

Supporting Information

Side chain engineering on D18 polymers yields 18.74% power conversion efficiency

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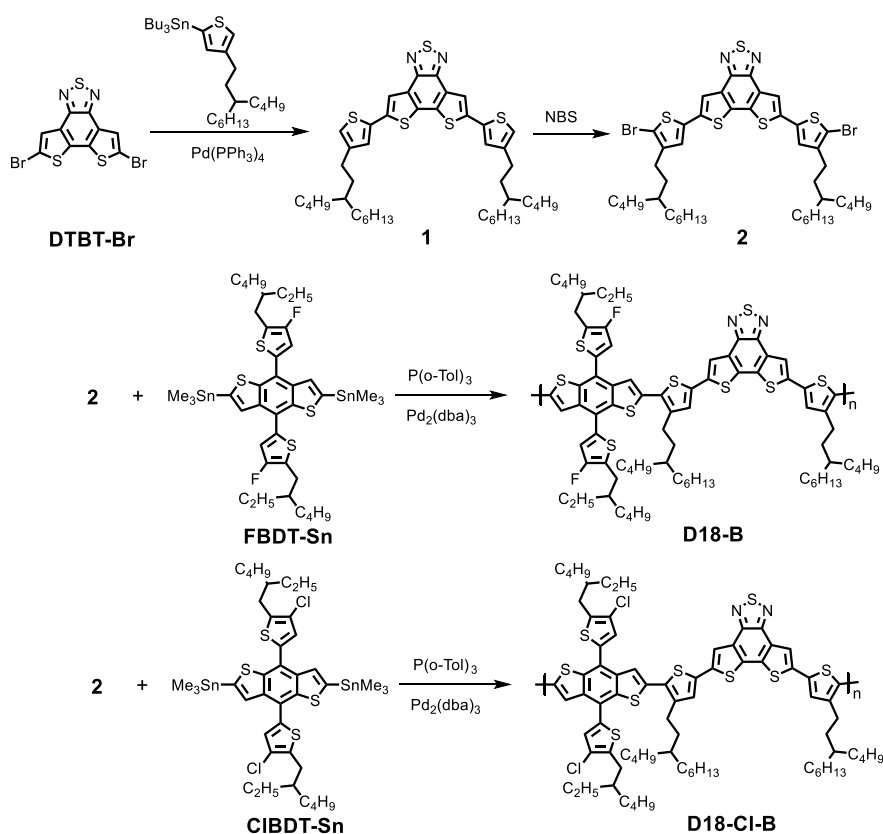
[‡] Xianyi Meng and Ke Jin contributed equally to this work.

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. D18-B or D18-Cl-B was coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc⁺. AFM was performed on a Multimode microscope (Bruker-M8-HR) 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. N3 was purchased from eFlexPV Co. 5,8-Dibromodithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (DTBT-Br) was purchased from Henan Psai Co. FBDT-Sn and ClBDT-Sn were recrystallized twice in isopropyl alcohol before use. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.



Scheme S1. The synthetic routes for D18-B and D18-Cl-B.

Compound 1. To a solution of DTBT-Br (1.45 g, 3.57 mmol) and tributyl(4-(3-butylnonyl)thiophen-2-yl)stannane (5.7 g, 10.26 mmol) in toluene (34 mL) and DMF (7 mL) was added Pd(PPh₃)₄ (412 mg, 0.37 mmol) under N₂. The mixture was heated to reflux and stirred overnight. The reaction mixture was poured into water and extracted with petroleum ether (PE) three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:PE (1:2) as eluent to give **compound 1** as an orange solid (2.1 g, 76%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.86 (s, 2H), 7.11 (d, *J* = 1.3 Hz, 2H), 6.89 (s, 2H), 2.62-2.55 (m, 4H), 1.66-1.58 (m, 4H), 1.30 (m, 34H), 0.95-0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 150.14, 144.71, 137.58, 136.01, 133.27, 129.37, 126.34, 120.37, 119.19, 37.15, 34.38, 33.53, 33.21, 31.97, 29.82, 28.90, 27.75, 26.63, 23.17, 22.74, 14.19, 14.14. MALDI-TOF HRMS (*m/z*): C₄₄H₆₀N₂S₅ (M⁺) calc. 776.3360, found 776.3357.

Compound 2. To a solution of compound 1 (1.48 g, 1.9 mmol) in CHCl₃ (25 mL) and DMF (5 mL) was added NBS (650 mg, 3.65 mmol) at room temperature. The mixture was stirred for 2 h. The reaction mixture was poured into water and extracted with PE three times. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:PE (1:3) as eluent to afford a crude product. The crude product was further recrystallized with CHCl₃/MeOH to yield **compound 2** as an orange solid (1.6 g, 90%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm):

7.68-7.62 (m, 2H), 6.88 (s, 2H), 2.50 (dd, $J = 9.5, 6.9$ Hz, 4H), 1.59-1.50 (m, 4H), 1.31 (m, 34H), 0.97-0.88 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, δ/ppm): 149.82, 143.56, 136.56, 135.70, 132.95, 129.28, 125.52, 119.17, 109.35, 37.21, 33.50, 33.46, 33.14, 31.99, 29.82, 28.91, 26.93, 26.65, 23.17, 22.75, 14.22, 14.16. MALDI-TOF HRMS (m/z): $\text{C}_{44}\text{H}_{58}\text{Br}_2\text{N}_2\text{S}_5$ (M^+) calc. 934.1550, found 934.1544.

