

Supporting Information

D-A copolymers with benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione acceptor unit for 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 1515-2410 series GPC coupled with differential refractive index detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was done using a NETZSCH TG209-F3 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. X-ray diffraction (XRD) of thin films was performed on a Rigaku D/max-2500 X-ray diffractometer in reflection mode using Cu K α radiation (40 kV, 200 mA).

2. Synthesis

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co., Lyntech Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 5,7-Dibromo-2-(2-ethylhexyl)benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (**1**) was prepared according to literature.¹

5,7-Bis(4-(2-butyloctyl)thiophen-2-yl)-2-(2-ethylhexyl)benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (2). To a solution of compound **1** (400 mg, 0.82 mmol) in 70 mL toluene were added tributyl(4-butyloctylthiophen-2-yl)stannane (1.06 g, 1.96 mmol) and Pd(PPh₃)₄ (70 mg) under Ar. The mixture was stirred at 110 °C for 12 h and then cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified via column chromatography over silica gel by using petroleum ether/CH₂Cl₂ (3:1) as eluent to

give compound **2** as a red viscous liquid (488 mg, 72%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.68-7.66 (m, 2H), 7.33 (s, 1H), 7.11 (d, 2H), 2.83 (d, *J* = 6.7 Hz, 2H), 2.59 (d, *J* = 6.3 Hz, 4H), 1.67-1.60 (m, 1H), 1.41-1.28 (m, 42H), 0.94-0.86 (m, 18H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 176.10, 174.48, 155.26, 145.60, 144.42, 144.37, 144.07, 142.52, 142.46, 133.07, 133.02, 132.31, 132.24, 130.08, 129.69, 126.09, 124.50, 41.44, 38.95, 34.87, 34.83, 33.31, 33.00, 32.39, 31.92, 29.71, 28.88, 28.84, 26.60, 25.57, 23.07, 22.93, 22.17, 14.16, 14.13, 14.09, 10.80. MALDI-TOF MS (*m/z*): 834.6 (M+H⁺).

5,7-Bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)-2-(2-ethylhexyl)benzo[1,2-*b*:4,5-*c'*]dithiophene-4,8-dione (3). To a solution of compound **2** (470 mg, 0.56 mmol) in a mixed solvent of CHCl₃ (20 mL) and DMF (20 mL) was added NBS (245 mg, 1.38 mmol) under Ar. The mixture was stirred at room temperature for 24 h and then poured into water and extracted with CHCl₃ for three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified via column chromatography over silica gel by using petroleum ether/CH₂Cl₂ (6:1) as eluent to give compound **3** as a red solid (470 mg, 84%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.46 (d, 2H), 7.34 (s, 1H), 2.84 (d, *J* = 6.7 Hz, 2H), 2.55-2.53 (m, 4H), 1.70 (br, 1H), 1.38-1.28 (m, 42H), 0.93-0.86 (m, 18H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 175.84, 174.19, 155.79, 145.15, 144.09, 143.21, 142.84, 142.47, 142.44, 132.20, 132.16, 131.55, 131.52, 129.51, 129.15, 124.45, 116.46, 41.39, 34.84, 32.38, 31.94, 29.77, 29.70, 29.68, 29.67, 29.62, 29.51, 29.43, 29.38, 29.33, 28.83, 25.55, 22.94, 22.71, 14.13, 14.10, 10.80. MALDI-TOF MS (*m/z*): 992.4 (M+H⁺).

PThBDTD. Compound **3** (100 mg, 0.10 mmol) and 2,5-bis(trimethylstannyl)thiophene (41.3 mg, 0.10 mmol) were dissolved in 30 mL toluene, and the solution was flushed with argon for 15 min, then 8 mg Pd(PPh₃)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 via Soxhlet extraction by using 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 **PThBDTD** as a purple-black solid (45mg, 49%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 8.04-7.45 (br, 2H), 7.30-7.25 (br, 1H), 7.08 (br, 2H), 2.72-2.71 (br, 6H), 1.73-1.23 (br, 43H), 0.87-0.81 (br, 18H). Elemental analysis (%) calcd for $\text{C}_{54}\text{H}_{72}\text{O}_2\text{S}_5$: C, 71.00; H, 7.94. Found: C, 68.38; H, 7.94.

