Supporting Information

High-performance wide-bandgap copolymers with dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one unit

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1. General characterization

¹H and ¹³C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. 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 copolymer 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 D/MAX-TTR III (CBO) X-ray diffractometer in reflection mode by using Cu Kα radiation (45 kV, 200 mA).

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., Derthon Co., SunaTech Co. and other commercial suppliers. All reactions dealing with air- or moisturesensitive compounds were carried out by using standard Schlenk techniques. 2,7-Dibromo-4-(2-hexyldecyl)dithieno[3,2-b:2',3'-d]pyridin-5(4H)-one (DTP1)^[1] and trimethyl(4octylthiophen-2-yl)stannane^[2] were prepared according to literature. (4,8-Bis(5-(2ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-T-Sn) was purchased from Derthon Co.



Scheme S1 The synthetic routes for PBD and PBD2T.

PBD. To a mixture of DTP1 (100 mg, 0.17 mmol), BDT-T-Sn (153.4 mg, 0.17 mmol), $Pd_2(dba)_3$ (6.2 mg, 0.0068 mmol) and P(o-Tol)₃ (16.5 mg, 0.054 mmol) in a Schlenk flask was added toluene (3 mL) under argon. The mixture was heated to reflux for 24 h. Then the mixture was cooled to room temperature and added into methanol (150 mL) 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. The precipitate was collected and dried under vacuum overnight to give **PBD** as a black solid (165 mg, 94%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 6.98 (br, aromatic protons), 2.99 (br, aliphatic protons), 0.83-1.82 (br, aliphatic protons).

Compound 1. To a solution of DTP1 (200 mg, 0.34 mmol) and trimethyl(4-octylthiophen-2yl)stannane (304.6 mg, 0.85 mmol) in toluene (10 mL) and DMF (2 mL) was added Pd(PPh₃)₄ (39.2 mg, 0.034 mmol) under N₂. The mixture was heated to reflux and stirred overnight. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:petroleum ether (1:1) as eluent to give **compound 1** as a yellow solid (185 mg, 66%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.69 (s, 1H), 7.11 (s, 1H), 7.06 (s, 1H), 7.05 (s, 1H), 6.91 (s, 1H), 6.86 (s, 1H), 4.19 (br, 2H), 2.60 (m, 2H), 1.99 (br, 1H), 1.64 (m, 4H), 1.24-1.33 (m, 44H), 0.84-0.90 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 158.45, 144.66, 144.30, 140.84, 139.60, 137.63, 136.04, 135.93, 134.85, 129.22, 126.32, 126.00, 121.65, 120.75, 120.25, 112.83, 112.65, 49.02, 37.23, 31.88, 31.84, 31.61, 31.56, 30.46, 30.39, 30.37, 29.96, 29.65, 29.57, 29.41, 29.31, 29.28, 29.26, 26.66, 22.67, 22.63, 14.11, 14.08. MALDI-TOF MS (m/z): 820.4 (M + H⁺).

DTP2. To a solution of compound 1 (165 mg, 0.20 mmol) in CHCl₃ (5 mL) was added NBS (71.6 mg, 0.40 mmol) at room temperature. The mixture was stirred for 1 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:petroleum ether (1:1) as eluent to give **DTP2** as a yellow solid (162 mg, 82%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.55 (s, 1H), 6.92 (s, 1H), 6.90 (s, 1H), 6.86 (s, 1H), 4.11 (br, 2H), 2.53 (m, 4H), 1.92 (br, 1H), 1.60 (m, 4H), 1.23-1.34 (m, 44H), 0.84-0.91 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 158.14, 143.51, 143.12, 140.83, 139.35, 136.60, 135.72, 135.60, 133.89, 129.25, 125.60, 125.25, 121.80, 112.82, 112.53, 109.70, 109.10, 48.95, 37.21, 31.89, 31.87, 31.85, 31.57, 31.53, 29.96, 29.66, 29.61, 29.58, 29.55, 29.36, 29.30, 29.24, 26.64, 22.67, 22.64, 14.11. MALDI-TOF MS (m/z): 977.3 (M⁺).

PBD2T. To a mixture of DTP2 (100 mg, 0.10 mmol), BDT-T-Sn (92.5mg, 0.10 mmol), $Pd_2(dba)_3$ (3.7 mg, 0.0041 mmol) and P(o-Tol)₃ (9.96 mg, 0.033 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 methanol (150 mL) 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. The precipitate was collected and dried under vacuum overnight to give **PBD2T** as a black solid (139 mg, 95%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 6.95 (br, aromatic protons), 2.90 (br, aliphatic protons), 0.84-1.83 (br, aliphatic protons).





Fig. S1 ¹H NMR spectrum of PBD.











Fig. S5 ¹³C NMR spectrum of DTP2.





4. UV-Vis



Fig. S7 Absorption spectra of PBD and PBD2T in CHCl₃.

5. CV



Fig. S8 Cyclic voltammograms for PBD and PBD2T.

6. Device fabrication and measurements

Inverted solar cells

The ZnO precursor solution was prepared according to literature.^[3] 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 donor:IT-M blend in chlorobenzene (CB) with DIO additive was spin-coated onto ZnO layer. MoO₃ (~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 devices is 4 mm². 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/cm²). 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/donor (or donor:IT-M)/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 pure donor (or donor:IT-M blend) in CB was spin-coated onto PEDOT layer. Finally, MoO₃ (~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.

