

Supporting Information

A pentacyclic building block containing azepine-2,7-dione moiety 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) was 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 by using a NETZSCH TG209 F3 thermal analyzer under nitrogen. Cyclic voltammetry was done by using 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 by 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., Solarmer Materials Inc. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. Ethyl thieno[3,2-*b*]thiophene-3-carboxylate (**1**), T₃PMgCl·LiCl,¹ and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane)² were prepared according to literatures.

Ethyl 2-(tributylstannyl)thieno[3,2-*b*]thiophene-3-carboxylate (2). To a solution of compound **1** (1.06 g, 5 mmol) in dry THF (20 mL) was added THF solution of T₃PMgCl·LiCl (6.8 mL, 1.1 M) dropwise under N₂ at -20 °C. The mixture was

stirred at -20 °C for 2 h. Then tributylchlorostannane (2.2 mL, 7.5 mmol) was added to the mixture. The solution was allowed to warm to room temperature and stirred overnight. After that, the mixture was poured into water and extracted with petroleum ether twice. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (Al₂O₃) using petroleum ether/CH₂Cl₂ (3:1) as eluent to give compound **2** (1.5 g, 60%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.40 (d, *J* = 5.3 Hz, 1H), 7.22 (d, *J* = 5.3 Hz, 1H), 4.42 (q, *J* = 7.12 Hz, 2H), 1.55 (m, 6H), 1.45 (t, *J* = 7.11 Hz, 3H), 1.32 (m, 6H), 1.20 (m, 6H), 0.88 (t, *J* = 7.31 Hz, 9H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 163.26, 155.13, 144.91, 141.34, 130.81, 128.64, 118.75, 61.03, 29.00, 27.23, 14.42, 13.63, 11.64.

Ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate (3). To a solution of compound **1** (636 mg, 3 mmol) in dry THF (13 mL) was added THF solution of TMPMgCl·LiCl (4.1 mL, 1.1 M) dropwise under N₂ at -20 °C. The mixture was stirred at -20 °C for 2 h. Then 1,2-dibromo-1,1,2,2-tetrachloroethane (1.47 g, 4.5 mmol) was added to the mixture in one portion, and the mixture was stirred at -20 °C for 2 h further. The mixture was poured into water and extracted with petroleum ether twice. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (3:1) as eluent to give compound **3** (648 mg, 74%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.50 (d, *J* = 5.3 Hz, 1H), 7.18 (d, *J* = 5.3 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 161.07, 138.25, 136.44, 128.59, 123.96, 121.37, 118.52, 61.43, 14.25.

Diethyl [2,2'-bithieno[3,2-b]thiophene]-3,3'-dicarboxylate (4). To a solution of compound **2** (1.75 g, 3.5 mmol) and compound **3** (846 mg, 2.9 mmol) in fresh distilled toluene (100 mL) in a two-necked flask were added Pd(PPh₃)₄ (400 mg) and CuI (330 mg) in sequence under N₂. The mixture was heated to reflux and stirred overnight. Then it was poured into water and extracted with toluene twice. The

organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (2:1) as eluent to give compound **4** (1.21 g, 99%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.51 (d, *J* = 5.3 Hz, 2H), 7.28 (d, *J* = 5.3 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 4H), 1.17 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 161.68, 141.46, 139.96, 137.54, 129.58, 124.44, 118.75, 60.99, 13.87.

[2,2'-Bithieno[3,2-b]thiophene]-3,3'-dicarboxylic acid (5). A mixture of compound **4** (500 mg, 1.2 mmol) and sodium hydroxide (400 mg, 10 mmol) in ethanol/THF/water (20 mL/20 mL/5 mL) was refluxed overnight. The solvent was removed under vacuum to ~1/4 of its original volume. 50 mL water was added to the solution and the resulting mixture was treated with dilute HCl. The precipitate was filtered and washed with water to give compound **5** (424 mg, 98%). ¹H NMR (*d*₆-DMSO, 400 MHz, δ/ppm): 13.18 (br, 2H), 7.82 (d, *J* = 5.3 Hz, 2H), 7.51 (d, *J* = 5.3 Hz, 2H). ¹³C NMR (*d*₆-DMSO, 100 MHz, δ/ppm): 162.76, 140.63, 139.76, 137.13, 130.54, 125.00, 119.79.

