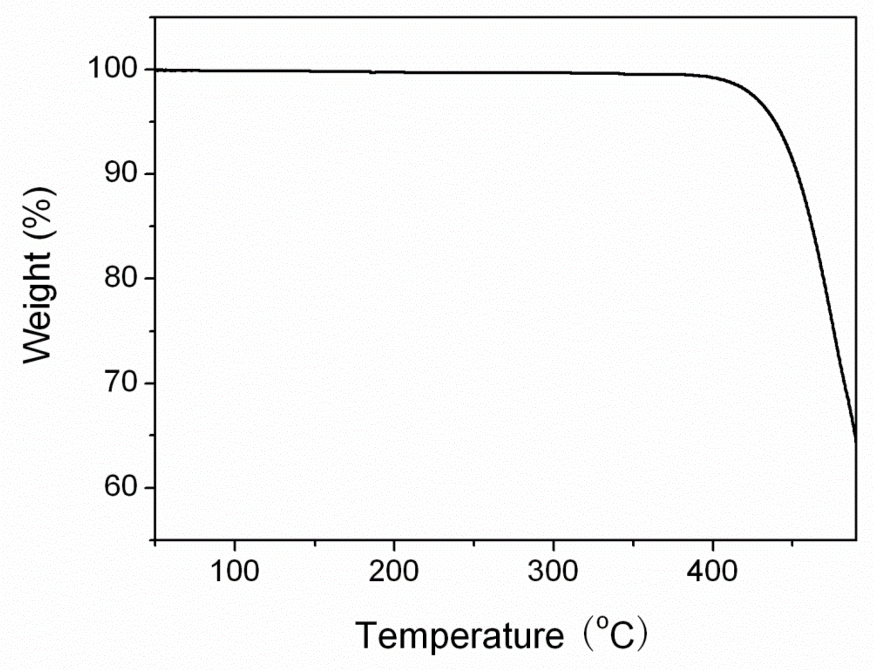

Figure S3 TGA curve for **PThBDTP**.

5. CV

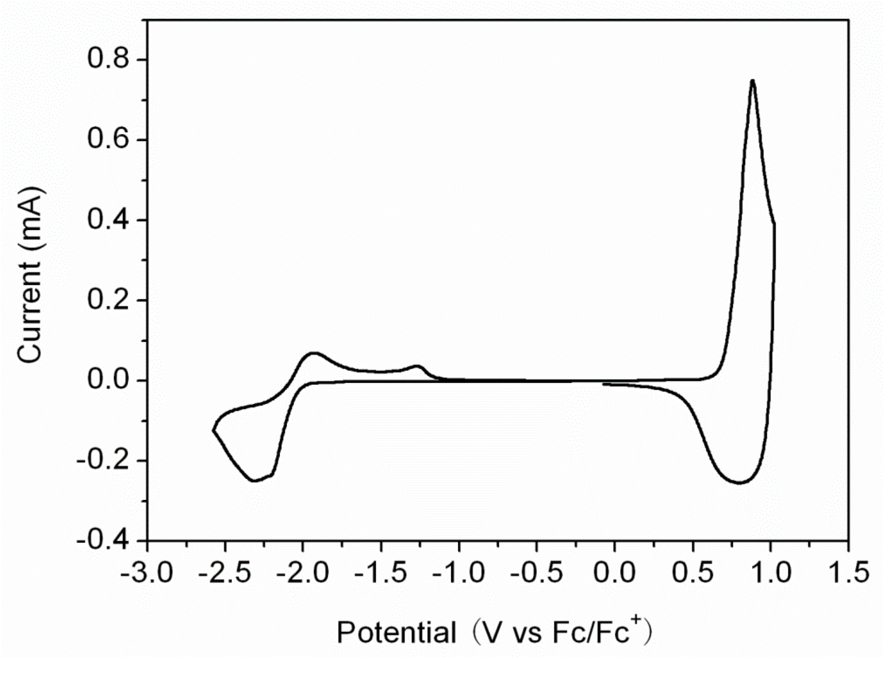

Figure S4 Cyclic voltammogram for **PThBDTP**.

