

Supporting Information

**Enhanced photovoltaic performance of donor polymers effected by
asymmetric π -bridges**

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Materials Synthesis

All reagents were purchased from Sigma–Aldrich. All of the commercially available compounds and reagents were used without any further treatment unless stated otherwise.

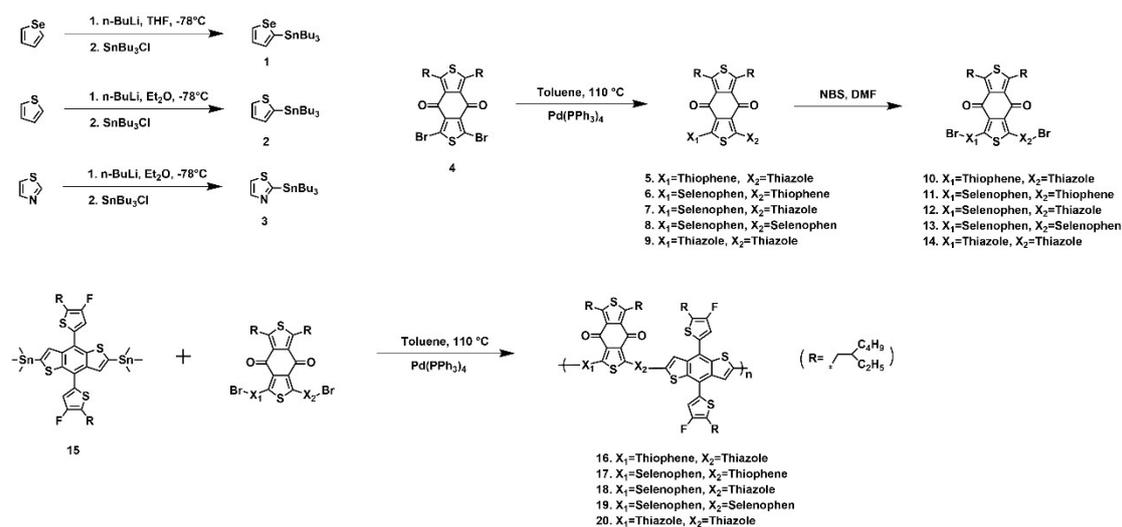


Figure S1. The synthetic routes of the monomers and polymers.

(1). tributyl(selenophen-2-yl)stannane.

Selenophene (2.00 g, 15.26 mmol) was dissolved in dry THF (20 mL) and placed under argon atmosphere. The solution was placed into an ice bath and stirred while 2.4 M *n*-butyllithium in hexane (8.27 mL, 19.84 mmol) was added dropwise. The mixture was stirred for another 2.5 hours at -78°C , then tributylchlorostannane (7.45 g, 22.89 mmol) was added. The solution was warmed to room temperature and stirred overnight. Then it was poured into water and extracted with petroleum ether. The organic phase was combined and dried over anhydrous Na_2SO_4 . After removal of the solvent, the crude product (1) was utilized for the next step without further purification.

(2). tributyl(thiophen-2-yl)stannane.

Thiophen (2.00 g, 23.77 mmol) was dissolved in dry ether (25 mL) and placed under argon atmosphere. The solution was cooled to -78 °C and stirred while 2.4 M *n*-butyllithium in hexane (10.40 mL, 24.96 mmol) was added dropwise. The mixture was stirred for another 2.0 hours at -78 °C, then tributylchlorostannane (8.51 g, 26.15 mmol) was added. The solution was warmed to room temperature and stirred overnight. Then it was poured into water and extracted with petroleum ether. The organic phase was combined and dried over anhydrous Na_2SO_4 . After removal of the solvent, the crude product (2) was utilized for the next step without further purification.

(3). *2-(tributylstannyl)thiazole*.

Thiazole (3.00 g, 35.24 mmol) was dissolved in dry ether (30 mL) and placed under argon atmosphere. The solution was cooled to -78 °C and stirred while 2.4 M *n*-butyllithium in hexane (15.41 mL, 37.01 mmol) was added dropwise. The mixture was stirred for another 2.0 hours at -78 °C, then tributylchlorostannane (12.62 g, 38.71 mmol) was added. The solution was warmed to room temperature and stirred overnight. Then it was poured into water and extracted with petroleum ether. The organic phase was combined and dried over anhydrous Na_2SO_4 . After removal of the solvent, the crude product (3) was utilized for the next step without further purification.

