

Supporting Information for

Benzobisthiazole Unit in 4, 8-Connection Mode to Build D-A Polymer Donors Achieving High Short-circuit Current Density for Organic Solar Cells

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Instruments and measurements

¹H-NMR and ¹³C-NMR were measured on a Bruker AVANCE III HD 400 MHz. The thermogravimetric analysis (TGA) was performed on TA thermal analyzer (model Q600 SDT) under a nitrogen flow at a heating rate of 10 °C min⁻¹. The molecular weight and dispersion of the polymer were measured by gel permeation chromatography (GPC) (PL-GPC220 of Polymer Laboratories Ltd). The thickness of active layer was measured on a Bruker DektakXT profilometer. The cyclic voltammetry (CV) was conducted on a CHI voltammetric analyzer with glassy carbon disk, Pt wire and Ag/Ag⁺ electrode as working electrode, counter electrode and reference electrode respectively in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. The electronic energy levels were obtained from CV measurement according to the Leeuw empirical formula: $E_{(\text{HOMO})}$ (eV) = -e

$(4.8 + E_{\text{ox}}^{\text{onset}} - E_{\text{Fc}/\text{Fc}^+})$. The UV-vis absorption spectra were measured by a Varian Cary 5000 UV-vis-NIR spectrophotometer. Atomic force microscope (AFM) images were measured on Multimode 8 scanning probe microscopy (Bruker Daltonics Inc., United States) in the tapping mode to investigate the nanoscale morphology of the blends. The transmission electron microscopy (TEM) characterization was carried out on a JEM-ARM200F transmission electron microscope. The grazing incident wide-angle X-ray scattering (GIWAXS) measurements were carried out with a Xeuss 2.0 WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector.

Fabrication and characterization of organic solar cells

The OSC devices were fabricated with the structure: ITO/PEDOT:PSS/active layer/F3N/Ag. The indium tin oxide (ITO) glass (sheet resistance = $10 \Omega \text{ sq}^{-1}$) was pre-cleaned in an ultrasonic bath of deionized water, acetone and isopropanol. PEDOT:PSS layer (*ca.* 30 nm) was spin-coated onto the ITO glass, and baked at 150 °C for 15 min. A chloroform solution of active layer (16 mg mL^{-1} in total) was spin-coated on PEDOT:PSS layer to form a photoactive layer. The Ag (70 nm for opaque devices) was successively evaporated onto the surface of the photoactive layer under vacuum (*ca.* 10^{-5} Pa). The active area of the device was 4.0 mm^2 , defined under an optical microscope. The J - V curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, $70 \times 70 \text{ mm}^2$ photobeam size) coupled with AM 1.5G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm^{-2} . A $2 \times 2 \text{ cm}^2$ monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Mobility measurements

Hole-only and electron-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/ active layer /Au for holes and ITO/ZnO/ active layer/Al for electrons. Mobilities were extracted by fitting the current density–voltage curves using space-charge-

limited current (SCLC) method. The J - V curves of the devices were plotted as $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ using the equation $\ln(Jd^3/V^2) \cong 0.89(1/E_0)^{0.5}(V/d)^{0.5} + \ln(9\epsilon_0\epsilon_r\mu/8)$, where J is the current density, d is the film thickness of active layer, μ is the hole or electron mobility, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes (for hole-only diodes, V_{bi} is 0.2 V; for electron-only diodes, V_{bi} is 0 V).

Materials and synthesis

The intermediate 1 were synthesized according to the literature method.¹ The tributyl(5-(2-hexyldecyl)thiophen-2-yl)stannane, tributyl(4-fluoro-5-(2-hexyldecyl)thiophen-2-yl)stannane, tributyl(4-chloro-5-(2-hexyldecyl)thiophen-2-yl)stannane and BDT monomer was purchased from SunaTech Inc. Other chemicals were purchased from commercial sources as used directly unless otherwise noted.

Synthesis of compound 2: To a 250 mL of dried Schlenk tube, magnetic stir bar, intermediate 1 (5 g, 14.28 mmol, 1eq), tributyl(thiophen-2-yl)stannane (16.02 g, 42.84 mmol, 3eq), Pd(Ph₃)₄ (0.49 g, 0.43 mmol, 0.03 eq) and anhydrous toluene (120 mL) were added. Then, the reaction mixture was degassed for 30 min under Ar and was heated to 110 °C for 36 h. After cooling to room temperature, the solvent of reaction system was removed. In the final, the residue was purified by column chromatography (PE:DCM = 1:1, v/v) to obtain a yellow solid (3.67 g, 10.28 mmol, 72% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.16 (s, 2H), 7.89 (dd, $J = 3.7, 1.1$ Hz, 2H), 7.59 (dd, $J = 5.1, 1.1$ Hz, 2H), 7.28 (dd, $J = 5.1, 3.7$ Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 155.33, 148.60, 138.46, 133.69, 128.81, 127.92, 127.20, 123.03.