6. Device fabrication and measurements

Conventional solar cells

Patterned ITO glass with a sheet resistance of 15 Ω 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^{TM} P VP Al 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A PThBDTP/$PC_{71}BM$ blend (1:1.2 w/w) in ODCB (14 mg/mL) with 3 vol% DIO was spin-coated onto PEDOT:PSS layer (1400 rpm for 85 s). The thicknesses for the active layers were measured by KLA Tencor D-120 profilometer. 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 devices is 4 mm^2. *J-V* curves were measured in air using a computerized Keithley 2420 SourceMeter and a Xenon-lamp-based solar simulator (Newport, Oriel 91159A, 150 W, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined using a monocrystalline silicon solar cell (Oriel 91150, 2×2 cm) calibrated by NREL. The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Technology Co.).

Inverted solar cells

ZnO precursor was prepared according to literature.[4] The precursor solution was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C for 30 min in air. ZnO film thickness is about 30 nm. A PThBDTP/$PC_{71}BM$ blend in ODCB (14 mg/mL) with 3 vol% DIO was spin-coated onto ZnO layer (1400 rpm for 85 s). MoO_3 (~6 nm) and Ag (~80 nm) was successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa).

Hole-only devices

The structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/Al. A 30 nm thick PEDOT:PSS layer was made by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A

PThBDTP/PC$_{71}$BM blend in ODCB (14 mg/mL) with 3 vol% DIO was spin-coated onto PEDOT:PSS layer (1000 rpm for 60 s). Finally, MoO$_3$ (~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 with a computerized Keithley 2420 SourceMeter in the dark.

Electron-only devices

The structure of electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was first evaporated onto a glass substrate. A PThBDTP/PC$_{71}$BM blend in ODCB (14 mg/mL) with 3 vol% DIO was spin-coated onto Al (1000 rpm for 60 s). Ca (~5 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured with a computerized Keithley 2420 SourceMeter in the dark.

7. Device optimization

Table S1 Optimization of the D/A ratio for **PThBDTP**/PC$_{61}$BM conventional solar cells.[a]

D:A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.6	0.84	7.45	39.7	2.48 (2.30)[b]
1:0.8	0.87	10.87	47.3	4.46 (4.03)
1:1.0	0.89	10.93	51.5	5.00 (4.82)
1:1.2	0.83	9.53	49.0	3.98 (3.70)
1:1.4	0.82	9.89	54.2	4.39 (4.18)

[a]Blend solution: 14 mg/mL in a mixed solvent (CB/CF, 3/1, v/v) with 3 vol% DIO; spin-coating: 800 rpm for 85 s. [b]Data in parentheses stand for the average PCEs for 10 cells.

Table S2 Optimization of the active layer thickness for **PThBDTP**/PC$_{61}$BM conventional solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
116	0.87	9.10	53.5	4.23 (4.08)[b]
132	0.88	9.30	51.6	4.22 (4.09)
150	0.89	10.93	51.5	5.00 (4.82)
162	0.87	11.42	48.1	4.78 (4.57)

[a]D/A ratio: 1:1, w/w; blend solution: 14 mg/mL in a mixed solvent (CB/CF, 3/1, v/v) with 3 vol% DIO. [b]Data in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of the additive content for **PThBDTP**/PC$_{61}$BM conventional solar cells.[a]

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.90	8.82	45.7	3.63 (3.30)[b]
1	0.89	10.12	46.9	4.22 (4.06)
2	0.90	11.63	47.9	5.00 (4.85)
3	0.91	12.02	48.8	5.33 (4.93)
4	0.90	11.21	47.1	4.75 (4.27)

[a]D/A ratio: 1:1, w/w; blend solution: 14 mg/mL in a mixed solvent (CB/CF, 3/1, v/v); spin-coating:1000 rpm for 85 s. [b]Data in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of solvent for **PThBDTP**/PC$_{61}$BM conventional solar cells.[a]

Solvent	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
CB:CHCl$_3$ (3:1)	0.91	11.56	49.1	5.16 (4.73)[b]
CB	0.91	12.02	48.8	5.33 (4.75)
ODCB	0.96	10.76	61.0	6.30 (6.12)

[a] D/A ratio: 1:1, w/w; blend solution: 14 mg/mL with 3 vol% DIO; spin-coating: 1000 rpm for 85 s. [b] Data in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of D/A ratio for **PThBDTP**/PC$_{71}$BM conventional solar cells.[a]

D:A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.6	0.97	11.27	62.6	6.85 (6.60)[b]
1:0.8	0.96	11.44	63.4	6.96 (6.74)
1:1.0	0.96	11.98	64.3	7.40 (7.15)
1:1.2	0.96	11.72	66.5	7.48 (7.28)
1:1.4	0.94	11.43	65.6	7.05 (6.89)

