Supporting Information

A facilely synthesized lactam acceptor unit for high-performance polymer donors

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1. General characterization

^{1}H 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 THF as eluent and polystyrenes as standards. Thermogravimetric analysis was done by using a Perkin Elmer Diamond TG/DTA 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. The polymer was coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc$^+$. AFM was performed on a Multimode 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 Kα radiation (40 kV, 200 mA).

2. Synthesis

All reagents were purchased from J&K Co., Lyntech Co., Innochem Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 4-(2-Octyldodecyl)-dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (**DTP**) was prepared according to literature. [1]

7-Bromo-4-(2-octyldodecyl)-dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (DTP-Br). To a solution of **DTP** (150 mg, 0.31 mmol) in DMF (15 mL) was added NBS (55 mg, 0.31 mmol). The mixture was stirred at room temperature for 7 h and then was poured into water and extracted with petroleum ether three times. The organic layer was dried over anhydrous Na$_2$SO$_4$. After removal of the solvent, the crude product was purified

via column chromatography (silica gel) using CH_2Cl_2 as eluent to give **DTP-Br** as a yellow oil (148 mg, 85%). ^1H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.63 (s, 1H), 7.45 (d, $J = 5.4$ Hz, 1H), 7.06 (d, $J = 5.4$ Hz, 1H), 4.18 (d, $J = 3.6$ Hz, 2H), 1.96 (m, 1H), 1.31-1.13 (m, 28H), 0.87-0.84 (m, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 157.57, 142.57, 140.85, 128.83, 128.71, 126.07, 117.51, 113.25, 110.52, 49.25, 37.20, 31.89, 31.85, 31.49, 29.91, 29.59, 29.53, 29.48, 29.31, 29.24, 26.58, 22.66, 22.63, 14.10. MALDI-TOF MS (m/z): 566.4 (M$^+$).

7,7'-Dibromo-4,4'-bis(2-octyldodecyl)-[2,2'-bidithieno[3,2-b:2',3'-d]pyridine]-5,5'(4H,4'H)-dione (BDTP$_i$ monomer). To a solution of **DTP-Br** (800 mg, 1.41 mmol) and Ag$_2$O (654 mg, 2.82 mmol) in DMSO (8 mL) was added Pd(OAc)$_2$ (7.9 mg, 0.035 mmol) under Ar. The reaction mixture was stirred at 80 °C for 5 h. After cooling to room temperature, the mixture was diluted with petroleum ether (50 mL) and washed with water three times. The organic layer was dried over anhydrous Na$_2$SO$_4$. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using CS$_2$/CH$_2$Cl$_2$ (1:1) as eluent to give **BDTP$_i$ monomer** as a yellow solid (246 mg, 31%). ^1H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.68 (s, 2H), 7.17 (s, 2H), 4.20 (br, 4H), 1.99 (m, 2H), 1.31-1.18 (m, 64H), 0.89-0.83 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 157.32, 141.55, 140.94, 135.80, 129.46, 129.08, 114.23, 113.10, 111.60, 49.18, 37.31, 31.92, 31.55, 29.99, 29.67, 29.60, 29.36, 29.32, 26.68, 22.68, 14.11. MALDI-TOF MS (m/z): 1131.8 (M$^+$).

PThBDTP$_i$. To a mixture of **BDTP$_i$ monomer** (50 mg, 0.04 mmol), 2,5-bis(trimethylstannyl)thiophene (18.1 mg, 0.04 mmol), Pd$_2$(dba)$_3$ (1.6 mg, 0.0017 mmol) and P(o-Tol)$_3$ (4.3 mg, 0.014 mmol) in a Schlenk flask was added toluene (3 mL) under argon. The mixture was heated to reflux for 24 h. Then the solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum

overnight to give **PThBDTP$_i$** as a black solid (47.5 mg, 97%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.76-6.66 (br, aromatic protons), 2.04-0.84 (br, aliphatic protons).