Synthesis of compound 3: To a 100 mL of dried two-neck round-bottom flask, magnetic stir bar, intermediate 2 (3.67 g, 10.28 mmol, 1 eq), toluene (50 mL), potassium tert-butoxide (2.88 g, 25.7 mmol, 2.5 eq) was added under a certain order. This reaction system was stirred for 2 hours and 1,2,3,4,5-pentafluoro-6-iodobenzene (9.06 g, 30.84 mmol, 3eq) was added, followed by stirring at 25 °C for 12 h. After reaction, the water was added to quenched the reaction system and the crude product was collected by filtration, washed with water. The title

compound was dried under vacuum and used directly without further purification. (3.86 g, 6.37 mmol, 62% yield).

Synthesis of compound 4-H: Intermediate 3 (1.2 g, 1.97 mmol, 1 eq), tributyl(5-(2-hexyldecyl)thiophen-2-yl)stannane (3.54 g, 5.91 mmol, 3 eq), Pd(Ph₃)₄ (232 mg, 0.20 mmol, 0.1 eq) and anhydrous toluene (50 mL), magnetic stir bar were added to a 100 mL of dried Schlenk tube. The reaction mixture was degassed for 30 min under Ar and was stirred at 110 °C for 24 h. After cooling to room temperature, the solvent of reaction system was removed. In the final, the residue was purified by column chromatography (PE: DCM = 6:1, v/v) to obtain a yellow solid (0.61 g, 0.63 mmol, 32% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.99 (d, *J* = 2.8 Hz, 2H), 7.58 (d, *J* = 4.3 Hz, 2H), 7.54 (d, *J* = 3.7 Hz, 2H), 7.28 (d, *J* = 3.8 Hz, 2H), 6.80 (d, *J* = 3.7 Hz, 2H), 2.80 (d, *J* = 6.7 Hz, 4H), 1.78-1.65 (m, 2H), 1.38-1.22 (m, 48H), 0.92-0.84 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 161.05, 150.48, 148.35, 139.17, 135.00, 133.19, 128.91, 128.26, 127.93, 126.68, 126.48, 121.19, 40.14, 34.99, 33.19, 31.90, 29.96, 29.62, 29.32, 26.53, 22.68, 14.11.

Synthesis of compound 4-F: The procedure is the same as **4-H**. compound 3 (1.44 g, 2.36 mmol, 1 eq), tributyl(4-fluoro-5-(2-hexyldecyl)thiophen-2-yl)stannane (4.37 g, 7.09 mmol, 3 eq), Pd(Ph₃)₄ (278 mg, 0.24 mmol, 0.1 eq). The product was obtained as a yellow solid (1.04 g, 1.04 mmol, 44% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.91 (dd, *J* = 3.7, 1.0 Hz, 2H), 7.57 (dd, *J* = 5.1, 1.0 Hz, 2H), 7.31 (s, 2H), 7.24 (dd, *J* = 5.1, 3.8 Hz, 2H), 2.72 (d, *J* = 6.7 Hz, 4H), 1.77-1.65 (m, 2H), 1.40-1.19 (m, 48H), 0.94-0.83 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 160.23, 160.21, 155.81, 153.26, 148.14, 138.79, 133.28, 131.43, 131.34, 128.34, 128.11, 127.14, 126.96, 126.71, 121.41, 118.16, 117.88, 39.54, 33.24, 31.90, 31.86, 29.96, 29.89, 29.62, 29.60, 29.33, 26.51, 26.48, 22.68, 22.67, 14.12.

Synthesis of compound 4-Cl: The procedure is the same as **4-H**. Compound 3 (1.56 g, 2.56 mmol, 1 eq), tributyl(4-chloro-5-(2-hexyldecyl)thiophen-2-yl)stannane (4.85 g, 7.68 mmol, 3 eq), Pd(Ph₃)₄ (301 mg, 0.26 mmol, 0.1 eq). The product was obtained as a yellow solid (1.14 g, 1.10 mmol, 43% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.90 (dd, *J* = 3.7, 0.9 Hz, 2H), 7.56 (dd, *J* = 5.1, 0.9 Hz, 2H), 7.41 (s, 2H), 7.25-7.19 (m, 2H), 2.76 (d, *J* = 7.0 Hz, 4H), 1.83-1.69 (m, 2H), 1.42-1.19 (m, 48H), 0.96-0.83 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 159.85, 148.16, 142.71, 138.85, 133.44, 133.23, 128.58, 128.39, 128.15, 126.73, 123.71,

121.44, 39.66, 33.29, 32.81, 31.93, 31.90, 29.99, 29.66, 29.64, 29.36, 26.53, 26.49, 22.71, 14.15.

Synthesis of monomer M-H: Intermediate 4-H (0.61 g, 0.63 mmol, 1eq) were dissolved in CHCl₃ (30 mL) in a 50 mL of dried two-neck round-bottom flask. The solution of NBS (0.22 g, 1.26 mmol, 2 eq) in chloroform was added dropwise. Then, this reaction was carried out at 25 °C for 12 h. The water was poured into to quenched the system. The crude product was extracted with dichloromethane, washed with brine, and dried over anhydrous Na₂SO₄. Finally, the solvent of reaction system was removed and the residue was purified by column chromatography (PE:DCM = 8:1, v/v) to obtain a yellow solid (0.56 g, 0.50 mmol, 79% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.59 (d, *J* = 4.1 Hz, 2H), 7.49 (d, *J* = 3.7 Hz, 2H), 7.14 (d, *J* = 4.1 Hz, 2H), 6.79 (d, *J* = 3.7 Hz, 2H), 2.82 (d, *J* = 6.7 Hz, 4H), 1.81-1.66 (m, 2H), 1.40-1.19 (m, 48H), 0.93-0.85 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 160.32, 150.47, 147.45, 140.31, 134.60, 130.68, 129.05, 129.01, 127.63, 126.39, 119.91, 116.36, 40.05, 34.96, 33.25, 31.96, 30.07, 29.73, 29.70, 29.40, 26.62, 26.57, 22.73, 14.17, 14.16. MS (MALDI-TOF): calcd for C₅₆H₇₄Br₂N₂S₆, 1125.26; found:1125.18.