Electron-only devices

The structure for electron-only devices is Al/donor:IT-M/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. A donor:IT-M blend in CB was spin-coated onto Al. Ca (~5 nm) and Al (~80 nm) were 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.

7. Optimization of device performance

D/A	V _{OC}	$J_{ m SC}$	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:1	1.00	13.21	51.3	$6.76(6.64)^b$
1:1.4	0.98	13.46	51.9	6.88 (6.76)
1:1.8	0.98	13.30	56.8	7.43 (7.18)
1:2.2	0.99	13.19	53.2	6.92 (6.59)

Table S1 Optimization of D/A ratio for PBD:IT-M inverted solar cells.^a

^{*a*} Blend solution: 12 mg/mL in CB; spin-coating: 1800 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 PBD:IT-M inverted solar cells.^a

-	Thickness	Voc	$J_{ m SC}$	FF	PCE
	[nm]	[V]	[mA/cm ²]	[%]	[%]
	130	0.99	13.16	55.8	$7.29(7.03)^b$
	106	0.98	13.30	56.8	7.43 (7.18)
	87	0.99	12.63	58.7	7.36 (7.15)

^{*a*} D/A ratio: 1:1.8 (w/w); blend solution: 12 mg/mL in CB.

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

DIO	Voc	$J_{ m SC}$	FF	PCE
[vol%]	[V]	[mA/cm ²]	[%]	[%]
0	0.98	13.30	56.8	7.43 (7.18) ^b
0.3	0.98	13.45	56.2	7.44 (7.19)
0.6	1.00	13.97	59.6	8.33 (8.04)
0.9	1.00	13.00	58.6	7.63 (7.31)

Table S3 Optimization of DIO content for PBD:IT-M inverted solar cells.^a

^a D/A ratio: 1:1.8 (w/w); blend solution: 12 mg/mL in CB; spin-coating: 1800 rpm for 60 s.
^b Data in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of D/A ratio for PBD2T:IT-M inverted solar cells.^a

D/A	$V_{\rm OC}$	$J_{ m SC}$	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:0.6	0.89	14.11	66.1	$8.32(8.04)^b$
1:1	0.90	14.63	71.7	9.41 (9.15)
1:1.4	0.90	14.33	70.6	9.09 (8.94)
1:1.8	0.87	13.79	70.4	8.48 (8.24)

^{*a*} Blend solution: 12 mg/mL in CB; spin-coating: 2300 rpm for 60 s.

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

Thickness	Voc	$J_{ m SC}$	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
122	0.89	13.92	71.1	$8.82(8.63)^b$
103	0.90	14.63	71.7	9.41 (9.15)
85	0.90	13.64	72.8	8.94 (8.72)

Table S5 Optimization of the active layer thickness for PBD2T:IT-M inverted solar cells.^a

^{*a*} D/A ratio: 1:1 (w/w); blend solution: 12 mg/mL in CB.

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

Table S6 Optimization of DIO content for PBD2T:IT-M inverted solar cells.^a

DIO	V _{OC}	$J_{ m SC}$	FF	PCE
[vol%]	[V]	[mA/cm ²]	[%]	[%]
0	0.90	14.63	71.7	9.41 $(9.15)^b$
0.2	0.89	15.95	72.8	10.34 (10.02)
0.4	0.88	15.14	70.6	9.42 (9.14)
0.6	0.88	15.02	68.1	9.04 (8.75)

^a D/A ratio: 1:1 (w/w); blend solution: 12 mg/mL in CB; spin-coating: 2300 rpm for 60 s.
^b Data in parentheses stand for the average PCEs for 10 cells.

8. SCLC

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 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 for hole-only devices, $V_{bi} = 0$ V for electron-only devices.^[4] The mobility was calculated from the slope of $J^{1/2}$ -V plots.



Fig. S9 *J-V* curves (a) and corresponding $J^{1/2}$ -*V* plots (b) for the hole-only devices (in dark). The thicknesses for PBD and PBD2T films are 59 nm and 63 nm, respectively. The μ_h for pure PBD and PBD2T films are 9.7×10⁻⁵ cm² V⁻¹ s⁻¹ and 1.3×10⁻⁴ cm² V⁻¹ s⁻¹, respectively.



Fig. S10 *J-V* curves (a) and corresponding $J^{1/2}$ -*V* plots (b) for the hole-only devices (in dark). The thicknesses for PBD:IT-M and PBD2T:IT-M blend films are 109 nm and 137 nm, respectively.



Fig. S11 *J*-*V* curves (a) and corresponding $J^{1/2}$ -*V* plots (b) for the electron-only devices (in dark). The thicknesses for PBD:IT-M and PBD2T:IT-M blend films are 90 nm and 110 nm, respectively.

Table S7. Hole and electron mobilities for donor:IT-M blend films.

Donor:IT-M	$\mu_{ m h}$ [cm ² V ⁻¹ s ⁻¹]	$\mu_{ m e}$ [cm ² V ⁻¹ s ⁻¹]	$\mu_{ m h}/\mu_{ m e}$
PBD:IT-M	1.89×10^{-4}	3.98×10 ⁻⁵	4.7
PBD2T:IT-M	5.14×10 ⁻⁴	1.44×10 ⁻⁴	3.6

9. XRD



Fig. S12 XRD profiles for pure PBD and PBD2T films.

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