Supporting Information

Hexacyclic lactam building blocks for highly efficient polymer solar cells

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1. General characterization

^{1}H and ^{13}C NMR spectra were measured with 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 series GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was measured by 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 was coated on the surface of 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 in the reflection mode using Cu Kα radiation (40 kV, 200 mA) on a 2 kW Rigaku D/max-2500 X-ray diffractometer.

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. Diethyl thieno[3,2-*b*]thiophene-3,6-dicarboxylate (**1**),[1] *N*-(2-octyldodecyl)thiophen-3-amine,[2] *N*-(2-hexyldecyl)thiophen-3-amine,[2] and 2,5-bis(trimethylstannyl)selenophene[3] were prepared according to literatures.

Diethyl 2,5-dibromothieno[3,2-*b*]thiophene-3,6-dicarboxylate (2). Bromine (1.2 mL, 23.4 mmol) was added dropwise to compound **1** (0.97 g, 3.41 mmol) in chloroform (30 mL). The mixture was stirred at room temperature for 6 h and then poured into aq.

Na_2SO_3 solution and extracted with $CHCl_3$. The organic layer was washed with water, and brine. After removal of the solvent, the crude product was purified through a silica gel column with petroleum ether/CH_2Cl_2 (1:2) to give compound **2** as a white solid (1.44 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 4.44 (q, J = 7.1 Hz, 4H), 1.46 (t, J = 7.1 Hz, 6H).

2,5-Dibromothieno[3,2-*b*]thiophene-3,6-dicarboxylic acid (3). A mixture of compound **2** (1.31 g, 3.0 mmol) and sodium hydroxide (1.5 g, 37.5 mmol) in ethanol/THF/water (50 mL/50 mL/5 mL) was refluxed overnight. The solvent was evaporated under vacuum to about half of its original volume. Water (50 mL) was added to the solution, and the resulting mixture was treated with HCl. The precipitate was filtered and washed with water to give compound **3** as a white solid (1.02 g, 89%). ^{13}C NMR (d_6-DMSO, 100 MHz, δ/ppm): 161.54, 135.35, 124.50, 122.44.

2,5-Dibromo-*N*^{3},*N*^{6}-bis(2-octyldodecyl)-*N*^{3},*N*^{6}-di(thiophen-3-yl)thieno[3,2-*b*]thiophene-3,6-dicarboxamide (4a). To a solution of compound **3** (1.0 g, 2.6 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 2,5-dibromothieno[3,2-*b*]thiophene-3,6-dicarbonyl dichloride, which was used in next step without purification. To the solution of 2,5-dibromothieno[3,2-*b*]thiophene-3,6-dicarbonyl dichloride in dry CH_2Cl_2 (30 mL) was slowly added a solution of *N*-(2-octyldodecyl)thiophen-3-amine (4.0 g, 10.5 mmol) and Et_3N (2 mL) in dry CH_2Cl_2 (30 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 **4a** as a light yellow oil (2.58 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.08 (s, 2H), 6.84 (br, 2H), 6.74 (br, 2H), 3.80 (d, J = 5.6 Hz, 4H), 1.60 (br, 2H), 1.30-1.25 (m, 64H), 0.90-0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 163.36, 139.59, 135.57, 130.80, 125.12, 119.21, 114.40, 113.35, 53.26, 36.41, 31.97, 31.95,

31.13, 30.13, 29.72, 29.68, 29.65, 29.60, 29.38, 29.36, 26.44, 22.71, 14.09, 14.08.

2,5-Dibromo-*N*^{3},*N*^{6}-bis(2-hexyldecyl)-*N*^{3},*N*^{6}-di(thiophen-3-yl)thieno[3,2-*b*]thiophene-3,6-dicarboxamide (4b). **4b** was synthesized by following the same procedures for **4a**. Compound **3** (1.05 g, 2.73 mmol) and *N*-(2-hexyldecyl)thiophen-3-amine (2.1 g, 6.48 mmol) were used as start materials. **4b** was obtained as a light yellow oil (1.75 g, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.08 (s, 2H), 6.84 (br, 2H), 6.74 (br, 2H), 3.80 (d, *J* = 5.6 Hz, 4H), 1.60 (br, 2H), 1.30-1.19 (m, 48H), 0.90-0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 163.36, 139.57, 135.55, 130.79, 125.10, 119.21, 114.39, 113.34, 53.23, 36.39, 31.94, 31.85, 31.21, 30.07, 29.71, 29.59, 29.35, 26.43, 26.38, 22.70, 22.68, 14.09, 14.08.

TD1. To a solution of compound **4a** (0.73 g, 0.66 mmol) in N,N-dimethylacetamide (80 mL) were added $PCy_3{\cdot}HBF_4$ (300 mg, 0.82 mmol), Cs_2CO_3 (2.5 g, 7.7 mmol) and $Pd(OAc)_2$ (150 mg, 0.65 mmol) under Ar. The mixture was stirred at 115 °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 (1:1) as eluent to give **TD1** as a yellow solid (262 mg, 42%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.50 (d, *J* = 5.4 Hz, 2H), 7.13 (d, *J* = 5.5 Hz, 2H), 4.29 (br, 4H), 2.07 (br, 2H), 1.39-1.22 (m, 64H), 0.87-0.83 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 157.88, 144.46, 141.17, 133.00, 126.16, 121.34, 117.59, 115.42, 49.46, 37.34, 31.90, 31.86, 31.72, 29.97, 29.60, 29.53, 29.48, 29.30, 29.25, 26.65, 22.65, 22.62, 14.02. MALDI-TOF-MS (m/z): 947.7 (M^+).