D18-B with moderate M_n (D18-B_M). Compound 2 (80.0 mg, 0.086 mmol), FBDT-Sn (76.4 mg, 0.081 mmol), $\text{Pd}_2(\text{dba})_3$ (2.4 mg, 0.0026 mmol) and $\text{P}(\text{o-Tol})_3$ (7.8 mg, 0.026 mmol) in a Schlenk flask was added dry toluene (1.6 mL) under argon. The mixture was heated to reflux and stirred for 16 h. Then the mixture was diluted with chlorobenzene and added into 150 mL MeOH dropwise. The precipitate was collected and further purified via Soxhlet extraction by using $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$ (1:1), CHCl_3 and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into MeOH dropwise. The precipitate was collected and dried under vacuum overnight to give **D18-B_M** as a brown solid (84 mg, 72%). The M_n is 47.2 kDa, with a PDI of 1.89. ^1H NMR (CDCl_3 , 400 MHz, δ/ppm): 7.11 (br, aromatic protons), 2.85 (br, aliphatic protons), 1.69-0.67 (br, aliphatic protons).

D18-B with low M_n (D18-B_L). Compound 2 (80.0 mg, 0.086 mmol), FBDT-Sn (74.0 mg, 0.079 mmol), $\text{Pd}_2(\text{dba})_3$ (2.4 mg, 0.0026 mmol) and $\text{P}(\text{o-Tol})_3$ (7.8 mg, 0.026 mmol) in a Schlenk flask was added dry toluene (1.6 mL) under argon. The mixture was heated to reflux and stirred for 16 h. Then the mixture was diluted with chlorobenzene and added into 150 mL MeOH dropwise. The precipitate was collected and further purified via Soxhlet extraction by using $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$ (1:1) and CHCl_3 in sequence. The CHCl_3 fraction was concentrated and added into MeOH dropwise. The precipitate was collected and dried under vacuum overnight to give **D18-B_L** as a brown solid (111 mg, 97%). The M_n is 33.0 kDa, with a PDI of 1.84.

D18-B with high M_n (D18-B_H). Compound 2 (80.0 mg, 0.086 mmol), FBDT-Sn (77.2 mg, 0.082 mmol), $\text{Pd}_2(\text{dba})_3$ (2.4 mg, 0.0026 mmol) and $\text{P}(\text{o-Tol})_3$ (7.8 mg, 0.026 mmol) in a Schlenk flask was added dry toluene (1.6 mL) under argon. The mixture was heated to reflux and stirred for 16 h. Then the mixture was diluted with chlorobenzene and added into 150 mL MeOH dropwise. The precipitate was collected and further purified via Soxhlet extraction by using $\text{CH}_2\text{Cl}_2:\text{CHCl}_3$ (1:1), CHCl_3 and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into MeOH dropwise. The precipitate was collected and dried under vacuum overnight to give **D18-B_H** as a brown solid (103 mg, 89%). The M_n is 57.0 kDa, with a PDI of 1.95.

D18-Cl-B with moderate M_n (D18-Cl-B_M). Compound 2 (80.0 mg, 0.086 mmol), ClBDT-Sn (80.0 mg, 0.082 mmol), $\text{Pd}_2(\text{dba})_3$ (2.4 mg, 0.0026 mmol) and $\text{P}(\text{o-Tol})_3$ (7.8 mg, 0.026 mmol) in a Schlenk flask was added dry toluene (1.6 mL) under argon. The mixture was heated to reflux and stirred for 16 h. Then the mixture was diluted with chlorobenzene and added into 150 mL MeOH dropwise. The precipitate was

collected and further purified via Soxhlet extraction by using CH₂Cl₂:CHCl₃ (1:1), CHCl₃ and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into MeOH dropwise. The precipitate was collected and dried under vacuum overnight to give **D18-CI-B_M** as a brown solid (86 mg, 72%). The *M_n* is 60.6 kDa, with a PDI of 1.95. ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.12 (br, aromatic protons), 2.93 (br, aliphatic protons), 1.65-0.67 (br, aliphatic protons).

D18-CI-B with low *M_n* (D18-CI-B_L). Compound 2 (80.0 mg, 0.086 mmol), CIBDT-Sn (77.4 mg, 0.080 mmol), Pd₂(dba)₃ (2.4 mg, 0.0026 mmol) and P(o-Tol)₃ (7.8 mg, 0.026 mmol) in a Schlenk flask was added dry toluene (1.6 mL) under argon. The mixture was heated to reflux and stirred for 16 h. Then the mixture was diluted with chlorobenzene and added into 150 mL MeOH dropwise. The precipitate was collected and further purified via Soxhlet extraction by using CH₂Cl₂:CHCl₃ (1:1) and CHCl₃ in sequence. The CHCl₃ fraction was concentrated and added into MeOH dropwise. The precipitate was collected and dried under vacuum overnight to give **D18-CI-B_L** as a brown solid (100 mg, 85%). The *M_n* is 38.1 kDa, with a PDI of 1.98.

D18-CI-B with high *M_n* (D18-CI-B_H). Compound 2 (72.0 mg, 0.077 mmol), CIBDT-Sn (74.21 mg, 0.076 mmol), Pd₂(dba)₃ (2.1 mg, 0.0023 mmol) and P(o-Tol)₃ (7.0 mg, 0.023 mmol) in a Schlenk flask was added dry toluene (1.5 mL) under argon. The mixture was heated to reflux and stirred for 16 h. Then the mixture was diluted with chlorobenzene and added into 150 mL MeOH dropwise. The precipitate was collected and further purified via Soxhlet extraction by using CH₂Cl₂:CHCl₃ (1:1), CHCl₃ and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into MeOH dropwise. The precipitate was collected and dried under vacuum overnight to give **D18-CI-B_H** as a brown solid (76 mg, 70%). The *M_n* is 68.6 kDa, with a PDI of 2.06.