Synthesis of monomer M-F: The procedure is the same as **M-H**. Compound 4-F (0.87 g, 0.87 mmol, 1eq), NBS (0.31 g, 1.74 mmol, 2eq). The product was obtained as a yellow solid (0.86 g, 0.74 mmol, 85% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.24 (d, *J* = 4.1 Hz, 2H), 7.08 (s, 2H), 6.93 (d, *J* = 4.1 Hz, 2H), 2.74 (d, *J* = 6.7 Hz, 4H), 1.81-1.66 (m, 2H), 1.45-1.22 (m, 48H), 0.95-0.82 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 159.54, 159.51, 155.83, 153.28, 147.09, 139.76, 130.97, 130.87, 130.50, 129.04, 127.66, 127.40, 127.22, 119.93, 118.26, 117.99, 116.78, 39.50, 33.27, 31.96, 31.94, 30.07, 29.89, 29.73, 29.70, 29.40, 26.56, 26.51, 22.74, 14.18, 14.16. MS (MALDI-TOF): calcd for C₅₆H₇₂Br₂F₂N₂S₆, 1161.24; found:1161.19.

Synthesis of monomer M-Cl: The procedure is the same as **M-H**. Compound 4-Cl (0.88 g, 0.85 mmol, 1eq), NBS (0.3 g, 1.7 mmol, 2 eq). The product was obtained as a yellow powder (0.72 g, 0.60 mmol, 70% yield). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.20 (d, *J* = 4.1 Hz, 2H), 7.15 (s, 2H), 6.91 (d, *J* = 4.1 Hz, 2H), 2.77 (d, *J* = 7.0 Hz, 4H), 1.85-1.74 (m, 2H), 1.46-1.22 (m, 48H), 0.95-0.84 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃, δ ppm): 159.05, 147.05, 142.91, 139.69, 132.90, 130.37, 129.03, 128.63, 127.68, 123.81, 119.89, 116.79, 39.56, 33.31, 33.29,

32.80, 31.96, 30.08, 29.74, 29.71, 29.41, 26.55, 26.49, 22.74, 14.20, 14.17. MS (MALDI-TOF): calcd for $C_{56}H_{72}Br_2Cl_2N_2S_6$, 1193.18; found: 1193.12.

Preparation of *PBDT-BBTH*: To a 50 mL of dried Schlenk tube, M-H (56.4 mg, 0.05 mmol, 1eq), BDT monomer (56.5 mg, 0.05 mmol, 1eq), $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol, 0.04 eq), $P(o\text{-tolyl})_3$ (3.6 mg, 0.012 mmol, 0.24 eq) were dissolved in 10 mL of anhydrous toluene. The reaction mixture was degassed for 30 min under Ar and was heated to 110 °C for 48 h. After cooling to room temperature, the solution was added to methanol to form precipitate. The collected solid was extracted with methanol, acetone, hexane and $CHCl_3$ by the Soxhlet. The resulted chloroform fraction was precipitated in methanol. Finally, the product was collected and dried under vacuum to obtain a dark reddish solid (76.2 mg, 67%). GPC (THF): $M_n = 47$ kDa, PDI = 3.1.

Preparation of *PBDT-BBTF*: The procedure is the same as *PBDT-BBTH*. M-F (58.2 mg, 0.05 mmol, 1eq), BDT monomer (56.5 mg, 0.05 mmol, 1eq), $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol, 0.04 eq), $P(o\text{-tolyl})_3$ (3.6 mg, 0.012 mmol, 0.24 eq). The product was obtained as a dark reddish solid (67.2 mg, 59% yield). GPC (THF): $M_n = 66$ kDa, PDI = 3.0.

Preparation of *PBDT-BBTCl*. The procedure is the same as *PBDT-BBTH*. M-Cl (59.8 mg, 0.05 mmol, 1eq), BDT monomer (56.5 mg, 0.05 mmol, 1eq), $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol, 0.04 eq), $P(o\text{-tolyl})_3$ (3.6 mg, 0.012 mmol, 0.24 eq). The product was obtained as a dark reddish solid (80.3 mg, 69% yield). GPC (THF): $M_n = 41$ kDa, PDI = 2.9.

Table S1. The data of polymer donor:L8-BO based devices with different annealing temperature and D/A ratios.

