

Supporting Information

A pentacyclic aromatic lactam building block for efficient polymer solar cells

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1. General characterization

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co., Aldrich Chemical Co. and other commercial suppliers. ^1H and ^{13}C NMR spectra were measured with a Bruker Avance-400 spectrometer. NOE spectra were measured with a Bruker Avance-600 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 series GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was measured by a TA SDT-Q600 thermal analyzer. Cyclic voltammetry was conducted on a Shanghai Chenhua CHI620 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 on the surface of glassy-carbon electrode and all potentials were corrected against Fc/Fc^+ . X-ray diffraction (XRD) of thin films was performed in the reflection mode using $\text{Cu K}\alpha$ radiation (40 kV, 200 mA) on a 2 kW Rigaku D/max-2500 X-ray diffractometer. AFM was performed on a Multimode 8 microscope (Veeco). TEM was performed on a FEI Tecnai G2 F20 electron microscope operated at 200 kV.

2. 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)-polystyrene sulfonic acid (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 PThTPTI/PC₇₁BM blend (18 mg/mL) in a mixed solvent $\text{PhCl}:\text{CHCl}_3$ (v/v, 4/1) with 3 vol% DIO was spin-coated onto

PEDOT:PSS layer (800 rpm for 60 s). The thicknesses of the active layers (180 nm) 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 with a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport, Oriel 91159A Mode, 150 W, with AM 1.5G filter, 100 mW/cm^2). The illumination intensity of solar simulator was determined using a monocrystalline silicon solar cell (Oriel 91150 Mode, $2 \times 2 \text{ cm}$) calibrated by National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Technology, Inc.).

Inverted solar cells

ZnO precursor was prepared according to literature.^[1] ZnO precursor solution was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at $200 \text{ }^\circ\text{C}$ for 30 min in air. ZnO film thickness is about 30 nm. A PThTPTI/PC₇₁BM blend (18 mg/mL) in a mixed solvent PhCl:CHCl₃ (v/v, 4/1) with 3 vol% DIO was spin-coated onto ZnO layer (800 rpm for 60 s). 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 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 PThTPTI/PC₇₁BM blend (18 mg/mL) in a mixed solvent PhCl:CHCl₃ (v/v, 4/1) with 3 vol% DIO was spin-coated onto PEDOT:PSS layer (800 rpm for 60 s). 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 with a computerized Keithley 2420 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was firstly evaporated onto a glass substrate. A PThTPTI/PC₇₁BM blend (18 mg/mL) in a mixed solvent PhCl:CHCl₃ (v/v, 4/1) with 3 vol% DIO was spin-coated onto Al (800 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 using a computerized Keithley 2420 SourceMeter in the dark.

3. Synthetic procedures

All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. N-(2-hexyldecyl)thiophen-3-amine (**1**)² and 2,5-bis(trimethylstannyl)thiophene³ were synthesized according to the literature methods.

2,5-Dibromo-N¹,N⁴-bis(2-hexyldecyl)-N¹,N⁴-di(thiophen-3-yl)terephthalamide (2).

To a solution of 2,5-dibromoterephthalic acid (2.33 g, 7.2 mmol) in dry CH₂Cl₂ (50 mL) were added oxalyl chloride (4 mL, 45.6 mmol) and 3 drops of DMF. The mixture was stirred at room temperature overnight. The solvent was removed under vacuum to obtain 2,5-dibromoterephthaloyl dichloride, which was used in next step without purification. To the solution of 2,5-dibromoterephthaloyl dichloride in dry CH₂Cl₂ (20 mL) was slowly added a solution of compound **1** (4.7 g, 14.5 mmol) and Et₃N (2 mL) in dry CH₂Cl₂ (30 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with CHCl₃ three times. The organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified through a silica gel column with CH₂Cl₂ to give compound **2** as a yellow oil (4.85 g, 72%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.13 (dd, *J* = 5.1, 3.2 Hz, 2H), 7.09 (s, 2H), 6.85 (br, 2H), 6.76 (dd, *J* = 5.1, 1.2 Hz, 2H), 3.75 (br, 4H), 1.57-1.52 (m, 2H), 1.29-1.24 (m, 48H), 0.90-0.85 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 166.65, 140.32, 139.62, 131.92, 125.67, 125.38, 120.73, 117.91, 52.25, 36.13, 31.88,

31.80, 31.14, 29.99, 29.65, 29.54, 29.29, 26.24, 26.20, 22.66, 22.63, 14.10, 14.08.