3. NMR

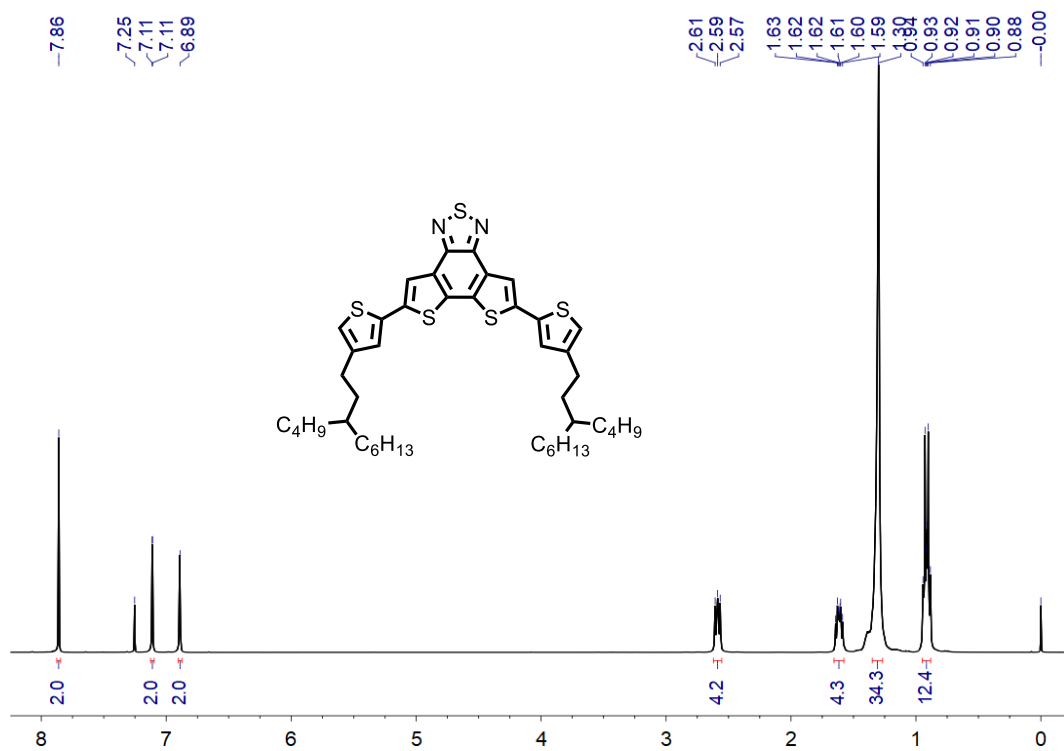


Fig. S1 ¹H NMR spectrum of compound 1.

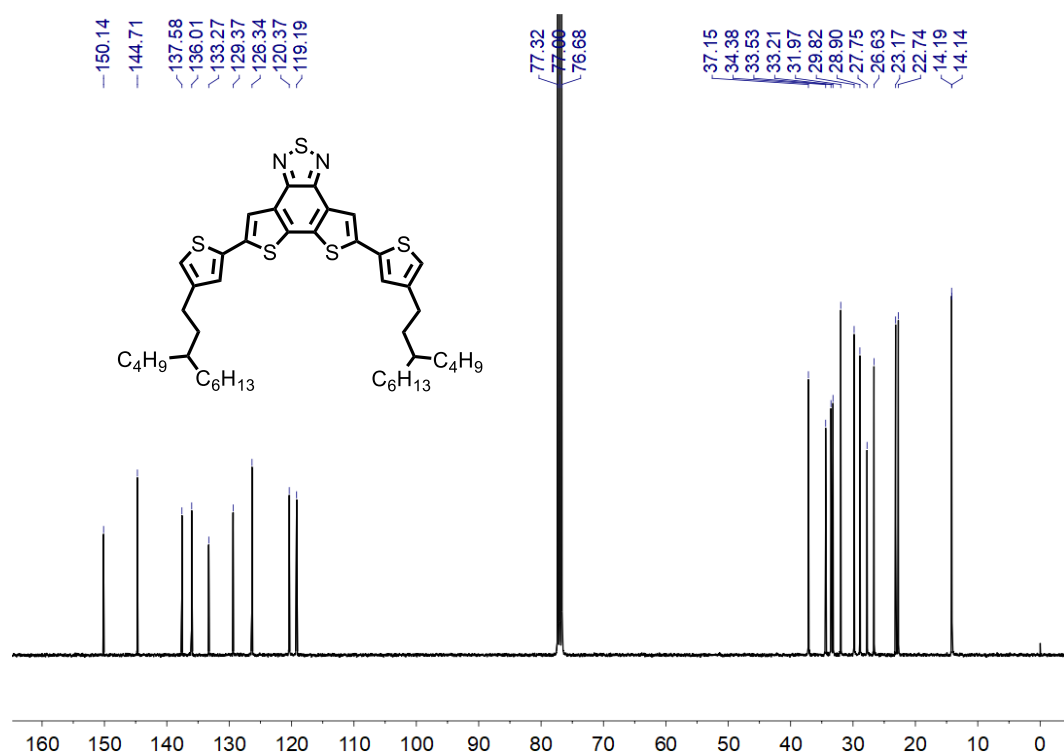


Fig. S2 ¹³C NMR spectrum of compound 1.