PSeBDTP$_i$. To a mixture of **BDTP$_i$ monomer** (50 mg, 0.04 mmol), 2,5-bis(trimethylstannyl)selenophene (20.2 mg, 0.04 mmol), Pd$_2$(dba)$_3$ (1.6 mg, 0.0017 mmol) and P(o-Tol)$_3$ (4.3 mg, 0.014 mmol) in a Schlenk flask was added toluene (3 mL) under argon. The mixture was heated to reflux for 24 h. Then the solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **PSeBDTP$_i$** as a black solid (43 mg, 88%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.66-6.76 (br, aromatic protons), 1.56-0.84 (br, aliphatic protons).
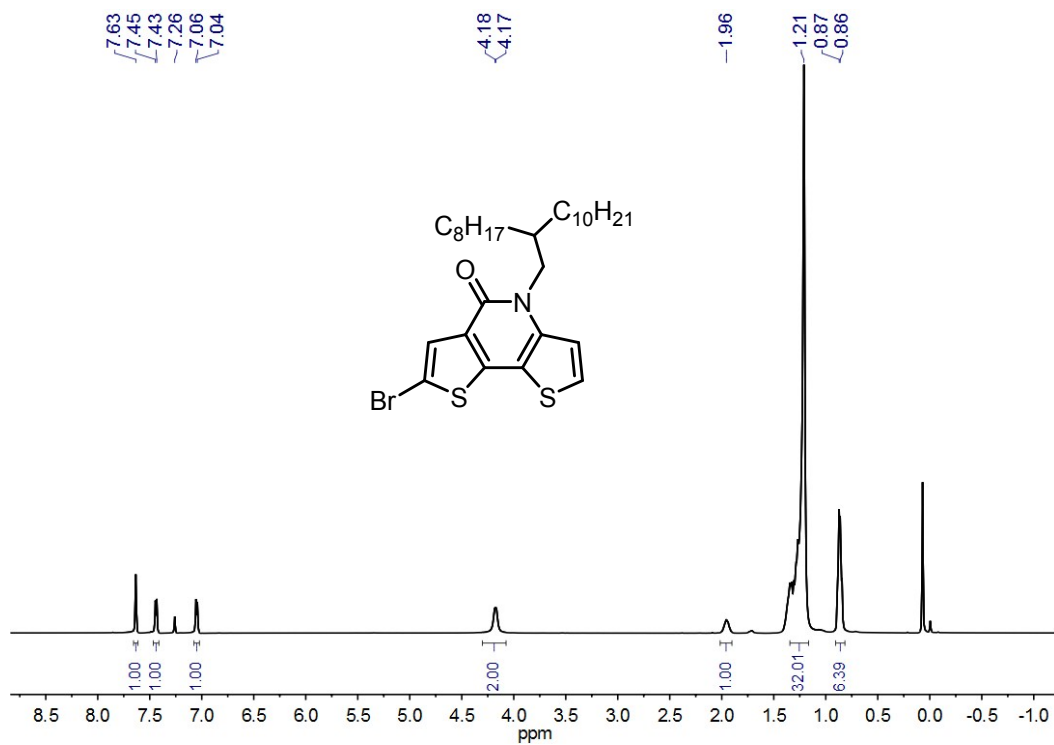
3. NMR
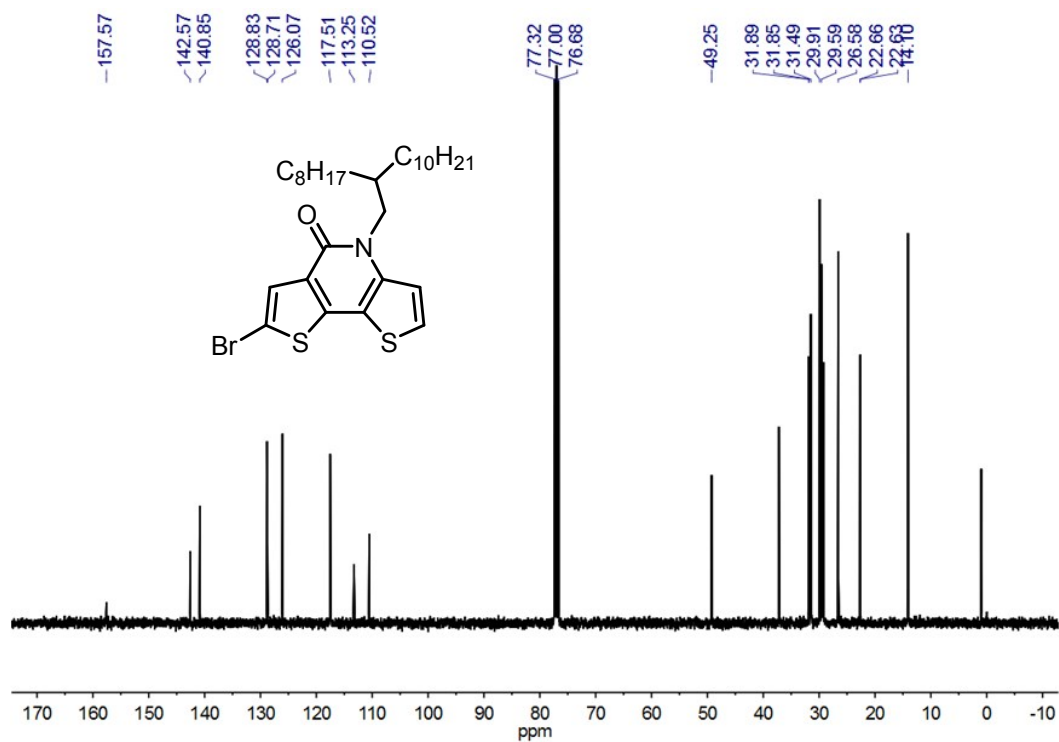

Fig. S1 ^{1}H NMR spectrum of **DTP-Br**.

Fig. S2 ^{13}C NMR spectrum of **DTP-Br**.