[a] Blend solution: 14 mg/mL in ODCB with 3 vol% DIO; spin-coating: 1000 rpm for 85 s.
[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of the active layer thickness for **PThBDTP**/PC$_{71}$BM conventional solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
105	0.95	11.52	67.3	7.36 (7.07)[b]
116	0.96	11.55	69.2	7.67 (7.38)
124	0.97	11.40	68.5	7.57 (7.32)
132	0.96	11.56	65.3	7.24 (7.02)
145	0.97	11.20	65.4	7.15 (6.99)

[a] D/A ratio: 1:1.2, w/w; blend solution: 14 mg/mL in ODCB with 3 vol% DIO. [b] Data in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of the additive content for **PThBDTP**/PC$_{71}$BM conventional solar cells.[a]

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1	0.96	11.21	69.0	7.43 (7.30)[b]
2	0.97	11.43	69.1	7.66 (7.45)
3	0.98	11.56	70.1	7.94 (7.60)
4	0.97	11.57	68.8	7.72 (7.51)
5	0.97	11.48	69.0	7.68 (7.45)

[a] D/A ratio: 1:1.2, w/w; blend solution: 14 mg/mL in ODCB; spin-coating:1400 rpm for 85 s. [b] Data in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of the active layer thickness for **PThBDTP**/$PC_{71}BM$ inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
90	0.96	11.78	76.0	8.59 (8.39)[b]
103	0.96	12.05	76.0	8.79 (8.60)
113	0.94	12.48	75.7	8.88 (8.61)
121	0.96	12.59	75.5	9.13 (8.98)
129	0.95	12.63	72.6	8.70 (8.56)

[a] D/A ratio: 1:1.2, w/w; blend solution: 14 mg/mL in ODCB with 3 vol% DIO. [b] Data in parentheses stand for the average PCEs for 10 cells.

8. AFM

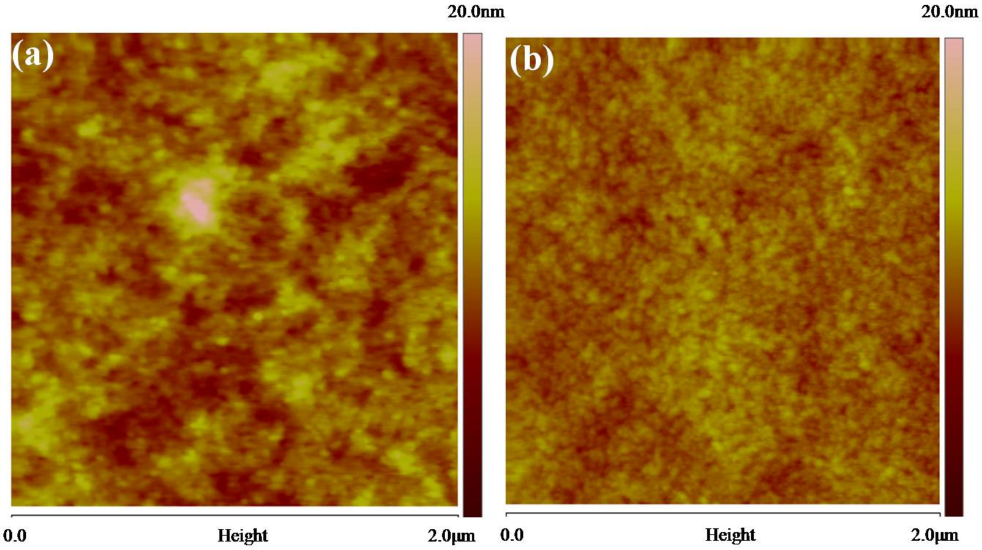

Figure S5 AFM height images for **PThBDTP**/$PC_{71}BM$ blend films without (a) and with 3 vol% DIO (b).

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:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where *J* is the current density, μ is the zero-field mobility of holes (μ_h) or electrons (μ_e), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, *d* is the thickness of the blend film, and *V* is the effective voltage, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode workfunction difference. Figure S6 and S7 show *J*-*V* curves for the hole-only devices and the electron-only devices, respectively. The mobilities were calculated from the slope of $J^{1/2}$-*V* curves.