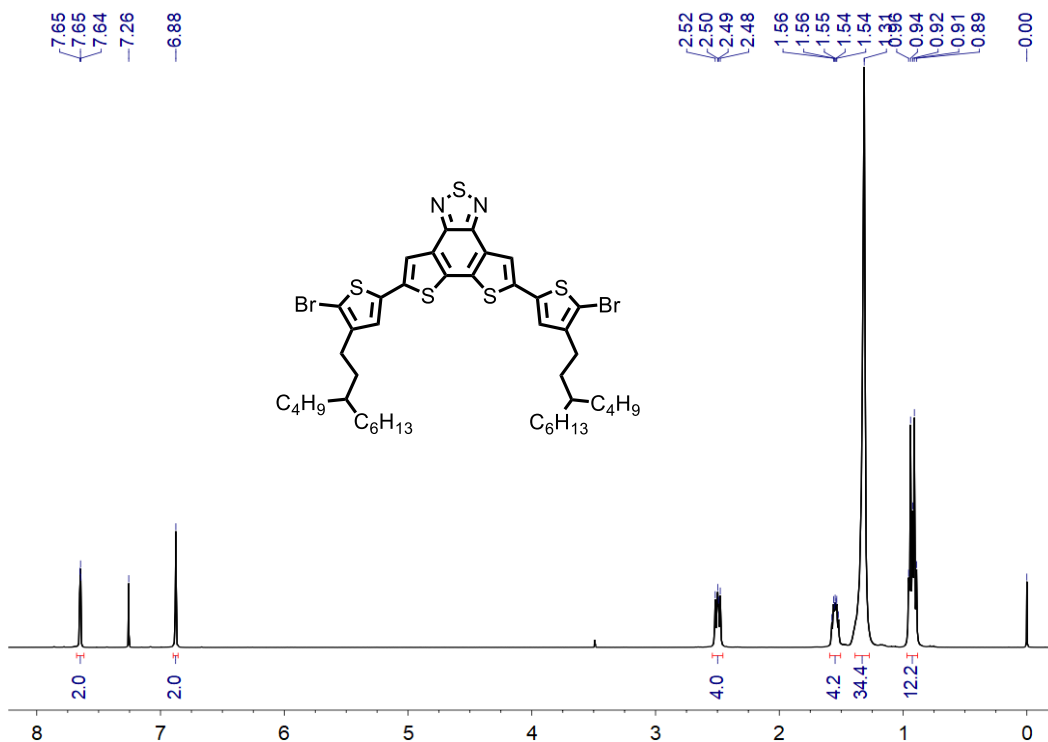


Fig. S3 ^1H NMR spectrum of compound 2.

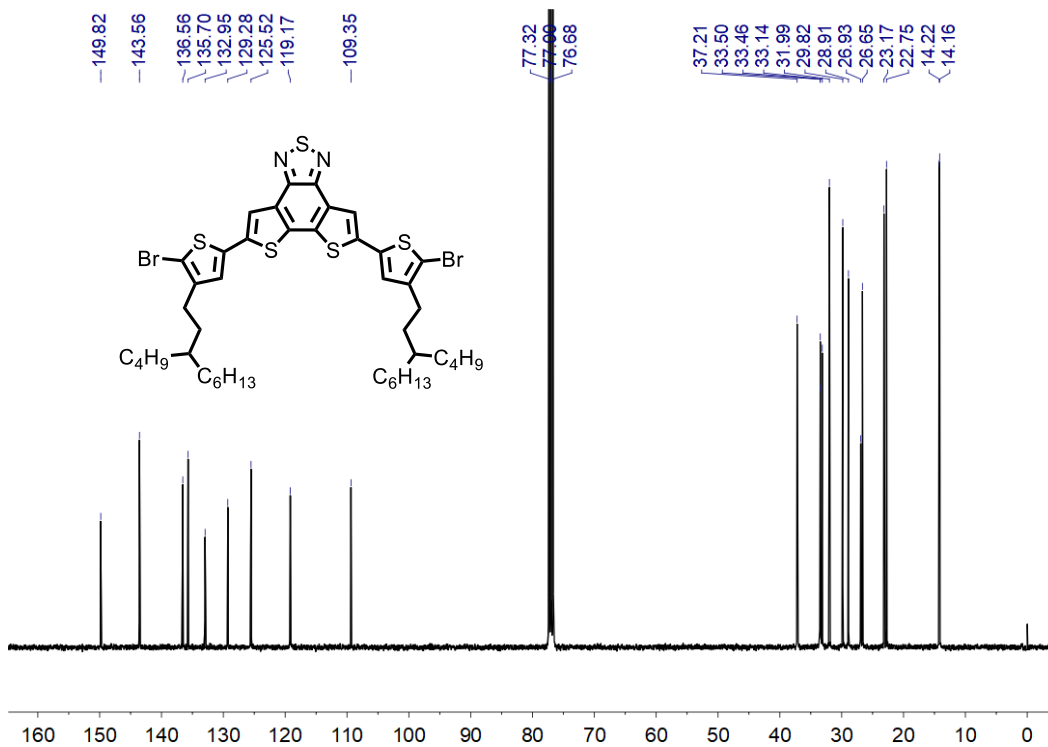


Fig. S4 ^{13}C NMR spectrum of compound 2.