(5). *1,3-bis(2-ethylhexyl)-5-(thiazol-2-yl)-7-(thiophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione*.

Compound 4 (1.00 g, 1.66 mmol), compound 2 (0.68 g, 1.83 mmol), compound 3 (0.68 g, 1.83 mmol) and $\text{Pd}(\text{PPh}_3)_4$, was mixed into 15 mL of toluene under argon protection. The reaction was stirred at 110 °C for 12 hours and then the solvent was removed by rotary evaporator. The product (5) was purified by silica gel

chromatographic column using DCM and PE as eluent. (0.86 g, yield=84 %). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.89–7.88(d, 1H), 7.81–7.79 (m, 1H), 7.49–7.46 (m, 2H), 7.08–7.06 (m, 1H), 3.24–3.21 (m, 4H), 1.74–1.68 (m, 2H), 1.39–1.31 (m, 6H), 1.29–1.18 (m, 10H), 0.91–0.80 (m, 12H).

(6).

1,3-bis(2-ethylhexyl)-5-(selenophen-2-yl)-7-(thiophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

The synthetic method for compound 6 is the same as that for compound 5 (0.76 g, yield=69 %). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.28–8.27(m, 1H), 7.94–7.93 (m, 1H), 7.77–7.76 (m, 1H), 7.51–7.49 (m, 1H), 7.39–7.37 (m, 1H), 7.14–7.11 (m, 1H), 3.37–3.26 (m, 4H), 1.81–1.70 (m, 2H), 1.29–1.18 (m, 10H), 1.42–1.33 (m, 10H), 1.31–1.25 (m, 6H), 0.96–0.91 (m, 5H), 0.90–0.86 (m, 7H).

(7).

1,3-bis(2-ethylhexyl)-5-(selenophen-2-yl)-7-(thiazol-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

The synthetic method for compound 7 is the same as that for compound 5 (0.73 g, yield=75 %). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.32–8.31(m, 1H), 8.11–8.10 (m, 1H), 7.97–7.96 (d, 1H), 7.56–7.55 (d, 1H), 7.42–7.39 (m, 1H), 3.37–3.30 (m, 4H), 1.83–1.78 (m, 2H), 1.46–1.36 (m, 9H), 1.32–1.25 (m, 7H), 0.97–0.93 (m, 6H), 0.91–0.88 (m, 6H).

(8).

1,3-bis(2-ethylhexyl)-5,7-di(selenophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophe

ne–4,8–dione.

The synthetic method for compound 8 is consistent with the findings of Hou.¹

(9).

1,3-bis(2-ethylhexyl)-5,7-di(thiazol-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

The synthetic method for compound 9 is consistent with the findings of Yang.²

(10).

1-(5-bromothiazol-2-yl)-3-(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

Compound 5 (0.36 g, 0.59 mmol) was dissolved into 12 mL of DMF at room temperature, and NBS (0.21 g, 1.20 mmol) was added into the flask in several portions. After the completion of the reaction, the resultant solution was poured into 100 mL water and extracted by petroleum ether. The raw product was obtained by concentrating the collected organic phase and compound 10 was then purified by silica gel chromatographic column using DCM and PE as eluent. (0.33 g, yield=73 %). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.73(s, 1H), 7.47–7.46 (d, 1H), 7.00–6.99 (d, 1H), 3.29–3.14 (m, 4H), 1.76–1.65 (m, 2H), 1.37–1.18 (m, 16H), 0.89–0.81 (m, 12H). ¹³C NMR (CDCl₃, 101 MHz), δ (ppm): 177.82, 158.39, 152.22, 147.55, 141.38, 133.47, 124.81, 40.11, 35.67, 31.23, 28.22, 26.06, 23.02, 15.12, 10.88.

(11).