4,10-Bis(2-hexyldecyl)thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4H,10H)-dione (TPTI). To a solution of compound **2** (0.61 g, 0.7 mmol) in N,N-dimethylacetamide (25 mL) were added PCy₃·HBF₄ (264 mg, 0.72 mmol), Cs₂CO₃ (2.82 g, 8.7 mmol) and Pd(OAc)₂ (100 mg, 0.45 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 CHCl₃ three times. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified through a silica gel column with petroleum ether/CH₂Cl₂ (1:1) as eluent to give **TPTI** as a yellow solid (309 mg, 57%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.89 (s, 2H), 7.49 (d, *J* = 5.2 Hz, 2H), 7.10 (d, *J* = 5.2 Hz, 2H), 4.24 (br, 4H), 2.04 (br, 2H), 1.38-1.22 (m, 48H), 0.84 (t, *J* = 6.6 Hz, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 161.59, 139.45, 130.00, 126.82, 126.10, 123.62, 117.94, 117.73, 49.71, 37.12, 31.84, 31.77, 31.69, 31.65, 29.94, 29.64, 29.49, 29.24, 26.64, 22.62, 22.59, 14.06, 14.04.

2,8-Dibromo-4,10-bis(2-hexyldecyl)thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4H,10H)-dione (TPTI-Br). To a solution of **TPTI** (288 mg, 0.37 mmol) in a mixed solvent of CHCl₃ (15 mL) and DMF (10 mL) was added NBS (136 mg, 0.76 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/CH₂Cl₂ (2:1) as eluent to give **TPTI-Br** as a yellow solid (316 mg, 91%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.70 (s, 2H), 7.07 (s, 2H), 4.15 (br, 4H), 1.99 (br, 2H), 1.36-1.23 (m, 48H), 0.85 (t, *J* = 6.8 Hz, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 161.04, 138.83, 129.29, 126.81, 123.31, 120.86, 118.78, 115.11, 49.73, 36.99, 31.85, 31.78, 31.55, 31.50, 29.94, 29.63, 29.50, 29.26, 26.53, 22.63, 22.61, 14.07, 14.06. TOF-MS ES+(*m/e*): 931.9 (M⁺, 100%).

Poly{2,5-thiophene-alt-2,8-(4,10-bis(2-hexyldecyl))thieno[2',3':5,6]pyrido[3,4-g]thie

no[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione} (PThTPTI). TPTI-Br (120 mg, 0.09 mmol) and 2,5-bis(trimethylstannyl)thiophene (71 mg, 0.09 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 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 **PThTPTI as a purple solid (103 mg, 93%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 8.10 (br, 2H), 6.84-6.30 (br, 4H), 4.89 (br, 4H), 1.56-1.25 (br, 50H), 0.86 (br, 12H). Elemental analysis (%) calcd for C₅₂H₇₂N₂O₂S₃: C, 73.19; H, 8.50; N, 3.28. Found: C, 72.82; H, 8.48; N, 3.36.**