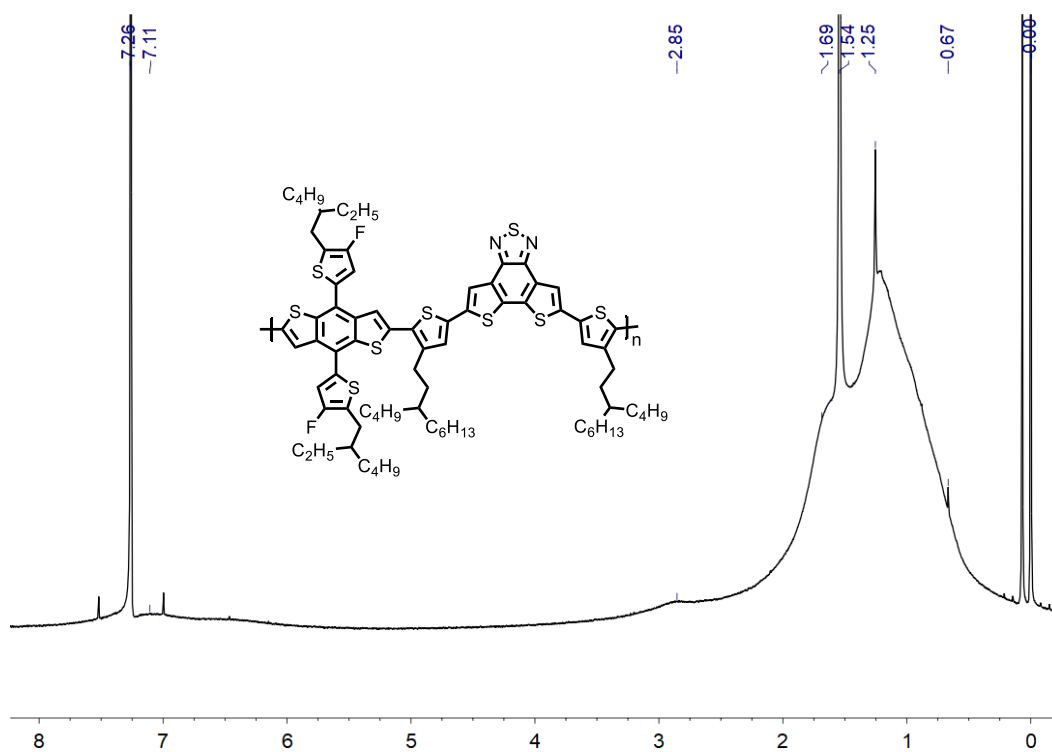


Fig. S5 ¹H NMR spectrum of **D18-B**.

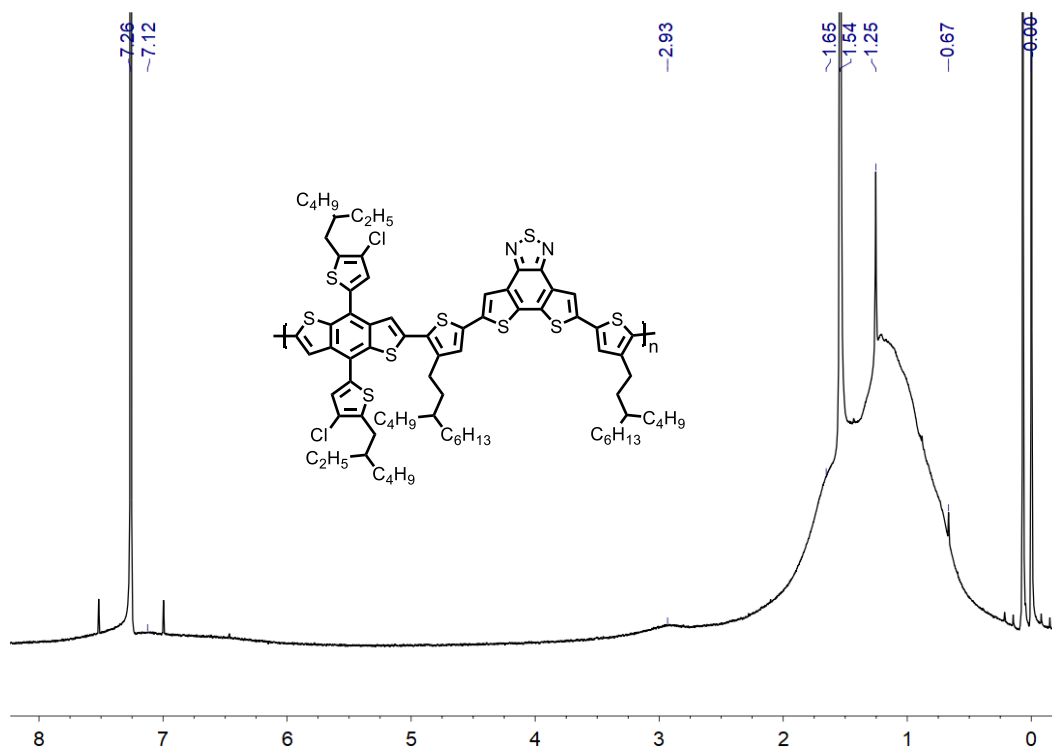


Fig. S6 ¹H NMR spectrum of **D18-Cl-B**.

4. UV-Vis

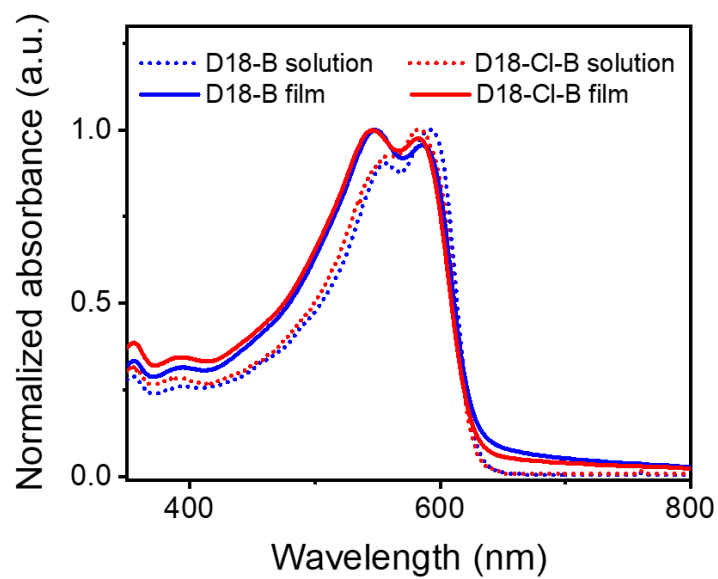


Fig. S7 Absorption spectra for D18-B and D18-Cl-B in chloroform and as films.