PTTBDTD. **PTTBDTD** was synthesized by following the same procedures for **PThBDTD**. Compound **3** (80 mg, 0.08 mmol) and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (37.6 mg, 0.08 mmol) were used as the starting materials. **PTTBDTD** was obtained as a dark blue solid (60 mg, 77%). ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 8.09-7.85 (br, 2H), 7.45-7.04 (br, 3H), 2.76-2.54 (br, 6H), 1.74-1.18 (br, 43H), 0.87-0.84 (br, 18H). Elemental analysis (%) calcd for $\text{C}_{56}\text{H}_{72}\text{O}_2\text{S}_6$: C, 69.37; H, 7.49. Found: C, 68.66; H, 7.45.

3. ^1H NMR

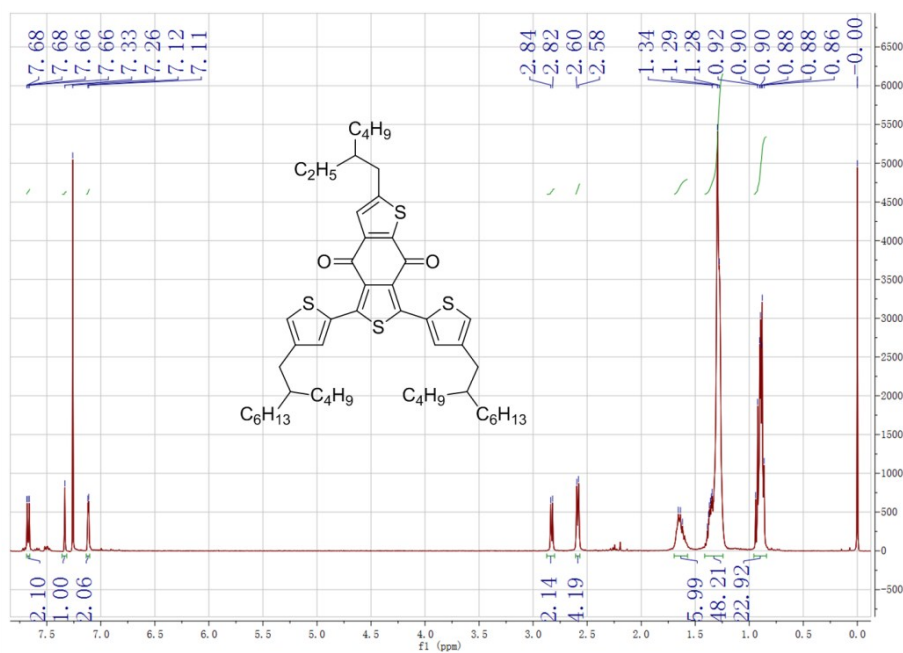


Fig. S1 ^1H NMR spectrum of compound **2**.