Thieno[2',3':4,5]thieno[3,2-c]thieno[2',3':4,5]thieno[2,3-e]oxepine-4,6-dione (6). Compound **5** (400 mg, 1.1 mmol) was added to acetic anhydride (10 mL) under N₂. The mixture was heated to reflux for 24 h. Then it was cooled to room temperature and filtered to afford compound **6** (372 mg, 98%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.67 (d, *J* = 5.2 Hz, 2H), 7.32 (d, *J* = 5.2 Hz, 2H). Note: ¹³C NMR spectrum cannot be obtained because of its poor solubility.

5-(2-Octyldodecyl)-4H-thieno[2',3':4,5]thieno[3,2-c]thieno[2',3':4,5]thieno[2,3-e]azepine-4,6(5H)-dione (TTA). To a solution of compound **6** (480 mg, 1.4 mmol) in dry CH₂Cl₂ (20 mL) was added 2-octyldodecan-1-amine (416 mg, 1.4 mmol) in dry CH₂Cl₂ (20 mL) dropwise at room temperature. The mixture was warmed to reflux for 2 h. Then the solvent was removed under reduced pressure. Through a flash column chromatography, the crude product was collected and used as the starting material for

next step. The crude product was dissolved in THF (20 mL). To this solution was added concentrated H₂SO₄ (2 mL). The mixture was heated to reflux and stirred overnight. After that, it was poured into water and extracted with CH₂Cl₂ twice. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (3:1) as eluent to give TTA (571 mg, 65%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.61 (d, *J* = 5.4 Hz, 2H), 7.28 (d, *J* = 5.3 Hz, 2H), 4.42 (d, *J* = 7.4 Hz, 2H), 2.05 (m, 1H), 1.44-1.11 (m, 32H), 0.86 (dt, *J* = 8.5, 7.0 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 160.58, 143.17, 139.99, 134.19, 132.21, 125.14, 118.41, 49.26, 36.01, 31.91, 31.88, 31.48, 30.09, 29.64, 29.61, 29.56, 29.33, 29.30, 26.33, 22.68, 22.65, 14.11.

2,8-Dibromo-5-(2-octyldodecyl)-4H-thieno[2',3':4,5]thieno[3,2-c]thieno[2',3':4,5]thieno[2,3-e]azepine-4,6(5H)-dione (TTA-Br). To a solution of TTA (500 mg, 0.8 mmol) in a mixed solvent of CHCl₃ (15 mL) and DMF (5 mL) was added NBS (299 mg, 1.7 mmol) under N₂. The mixture was stirred at room temperature overnight. Then it was poured into water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether/CH₂Cl₂ (3:1) as eluent to give TTA-Br (576 mg, 92%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.24 (s, 2H), 4.35 (d, *J* = 7.3 Hz, 2H), 1.99 (m, 1H), 1.44-1.12 (m, 32H), 0.87 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 160.05, 143.24, 138.21, 132.85, 124.93, 120.86, 119.95, 49.22, 36.07, 31.93, 31.90, 31.48, 30.11, 29.69, 29.64, 29.59, 29.36, 26.28, 22.69, 22.68, 22.65, 14.13. MALDI-TOF MS (*m/z*): 785.8 (M⁺).

PTTABT. TTA-Br (78.6 mg, 0.1 mmol) and (4,4'-ditetradecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (88.5 mg, 0.1 mmol) were dissolved in 20 mL toluene, and the solution was flushed with argon for 15 min, then 7 mg Pd(PPh₃)₄ was added into the solution. The mixture was flushed with argon again for 20 min. The reaction solution was heated to reflux for 120 h. Then the solution was cooled to room

temperature and added to 150 mL methanol dropwise. 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 into methanol dropwise. Subsequently, the precipitate was collected and dried under vacuum overnight to give PTTABT as a black solid (92 mg, 77%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.67-5.64 (br, 4H), 4.44 (br, 2H), 2.56-0.55 (br, 97H). Elemental analysis (%) calcd for C₇₀H₁₀₃NO₂S₆: C, 71.07; H, 8.78; N, 1.18. Found: C, 69.93; H, 8.53; N, 1.49.