1-(5-bromoselenophen-2-yl)-3-(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

The synthetic method for compound 11 is the same as that for compound 10 (0.2 g, yield=68 %). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.61–7.60 (d, 1H), 7.46–7.44 (d, 1H), 7.32–7.31 (d, 1H), 7.07–7.05 (d, 1H), 3.35–3.22 (m, 4H), 1.78–1.74 (m, 2H), 1.44–1.23 (m, 16H), 0.96–0.89 (m, 12H). ¹³C NMR (CDCl₃, 101 MHz), δ (ppm): 178.64, 176.53, 154.40, 152.85, 146.11, 140.63, 137.61, 134.17, 133.68, 132.59, 132.41, 131.68, 131.15, 130.75, 128.83, 127.21, 124.96, 116.89, 40.38, 34.55, 34.13, 32.91, 32.02, 30.41, 28.89, 28.37, 25.63, 24.02, 23.73, 17.27, 13.41, 11.79, 10.86, 9.68, 9.47, 2.10.

(12).

1-(5-bromoselenophen-2-yl)-3-(5-bromothiazol-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

The synthetic method for compound 12 is the same as that for compound 10 (0.2 g, yield=68 %). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.81 (s, 1H), 7.74–7.73 (d, 1H), 7.33–7.32 (d, 1H), 3.36–3.20 (m, 4H), 1.79–1.73 (m, 2H), 1.44–1.30 (m, 16H), 0.96–0.91 (m, 12H). ¹³C NMR (CDCl₃, 101 MHz), δ (ppm): 183.39, 159.37, 152.52, 148.71, 145.82, 140.17, 137.16, 134.68, 132.24, 130.23, 124.81, 112.99, 44.03, 37.40, 31.68, 26.08, 22.35, 15.12, 9.25, 0.62.

(13).

1,3-bis(5-bromoselenophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

The synthetic method for compound 13 is consistent with the findings of Hou.¹

(14).

1,3-bis(5-bromothiazol-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione.

The synthetic method for compound 14 is consistent with the findings of Yang.²

Polymerization (Compound 16, 17, 18, 19 and 20):

Compound 10 (0.1 mmol) and compound 15 (the BDT monomer part, 0.1 mmol) was dissolved into 7 mL of toluene. The mixture was purged by argon for 15 min and then Pd(PPh₃)₄ was added into the solution. The reactant was purged by argon for another 20 min and stirred at 110 °C overnight. The compound 16 was precipitated from 80 mL of methanol and the raw product was then filtered, dried, and further purified by silica gel chromatographic column using hot trichloromethane as eluent. The synthetic method for compound 17, 18, 19 and 20 is the same as that for compound 16. The yields of the polymers are over 55 %.