4. NMR spectra

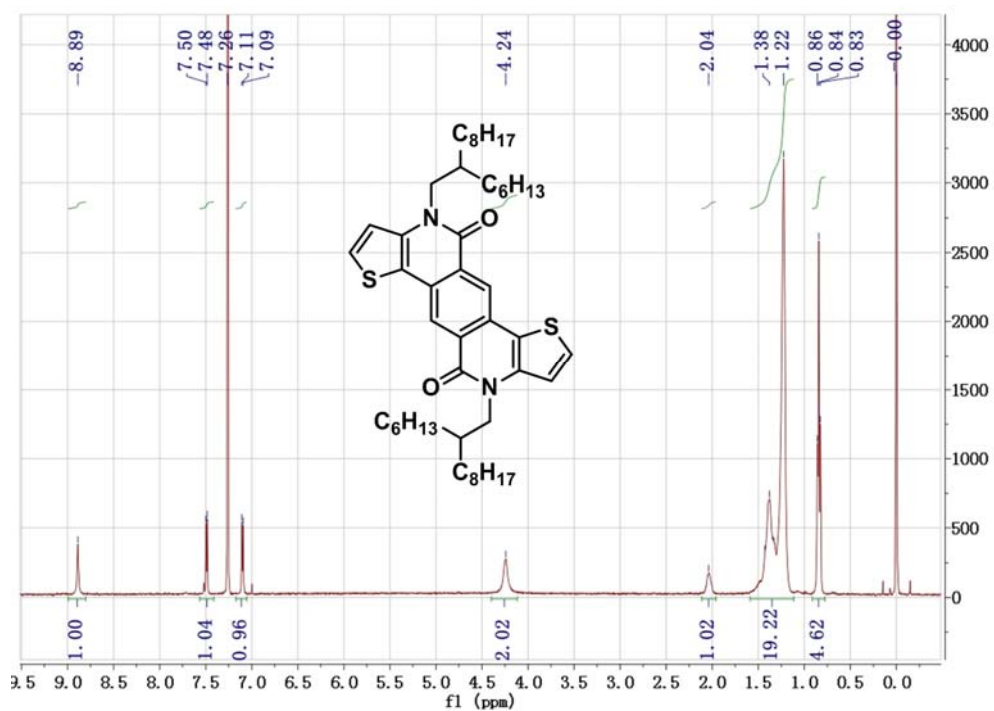


Figure S1 ¹H NMR spectrum of TPTI.

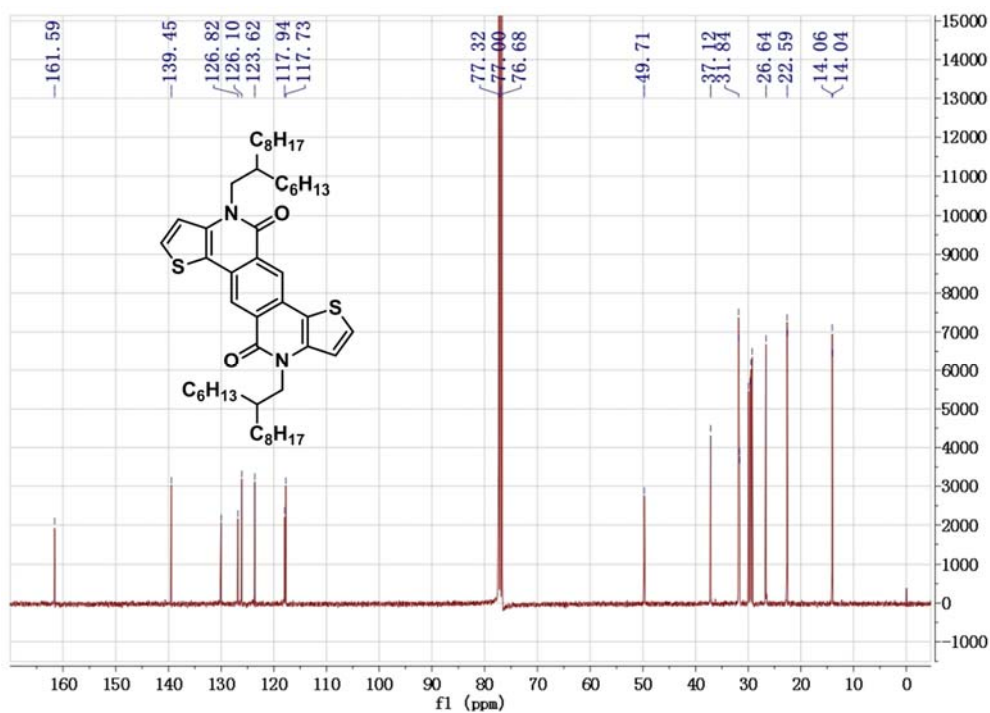


Figure S2 ¹³C NMR spectrum of TPTI.