PTTABDT. TTA-Br (78.6 mg, 0.1 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (90.5 mg, 0.1 mmol) were dissolved in 20 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 with argon again for 20 min. The reaction solution was heated to reflux for 24 h. Then the solution was cooled to room temperature and added to 150 mL methanol dropwise. 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 into methanol dropwise. Subsequently, the precipitate was collected and dried under vacuum overnight to give PTTABDT as a black solid (56 mg, 46%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.66-5.83 (br, 8H), 2.96 (br, 2H), 1.94-0.58 (br, 73H). Elemental analysis (%) calcd for C₆₈H₈₃NO₂S₈: C, 67.90; H, 6.96; N, 1.16. Found: C, 67.67; H, 6.99; N, 1.30.

3. NMR

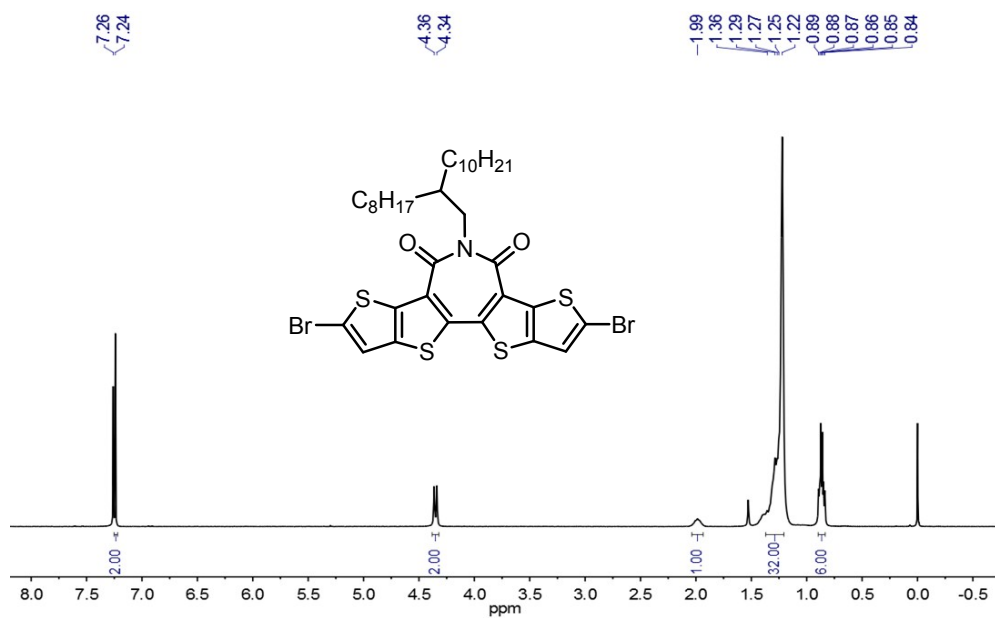


Fig. S1 ¹H NMR spectrum of TTA-Br.