TD2. **TD2** was synthesized by following the same procedures for **TD1**. Compound **4b** (0.85 g, 0.85 mmol), $PCy_3{\cdot}HBF_4$ (400 mg, 1.09 mmol), Cs_2CO_3 (3.5 g, 10.8 mmol) and $Pd(OAc)_2$ (200 mg, 0.87 mmol) were used as start materials. **TD2** was obtained as a yellow solid (369 mg, 52%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.50 (d, *J* = 5.4 Hz,

2H), 7.13 (d, *J* = 5.5 Hz, 2H), 4.28 (br, 4H), 2.07 (br, 2H), 1.39-1.22 (m, 48H), 0.86-0.83 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 157.84, 144.40, 141.07, 132.86, 126.25, 121.21, 117.58, 115.39, 49.36, 37.29, 31.85, 31.76, 31.61, 31.56, 29.95, 29.64, 29.48, 29.25, 26.58, 22.63, 22.59, 14.07, 14.04. MALDI-TOF-MS (m/z): 835.6 (M^+).

TD1-Br. To a solution of **TD1** (223 mg, 0.24 mmol) in a mixed solvent of $CHCl_3$ (20 mL) and DMF (10 mL) was added NBS (88 mg, 0.49 mmol) under Ar. The mixture was stirred at room temperature for 24 h and then poured into 100 mL methanol. The precipitate was filtered and purified through a silica gel column with petroleum ether/CH_2Cl_2 (3:2) as eluent to give **TD1-Br** as a yellow solid (230 mg, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.11 (s, 2H), 4.20 (br, 4H), 2.02 (br, 2H), 1.38-1.22 (m, 64H), 0.88-0.83 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 157.29, 143.26, 140.16, 132.80, 121.15, 120.56, 116.22, 115.34, 49.39, 37.18, 31.90, 31.86, 31.43, 29.97, 29.62, 29.61, 29.56, 29.51, 29.33, 29.28, 26.50, 22.67, 22.65, 14.10. MALDI-TOF-MS (m/z): 1106.0 ($M+H^+$).

TD2-Br. TD2-Br was synthesized by following the same procedures for **TD1-Br**. **TD2** (135 mg, 0.16 mmol) and NBS (60 mg, 0.34 mmol) were used as start materials. **TD2-Br** was obtained as a yellow solid (135 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.11 (s, 2H), 4.19 (br, 4H), 2.02 (br, 2H), 1.37-1.23 (m, 48H), 0.87-0.83 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 157.23, 143.27, 140.16, 132.77, 121.10, 120.56, 116.23, 115.35, 49.38, 37.19, 31.86, 31.78, 31.46, 31.41, 29.96, 29.65, 29.50, 29.27, 26.48, 22.65, 22.62, 14.10, 14.07. MALDI-TOF-MS (m/z): 993.5 (M^+).

PThTD1. TD1-Br (100 mg, 0.090 mmol) and 2,5-bis(trimethylstannyl)thiophene (37 mg, 0.090 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 150 mL methanol dropwise. 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 **PThTD1** as a blue-black solid (86 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.52-6.38 (br, 4H), 4.86 (br, 4H), 2.60-0.84 (br, 78H). Elemental analysis (%) calcd for $C_{60}H_{86}N_2O_2S_5$: C, 70.12; H, 8.43; N, 2.73. Found: C, 69.88; H, 8.52; N, 2.75.

PSeTD1. PSeTD1 was synthesized by following the same procedures for **PThTD1**. **TD1-Br** (88 mg, 0.080 mmol) and 2,5-bis(trimethylstannyl)selenophene (36 mg, 0.080 mmol) were used as start materials. **PSeTD1** was obtained as a blue-black solid (83 mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.52-6.46 (br, 4H), 4.83 (br, 4H), 2.45-0.87 (br, 78H). Elemental analysis (%) calcd for $C_{60}H_{86}N_2O_2S_4Se$: C, 67.06; H, 8.07; N, 2.61. Found: C, 66.70; H, 7.96; N, 2.63.

PThTD2. PThTD2 was synthesized by following the same procedures for **PThTD1**. **TD2-Br** (113 mg, 0.114 mmol) and 2,5-bis(trimethylstannyl)thiophene (46 mg, 0.114 mmol) were used as start materials. **PThTD2** was obtained as a blue-black solid (97 mg, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.52-6.31 (br, 4H), 4.82 (br, 4H), 2.52-0.86 (br, 62H). Elemental analysis (%) calcd for $C_{52}H_{70}N_2O_2S_5$: C, 68.22; H, 7.71; N, 3.06. Found: C, 68.10; H, 7.72; N, 3.06.