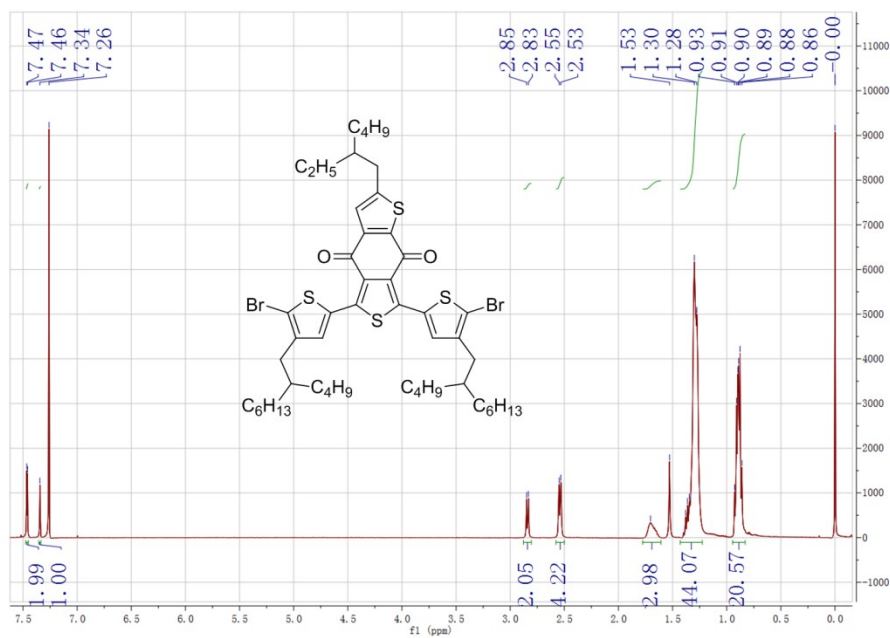


Fig. S2 ^1H NMR spectrum of compound **3**.

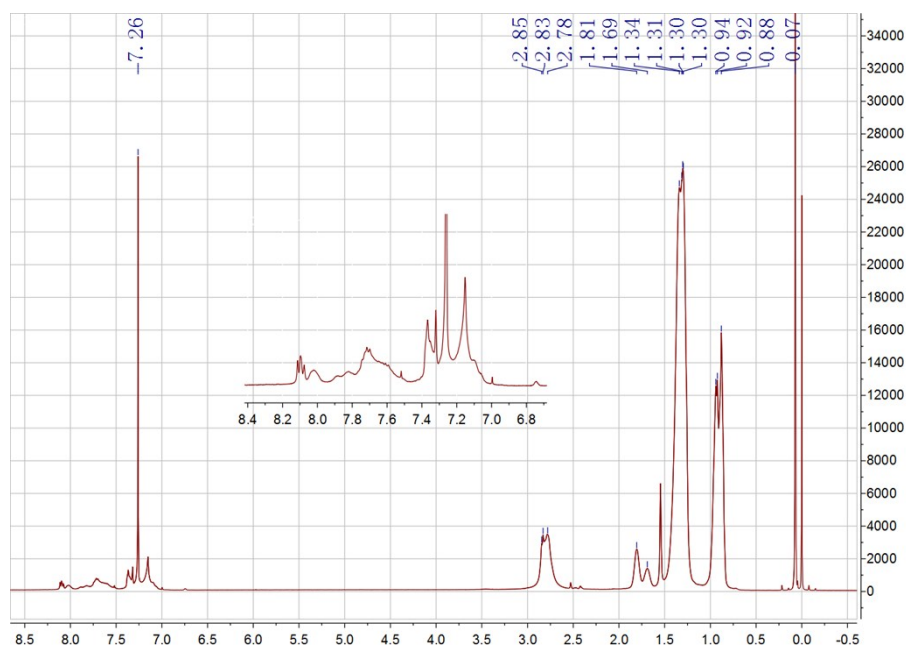


Fig. S3 ^1H NMR spectrum of PThBDTD.

