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SHORT COMMUNICATION

Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]oxadiazole-based polymer donors with deep HOMO levels

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SUPPORTING INFORMATION

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. 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 multimode microscope (Veeco) by using tapping mode.

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., Derthon Co., SunaTech Co. and other commercial suppliers. Y6 was purchased from eFlexPV Co. 5,8-Dibromodithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]oxadiazole (DTBO-Br) was purchased from Henan Psai Co. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.

Compound 1. To a solution of DTBO-Br (150 mg, 0.385 mmol) and tributyl(4-(2-butyloctyl)thiophen-2-yl)stannane (624 mg, 1.155 mmol) in toluene (15 mL) was added Pd(PPh$_3$)$_4$ (44.5 mg, 0.039 mmol) under N$_2$. 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 CH$_2$Cl$_2$:petroleum ether (1 : 1) as eluent to give **compound 1** as an orange oil (174 mg, 62%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.81 (s, 2H), 7.10 (s, 2H), 6.90 (s, 2H), 2.55 (d, *J* = 8 Hz, 4H) 1.64 (m, 2H), 1.29 (m, 34H), 0.91–0.88 (m, 12H). ^{13}C NMR (CDCl$_3$, 400 MHz, δ/ppm): 145.52, 143.36, 138.81, 135.15, 134.69, 127.17, 122.96, 121.89, 119.04, 38.83, 34.92, 33.30, 32.98, 31.91, 29.68, 28.85, 26.58, 23.05, 22.69, 14.16, 14.13. MALDI-TOF MS (m/z): $C_{42}H_{56}N_2OS_4$ (M$^+$) calc. 732.33, found 732.53.

Compound 2. To a solution of compound 1 (144 mg, 0.196 mmol) in CHCl$_3$ (12 mL) was added NBS (70 mg, 0.393 mmol) at room temperature. The mixture was stirred for 2 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH$_2$Cl$_2$:petroleum ether (1 : 2) as eluent to give **compound 2** as an orange solid (140 mg, 80%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.86 (s, 2H), 7.01 (s, 2H), 2.52 (d, *J* = 8.0 Hz, 4H), 1.74–1.66 (m, 2H), 1.38–1.22 (m, 32H), 0.91–0.87 (m, 12H). ^{13}C NMR (CDCl$_3$, 400 MHz, δ/ppm): 145.40, 142.77, 137.84, 134.84, 134.67, 126.65, 123.15, 119.33, 110.75, 38.55, 34.23, 33.33, 33.04, 31.91, 29.69, 28.77, 26.51, 23.06, 22.71, 14.15. MALDI-TOF MS (m/z): $C_{42}H_{54}Br_2N_2OS_4$ (M$^+$) calc. 890.15, found 890.38.

P1. To a mixture of compound 2 (50 mg, 0.056 mmol), FBDT-Sn (50.67 mg, 0.054 mmol), Pd$_2$(dba)$_3$ (1.54 mg, 0.0017 mmol) and P(o-Tol)$_3$ (5.12 mg, 0.017 mmol) in a Schlenk flask was added toluene (1 mL) under argon. The mixture was heated to reflux for 16 h. Then, 5 mL chlorobenzene was added and the mixture was stirred for 10 min. The solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using CH$_2$Cl$_2$:CHCl$_3$ (1 : 1), CHCl$_3$ in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **P1** as a brown solid (66 mg, 90%). The M_n for P1 is 38.0 kDa, with a PDI of 2.08. ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.07 (br, aromatic protons), 2.91–3.54 (br, aliphatic protons), 0.87–1.68 (br, aliphatic protons).

P2. To a mixture of compound 2 (50 mg, 0.056 mmol), BDT-Sn (48.73 mg, 0.054 mmol), Pd$_2$(dba)$_3$ (1.54 mg, 0.0017 mmol) and P(o-Tol)$_3$ (5.12 mg, 0.017 mmol) in a Schlenk flask was added toluene (1 mL) under argon. The mixture was heated to reflux for 16 h. Then, 5 mL chlorobenzene was added and the mixture was stirred for 10 min. The solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using CH$_2$Cl$_2$:CHCl$_3$ (1 : 1), CHCl$_3$ and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **P2** as a brown solid (42 mg, 58%). The M_n for P2 is 47.0 kDa, with a PDI of 1.67. ^{1}H NMR (CDCl$_3$, 400 MHz,

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Xiongfeng Li and Jingui Xu contributed equally to this work.