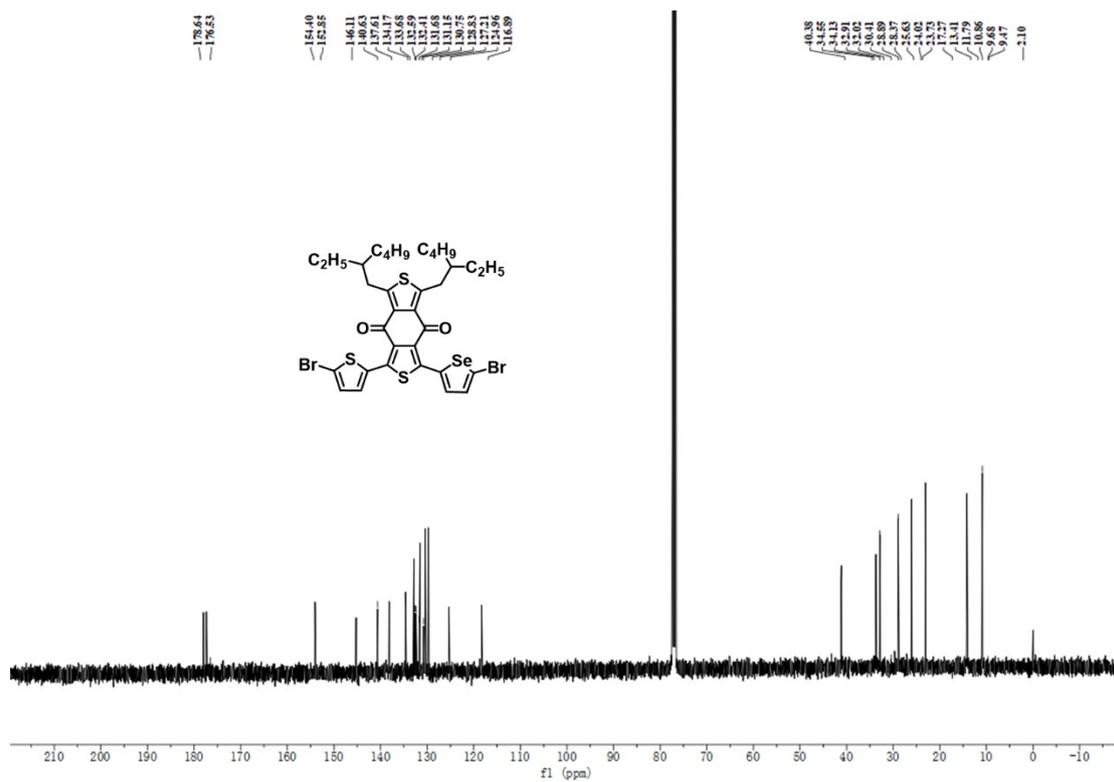


Figure S8. ¹³C NMR spectrum of compound 11 in CDCl₃.

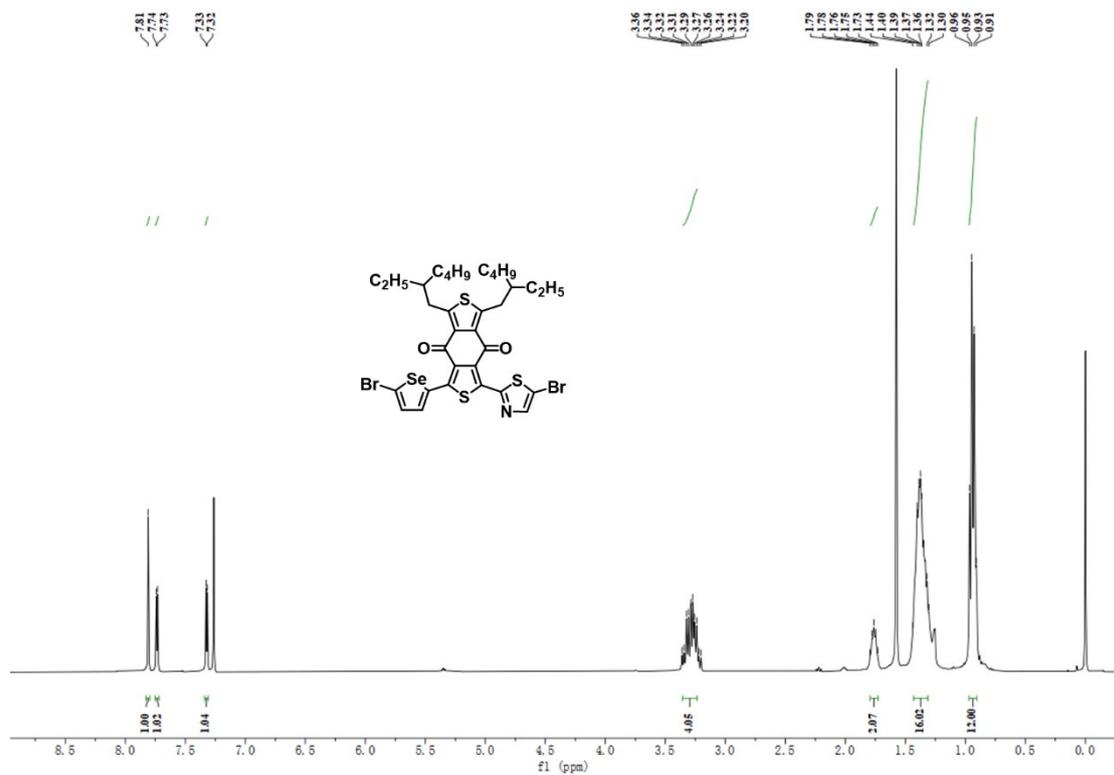


Figure S9. ¹H NMR spectrum of compound 12 in CDCl₃.