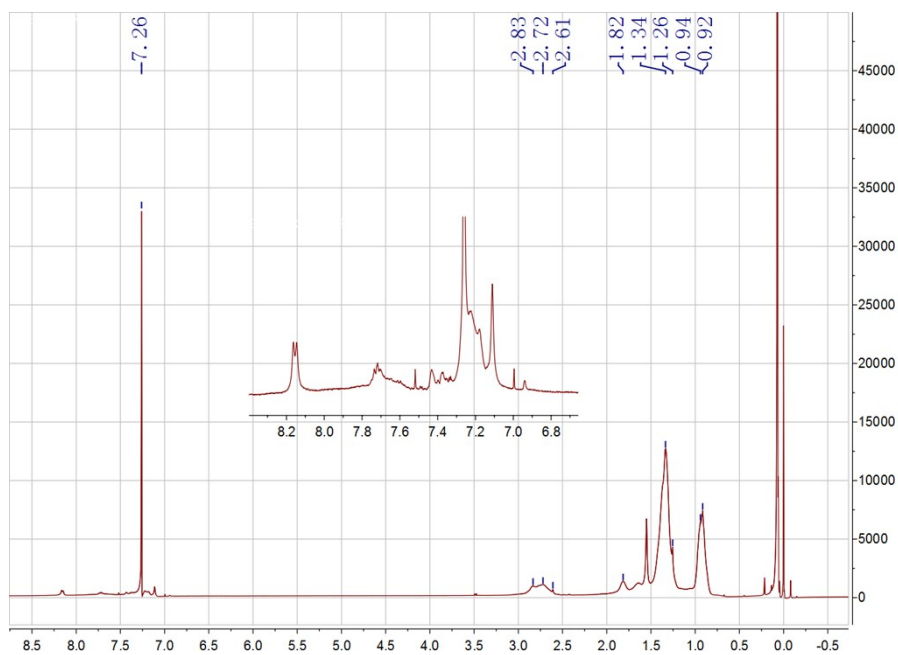


Fig. S4 ^1H NMR spectrum of PTTBDTD.

4. TGA

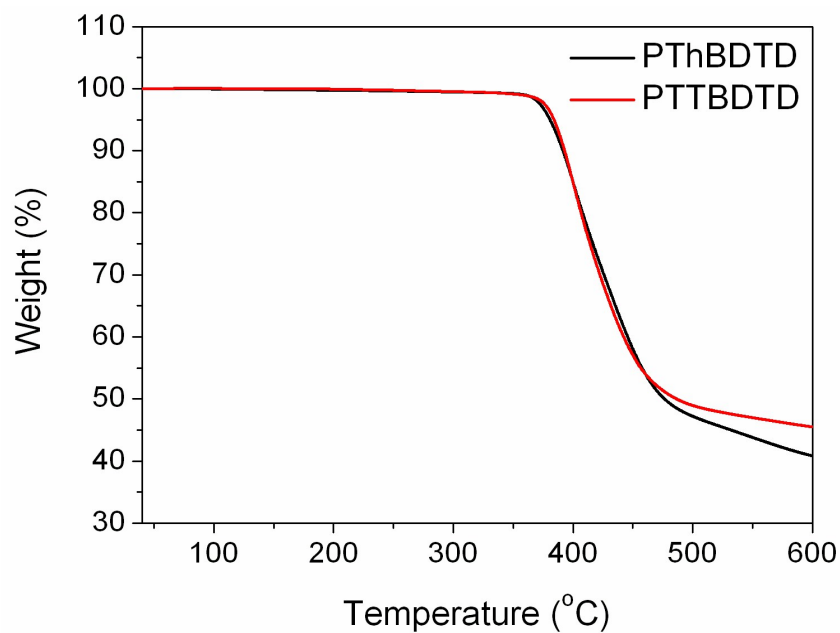


Fig. S5 TGA curves for PThBDTD and PTTBDTD.

5. CV

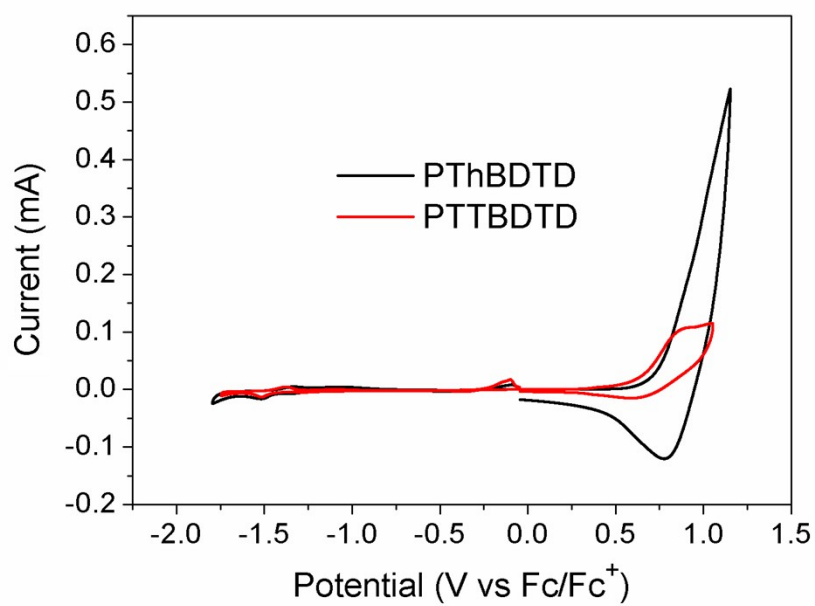


Fig. S6 Cyclic voltammograms for PThBDTD and PTTBDTD.