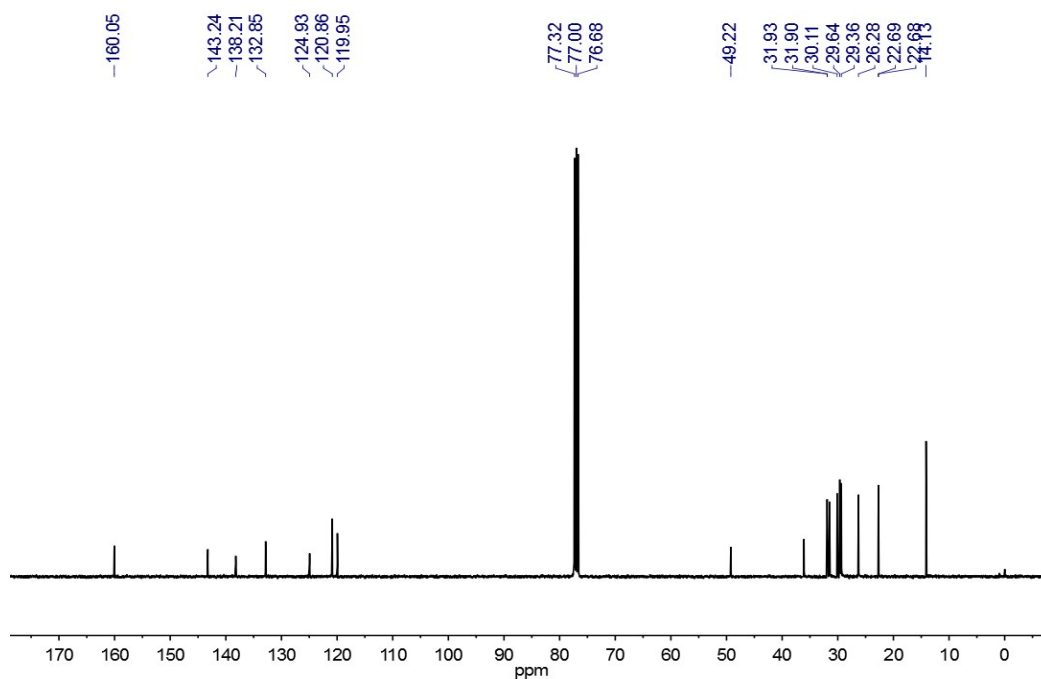


Fig. S2 ¹³C NMR spectrum of TTA-Br.

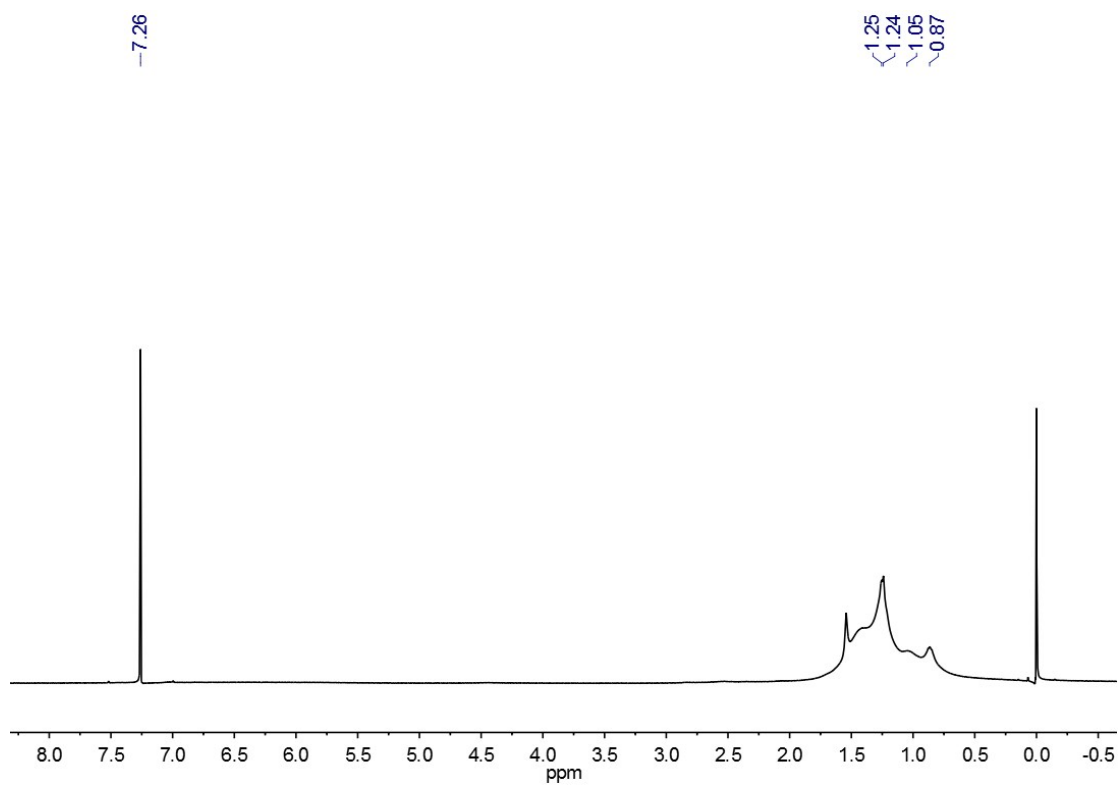


Fig. S3 ^1H NMR spectrum of PTTABT.