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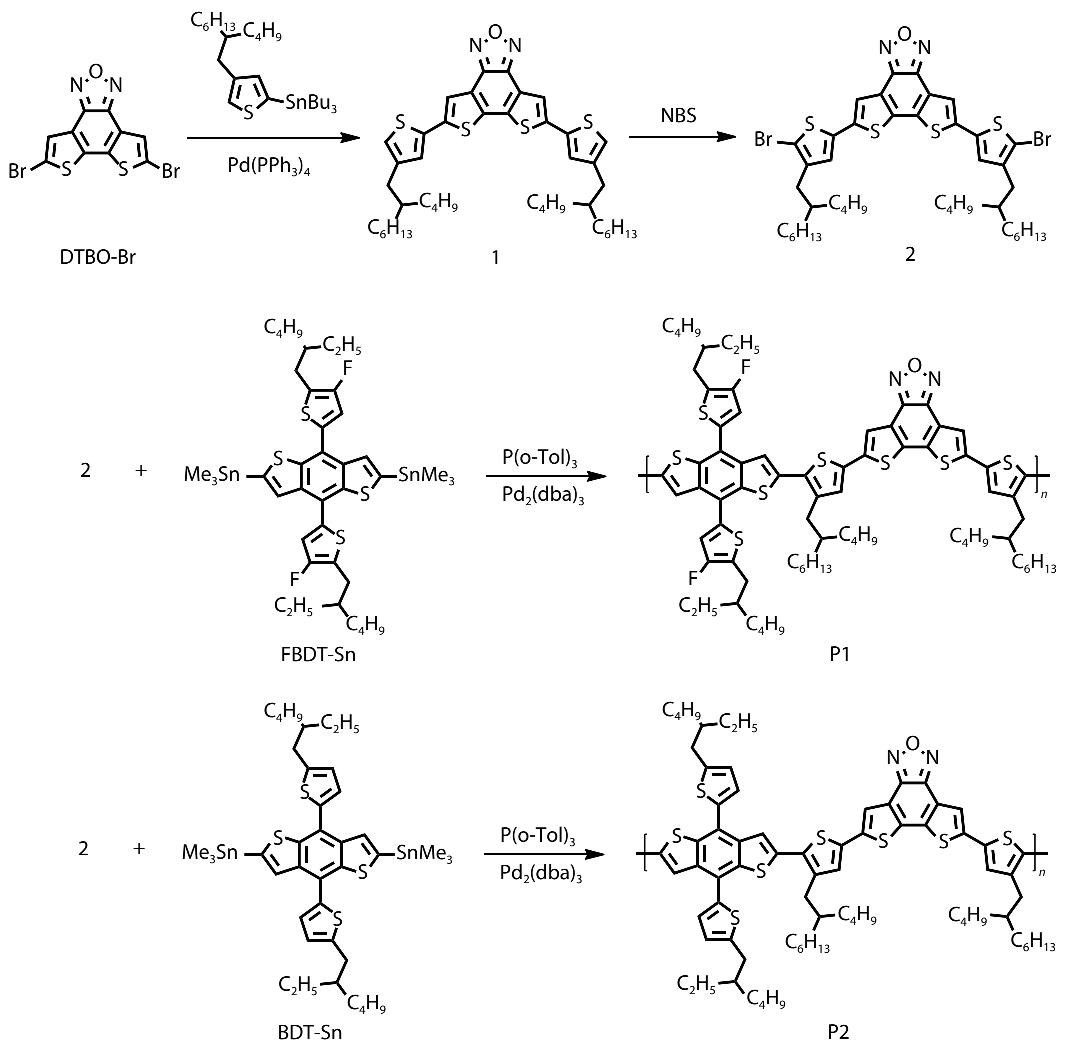

Scheme 1. The synthetic routes for P1 and P2.

δ/ppm): 7.07 (br, aromatic protons), 3.53 (br, aliphatic protons), 0.91–1.67 (br, aliphatic protons).