PSeTD2. PSeTD2 was synthesized by following the same procedures for **PThTD1**. **TD2-Br** (80 mg, 0.081 mmol) and 2,5-bis(trimethylstannyl)selenophene (36 mg, 0.081 mmol) were used as start materials. **PSeTD2** was obtained as a blue-black solid (74 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.52-6.28 (br, 4H), 4.83 (br, 4H), 2.11-0.85 (br, 62H). Elemental analysis (%) calcd for $C_{52}H_{70}N_2O_2S_4Se$: C, 64.90; H, 7.33; N, 2.91. Found: C, 64.74; H, 7.35; N, 3.02.

3. ^{1}H NMR

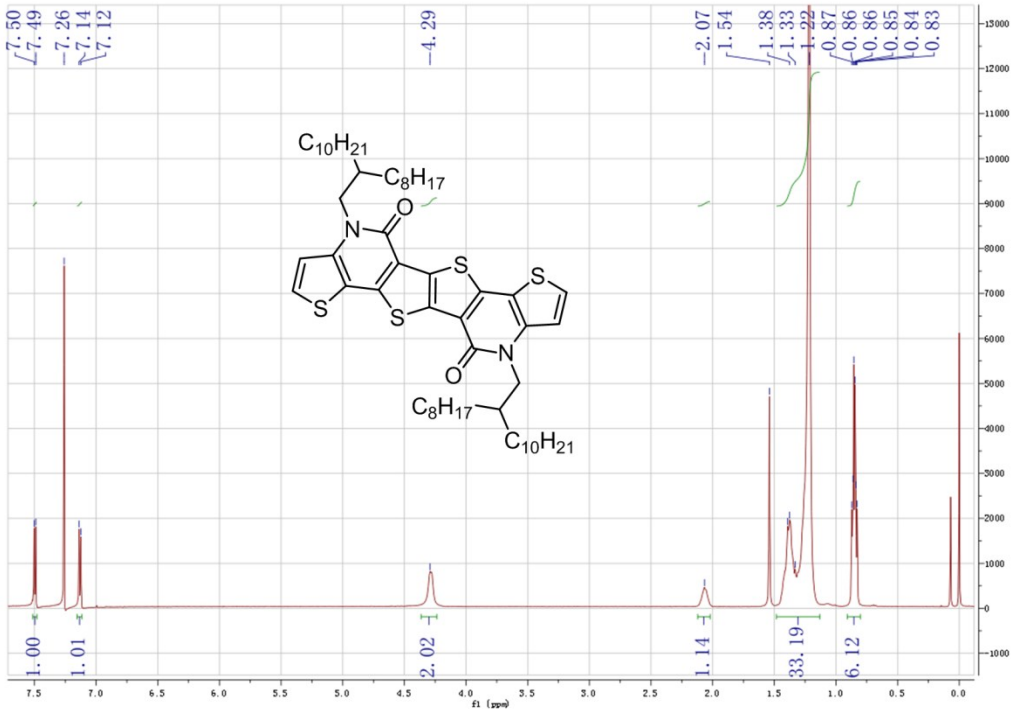

Figure S1 ^{1}H NMR spectrum of TD1.

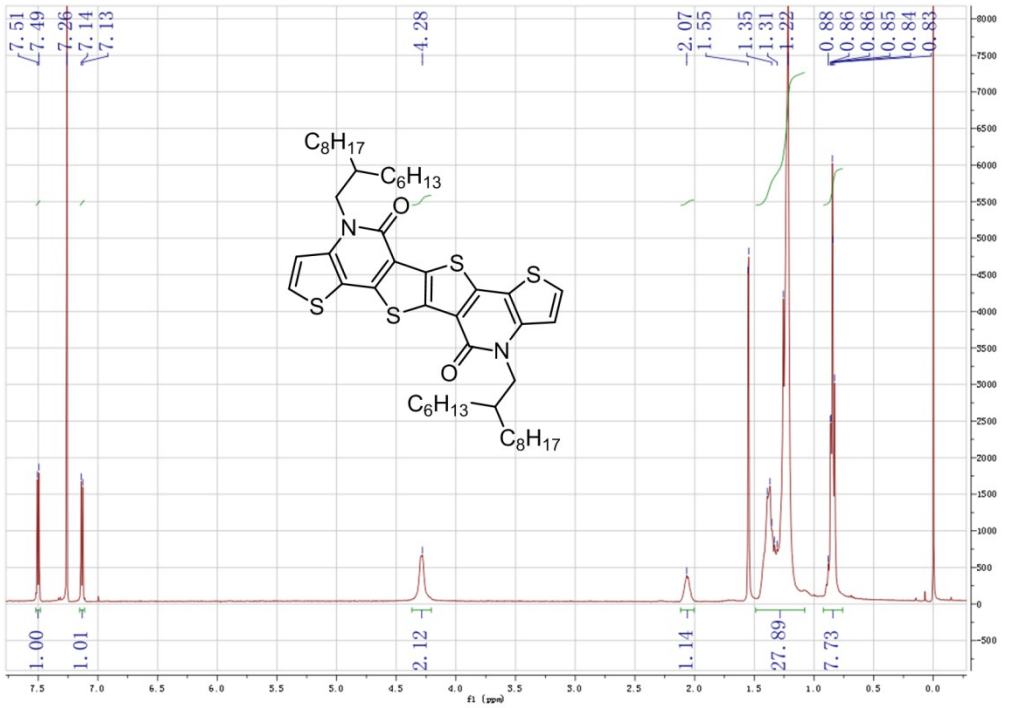

Figure S2 ^{1}H NMR spectrum of TD2.