"C7" bromination   vs   "C2" bromination

H (7.63 ppm) correlates with C (157.57 ppm)
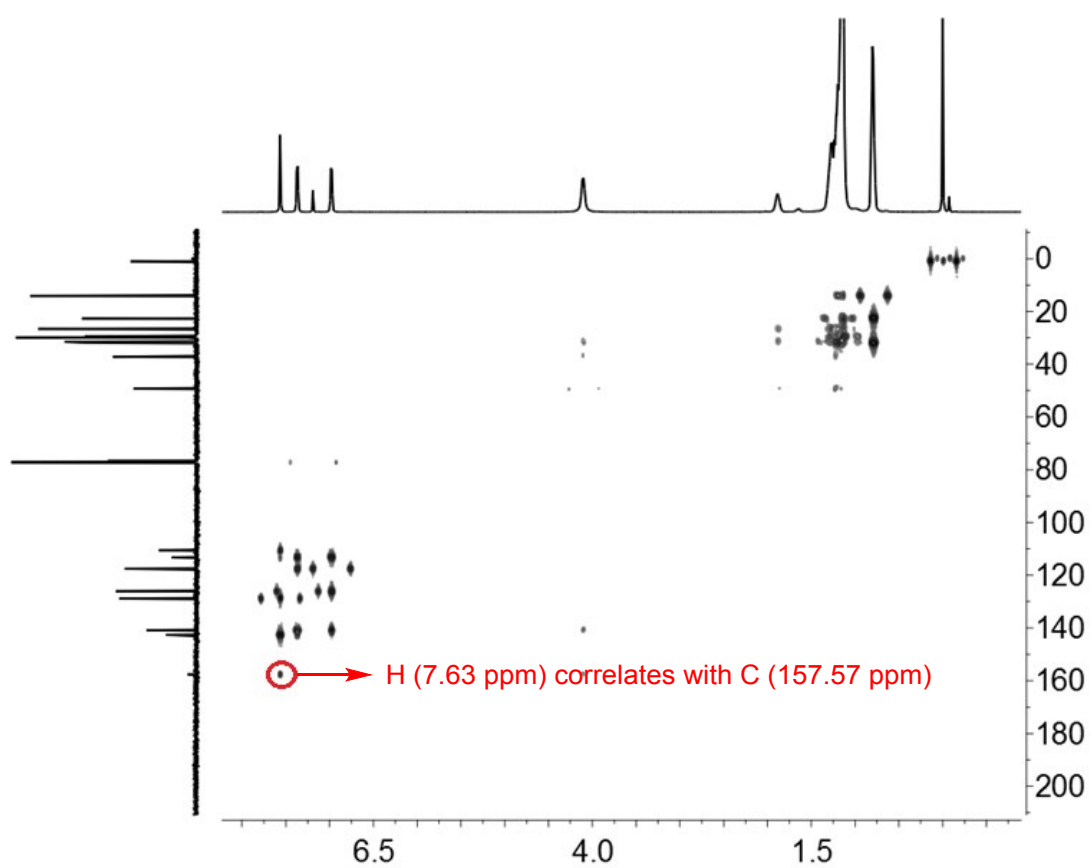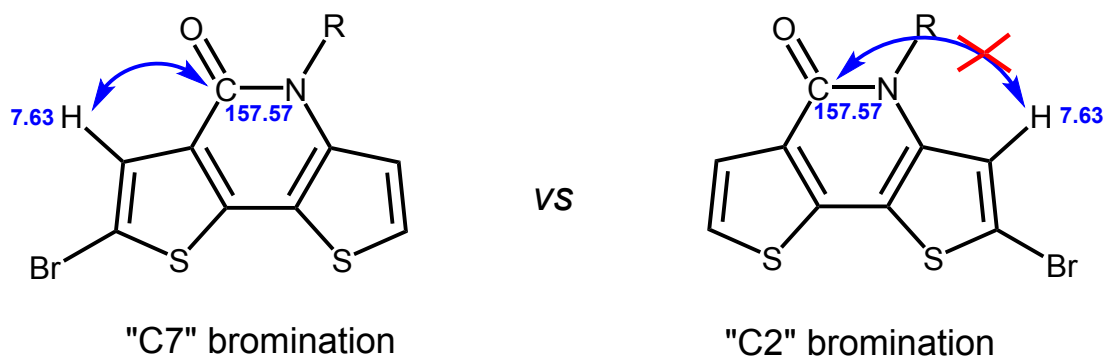
Fig. S3 HMBC spectrum of **DTP-Br**.
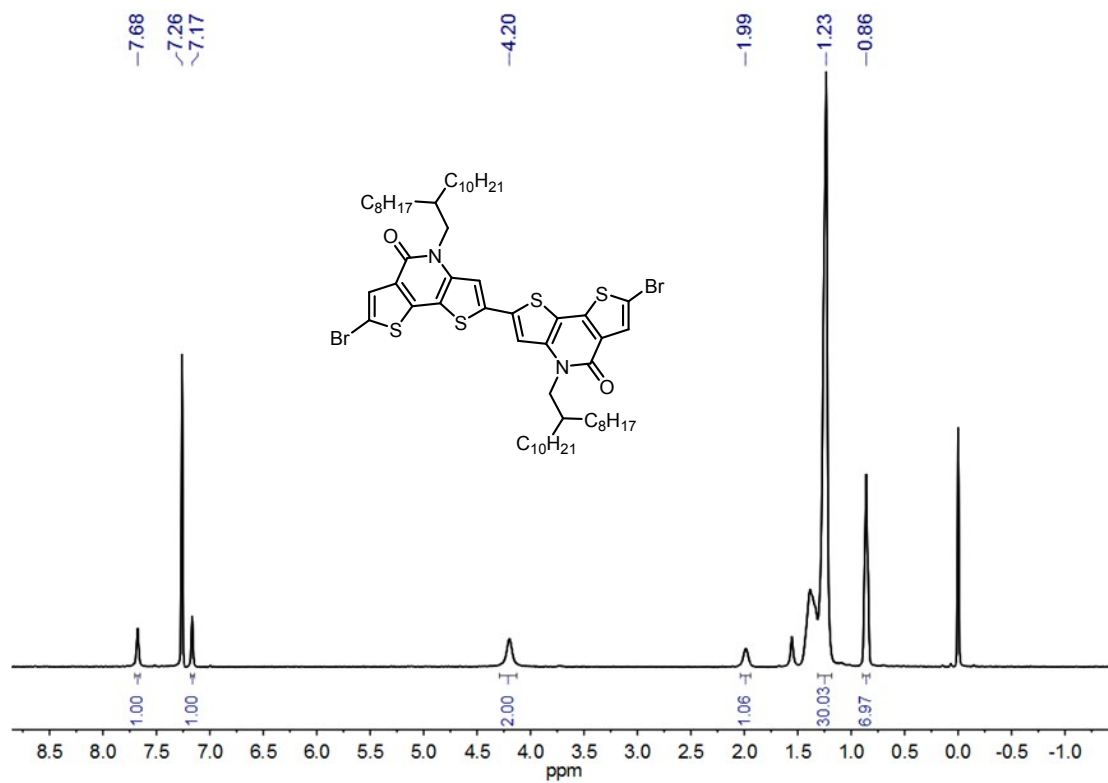
Fig. S4 ^{1}H NMR spectrum of **BDTP$_i$ monomer**.