3. NMR

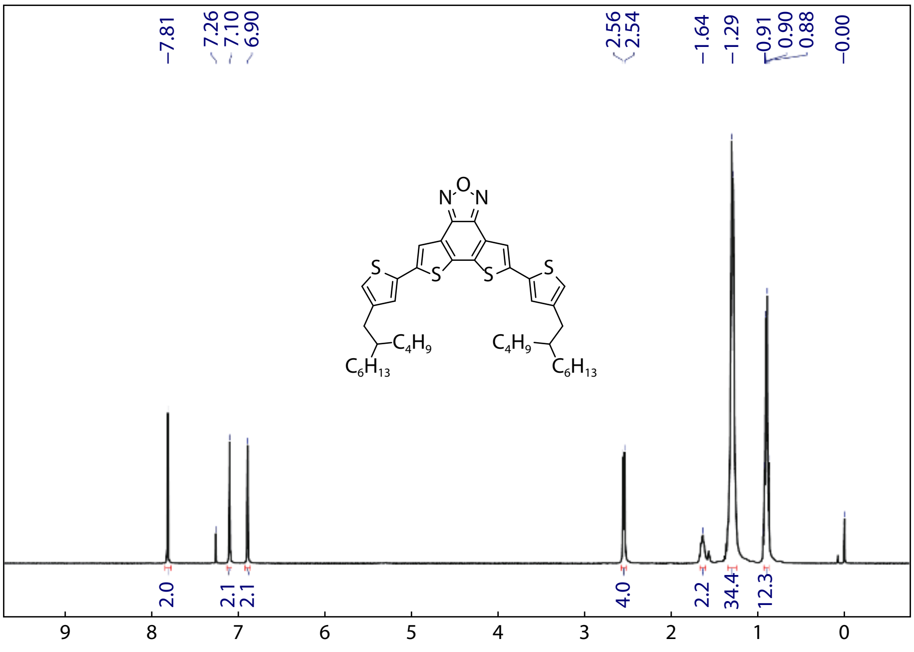

Fig. S1. ^{1}H NMR spectrum of **compound 1**.

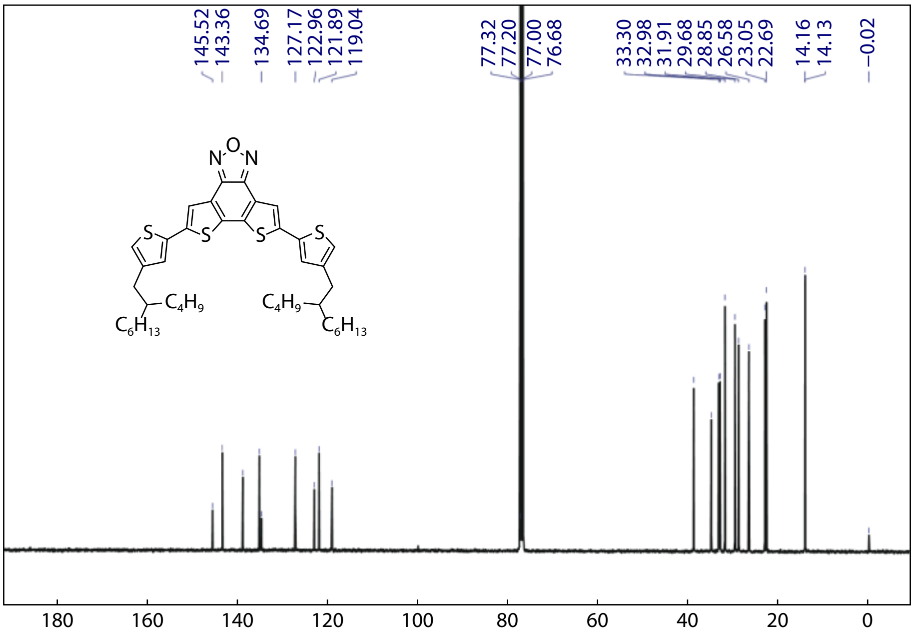

Fig. S2. ^{13}C NMR spectrum of **compound 1**.

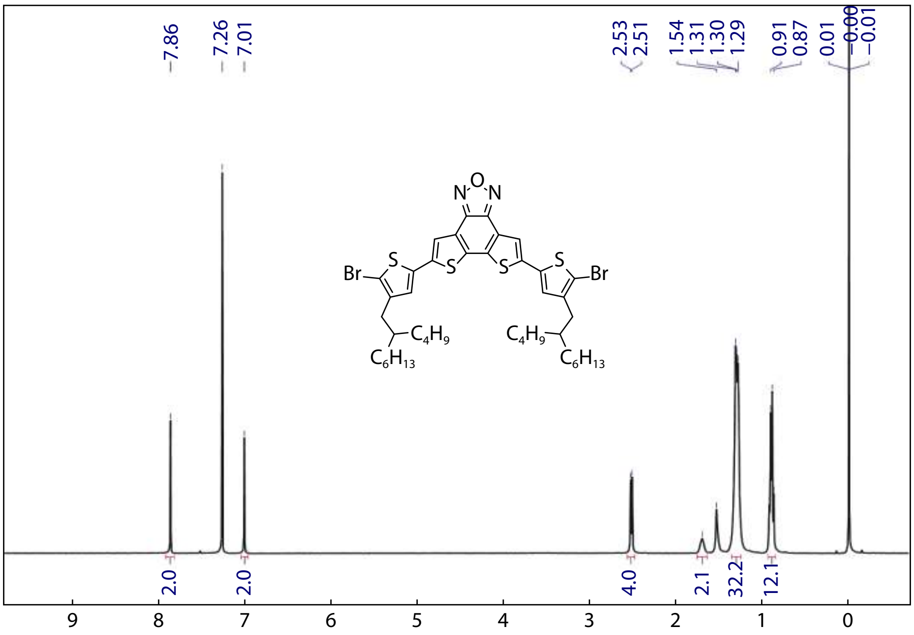

Fig. S3. ^{1}H NMR spectrum of **compound 2**.