5. CV

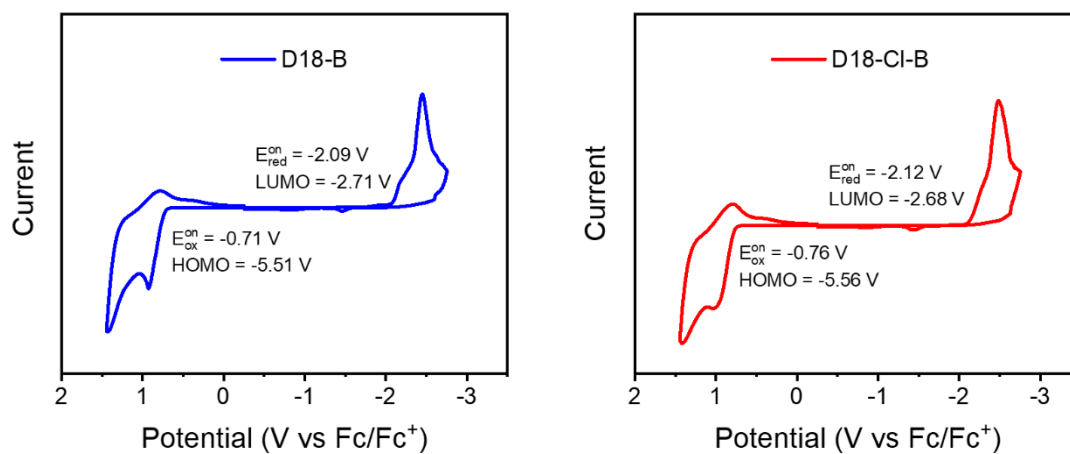


Fig. S8 Cyclic voltammograms for D18-B and D18-Cl-B.

6. 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 D18-B:N3:PC₆₁BM (or D18-Cl-B:N3:PC₆₁BM) blend in chloroform (CF) was spin-coated onto PEDOT:PSS layer. 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 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 the National Institute of Metrology (NIM). The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech). The best cells were further tested at NIM for certification. A metal mask with an aperture (2.580 mm²) was used to define the effective area.

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/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:PSS substrates were dried at 150 °C for 10 min. A pure D18-B (or D18-Cl-B) in CF was spin-coated onto PEDOT:PSS 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.

7. 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, 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 work function difference). Here, $V_{\text{bi}} = 0.1$ V for hole-only devices.^[1] The mobility was calculated from the slope of $J^{1/2}$ - V plot.

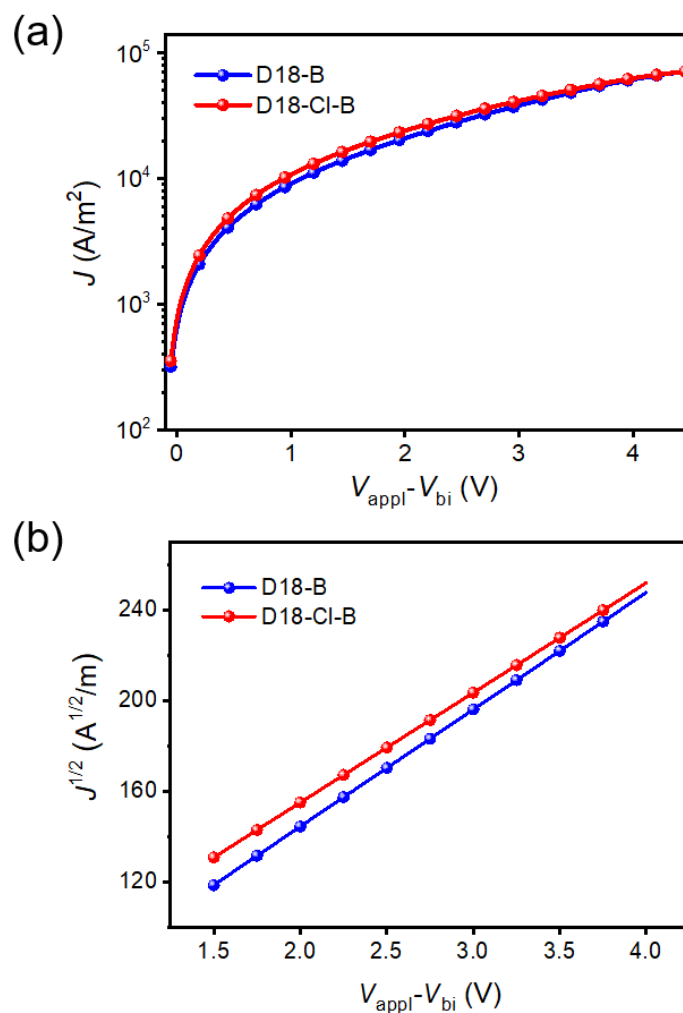


Fig. S9 J - V curves (a) and corresponding $J^{1/2}$ - V plots (b) for the hole-only devices (in dark). The thicknesses for D18-B and D18-Cl-B films are 99 nm and 96 nm, respectively.