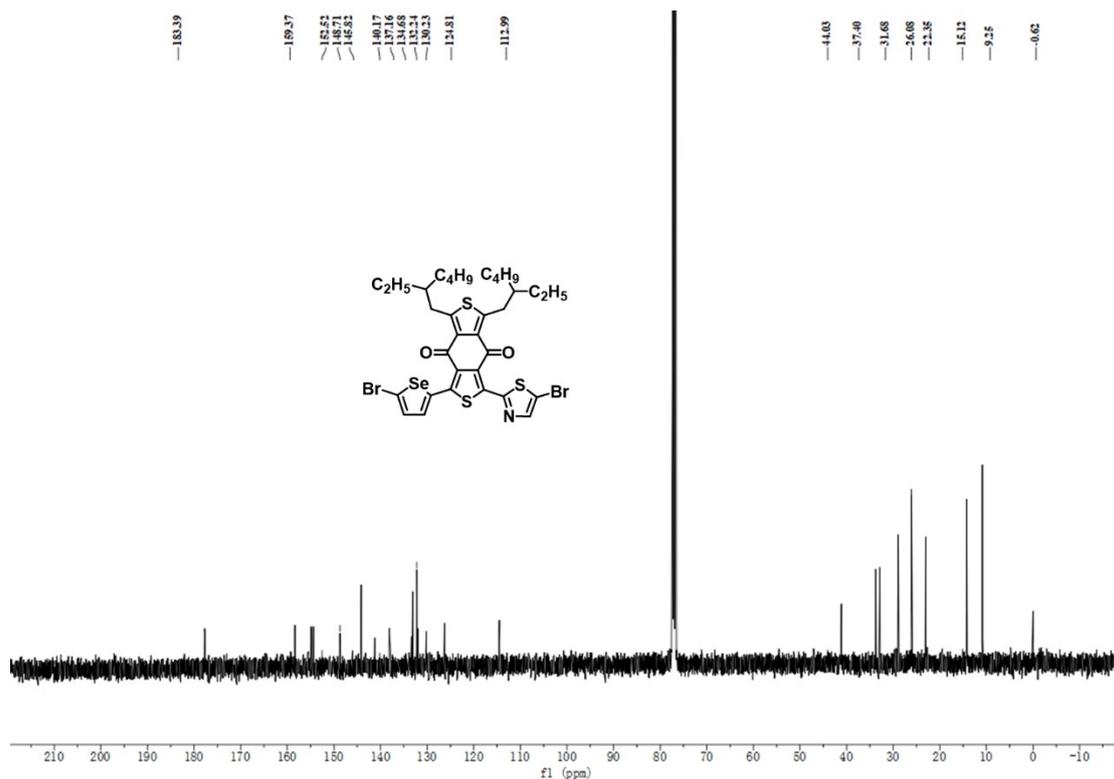


Figure S10. ¹³C NMR spectrum of compound 12 in CDCl₃.

Instruments and Measurements

The ¹H NMR spectra of the monomers were recorded on a Bruker AVANCE–III 400 Spectrometer with CDCl₃ as the solvent. The UV–vis absorption spectra of the polymers were recorded using a Hitachi U–4100 spectrophotometer. Cyclic voltammetry (CV) measurement was performed on a CHI660D electrochemical workstation with a three–electrode system (a glassy carbon working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire counter electrode) using a scan rate of 100 mV/s with a nitrogen saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile. Atom Force Microscopy (AFM) measurement were conducted with an Agilent–5400 scanning probe microscope with a Nanodrive controller in tapping mode with MikroMasch

NSC-15 AFM tips with resonant frequencies of 300 kHz. Transmission electron microscopy (TEM) measurement was performed by using a HITACHI H-7650 electron microscope with an acceleration voltage of 120 kV. The n and k curves of the blend film was recorded using a Mueller matrix ellipsometer (ME-L-VI).