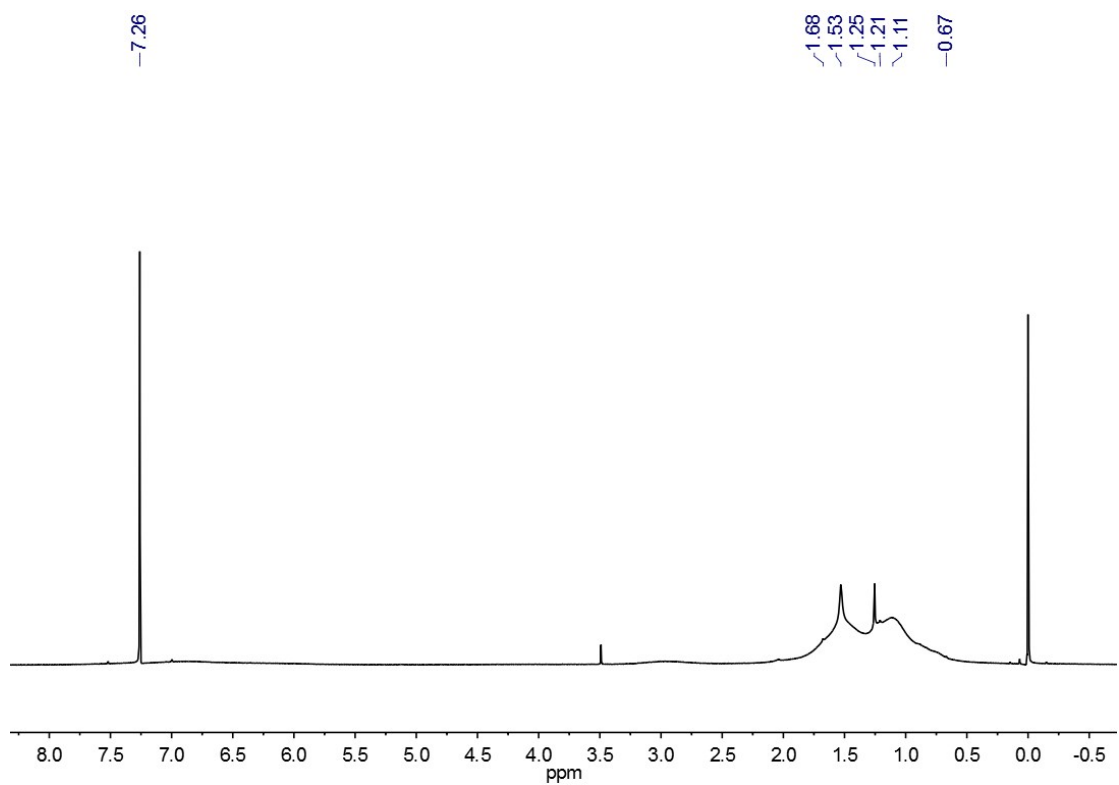


Fig. S4 ^1H NMR spectrum of PTTABDT.