4. TGA

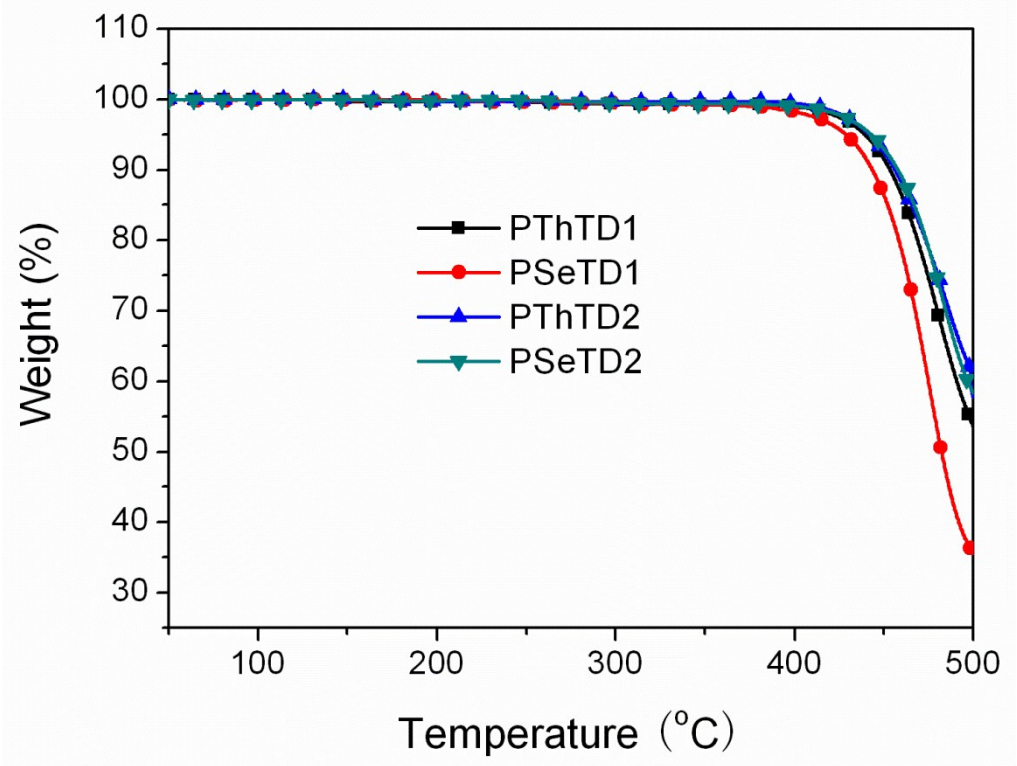

Figure S3 TGA curves for the polymers.

Table S1 GPC and TGA data.

Polymers	M_n [kDa][a]	M_w [kDa][a]	PDI[a]	T_d [°C][b]
PThTD1	58.1	336.2	5.78	439
PSeTD1	70.8	253.0	3.58	429
PThTD2	33.2	146.3	4.41	442
PSeTD2	35.5	93.4	2.63	443

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

[b]The temperature at which 5% weight loses under nitrogen.