Devices	D:A (w/w)	TA Temp/Time	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDT-BBTH:L8-BO	1:1	130°C/5min	0.81	20.73	62.87	10.60
	1:1.2	/	0.86	16.86	55.92	8.07
	1:1.2	130°C/5min	0.81	22.53	61.32	11.18
	1:1.5	80°C/5min	0.81	22.80	58.89	10.89
PBDT-BBTF:L8-BO	1:1	130°C/5min	0.85	21.00	58.57	12.28
	1:1.2	/	0.91	18.30	64.25	10.64
	1:1.2	130°C/5min	0.86	22.37	69.88	13.43
	1:1.5	80°C/5min	0.85	21.54	69.58	12.73
PBDT-BBTCl:L8-BO	1:1	130°C/5min	0.86	22.66	68.28	13.38
	1.2:1	80°C/5min	0.89	21.19	53.80	10.12
	1:1.2	/	0.91	20.41	58.69	10.87
	1:1.2	130°C/5min	0.87	21.94	70.56	13.40
	1:1.5	80°C/5min	0.89	22.38	58.54	11.67

Table S2. The data of polymer donor:L8-BO based devices with different annealing temperature and solvent additive.

Devices	Additive (v/v)	TA Temp/Time	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDT-BBTH:L8-BO	0.25%CN	130°C/5min	0.80	22.26	66.98	11.99
	0.25%DPE	80°C/5min	0.83	20.28	66.18	11.08
	0.50%DPE	130°C/5min	0.79	23.46	67.53	12.59
	0.75%DPE	130°C/5min	0.78	23.46	70.47	12.85
	1%DPE	130°C/5min	0.77	23.99	69.38	12.79
PBDT-BBTF:L8-BO	0.25%CN	80°C/5min	0.81	20.72	62.18	10.42
	0.25%DPE	80°C/5min	0.88	22.30	67.85	13.28
	0.50%DPE	130°C/5min	0.85	22.49	71.79	13.65
	0.75%DPE	130°C/5min	0.84	22.27	72.51	14.11
	1%DPE	130°C/5min	0.82	23.36	72.84	14.02
PBDT-BBTCl:L8-BO	0.25%CN	130°C/5min	0.86	18.33	70.09	11.04
	/	130°C/5min	0.86	22.03	69.78	13.26
	0.25%DPE	130°C/5min	0.86	22.16	69.21	13.11
	0.50%DPE	130°C/5min	0.85	21.39	69.03	12.49

Table S3. Carrier transport properties of optimized polymer donor:L8-BO blended films.

Devices	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_h/μ_e
PBDT-BBTH:L8-BO	2.36×10^{-4}	1.30×10^{-4}	1.82
PBDT-BBTF:L8-BO	1.86×10^{-4}	9.71×10^{-5}	1.92
PBDT-BBTCl:L8-BO	1.62×10^{-4}	7.49×10^{-5}	2.16

Table S4. 2D GIWAXS patterns of neat films along the in-plane (IP) directions.

Table 2D	q_r	Lamellar		S5.
		Peak (\AA^{-1})	d-spacing (\AA)	
	PBDT-BBTH	0.235	26.7	
	PBDT-BBTF	0.240	26.2	
	PBDT-BBTCl	0.255	24.6	
	L8BO	0.395	15.9	

GIWAXS patterns of neat films along the out-of-plane (OOP) directions.

q_z	Lamellar		π - π stacking	
	Peak (\AA^{-1})	d-spacing (\AA)	Peak (\AA^{-1})	d-spacing (\AA)
PBDT-BBTH	0.270	23.3	1.61	3.90
PBDT-BBTF	0.280	22.4	1.60	3.93
PBDT-BBTCl	0.290	21.7	1.60	3.93
L8BO	/	/	1.81	3.47

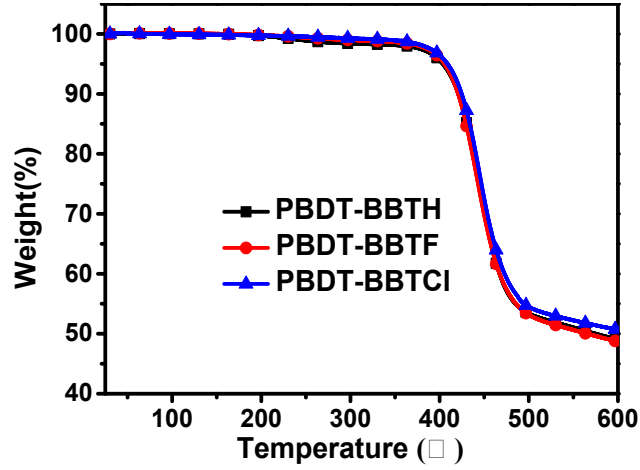


Fig. S1 The TGA curves of PBDT-BBTH, PBDT-BBTF and PBDT-BBTCI.

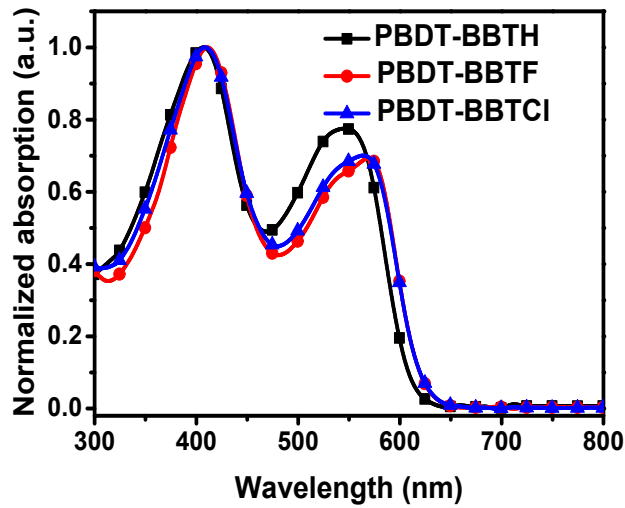


Fig. S2 The normalized UV-vis absorption spectra of polymer donors in solution.