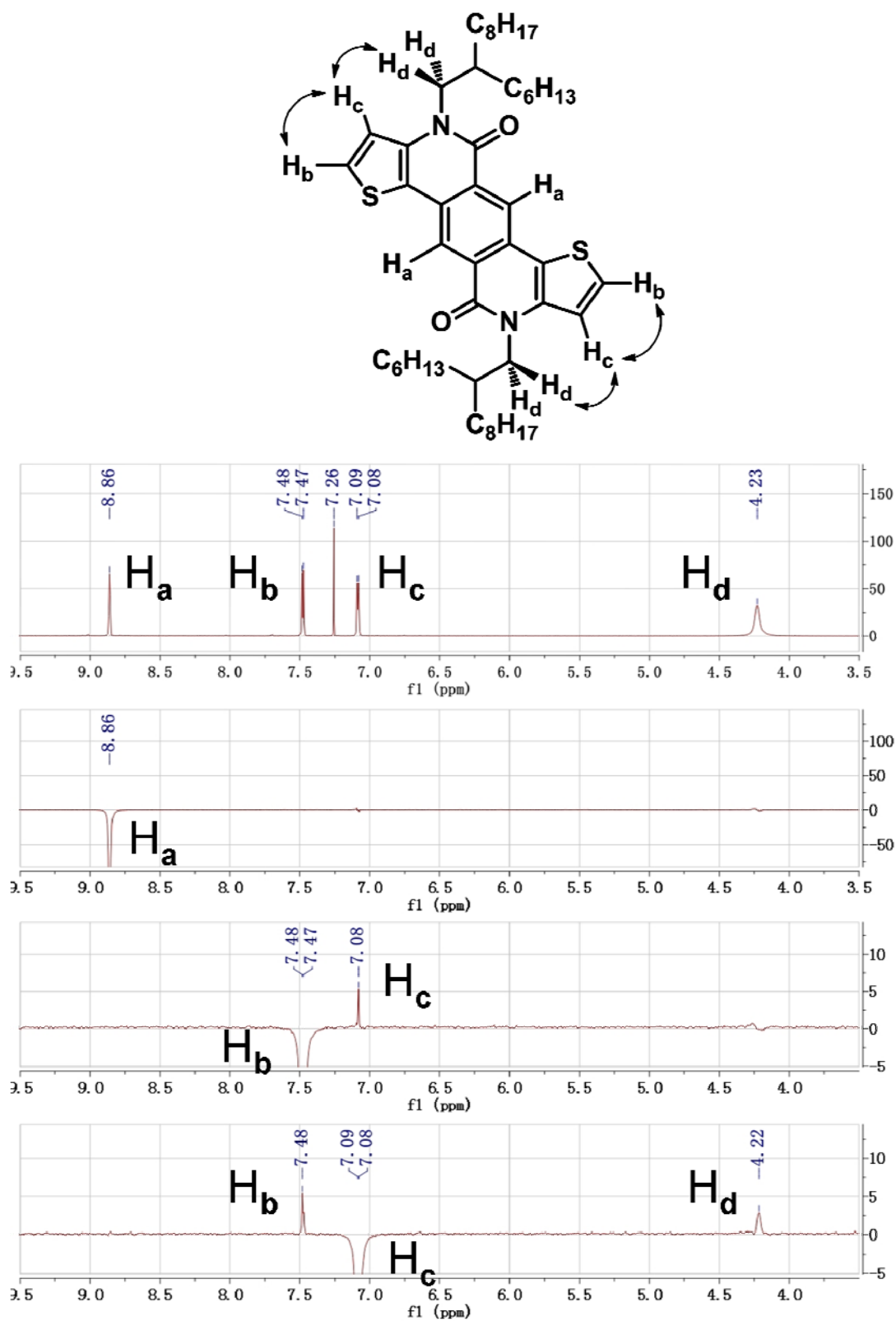


Figure S3 NOE spectra of TPTI.