5. Absorption spectra

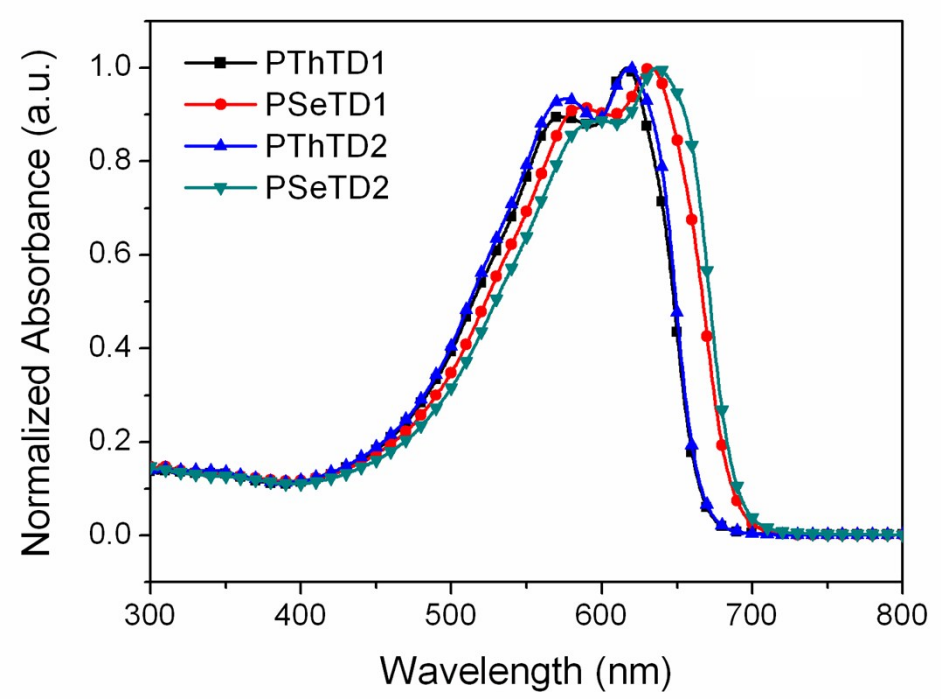

Figure S4 Absorption spectra for the polymers in chloroform.

6. CV

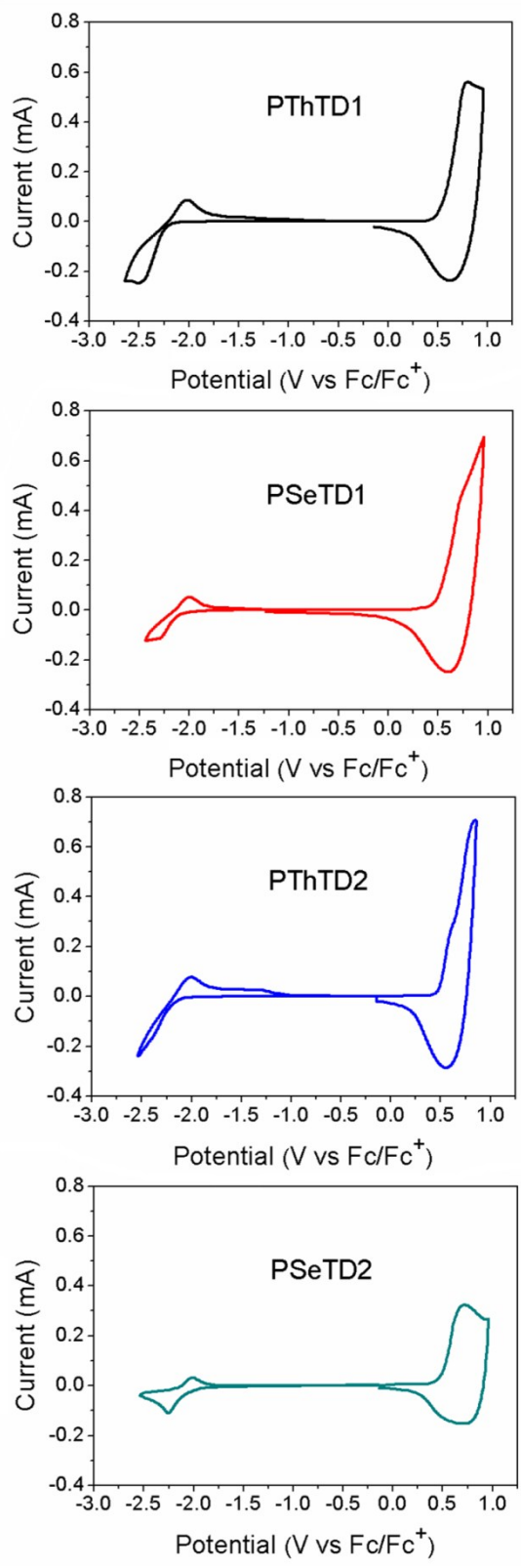

Figure S5 Cyclic voltammogram for the polymers.

7. 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)-polystyrene sulfonate (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 °C for 10 min. A polymer:$PC_{71}BM$ blend in chlorobenzene with DIO additive (0~4 vol%) was spin-coated onto PEDOT:PSS 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 devices is 4 mm^2. The thicknesses of the active layers were measured by a KLA Tencor D-120 profilometer. *J-V* curves were measured using a computerized Keithley 2420 SourceMeter. Device characterization was done in air using 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 Tech).

Inverted solar cells

ZnO precursor was prepared according to literature.[4] ZnO precursor solution was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C in air for 20 min. The thickness for ZnO film is about 30 nm. A polymer:$PC_{71}BM$ blend in chlorobenzene with DIO additive (0~4 vol%) was spin-coated onto ZnO layer. MoO_3 (~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_3/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 °C for 10 min. A polymer:$PC_{71}BM$ (1:0.8) blend in chlorobenzene with 3 vol% DIO additive was spin-coated onto PEDOT:PSS layer. 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.

8. Device optimization

Table S2 D/A ratio optimization for **PThTD1**:$PC_{71}BM$ solar cells.[a]

D:A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.6	0.90	9.51	60.03	5.14
1:0.8	0.89	9.29	68.80	5.69
1:1.0	0.88	8.87	69.38	5.42

[a] The active layer thickness is ~105 nm. DIO content in chlorobenzene is 3 vol%.