4. TGA

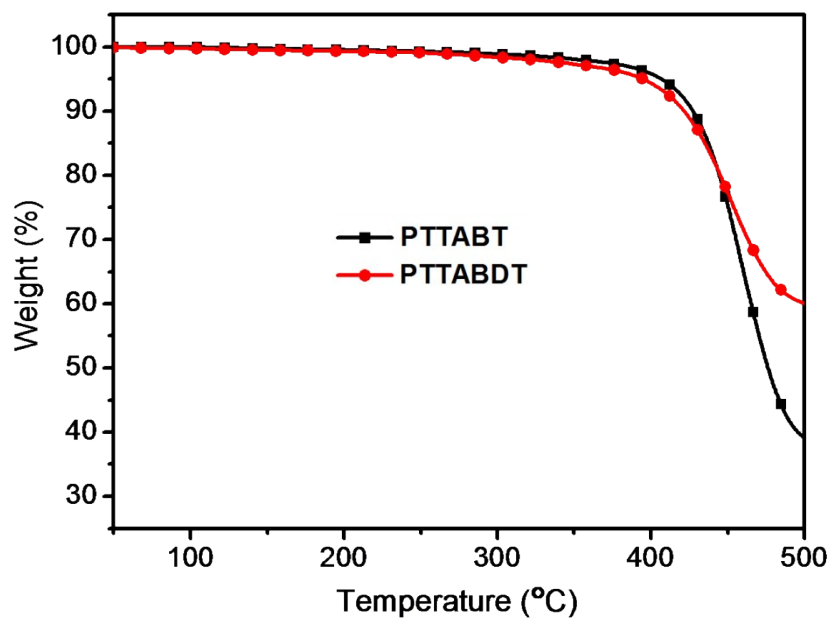


Fig. S5 TGA curves for PTTABT and PTTABDT.

Table S1 GPC and TGA data.

Polymer	M_n [kDa] ^a	M_w [kDa] ^a	PDI ^a	T_d [°C] ^b
PTTABT	54.0	106.6	1.97	407
PTTABDT	61.7	113.6	1.84	395

^a Number-average molecular weight (M_n), weight-average molecular weight (M_w) and PDI were determined by GPC with THF as eluent.

^b 5% weight loss under N₂.

5. CV

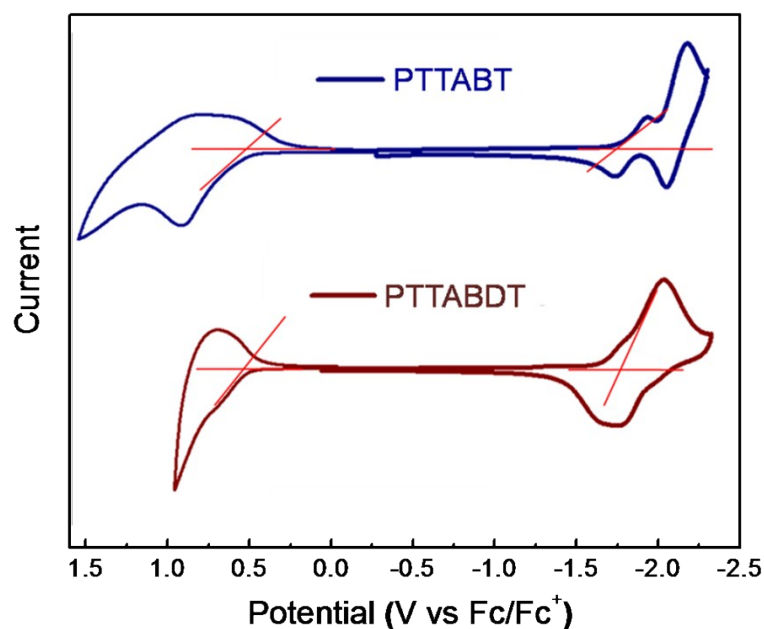


Fig. S6 Cyclic voltammograms for PTTABT and PTTABDT.

6. Device fabrication and measurements

Conventional solar cells

Patterned ITO glass with a sheet resistance of $15 \Omega \text{ sq}^{-1}$ was ultrasonically cleaned by 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 AI 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 $150 \text{ }^\circ\text{C}$ 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 mm^2 . 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 solar simulator was determined by using a monocrystalline silicon solar cell (S10-12008, 2 × 2 cm²) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured using a QE-R3011 measurement system (Enli Tech).

Inverted solar cells

ZnO precursor was prepared according to literature.³ 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 ~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 1 vol% DIO additive was spin-coated onto PEDOT layer. Finally, MoO₃ (~6 nm) and Al (~100 nm) was 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 S2 Optimization of D/A ratio for PTTABT:PC₇₁BM conventional solar cells.^a

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:0.6	0.72	5.61	45.5	1.84 (1.71) ^b
1:0.8	0.72	7.09	47.8	2.44 (2.34)
1:1	0.73	7.88	44.2	2.54 (2.45)
1:1.2	0.72	8.42	47.1	2.84 (2.63)
1:1.4	0.71	7.54	46.3	2.48 (2.39)

^a Blend solution: 20 mg/mL in CB with 3 vol% DIO; spin-coating: 1200 rpm for 60 s.