8. Optimization of device performance

Table S1 Optimization of D/A ratio for D18-B:N3 solar cells.^a

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:1	0.821	26.06	75.2	16.09 (16.06) ^b
1:1.2	0.825	26.59	76.9	16.87 (16.60)
1:1.4	0.827	26.75	77.3	17.09 (17.00)
1:1.6	0.825	25.95	78.6	16.84 (16.73)

^aBlend solution: 13 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S2 Optimization of PC₆₁BM content for D18-B:N3:PC₆₁BM solar cells.^a

D18-B:N3:PC ₆₁ BM	V_{oc}	J_{sc}	FF	PCE
[w/w/w]	[V]	[mA/cm ²]	[%]	[%]
1:1.4:0	0.827	26.75	77.3	17.09 (17.00) ^b
1:1.4:0.1	0.830	27.08	77.7	17.45 (17.33)
1:1.4:0.2	0.832	27.66	77.8	17.91 (17.70)
1:1.4:0.3	0.831	27.76	77.0	17.75 (17.57)

^aBlend solution: 13 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of DPE content for D18-B:N3:PC₆₁BM solar cells.^a

DPE [vol%]	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.832	27.66	77.8	17.91 (17.70) ^b
0.25	0.825	28.00	78.9	18.24 (18.20)
0.5	0.823	28.50	79.0	18.53 (18.40)
0.75	0.819	28.41	78.6	18.29 (18.12)

^aD18-B:N3:PC₆₁BM ratio: 1:1.4:0.2 (w/w/w); blend solution: 13 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of the active layer thickness for D18-B:N3:PC₆₁BM solar cells.^a

Thickness [nm]	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
140	0.815	28.32	76.9	17.75 (17.60) ^b
119	0.823	28.50	79.0	18.53 (18.40)
106	0.823	27.72	79.6	18.15 (18.11)
93	0.825	27.30	80.1	18.04 (17.99)

^aD18-B:N3:PC₆₁BM ratio: 1:1.4:0.2 (w/w/w); blend solution: 13 mg/mL in CF with 0.5 vol% DPE.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of D/A ratio for D18-Cl-B:N3 solar cells.^a

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:1	0.845	25.47	76.8	16.52 (16.50) ^b
1:1.2	0.844	26.89	76.2	17.30 (17.18)
1:1.4	0.844	27.25	76.9	17.69 (17.60)
1:1.6	0.841	27.24	76.1	17.43 (17.41)

^aBlend solution: 12.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of PC₆₁BM content for D18-Cl-B:N3:PC₆₁BM solar cells.^a

D18-Cl-B:N3:PC ₆₁ BM	V_{oc}	J_{sc}	FF	PCE
[w/w/w]	[V]	[mA/cm ²]	[%]	[%]
1:1.4:0	0.844	27.25	76.9	17.69 (17.60) ^b
1:1.4:0.1	0.846	27.18	79.2	18.21 (17.97)
1:1.4:0.2	0.845	27.50	78.5	18.23 (17.99)
1:1.4:0.3	0.844	27.52	76.3	17.73 (17.38)

^aBlend solution: 12.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of DPE content for D18-Cl-B:N3:PC₆₁BM solar cells.^a

DPE [vol%]	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.845	27.50	78.5	18.23 (17.99) ^b
0.25	0.837	27.96	78.4	18.35 (18.18)
0.5	0.836	28.50	78.7	18.74 (18.52)
0.75	0.833	28.28	78.8	18.55 (18.34)

^aD18-Cl-B:N3:PC₆₁BM ratio: 1:1.4:0.2 (w/w/w); blend solution: 12.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of the active layer thickness for D18-Cl-B:N3:PC₆₁BM solar cells.^a

Thickness [nm]	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
133	0.831	27.61	78.6	18.02 (17.71) ^b
118	0.836	28.50	78.7	18.74 (18.52)
109	0.834	28.03	79.6	18.61 (18.38)
95	0.835	27.53	79.8	18.33 (18.17)

^a D18-Cl-B:N3:PC₆₁BM ratio: 1:1.4:0.2 (w/w/w); blend solution: 12.5 mg/mL in CF with 0.5 vol% DPE.

^bData in parentheses stand for the average PCEs for 10 cells.