Fabrication of OSCs. All devices were fabricated with the conventional structure of ITO/PEDOT:PSS/Active layers/PDINN/Ag. The conductivity of ITO was $15 \Omega/\text{sq}$. The ITO-coated glass substrates were thoroughly cleaned by detergent, deionized water, acetone, and isopropanol, followed by drying with N_2 flow. Firstly, the PEDOT:PSS was spin-coated on the precleaned ITO substrates at 5000 rpm and annealed for 15 min at 155°C . All active layer materials were dissolved in CF with 0.3% v/v diiodomethane at a polymer concentration of 7.5 mg mL^{-1} , polymers and Y6 were mixed at a ratio of 1:1.2. The active layer was then spin-coated on the PEDOT:PSS and heated for 5 min at 85°C . Then PDINN dissolved in methanol (1 mg mL^{-1}) was spin-coated on the top of the active layers. Finally, the cathode Ag layer was thermally evaporated under high vacuum ($4 \times 10^{-4} \text{ Pa}$). All the operating area of solar cell devices are 0.042 cm^2 .

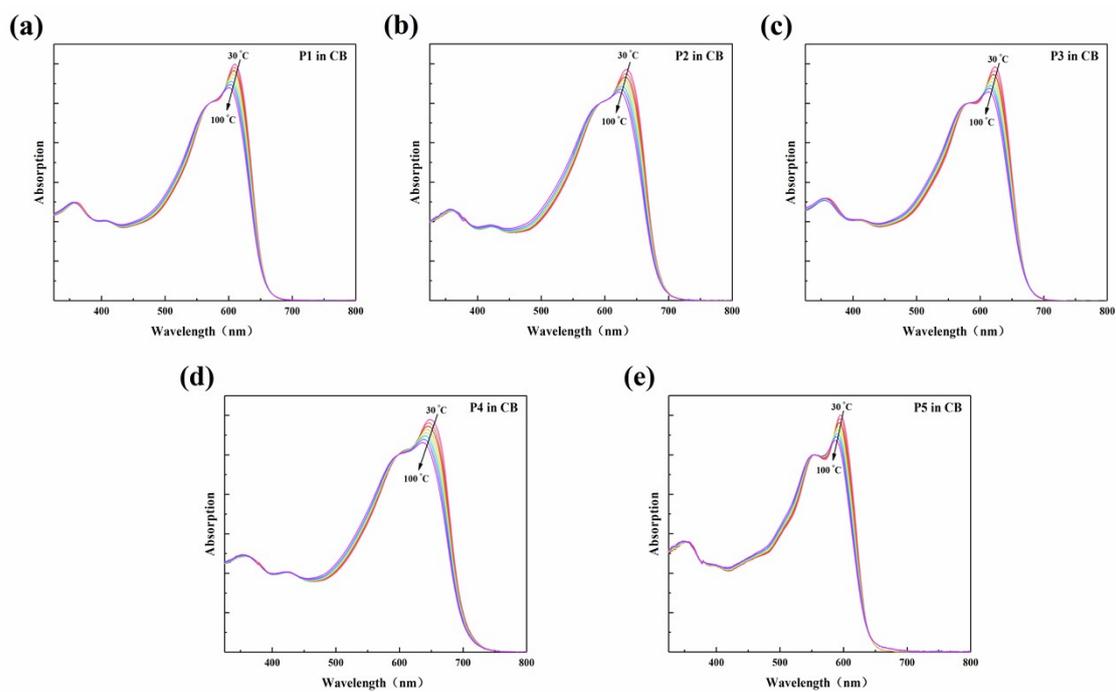


Figure S11. (a–e) The temperature–dependent absorption spectra of P1, P2, P3, P4, P5 from 30 °C to 100 °C.