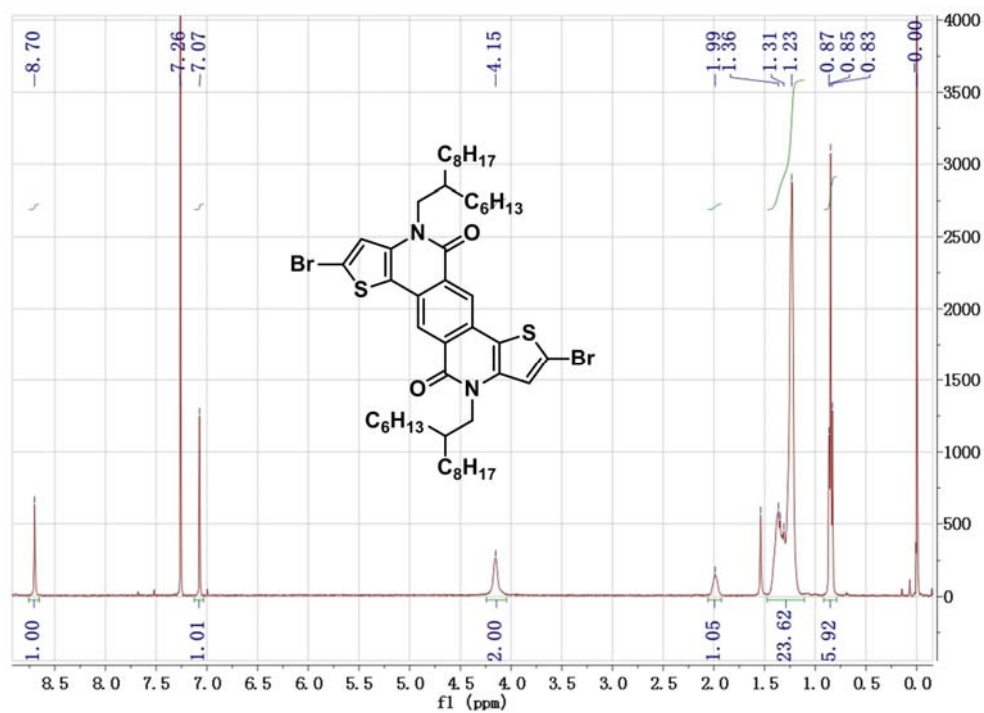


Figure S4 ¹H NMR spectrum of TPTI-Br.

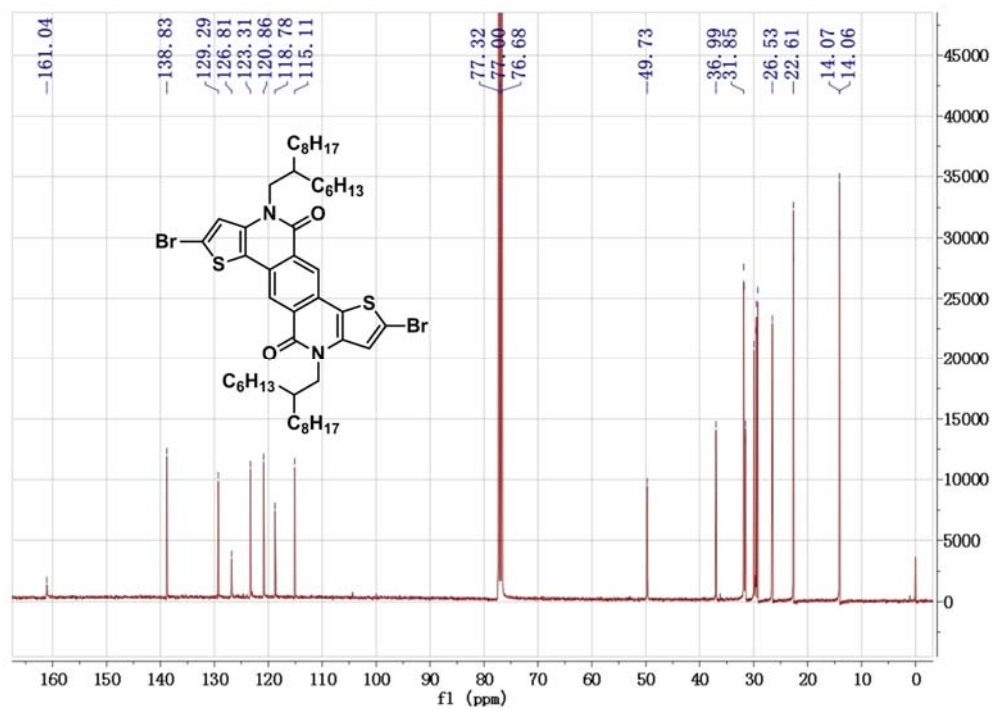


Figure S5 ¹³C NMR spectrum of TPTI-Br.