^b Data in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of the active layer thickness for PTTABT:PC₇₁BM conventional solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
93	0.72	7.34	49.8	2.63 (2.45) ^b
100	0.72	7.81	48.7	2.75 (2.63)
109	0.71	8.72	47.0	2.90 (2.85)
120	0.73	8.86	44.2	2.87 (2.82)
133	0.72	8.76	42.2	2.67 (2.60)

^a D/A ratio: 1:1.2 (w/w); blend solution: 20 mg/mL in CB with 3 vol% DIO. ^b Data in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of DIO content for PTTABT:PC₇₁BM conventional solar cells.^a

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.72	4.98	59.0	2.13 (2.00) ^b
1	0.72	8.81	56.3	3.59 (3.33)
2	0.71	8.26	51.8	3.04 (2.94)
3	0.72	8.64	48.0	3.00 (2.88)
4	0.73	8.04	49.5	2.89 (2.72)

^a D/A ratio: 1:1.2 (w/w); blend solution: 20 mg/mL in CB; spin-coating: 1500 rpm for 45 s. ^b Data in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of the active layer thickness for PTTABT:PC₇₁BM inverted solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
81	0.70	9.18	67.1	4.28 (4.11) ^b
90	0.69	10.06	63.0	4.38 (4.23)
98	0.69	10.19	65.8	4.65 (4.46)
112	0.69	10.23	64.0	4.54 (4.39)
123	0.69	9.88	64.9	4.46 (4.22)

^a D/A ratio: 1:1.2 (w/w); blend solution: 20 mg/mL in CB with 1 vol% DIO. ^b Data in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of D/A ratio for PTTABDT:PC₇₁BM inverted solar cells.^a

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
1:1.2	0.79	11.02	48.2	4.19 (3.98) ^b
1:1.4	0.78	10.97	49.7	4.26 (4.06)
1:1.5	0.78	11.76	52.2	4.80 (4.67)
1:1.6	0.78	11.06	53.6	4.62 (4.56)
1:1.8	0.77	11.21	52.5	4.55 (4.41)

^a Blend solution: 14 mg/mL in CB with 2 vol% DIO; spin-coating: 1400 rpm for 60 s.

^b Data in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of the active layer thickness for PTTABDT:PC₇₁BM inverted solar cells.^a

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
85	0.78	10.88	57.4	4.86 (4.69) ^b
90	0.78	11.28	55.8	4.92 (4.78)
101	0.78	12.11	51.2	4.84 (4.70)
112	0.78	12.39	45.5	4.41 (4.34)

^a D/A ratio: 1:1.5 (w/w); blend solution: 14 mg/mL in CB with 2 vol% DIO. ^b Data in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of DIO content for PTTABDT:PC₇₁BM inverted solar cells.^a

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.80	8.56	51.8	3.54 (2.98) ^b
1	0.79	10.52	65.4	5.46 (5.28)
2	0.78	12.00	54.0	5.05 (4.86)
3	0.78	11.37	54.6	4.84 (4.69)
4	0.78	11.22	53.9	4.74 (4.61)

^a D/A ratio: 1:1.5 (w/w); blend solution: 14 mg/mL in CB; spin-coating: 1600 rpm for 45 s. ^b Data in parentheses stand for the average PCEs for 10 cells.

8. 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), 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, $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference. The mobility was calculated from the slope of $J^{1/2}$ - V plots.