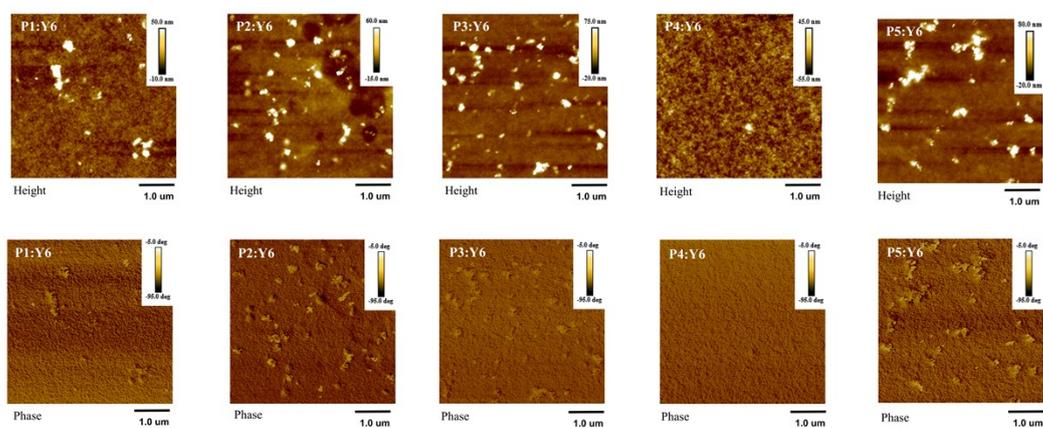


Figure S12. AFM photographs of five blend films in optimized conditions.

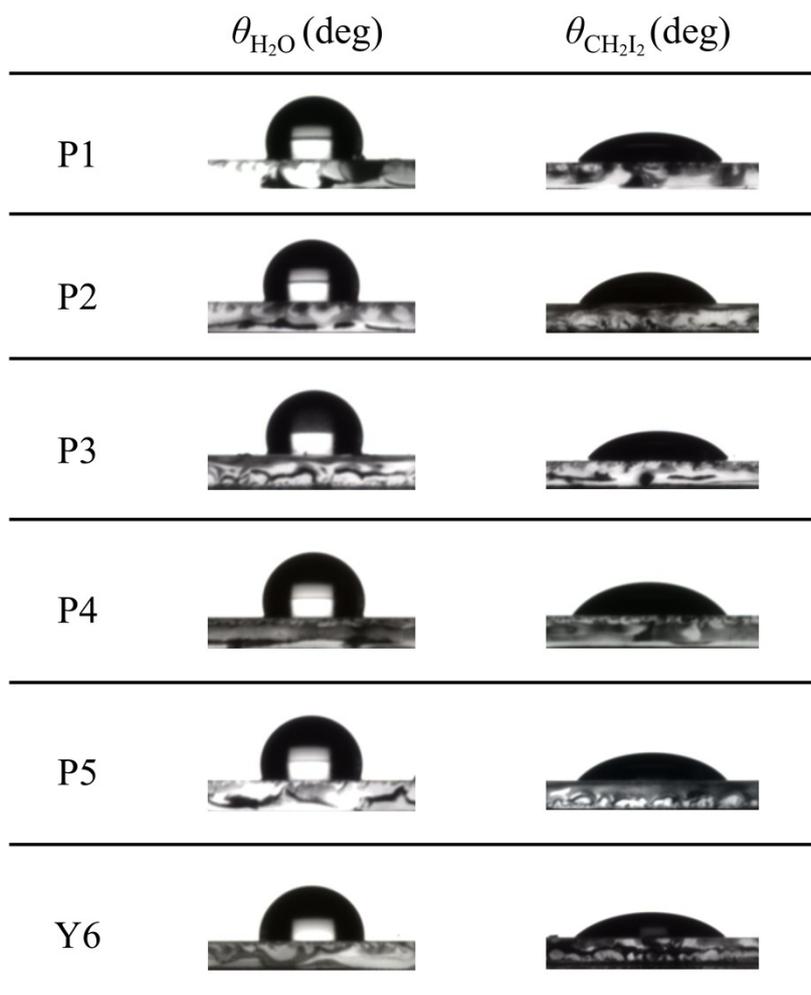


Figure S13. The contact angle images of neat films.

Table S1. The contact angle data of water and diiodomethane on neat films.

Material	$\theta_{\text{H}_2\text{O}}$ (deg)	$\theta_{\text{CH}_2\text{I}_2}$ (deg)	γ (mN m ⁻¹)	$\chi_{\text{Polymer:Y6}}$
P1	102.07	46.69	37.77	3.17×10^{-2} K
P2	104.70	49.70	36.47	8.11×10^{-2} K
P3	105.25	47.70	38.03	2.46×10^{-2} K

P4	105.53	48.98	37.22	4.97×10^{-2} K
P5	104.03	43.81	39.97	2.50×10^{-6} K
Y6	94.44	40.40	39.99	

References

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