Table S3 Active layer thickness optimization for **PThTD1**:$PC_{71}BM$ solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
82	0.88	8.85	69.38	5.40
112	0.89	9.30	68.85	5.70
140	0.89	8.27	66.92	4.93
175	0.89	7.95	50.42	3.57

[a] D/A ratio is 1:0.8. DIO content in chlorobenzene is 3 vol%.

Table S4 Additive content optimization for **PThTD1**:$PC_{71}BM$ solar cells.[a]

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.89	2.40	59.03	1.26
1	0.89	6.38	61.95	3.52
2	0.88	9.28	67.33	5.50
3	0.88	9.51	68.30	5.72
4	0.88	9.25	69.08	5.62

[a] D/A ratio is 1:0.8. Thickness of the active layer is ~110 nm.

Table S5 D/A ratio optimization for **PSeTD1**:$PC_{71}BM$ solar cells.[a]

D:A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.6	0.87	10.41	61.70	5.59
1:0.8	0.86	10.15	66.54	5.81
1:1.0	0.86	9.70	65.62	5.47

[a] Thickness of the active layer is ~110 nm. DIO content in chlorobenzene is 3 vol%.

Table S6 Active layer thickness optimization for **PSeTD1**:$PC_{71}BM$ solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
85	0.86	9.80	64.71	5.45
122	0.87	10.31	65.81	5.90
135	0.85	9.51	66.56	5.38
170	0.82	9.05	61.92	4.60

[a] D/A ratio is 1:0.8. DIO content in chlorobenzene is 3 vol%.

Table S7 Additive content optimization for **PSeTD1**:$PC_{71}BM$ solar cells.[a]

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.85	2.40	57.03	1.16
1	0.85	4.33	60.95	2.24
2	0.86	8.17	65.73	4.62
3	0.86	9.81	66.90	5.64
4	0.85	9.62	66.08	5.40

[a] D/A ratio is 1:0.8. Thickness of the active layer is ~115 nm.

Table S8 D/A ratio optimization for **PThTD2**:$PC_{71}BM$ solar cells.[a]

D:A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.6	0.89	9.28	69.26	5.72
1:0.8	0.87	11.51	62.14	6.22
1:1.0	0.86	11.24	63.01	6.09

[a] Thickness of the active layer is ~100 nm. DIO content in chlorobenzene is 3 vol%.

Table S9 Active layer thickness optimization for **PThTD2**:$PC_{71}BM$ solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
76	0.85	10.68	65.13	5.91
110	0.87	11.54	62.76	6.30
130	0.85	11.10	56.33	5.31
155	0.84	11.14	49.71	4.65

[a] D/A ratio is 1:0.8. DIO content in chlorobenzene is 3 vol%.

Table S10 Additive content optimization for **PThTD2**:$PC_{71}BM$ solar cells.[a]

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.85	2.11	57.02	1.02
1	0.87	8.88	60.23	4.65
2	0.86	11.36	62.74	6.13
3	0.87	11.55	67.06	6.74
4	0.84	10.98	66.24	6.11

[a] D/A ratio is 1:0.8. Thickness of the active layer is ~115 nm.

Table S11 D/A ratio optimization for **PSeTD2**:$PC_{71}BM$ solar cells.[a]

D:A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.6	0.88	12.75	63.46	7.12
1:0.8	0.88	12.71	66.38	7.42
1:1.0	0.87	12.51	65.76	7.16

[a] Thickness of the active layer is ~120 nm. DIO content in chlorobenzene is 3 vol%.

Table S12 Active layer thickness optimization for **PSeTD2**:$PC_{71}BM$ solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
85	0.86	11.10	67.74	6.47
98	0.86	12.20	67.66	7.10
115	0.87	12.73	68.12	7.54
150	0.85	12.26	63.10	6.58

[a] D/A ratio is 1:0.8. DIO content in chlorobenzene is 3 vol%.

Table S13 Additive content optimization for **PSeTD2**:$PC_{71}BM$ solar cells.[a]

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.88	3.47	50.11	1.53
1	0.87	12.02	67.22	7.03
2	0.86	12.66	65.07	7.08
3	0.86	12.91	66.46	7.38
4	0.86	13.07	65.45	7.36

[a] D/A ratio is 1:0.8. Thickness of the active layer is ~115 nm.

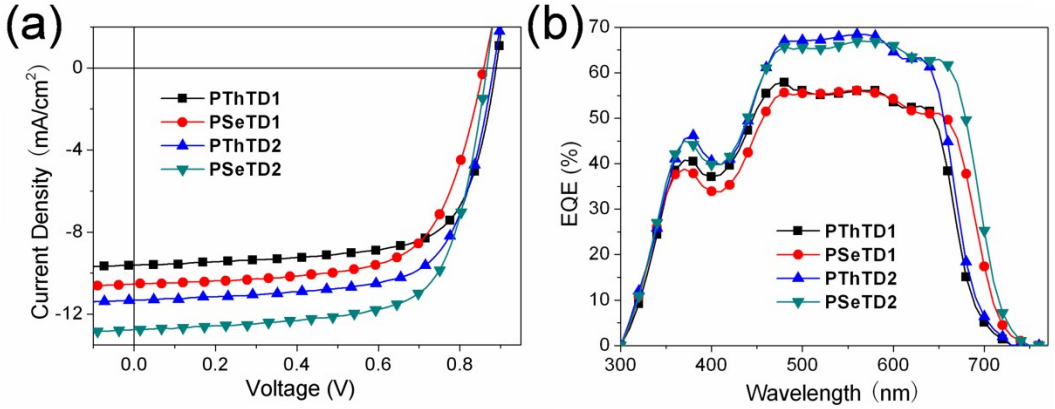

Figure S6 *J-V* curves (a) and EQE spectra (b) for conventional polymer:$PC_{71}BM$ solar cells.