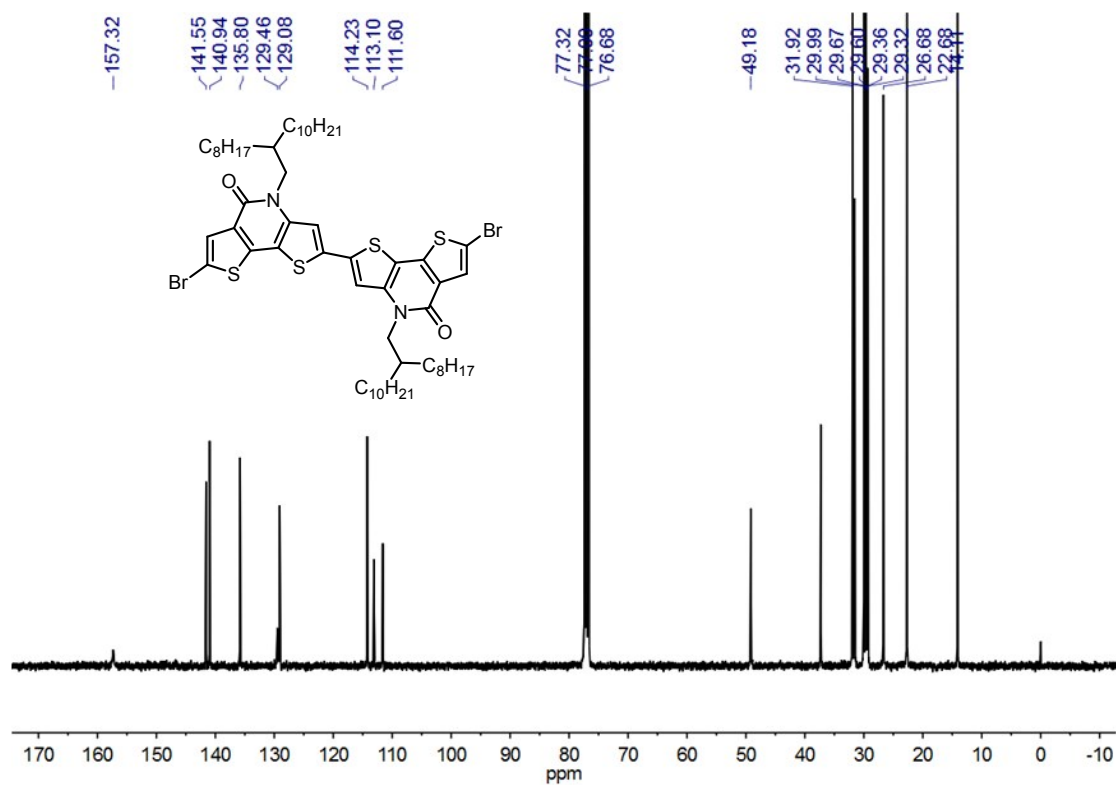
Fig. S5 ^{13}C NMR spectrum of **BDTP$_i$ monomer**.
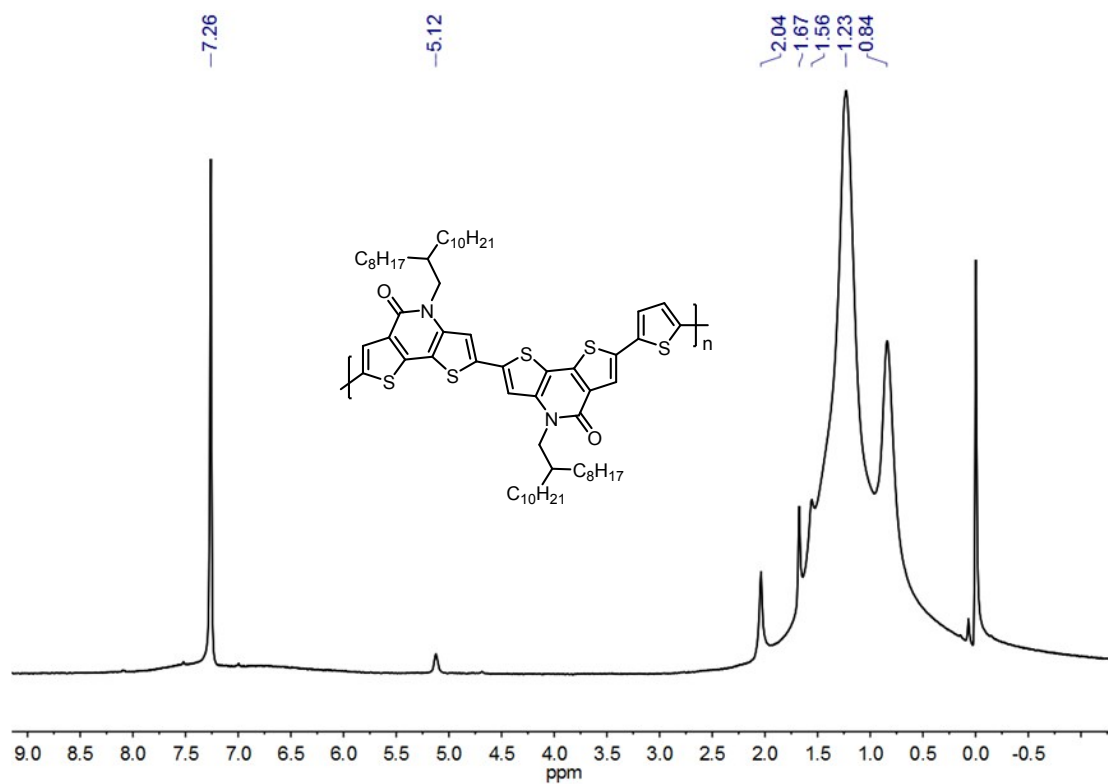
Fig. S6 ^{1}H NMR spectrum of **PThBDTP**$_i$.
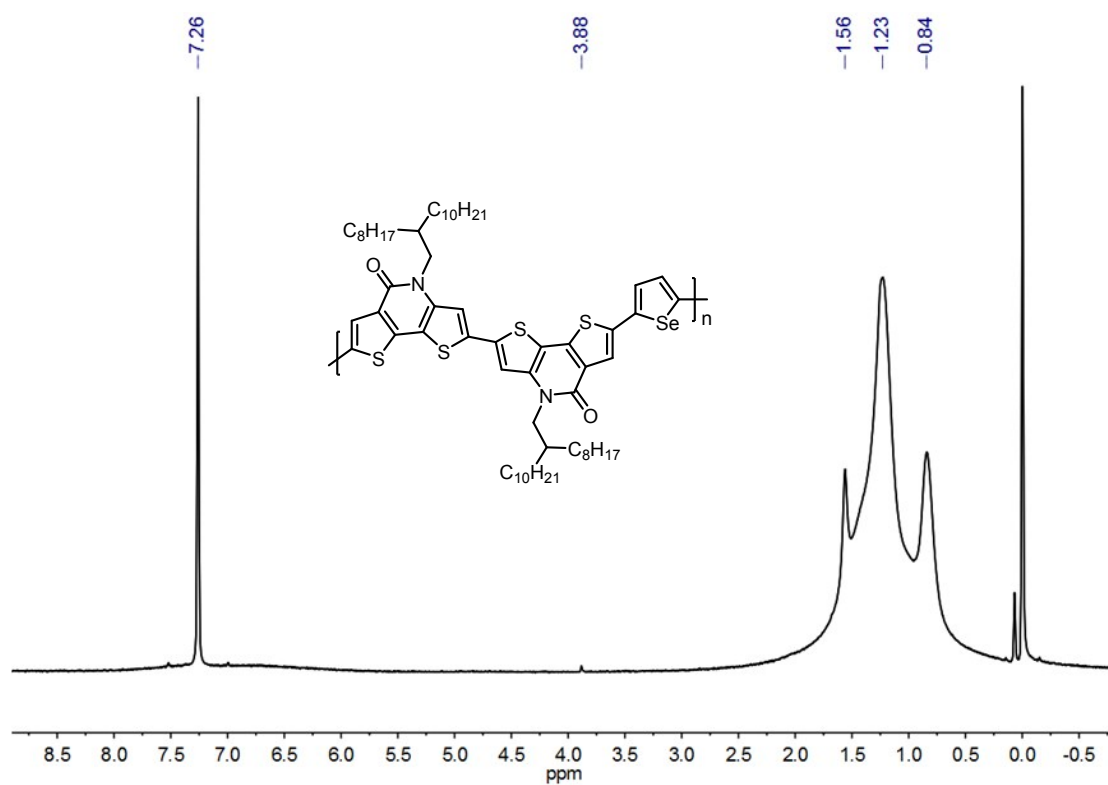
Fig. S7 ^{1}H NMR spectrum of **PSeBDTP**$_i$.
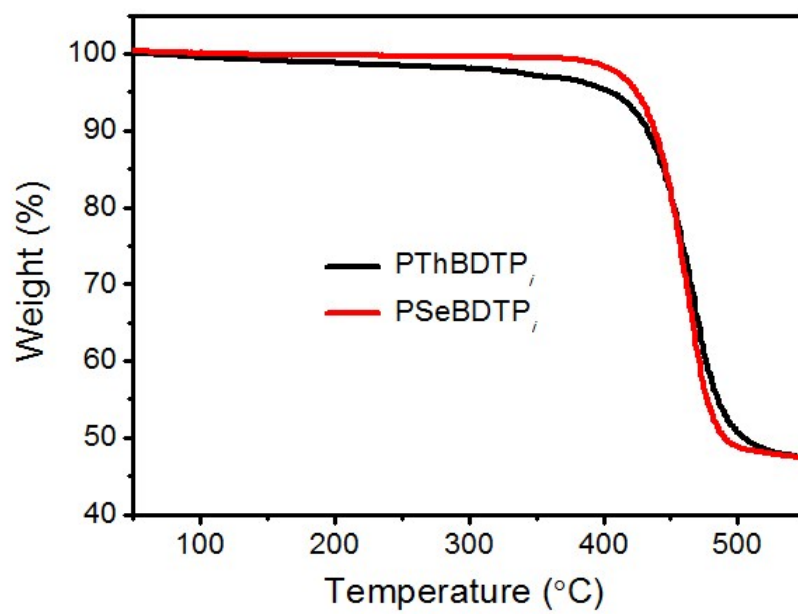
4. TGA