5. TGA for PThTPTI

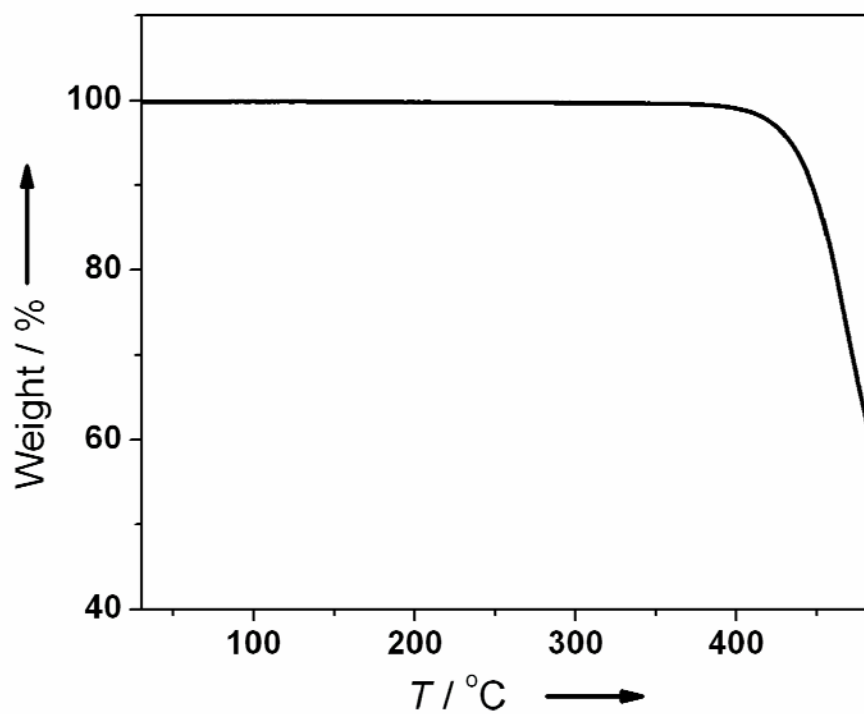


Figure S6 TGA curve of PThTPTI.

6. CV measurement for PThTPTI

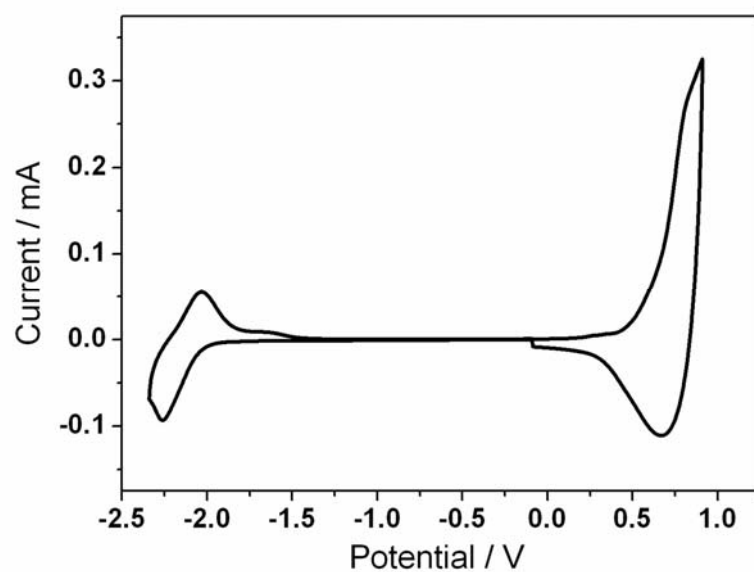


Figure S7 Cyclic voltammogram of PThTPTI.