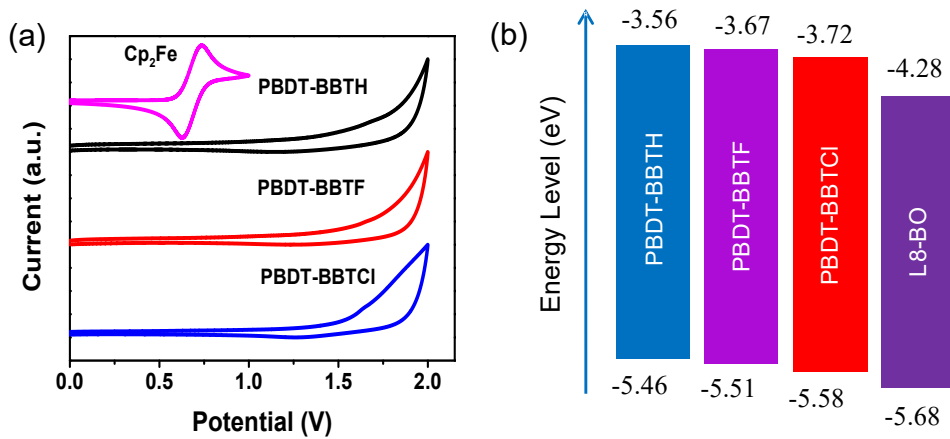


Fig. S3 The CV curves of the polymers (a) and the comparison of energy diagram for the polymer donors with acceptor L8-BO (b).

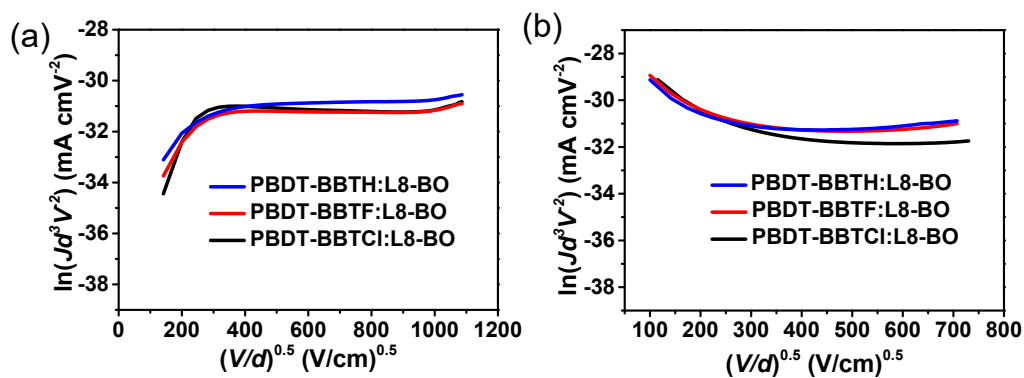


Fig. S4 The hole mobility (a) and electron mobility (b) of polymer donor:L8-BO based devices.

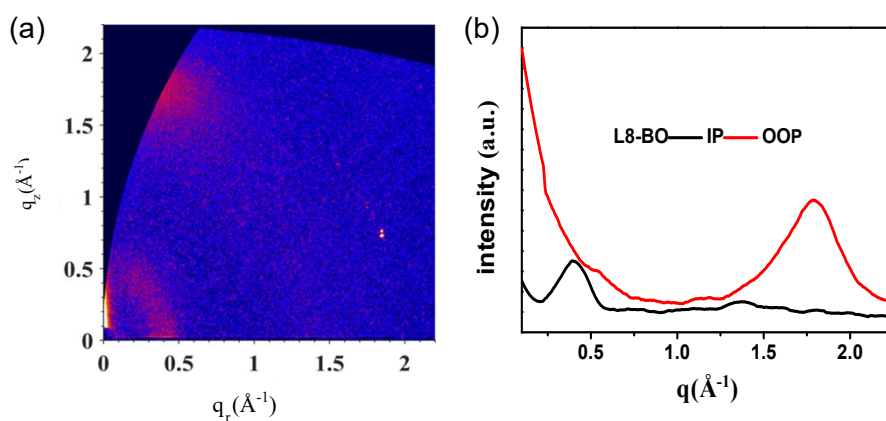


Fig. S5 (a) The 2D GIWAXS patterns of pure L8-BO; (b) The corresponding intensity profiles along the in-plane and out-of-plane directions.