Fig. S8 TGA curves for the polymers.
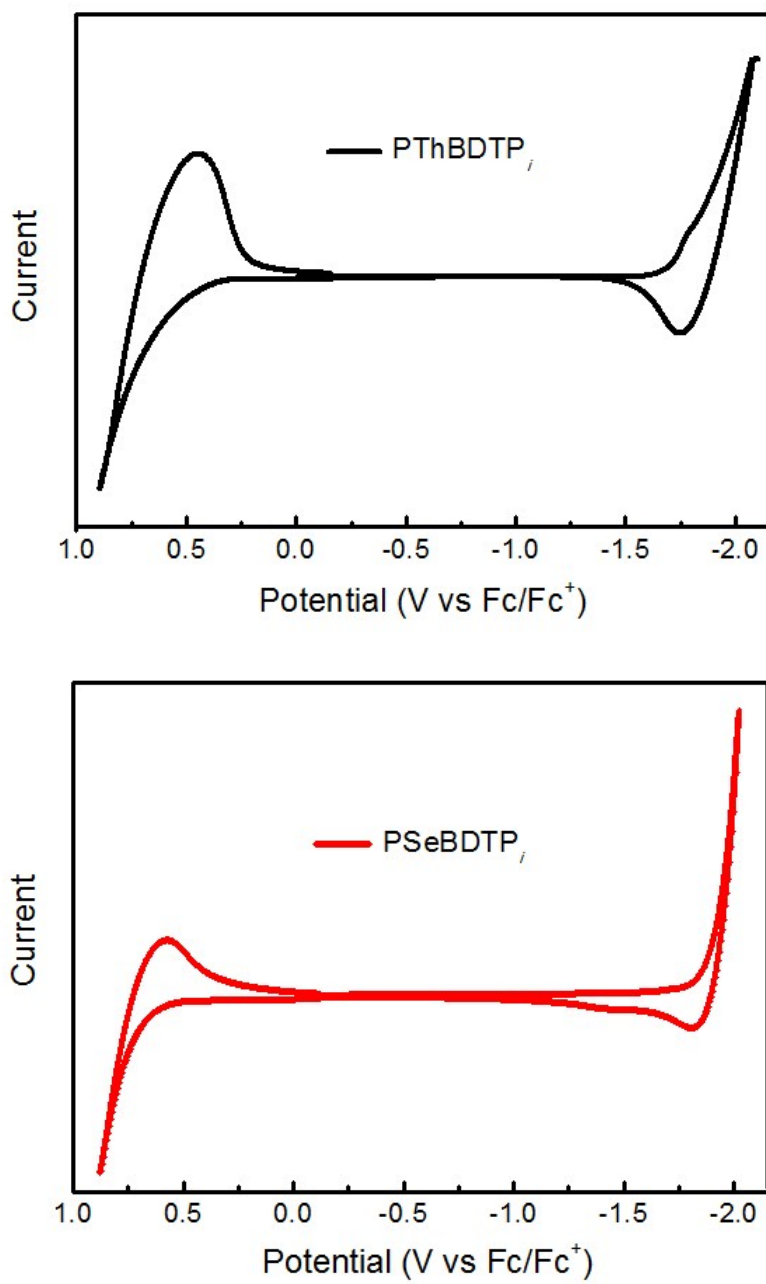
5. CV