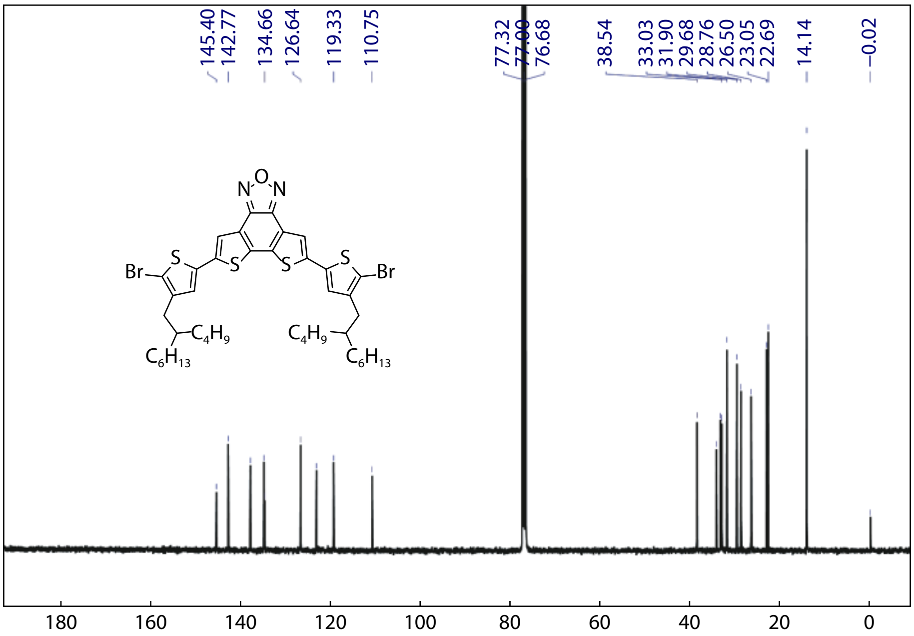

Fig. S4. ^{13}C NMR spectrum of **compound 2**.

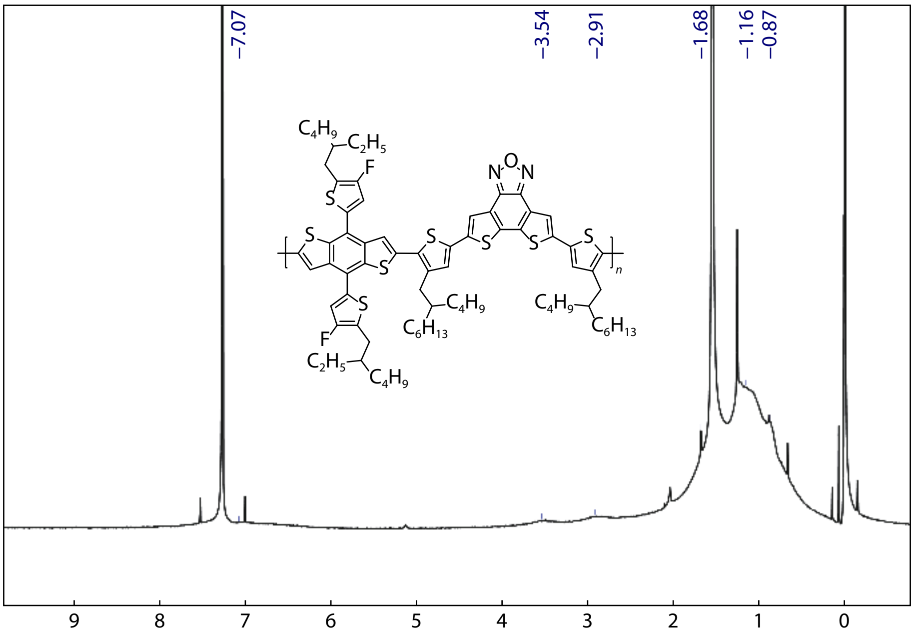

Fig. S5. ^{1}H NMR spectrum of **P1**.