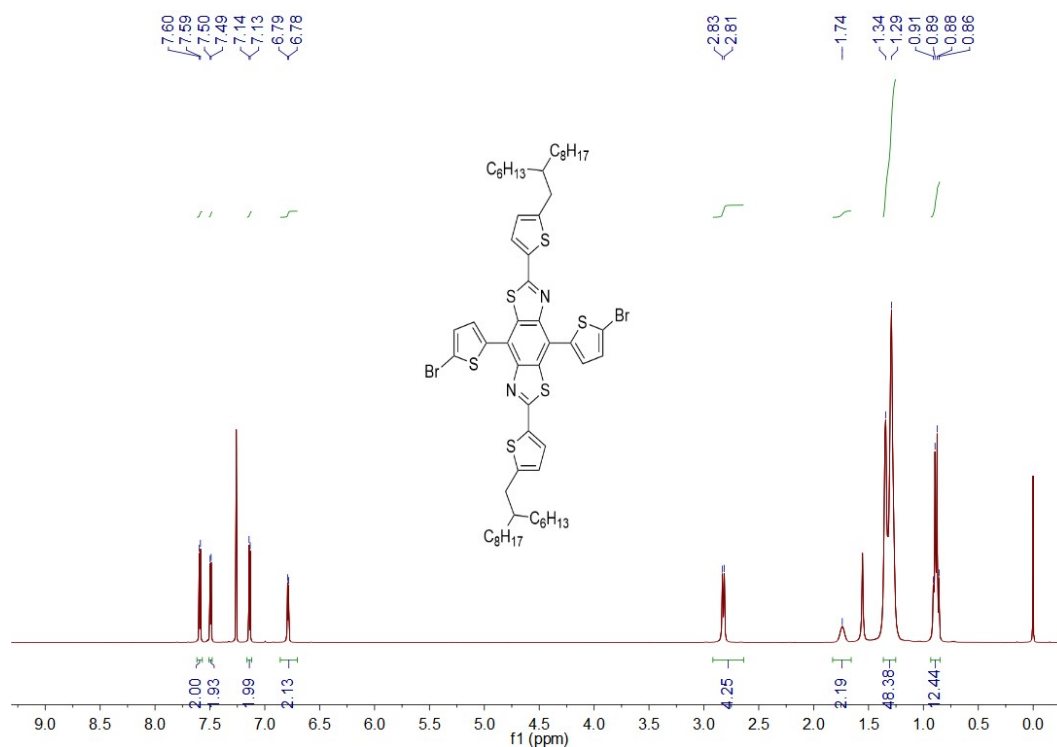


Fig. S6 ¹H NMR spectrum of compound M-H.

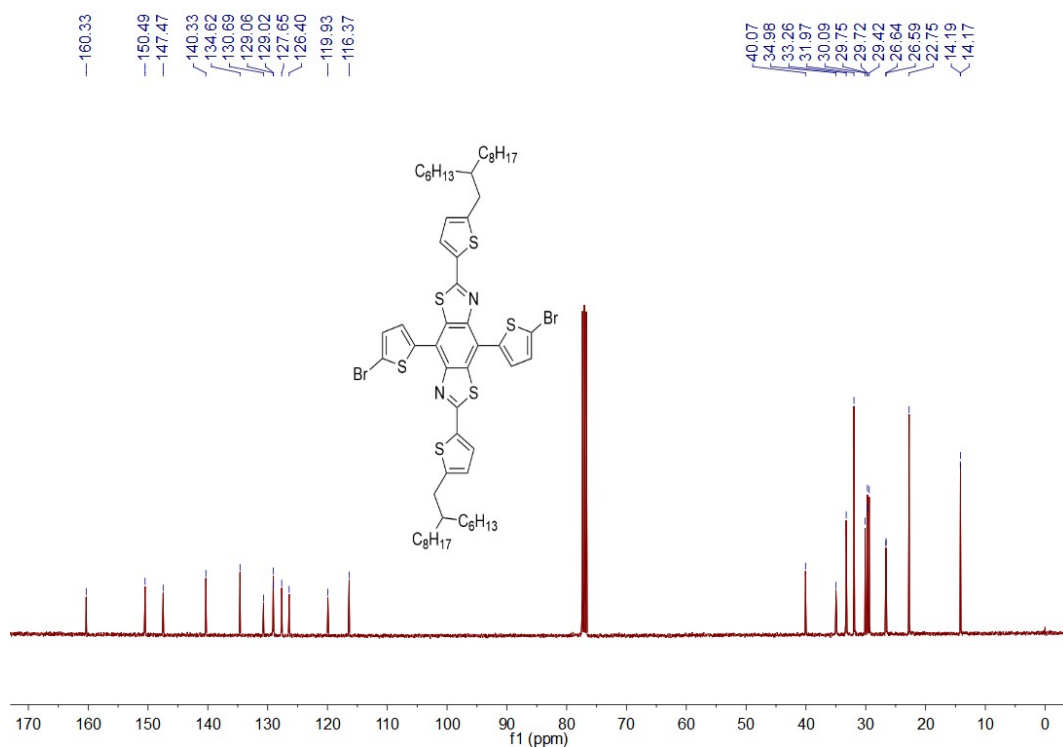


Fig. S7 ^{13}C NMR spectrum of compound M-H.