Fig. S9 Cyclic voltammograms for the polymers.

6. Device fabrication and measurements

Inverted solar cells

ZnO precursor solution was prepared according to literature.[2] It was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C in air for 30 min. ZnO film thickness is ~30 nm. A polymer:$PC_{71}BM$ blend in a mixed solvent of chloroform:chlorobenzene (3:2) or in CB with DIO additive was spin-coated onto ZnO layer. MoO_3 (~6 nm) and Ag (~80 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the cells is 4 mm^2. The thicknesses of 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/cm^2). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

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 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:$PC_{71}BM$ blend in a mixed solvent of chloroform:chlorobenzene (3:2) or in CB with DIO additive was spin-coated onto ZnO layer. Finally, MoO_3 (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

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7. Optimization of device performance

Table S1 Optimization of D/A ratio for PThBDTP$_i$:PC$_{71}$BM inverted solar cells.[a]

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm^2]	[%]	[%]
1:1	0.95	11.60	65.8	7.25 (7.01)[b]
1:1.5	0.95	11.58	69.1	7.61 (7.32)
1:2	0.96	11.64	68.9	7.70 (7.55)
1:2.5	0.94	11.02	72.9	7.56 (7.29)

[a]Blend solution: 6 mg/mL in CF:CB (3:2) with 1 vol% DIO; spin coating: 1400 rpm for 60 s.

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

Table S2 Optimization of the active layer thickness for PThBDTP$_i$:PC$_{71}$BM inverted solar cells.[a]

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm^2]	[%]	[%]
138	0.95	11.39	65.3	7.10 (6.64)[b]
121	0.96	11.77	67.7	7.62 (7.20)
106	0.96	11.78	69.2	7.84 (7.62)
92	0.96	11.88	69.4	7.89 (7.66)
73	0.96	11.64	68.9	7.72 (7.55)

[a]D/A ratio: 1:2 (w/w); blend solution: 6 mg/mL in CF:CB (3:2) with 1 vol% DIO.

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

Table S3 Optimization of DIO content for PThBDTP$_i$:PC$_{71}$BM inverted solar cells.[a]

DIO	V_{oc}	J_{sc}	FF	PCE
[vol%]	[V]	[mA/cm^2]	[%]	[%]
0	0.96	7.03	37.7	2.55 (2.32)[b]
0.5	0.95	12.13	70.5	8.11 (7.93)
1	0.95	11.88	69.9	7.89 (7.66)
1.5	0.97	11.34	59.2	6.52 (6.05)

[a]D/A ratio: 1:2 (w/w); blend solution: 6 mg/mL in CF:CB (3:2); spin coating: 1200 rpm for 60 s.