7. Device optimization

Table S1 Optimization of the D-A ratio for PThTPTI:PC₇₁BM cells.

D:A ratio	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.8	0.91	11.91	60.1	6.54
1:0.9	0.92	12.62	58.6	6.77
1:1.0	0.92	12.47	62.8	7.21
1:1.1	0.92	11.93	65.5	7.20
1:1.2	0.90	11.81	62.0	6.56

Table S2 Optimization of the active layer thickness for PThTPTI:PC₇₁BM cells.

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
145	0.91	10.23	63.9	5.97
162	0.91	10.58	64.5	6.24
180	0.92	11.79	65.5	7.10
193	0.90	12.33	57.0	6.33
238	0.91	12.13	55.8	6.17

Table S3 Optimization of the additive content for PThTPTI:PC₇₁BM cells.

DIO	V_{oc}	J_{sc}	FF	PCE
[v/v, %]	[V]	[mA/cm ²]	[%]	[%]
0	0.93	2.11	55.4	1.09
1	0.90	11.29	63.0	6.40
2	0.92	11.95	62.2	6.86
3	0.92	12.55	61.9	7.15
4	0.93	11.84	62.7	6.87
5	0.92	11.78	62.6	6.69
3 ^a	0.91	12.45	60.1	6.80
3 ^b	0.89	11.81	60.4	6.32

^a Annealed at 110 °C; ^b annealed at 150 °C.

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) 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, $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode workfunction difference. Figures S8 and S9 show J - V curves for the hole-only devices and the electron-only devices, respectively. The mobility was calculated from the slope of $J^{1/2}$ - V curves.

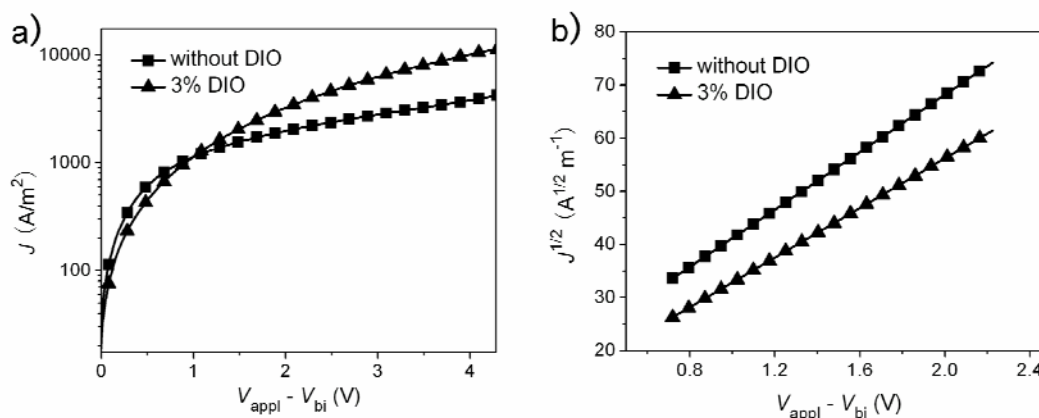


Figure S8 J - V curves (a) and the corresponding $J^{1/2}$ - V curves (b) for hole-only devices based on PThTPTI:PC₇₁BM blend film without or with 3% DIO (in dark). The thicknesses for the blend films are 179 and 180 nm, respectively.