Table S14 Best performance for conventional polymer:$PC_{71}BM$ solar cells.

Polymers	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
PThTD1	0.89	9.60	69.68	5.95
PSeTD1	0.86	10.53	66.54	6.03
PThTD2	0.88	11.31	68.94	6.86
PSeTD2	0.87	12.75	69.66	7.73

9. AFM

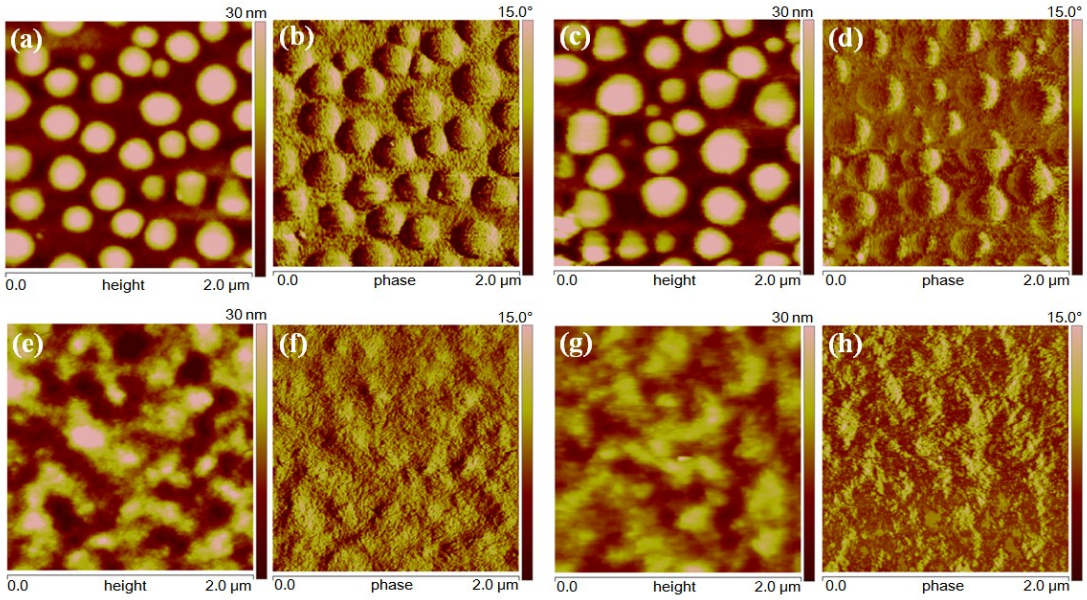

Figure S7 AFM height and phase images for PThTD1:$PC_{71}BM$ blend films without DIO (a, b) and with 3 vol% DIO (e, f); PSeTD1:$PC_{71}BM$ blend films without DIO (c, d) and with 3 vol% DIO (g, h).

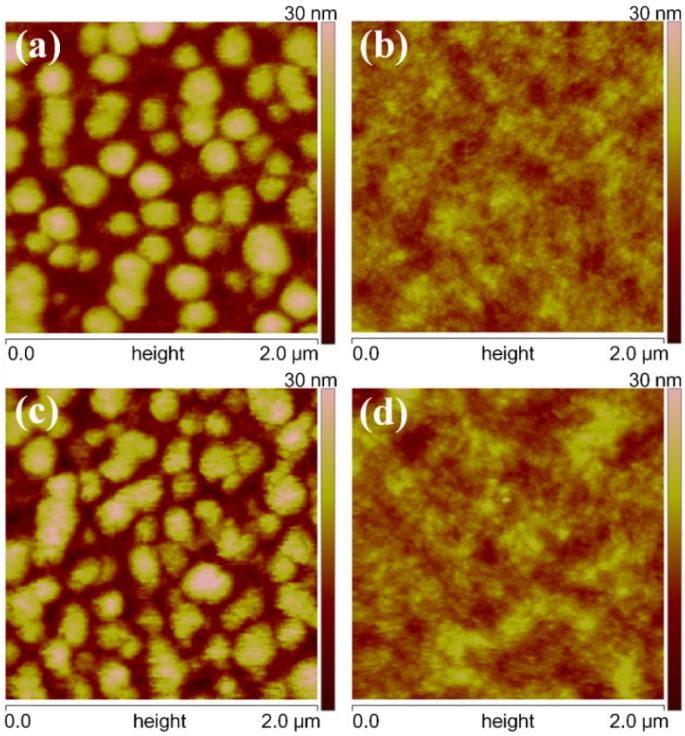

Figure S8 AFM height images for PThTD2:$PC_{71}BM$ blend films without DIO (a) and with 3 vol% DIO (b); PSeTD2:$PC_{71}BM$ blend films without DIO (c) and with 3 vol% DIO (d).