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, CleviosTM 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 polymer:PC₇₁BM blend in CB with DIO additive was spin-coated onto PEDOT:PSS layer. Finally, Ca (~10 nm) and Al (~100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm². The thicknesses for the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm²). The illumination intensity of the solar simulator was determined by using a monocrystalline silicon solar cell (Oriel 91150, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Inverted solar cells

ZnO precursor was prepared according to the literature.² 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 polymer:PC₇₁BM blend in CB with DIO additive was spin-coated onto ZnO layer. MoO₃ (~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/MoO₃/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 substrates were dried at 150 °C for 10 min. A polymer:PC₇₁BM blend in

CB with 2 vol% DIO additive was spin-coated onto PEDOT layer. Finally, MoO₃ (~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 by using a computerized Keithley 2400 SourceMeter in the dark.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for PThBDTD:PC₇₁BM conventional solar cells.^a

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.8	0.89	8.23	54.5	3.98 (3.79) ^b
1:1.0	0.87	9.63	51.3	4.26 (4.09)
1:1.2	0.87	9.06	52.8	4.18 (4.02)
1:1.4	0.87	9.10	51.7	4.09 (3.97)

^aBlend solution: 18 mg/mL in CB with 3 vol% DIO; spin coating: 1200 rpm for 60 s. ^bData in parentheses stand for the average PCEs for 10 cells.

Table S2 Optimization of the active layer thickness for PThBDTD:PC₇₁BM conventional solar cells.^a

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
106	0.87	9.01	53.0	4.13 (4.00) ^b
114	0.88	9.09	53.5	4.30 (4.13)
126	0.87	9.28	50.3	4.06 (3.88)
133	0.86	9.62	48.9	4.04 (3.86)
141	0.87	9.79	46.8	3.98 (3.84)

^aD/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in CB with 3 vol% DIO. ^bData in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of DIO content for PThBDTD:PC₇₁BM conventional solar cells.^a

DIO	V_{oc}	J_{sc}	FF	PCE
[v/v, %]	[V]	[mA/cm ²]	[%]	[%]
0	0.90	6.46	30.2	1.76 (1.60) ^b
1	0.87	5.65	50.0	2.47 (2.14)
2	0.89	10.07	59.1	5.28 (5.16)
3	0.87	8.42	55.1	4.03 (3.86)
4	0.84	7.11	49.3	2.94 (2.68)
5	0.81	5.64	48.4	2.20 (1.92)

^aD/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in CB; spin coating: 1000 rpm for 60 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of the active layer thickness for PThBDTD:PC₇₁BM inverted solar cells.^a

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
94	0.88	10.36	64.6	5.90 (5.81) ^b
101	0.88	10.40	65.4	6.02 (5.90)
112	0.88	10.81	66.2	6.32 (6.16)
121	0.88	11.53	61.9	6.22 (6.10)
134	0.88	10.98	63.4	6.11 (5.98)

^aD/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in CB with 2 vol% DIO. ^bData in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of D/A ratio for PTTBDTD:PC₇₁BM inverted solar cells.^a

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.8	0.73	13.80	53.1	5.35 (5.13) ^b
1:1.0	0.72	13.31	57.1	5.45 (5.26)
1:1.2	0.72	14.31	48.9	5.03 (4.80)
1:1.4	0.71	13.04	47.9	4.43 (4.26)

^aBlend solution: 16 mg/mL in CB with 3 vol% DIO; spin coating: 1200 rpm for 60 s. ^bData in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of the active layer thickness for PTTBDTD:PC₇₁BM inverted solar cells.^a