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

Table S4 Optimization of D/A ratio for PSeBDTP$_i$:PC$_{71}$BM inverted solar cells.[a]

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm^2]	[%]	[%]
1:1.0	0.92	9.77	63.4	5.71 (5.41)[b]
1:1.5	0.90	10.58	65.2	6.21 (6.06)
1:2	0.89	10.28	69.9	6.36 (6.22)
1:2.3	0.89	9.81	68.9	6.03 (5.82)

[a]Blend solution: 10 mg/mL in CB with 0.75 vol% DIO; spin coating: 1200 rpm for 60 s.

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

Table S5 Optimization of the active layer thickness for PSeBDTP$_i$:PC$_{71}$BM inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
126	0.88	10.08	64.4	5.73 (5.54)[b]
112	0.89	10.18	67.5	6.11 (5.93)
104	0.89	10.28	69.9	6.36 (6.22)
91	0.90	10.05	69.7	6.28 (6.09)
80	0.89	9.92	69.5	6.14 (5.88)

[a]D/A ratio: 1:2 (w/w); blend solution: 10 mg/mL in CB with 0.75 vol% DIO.

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

Table S6 Optimization of DIO content for PSeBDTP$_i$:PC$_{71}$BM inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.90	5.42	52.2	2.56 (2.47)[b]
0.5	0.90	9.87	68.2	6.07 (5.96)
0.75	0.90	10.53	67.6	6.39 (6.27)
1	0.91	10.32	69.6	6.50 (6.29)
1.5	0.90	10.03	67.8	6.15 (6.01)

[a]D/A ratio: 1:2 (w/w); blend solution: 10 mg/mL in CB; spin coating: 1000 rpm for 60 s.

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

8. SCLC

The charge carrier mobility was obtained by using 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 (here, V_{bi} = 0.1 V[3]). The mobility was calculated from the slope of $J^{1/2}$-V plots.