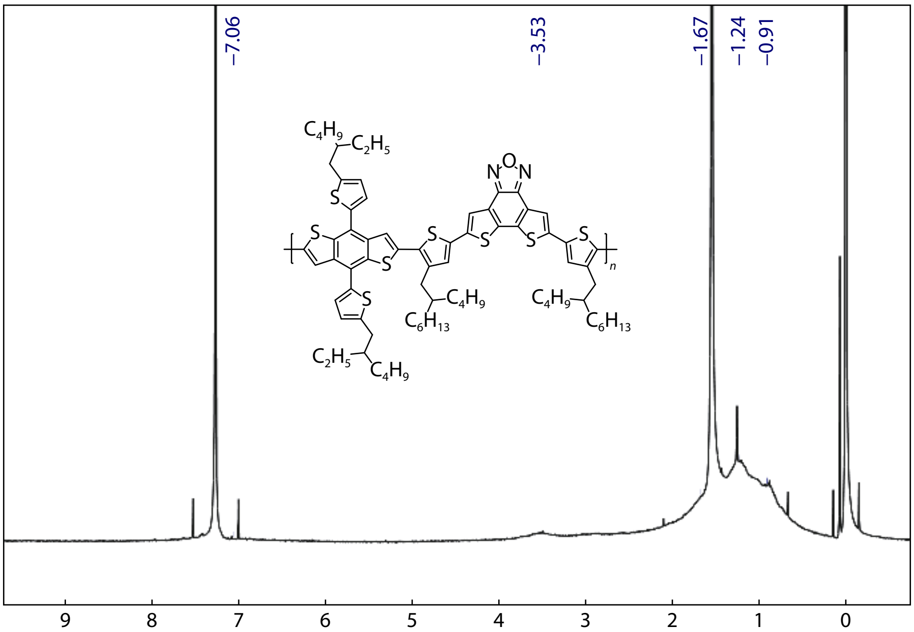

Fig. S6. ^{1}H NMR spectrum of **P2**.

4. Absorption spectra

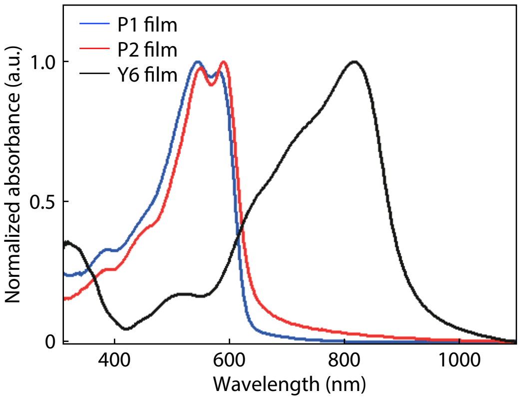

Fig. S7. Absorption spectra for P1, P2 and Y6 films

5. CV

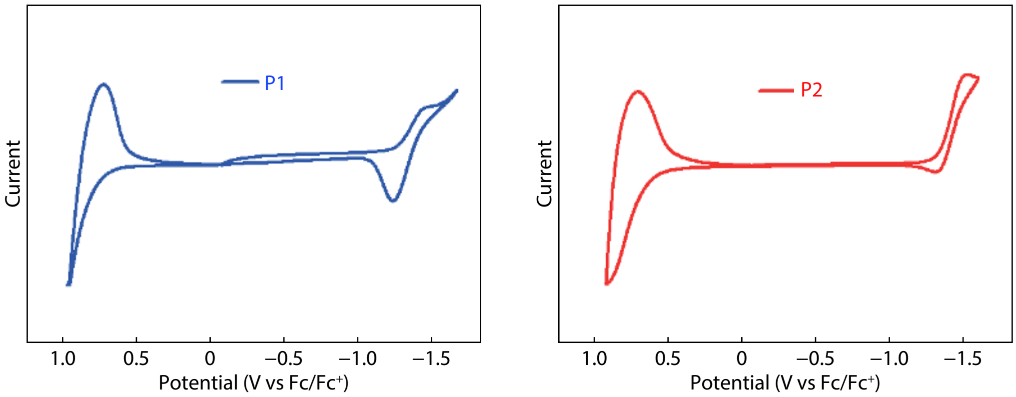

Fig. S8. Cyclic voltammogram for P1 and P2.