9. NIM certification for D18-Cl-B:N3:PC₆₁BM solar cells

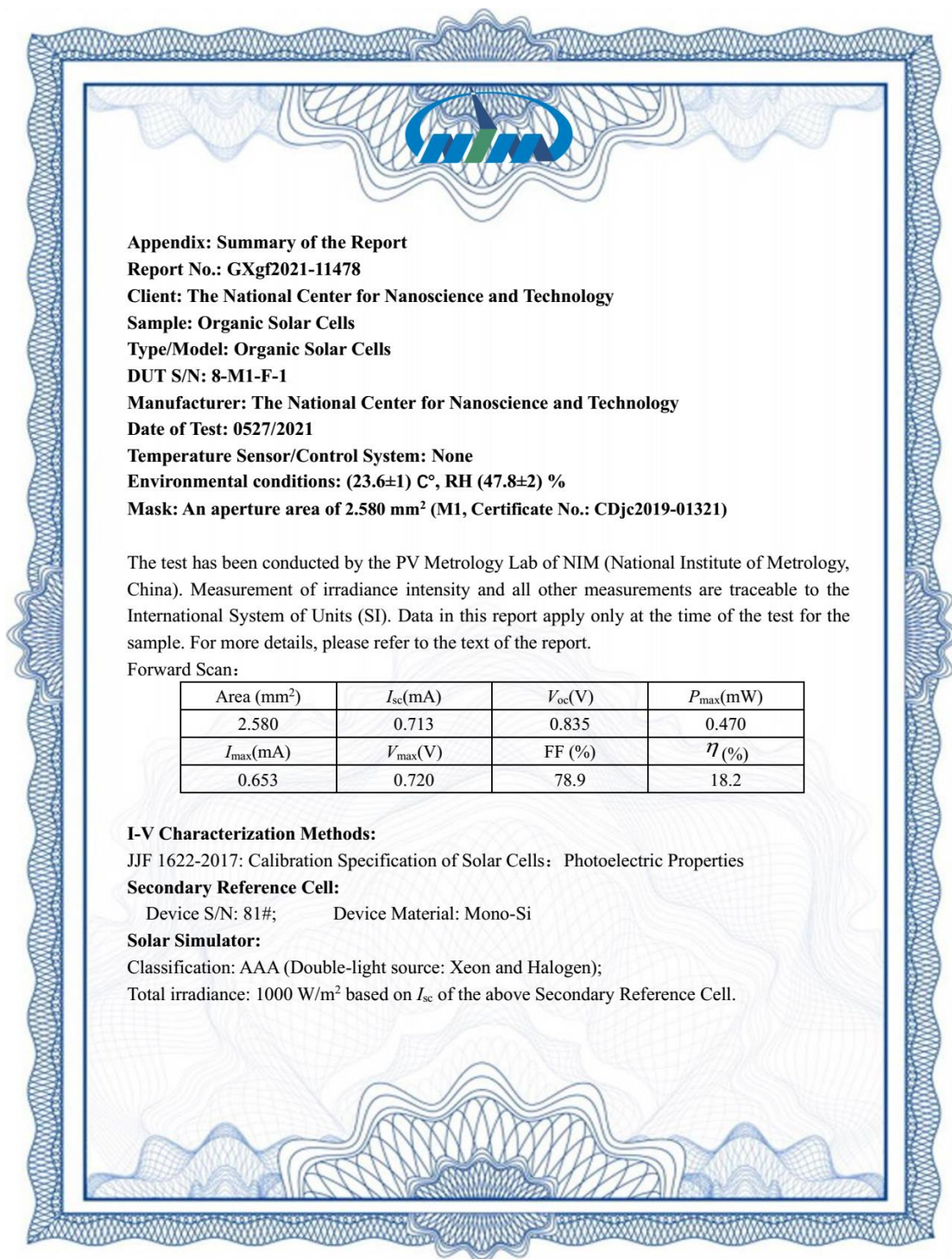


Fig. S10 NIM (Beijing) report for D18-Cl-B:N3:PC₆₁BM solar cells.

10. AFM

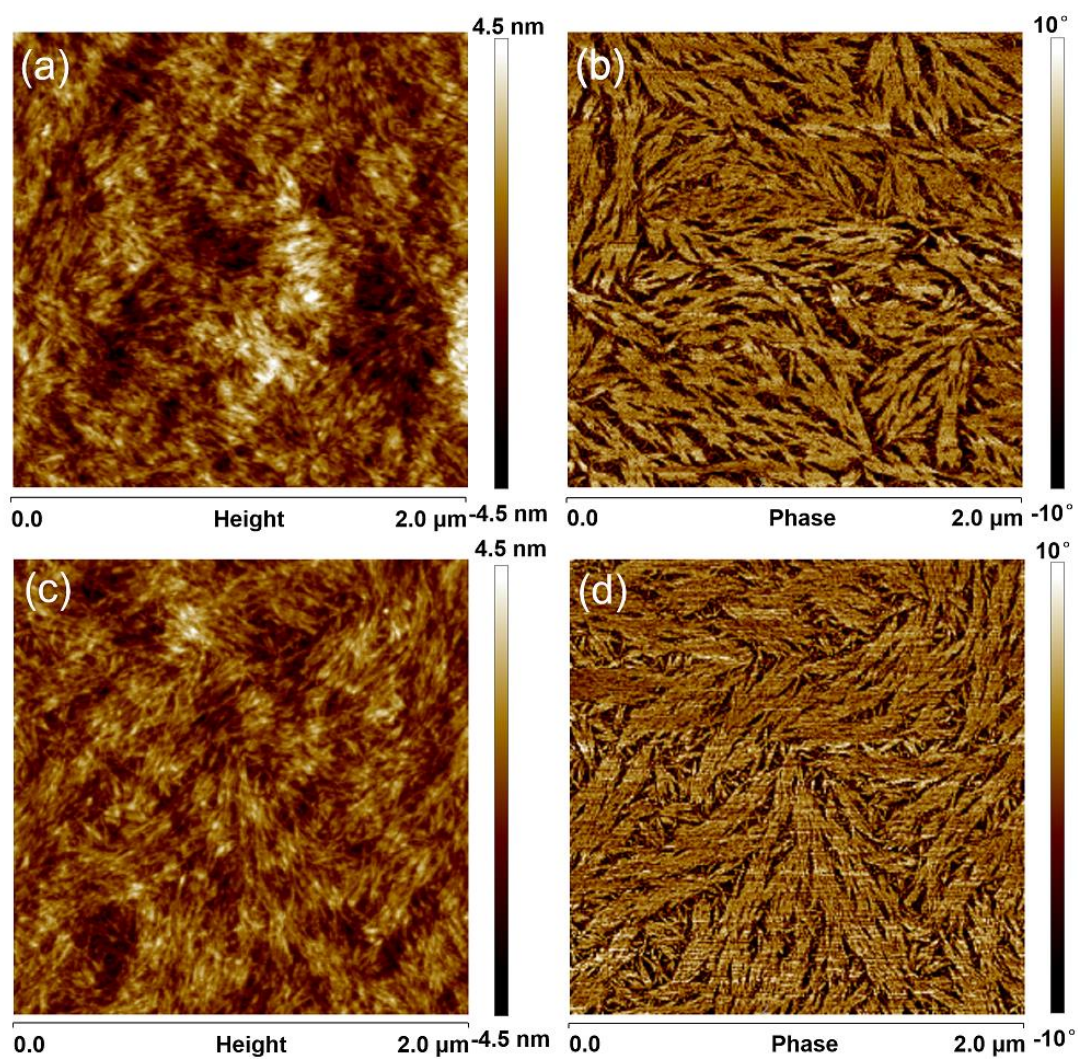


Fig. S11 AFM height (left) and phase (right) images for blend films. (a) and (b), D18-B:N3:PC₆₁BM ($R_{\text{rms}} = 1.27$ nm); (c) and (d), D18-Cl-B:N3:PC₆₁BM ($R_{\text{rms}} = 1.04$ nm). R_{rms} : root-mean-square roughness.

Reference

- [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