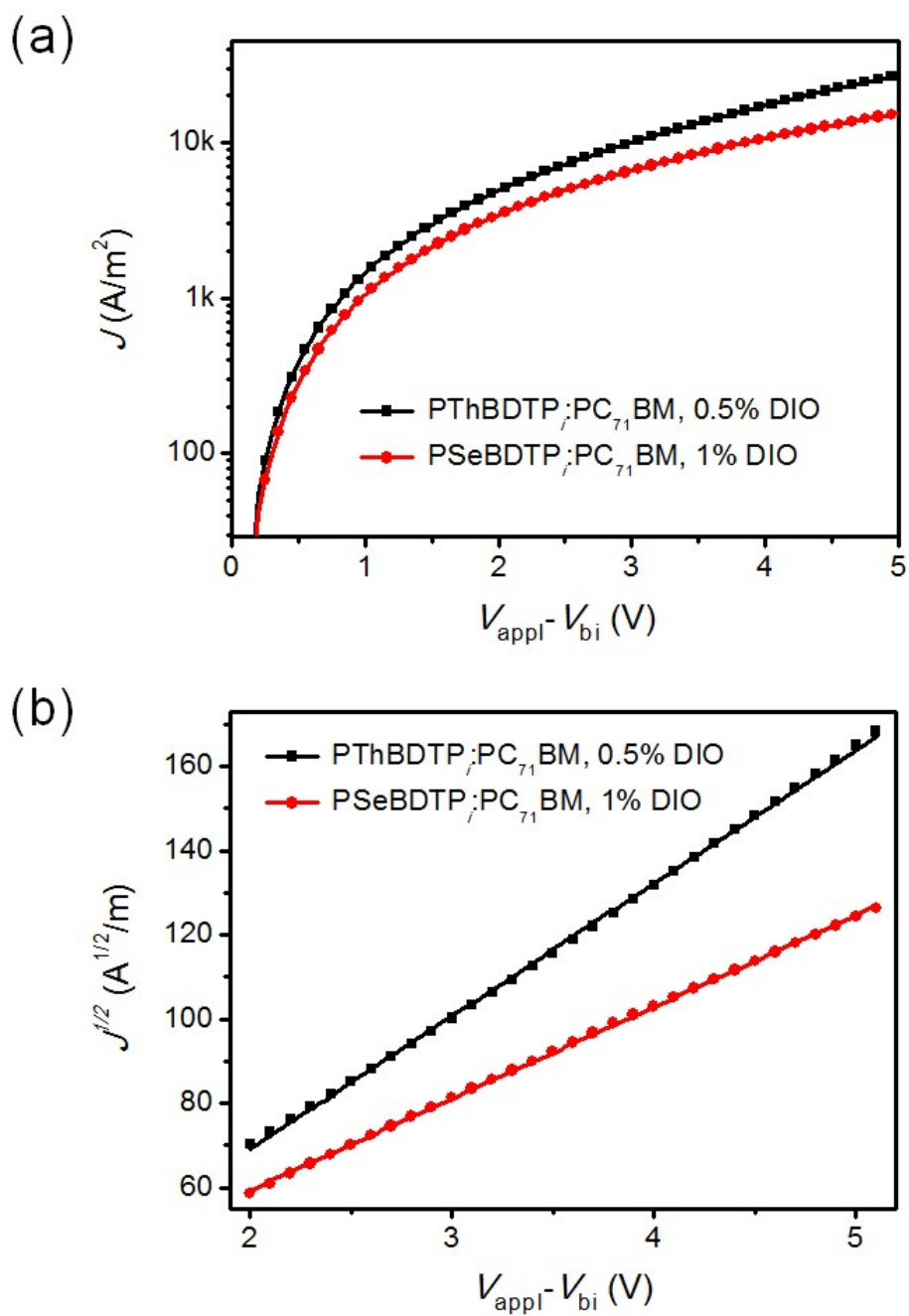**Fig. S10** *J-V* curves (a) and corresponding $J^{1/2}$-*V* plots (b) for the hole-only devices (in dark). The thicknesses for PThBDTP$_i$:PC$_{71}$BM and PSeBDTP$_i$:PC$_{71}$BM blend films are 92 and 104 nm, respectively.
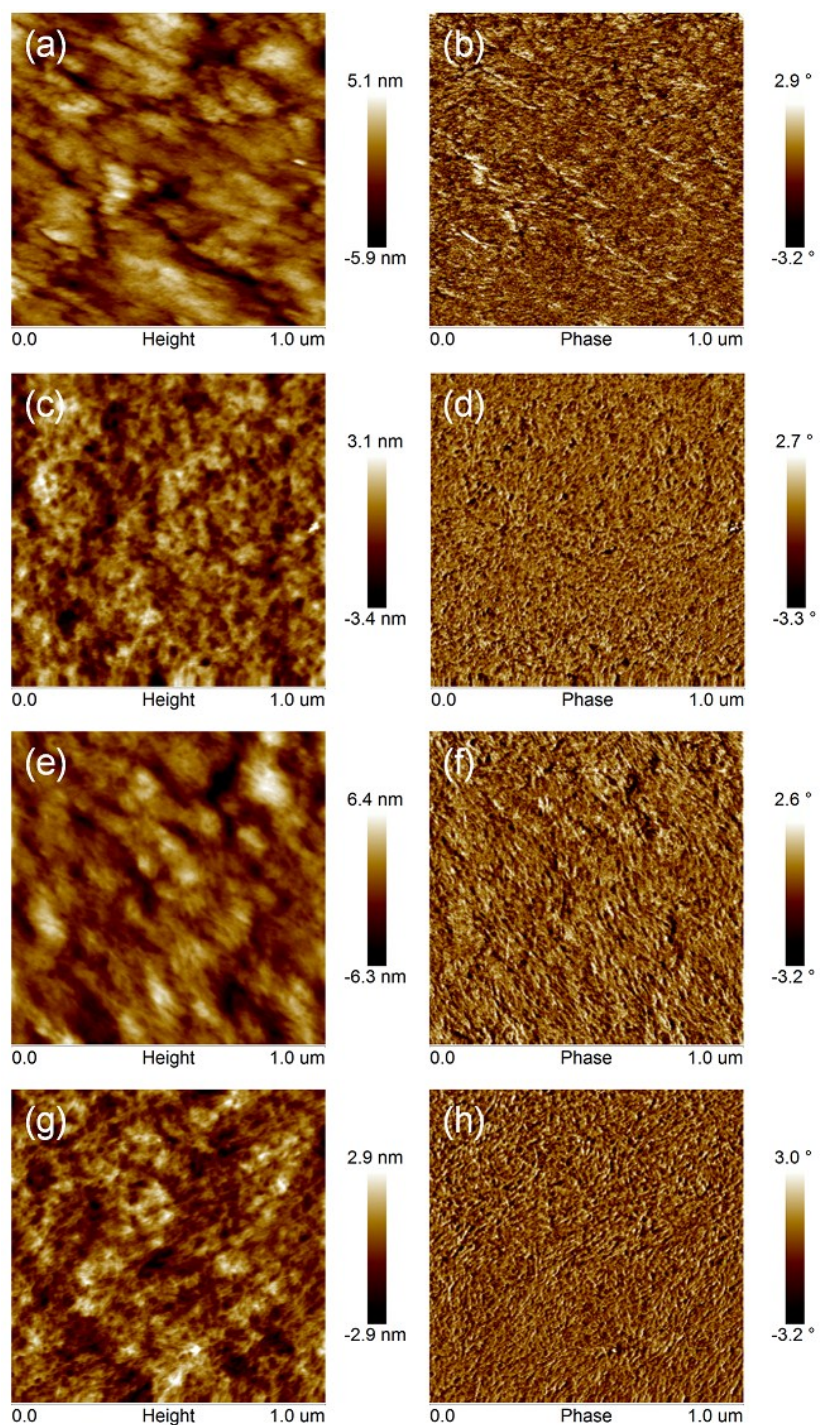
9. AFM

Fig. S11 AFM height (left) and phase (right) images for the blend films. (a) and (b), PThBDTP$_i$:PC$_{71}$BM blend without DIO; (c) and (d), PThBDTP$_i$:PC$_{71}$BM blend with 0.5 vol% DIO; (e) and (f), PSeBDTP$_i$:PC$_{71}$BM blend without DIO; (g) and (h), PSeBDTP$_i$:PC$_{71}$BM with 1 vol% DIO.

References

[1] M. Hao, G. Luo, K. Shi, G. Xie, K. Wu, H. Wu, G. Yu, Y. Cao and C. Yang, *J. Mater. Chem. A*, 2015, **3**, 20516.

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

[3] C. Duan, W. Cai, B. Hsu, C. Zhong, K. Zhang, C. Liu, Z. Hu, F. Huang, G. C. Bazan, A. J. Heeger and Y. Cao, *Energy Environ. Sci.*, 2013, **6**, 3022.