6. Energy level diagram

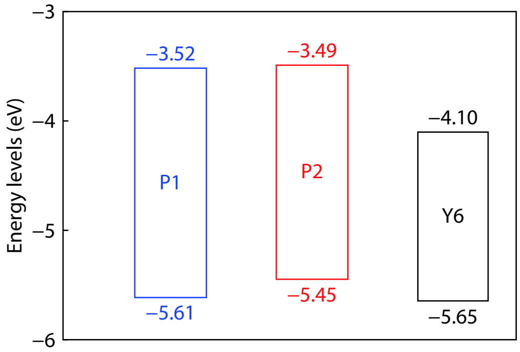

Fig. S9. HOMO and LUMO levels for P1 and P2.

7. Device fabrication and measurements

Conventional solar cells

A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A P1:Y6 (or P2:Y6) blend in chloroform (CF) was spin-coated onto PEDOT:PSS. PDIN (2 mg/mL) in MeOH:AcOH (1000 : 3) was spin-coated onto active layer (5000 rpm for 30 s). Ag (~80 nm) was evaporated onto PDIN through 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 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, 2 × 2 cm^2) 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:PSS substrates were dried at 150 °C for 10 min. A pure P1 (or P2) in CF or a P1:Y6 (or P2:Y6) blend in CF was spin-coated onto PEDOT:PSS. 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.

Electron-only devices

The structure for electron-only devices is ITO/ZnO/active layer/PDIN/Al. The 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. ZnO film thickness is ~30 nm. A P1:Y6 (or P2:Y6) blend in CF was spin-coated onto ZnO. PDIN (2 mg/mL) in MeOH:AcOH (1000:3) was spin-coated onto active layer (5000 rpm for 30 s). Al (~100 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.

8. Optimization of device performance

Table S1. Optimization of D/A ratio for P1:Y6 solar cells[a].

D/A (w/w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
1 : 0.8	0.89	15.90	50.8	7.21 (7.01)[b]
1 : 1.2	0.91	17.33	63.8	10.05 (9.82)
1 : 1.6	0.91	18.22	65.7	10.92 (10.73)
1 : 2	0.91	16.93	64.2	9.85 (9.52)

[a] Blend solution: 15.6 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b] Data in parentheses are averages for 8 cells.

Table S2. Optimization of active layer thickness for P1:Y6 solar cells[a].

Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
210	0.90	17.19	62.1	9.56 (9.36)[b]
160	0.90	17.26	62.2	9.66 (9.54)
110	0.91	18.22	65.7	10.92 (10.73)
100	0.91	17.60	65.4	10.47 (10.27)
70	0.91	17.28	65.3	10.30 (10.03)

[a] D/A ratio: 1 : 1.6 (w/w); blend solution: 15.6 mg/mL in CF.
[b] Data in parentheses are averages for 8 cells.

Table S3. Optimization of CN content for P1:Y6 solar cells[a].

CN (vol%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
0	0.91	18.22	65.7	10.92 (10.73)[b]
0.1	0.91	17.33	63.8	10.05 (9.86)
0.3	0.90	15.77	62.1	8.81 (8.53)
0.5	0.89	14.84	60.8	8.05 (7.81)

[a] D/A ratio: 1 : 1.6 (w/w); blend solution: 15.6 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

[b] Data in parentheses are averages for 8 cells.

Table S4. Optimization of D/A ratio for P2:Y6 solar cells[a].

D/A (w/w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
1 : 0.8	0.82	22.40	71.2	13.11 (12.88)[b]
1 : 1.2	0.82	25.77	72.4	15.33 (15.22)
1 : 1.6	0.83	26.72	70.6	15.64 (15.40)
1 : 2	0.81	25.52	69.9	14.48 (14.23)

[a] Blend solution: 13 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

[b] Data in parentheses are averages for 8 cells.

Table S5. Optimization of active layer thickness for P2:Y6 solar cells[a].

Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
230	0.81	23.28	71.8	13.53 (13.41)[b]
190	0.82	25.27	71.1	14.65 (14.41)
120	0.83	26.72	70.6	15.64 (15.40)
100	0.83	26.15	70.4	15.30 (15.14)
70	0.84	25.56	70.2	14.94 (14.70)

[a] D/A ratio: 1 : 1.6 (w/w); blend solution: 13 mg/mL in CF.

[b] Data in parentheses are averages for 8 cells.

Table S6. Optimization of CN content for P2:Y6 solar cells.[a]

CN (vol%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
0	0.83	26.72	70.6	15.64 (15.40)[b]
0.1	0.83	26.29	69.2	15.02 (14.87)
0.3	0.83	26.15	68.0	14.84 (14.61)
0.5	0.83	25.62	65.2	13.86 (13.77)

[a] D/A ratio: 1 : 1.6 (w/w); blend solution: 13 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

[b] Data in parentheses are averages for 8 cells.