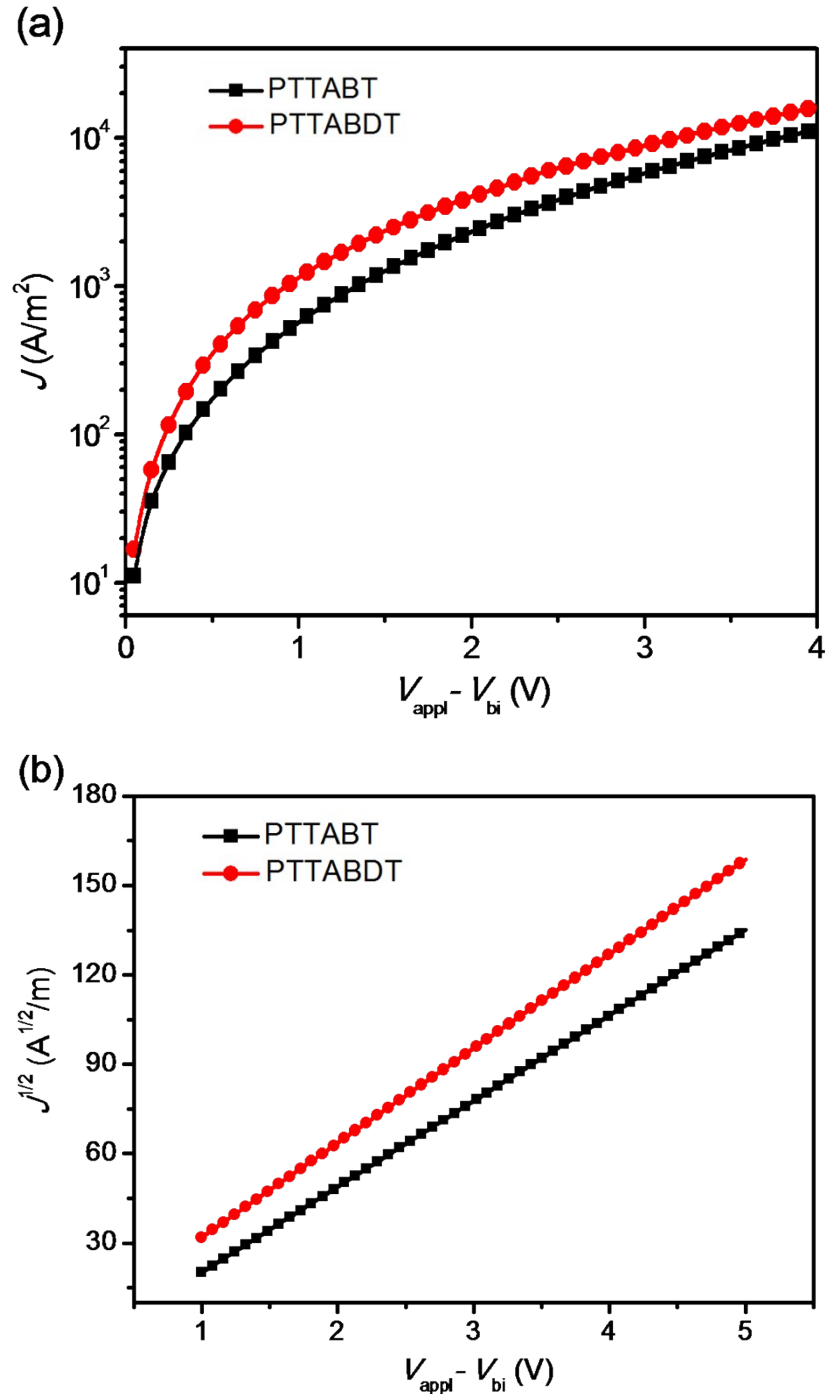


Fig. S7 J - V curves (a) and the corresponding $J^{1/2}$ - V plots (b) for the hole-only devices (in dark). The thicknesses for PTTABT:PC₇₁BM blend film and PTTABDT:PC₇₁BM blend film are 101 nm and 104 nm, respectively.

9. XRD

Table S9 XRD data.

Polymer	$2\theta_{(100)}$ [°]	d_{100} [Å]	$2\theta_{(010)}$ [°]	d_{010} [Å]
PTTABT	—	—	24.5	3.63
PTTABDT	4.58	19.3	24.1	3.69

References

- [1] T. Kunz and P. Knochel, *Chem. Eur. J.*, 2011, **17**, 866.
- [2] L. Huo, J. Hou, S. Zhang, H.-Y. Chen and Y. Yang, *Angew. Chem. Int. Ed.*, 2010, **49**, 1500.
- [3] Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679.