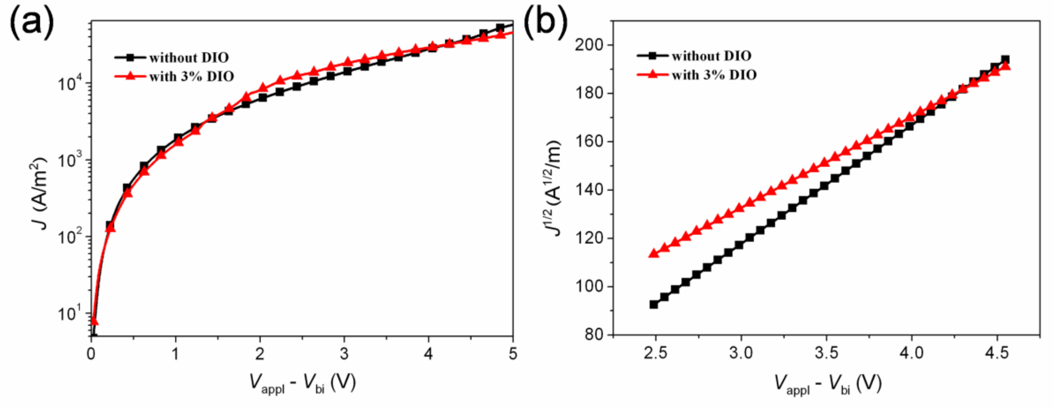

Figure S6 *J*-*V* curves (a) and the corresponding $J^{1/2}$-*V* curves (b) for hole-only devices based on **PThBDTP**:PC$_{71}$BM blend film without or with 3% DIO (in dark). The thicknesses for the blend films are 147 and 150 nm, respectively.

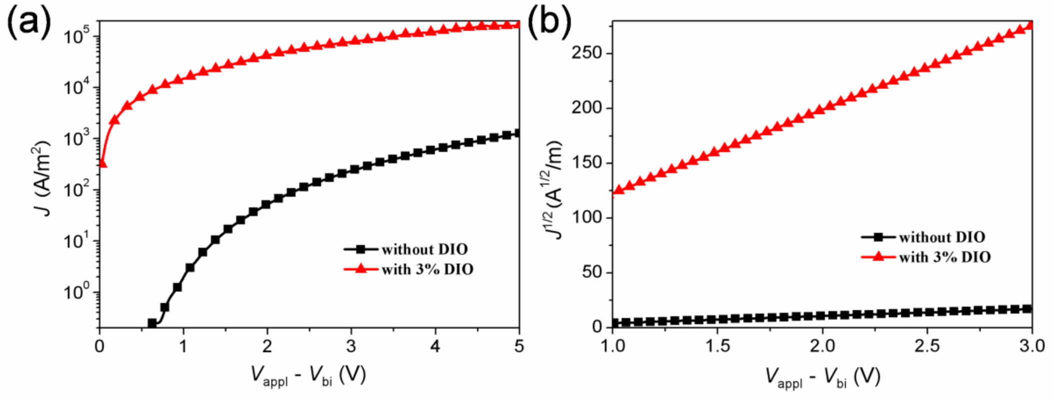

Figure S7 *J*-*V* curves (a) and the corresponding $J^{1/2}$-*V* curves (b) for electron-only devices based on **PThBDTP**:PC$_{71}$BM blend film without or with 3% DIO (in dark). The thicknesses for the blend films are 150 and 130 nm, respectively.

Table S9 Mobilities for **PThBDTP**:PC$_{71}$BM blend film

	Without DIO	With 3% DIO
μ_h (cm^2 V^{-1} s^{-1})	2.24×10^{-3}	1.61×10^{-3}
μ_e (cm^2 V^{-1} s^{-1})	4.84×10^{-5}	1.41×10^{-3}

References

[1] K. Sakamoto, Y. Takashima, N. Hamada, H. Ichida, H. Yamaguchi, H. Yamamoto and A. Harada, *Org. Lett.,* 2011, **13**, 672.

[2] R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus and I. McCulloch, *Chem. Commun.,* 2012, **48**, 3939.

[3] J. Hou, T. L. Chen, S. Zhang, L. Huo, S. Sista and Y. Yang, *Macromolecules,* 2009, **42**, 9217.

[4] Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter, A. J. Heeger, *Adv. Mater.,* 2011, **23**, 1679.