9. Exciton dissociation probability

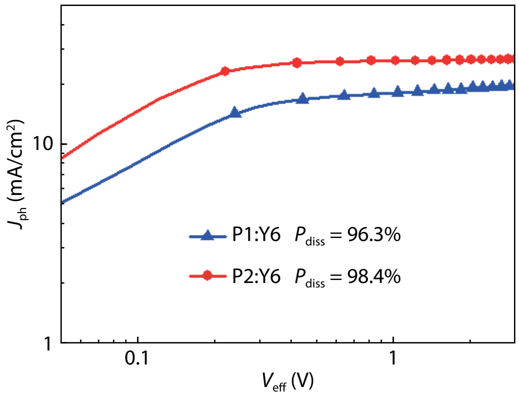

Fig. S10. J_{ph}–V_{eff} plots.

10. 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

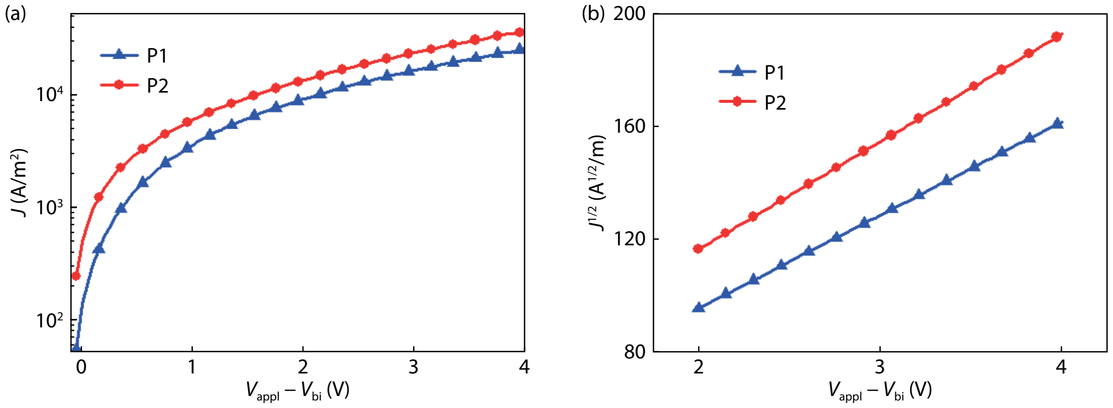

Fig. S11. J–V curves (a) and corresponding $J^{1/2}$–V plots (b) for the hole-only devices (in dark). The thicknesses for P1 and P2 pure films are 112 and 122 nm, respectively.

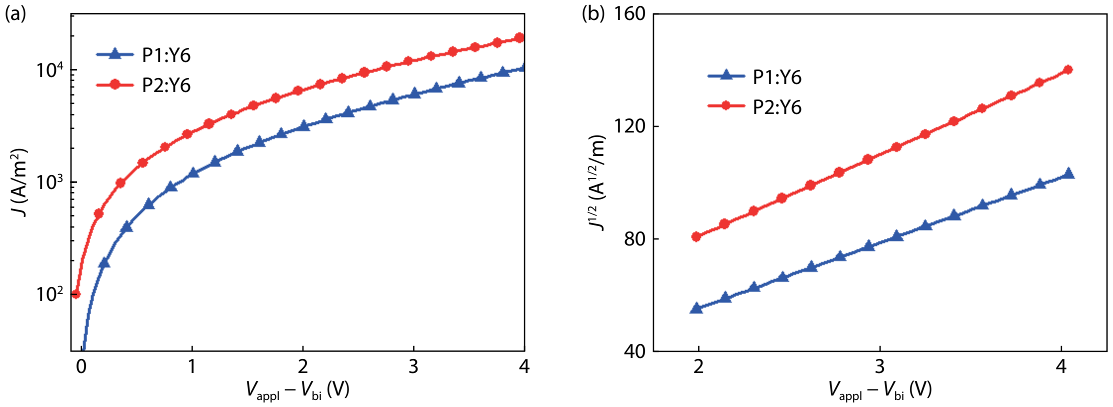

Fig. S12. J–V curves (a) and corresponding $J^{1/2}$–V plots (b) for the hole-only devices (in dark). The thicknesses for P1:Y6 (1 : 1.6) and P2:Y6 (1 : 1.6) blend films are 107 and 112 nm, respectively.