10. 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, $V = V_{appl} - V_{bi}$, 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 curves.

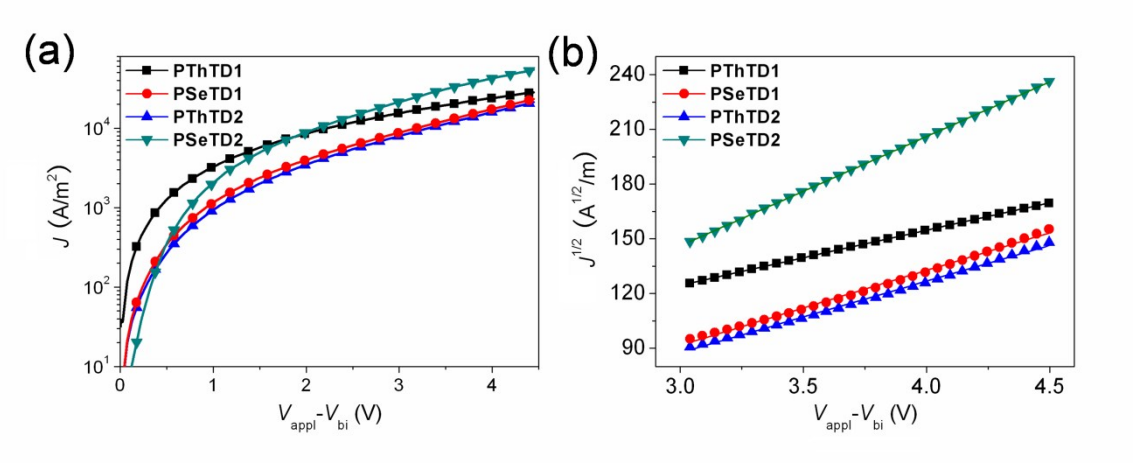

Figure S9 J-V curves (a) and corresponding $J^{1/2}$-V curves (b) for hole-only devices (in dark).

11. XRD

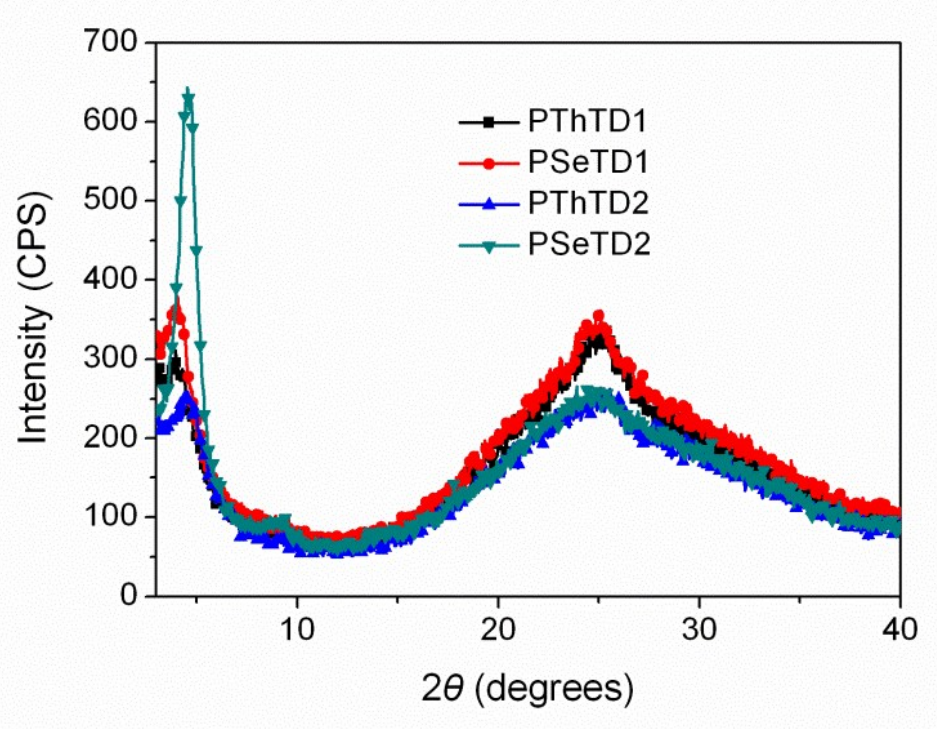

Figure S10 XRD patterns for as-cast polymer films.

Table S15 XRD analysis.

Polymers	$2\theta_{(100)}$ [°]	d_{100} [Å]	$2\theta_{(010)}$ [°]	d_{010} [Å]
PThTD1	3.97	22.23	25.04	3.55
PSeTD1	4.02	21.98	25.01	3.56
PThTD2	4.54	19.46	25.10	3.54
PSeTD2	4.58	19.29	24.93	3.57

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