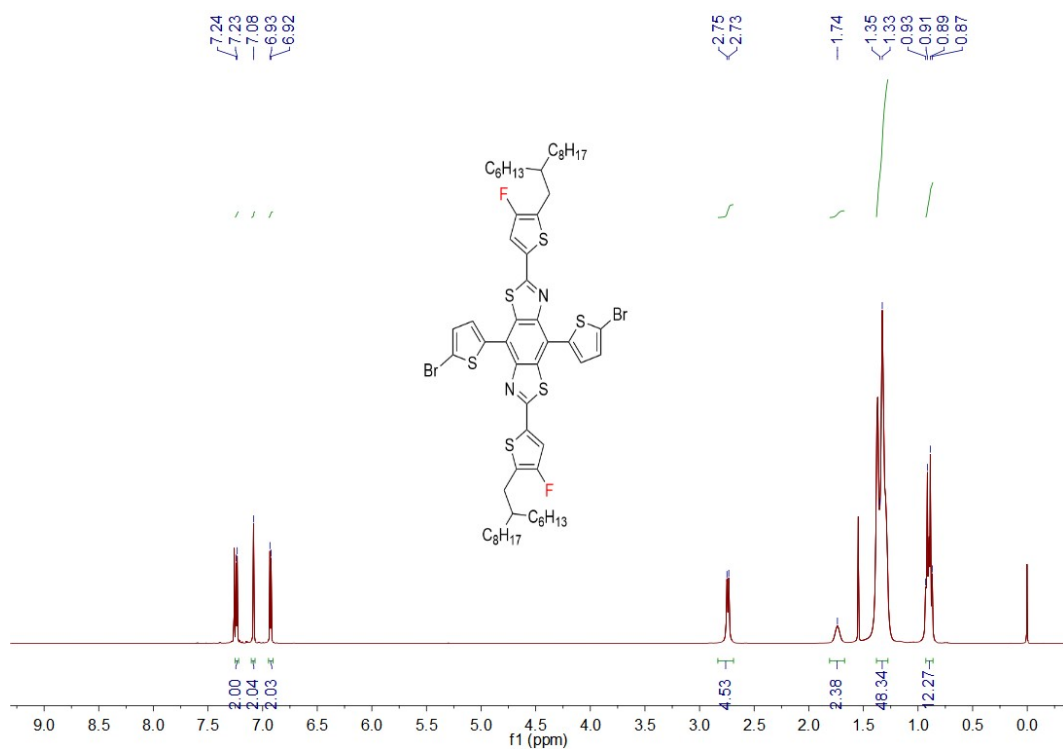


Fig. S8 ^1H NMR spectrum of compound M-F.

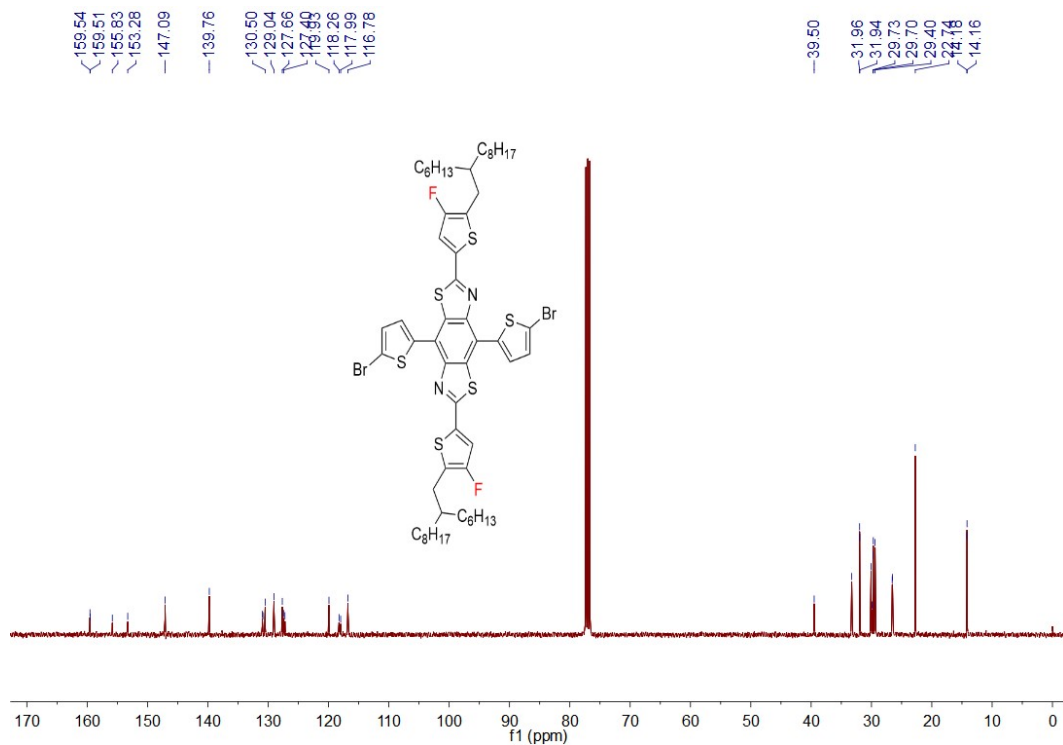


Fig. S9 ^{13}C NMR spectrum of compound M-F.