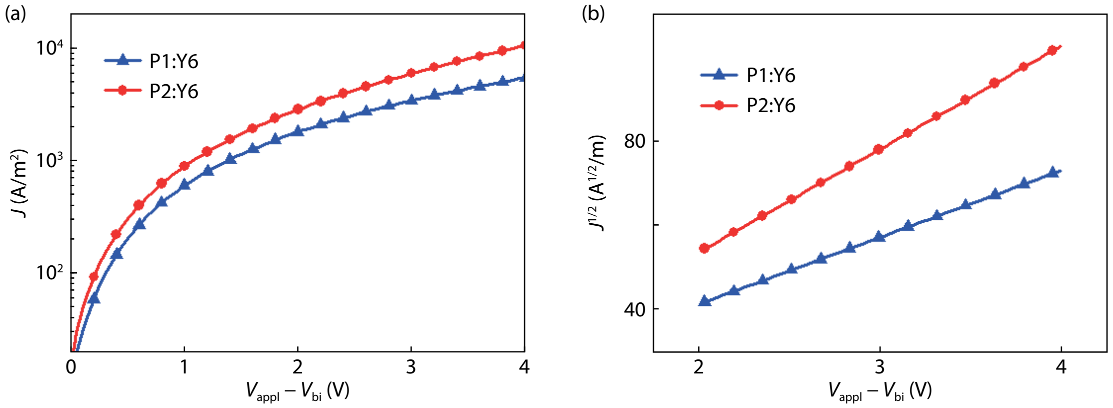

Fig. S13. J–V curves (a) and corresponding $J^{1/2}$–V plots (b) for the electron-only devices (in dark). The thicknesses for P1:Y6 (1 : 1.6) and P2:Y6 (1 : 1.6) blend films are 110 and 114 nm, respectively.

Table 7. Hole and electron mobilities.

Film	μ_h (cm²/(V·s))	μ_e (cm²/(V·s))	μ_h/μ_e
P1	5.13×10^{-4}	–	–
P2	8.82×10^{-4}	–	–
P1:Y6 (1 : 1.6)	2.21×10^{-4}	1.12×10^{-4}	1.97
P2:Y6 (1 : 1.6)	3.92×10^{-4}	2.97×10^{-4}	1.32

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 ($V = V_{appl} - V_{bi}$, 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.[1] The mobility was calculated from the slope of $J^{1/2}$–V plots.

11. Bimolecular recombination

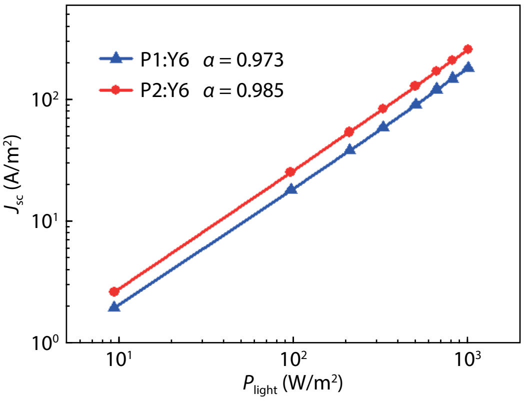

Fig. S14. J_{sc}–P_{light} plots.

12. AFM

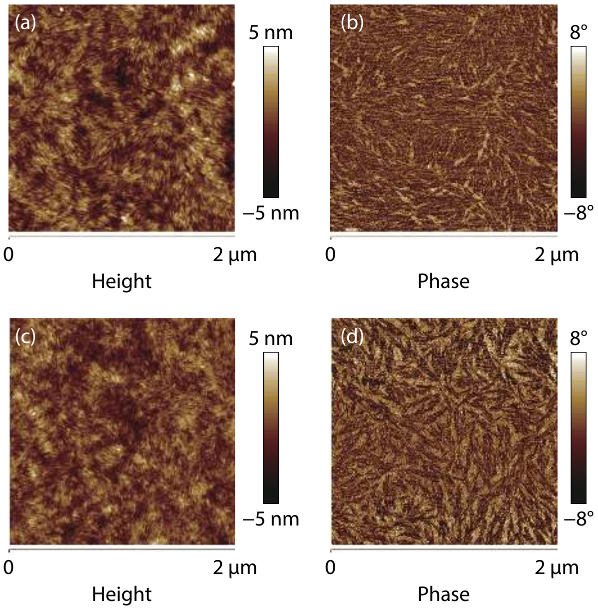

Fig. S15. AFM height (left) and phase (right) images for the blend films. (a, b) P1:Y6 film (R_{rms} = 1.20 nm). (c, d) P2:Y6 film (R_{rms} = 1.02 nm). R_{rms}: root-mean-square roughness.

References

[1] Duan C, Cai W, Hsu B, et al. Toward green solvent processable photovoltaic materials for polymer solar cells: the role of highly polar pendant groups in charge carrier transport and photovoltaic behavior. Energy Environ Sci, 2013, 6, 3022