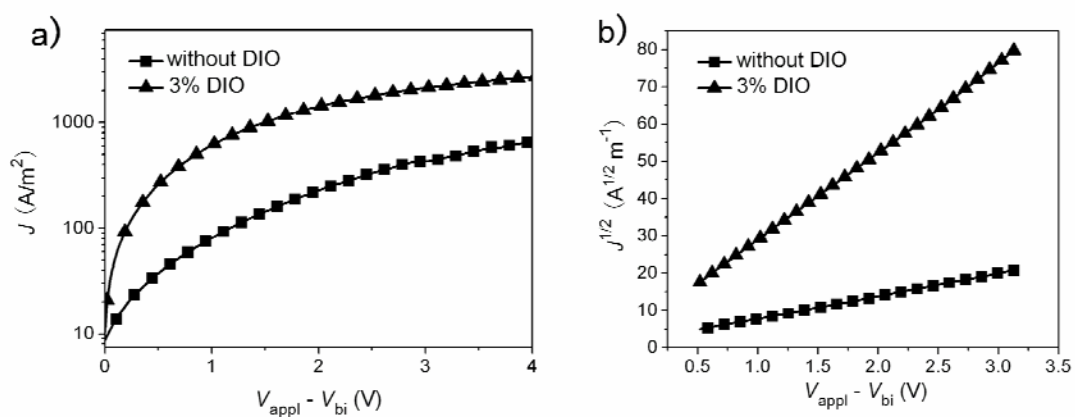


Figure S9 J - V curves (a) and the corresponding $J^{1/2}$ - V curves (b) for electron-only devices based on PThTPTI:PC₇₁BM blend film without or with 3% DIO (in dark). The thicknesses for the blend films are 175 and 195 nm, respectively.

PThTPTI:PC ₇₁ BM	μ_h (cm ² V ⁻¹ s ⁻¹)	μ_e (cm ² V ⁻¹ s ⁻¹)
Without DIO	1.40×10^{-3}	7.10×10^{-5}
3% DIO	1.07×10^{-3}	7.88×10^{-4}

9. XRD measurement for as-cast PThTPTI film

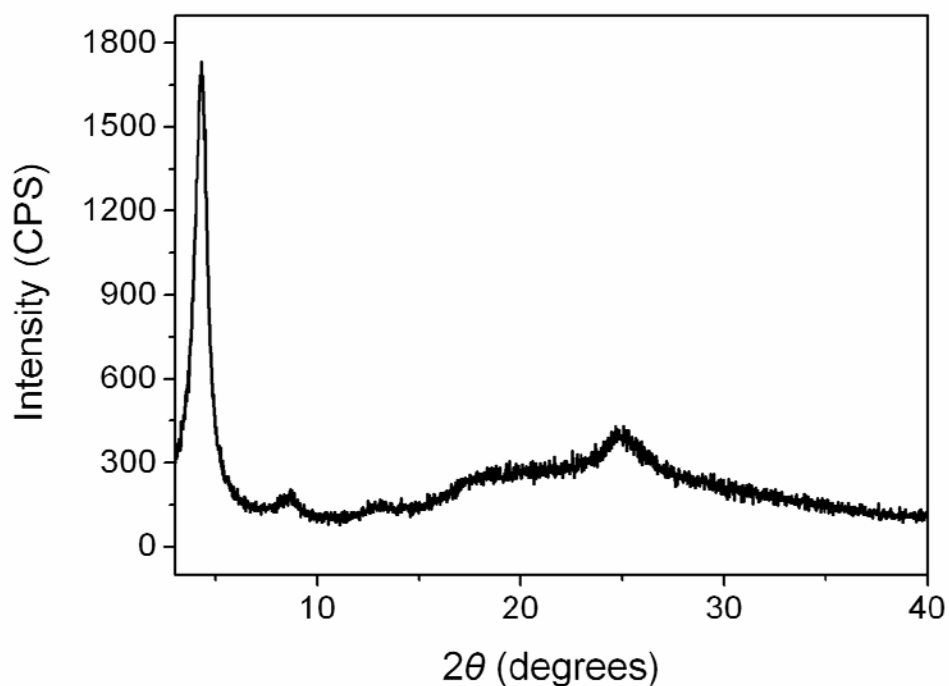


Figure S10 XRD pattern for PThTPTI film on glass substrate.

References

- [1] Y. Sun, J. H. Seo, C. J. Takacs, J. Seifert, A. J. Heeger, *Adv. Mater.* 2011, **23**, 1679.
- [2] a) R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus, I. McCulloch, *Chem. Commun.* 2012, **48**, 3939; b) *US Pat.* 20100297405.
- [3] C. van Pham, R. S. Macomber, H. B. Mark, H. Zimmer, *J. Org. Chem.* 1984, **49**, 5250.