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
98	0.72	12.41	59.9	5.39 (5.19) ^b
106	0.72	14.15	53.3	5.44 (5.23)
113	0.73	14.42	56.2	5.88 (5.59)
124	0.73	13.80	53.1	5.35 (5.14)
140	0.71	12.95	47.7	4.40 (4.33)

^aD/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in CB with 3 vol% DIO. ^bData in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of DIO content for PTTBDTD:PC₇₁BM inverted solar cells.^a

DIO	V_{oc}	J_{sc}	FF	PCE
[v/v, %]	[V]	[mA/cm ²]	[%]	[%]
0	0.79	6.61	32.9	1.72 (1.56) ^b
1	0.75	13.70	57.4	5.86 (5.66)
2	0.73	14.53	56.5	6.00 (5.89)
3	0.73	14.34	55.9	5.81 (5.68)
4	0.73	14.18	54.4	5.61 (5.45)
5	0.73	13.84	55.3	5.58 (5.42)

^aD/A ratio: 1:1 (w/w); blend solution: 18 mg/mL in CB; spin coating: 1000 rpm for 60 s.

^bData in parentheses stand for the average PCEs for 10 cells.

8. AFM

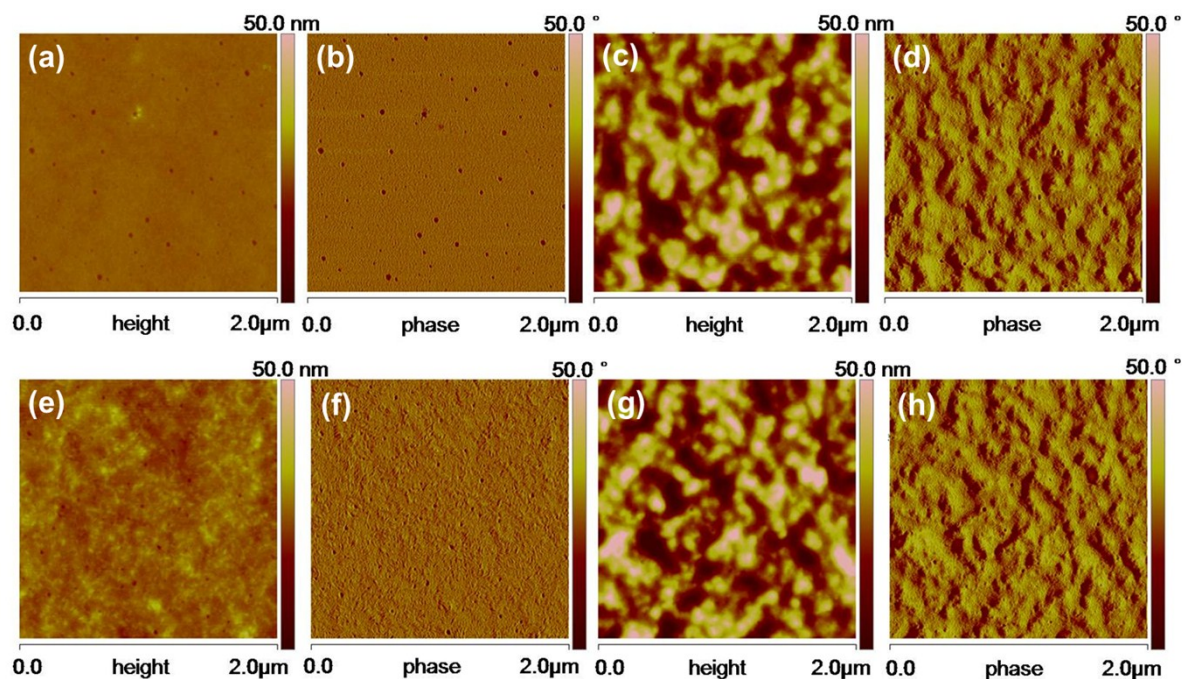


Fig. S7 AFM height and phase images for PThBDTD:PC₇₁BM blend films without (a, b) and with 2 vol% DIO (c, d); PTTBDTD:PC₇₁BM blend films without (e, f) and with 2 vol% DIO (g, h).

References

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