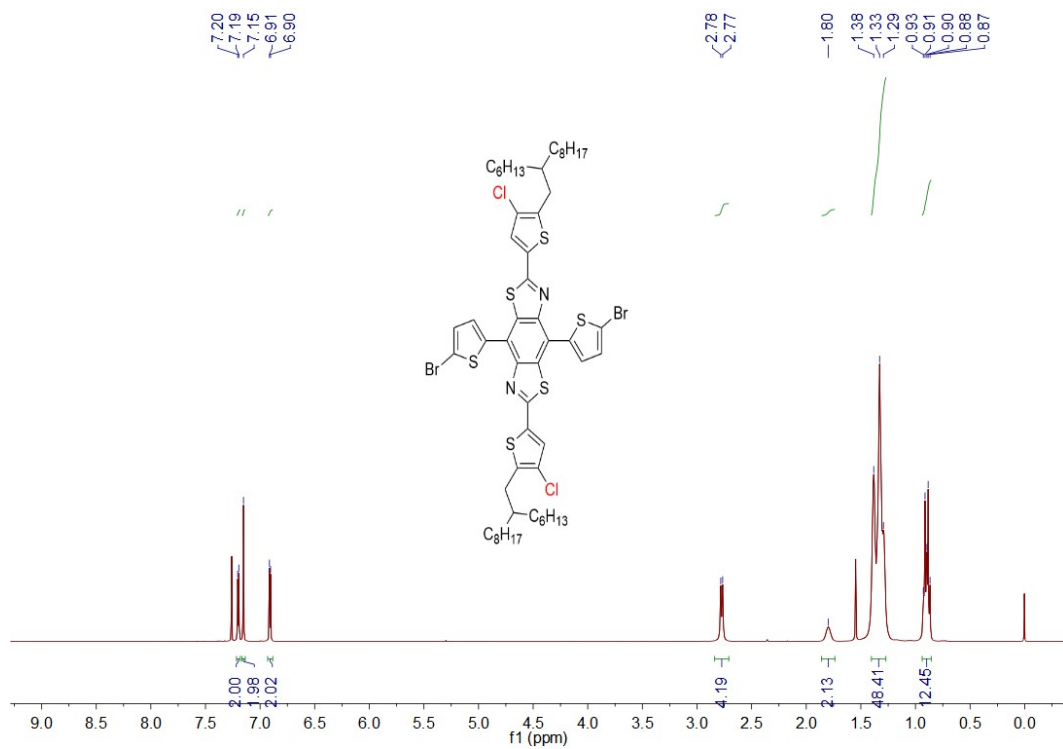


Fig. S10 ^1H NMR spectrum of compound M-Cl.

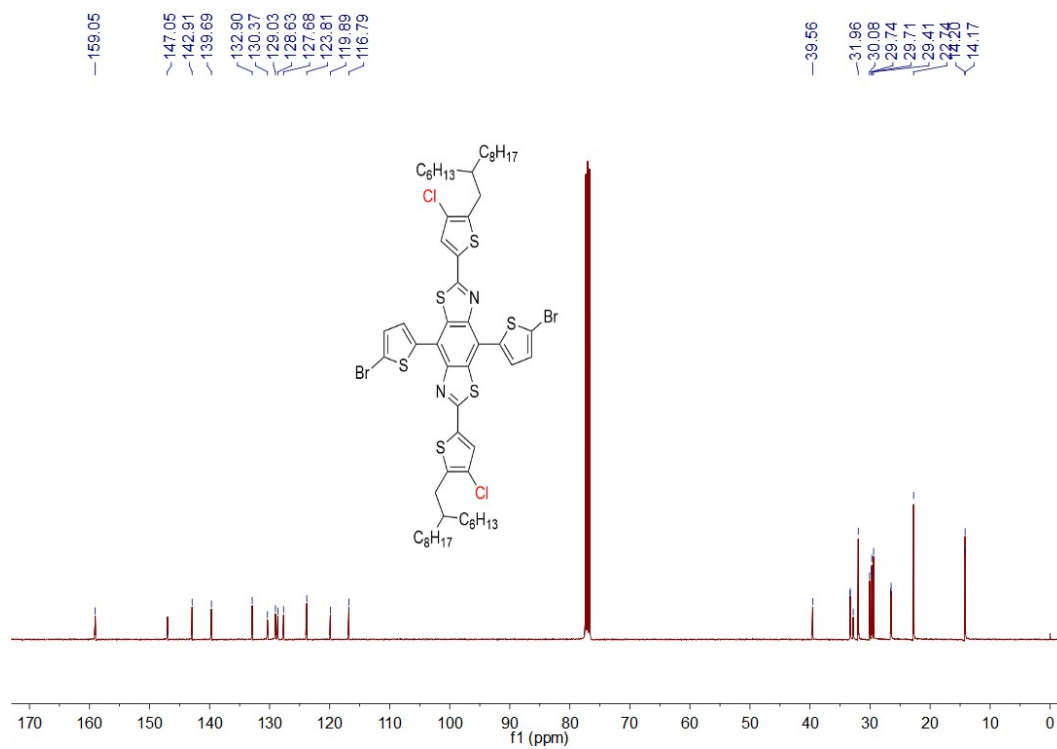


Fig. S11 ¹³C NMR spectrum of compound **M-Cl**.

References

- (1) J. Bon, D. Feng, S. Marder, S. Blakey. *J. Org. Chem*, 2014, **79**, 7766-7771.