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Electronic Supplementary information (ESI)

Rational Design of Asymmetric Benzodithiophene based Photovoltaic Polymers for Efficient Solar Cells

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1. Measurements and characterizations

^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker AVANCE-III 600 Spectrometer with $CDCl_3$ as the solvent. The molecular weight of the polymers was measured by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the eluent (40 ^{o}C) and polystyrene as the standard. Thermal gravimetric analysis (TGA) measurement was carried out by STA-409 at a heating rate of 10 °C/min under N_2. UV-vis absorption spectra were measured using a Hitachi U-4100 spectrophotometer. PL spectra were measured using a Fluoromax-4 fluorescence spectrometer. Cyclic voltammetry (CV) measurements was recorded on a CHI660D electrochemical workstation with a three-electrode system (a glassy carbon working electrode, a saturated calomel electrode (SCE) reference electrode and a platinum wire counter electrode) using a scan rate of 100 mV/s. 0.1 M tetrabutylammonium phosphorus hexafluoride in acetonitrile was used as the electrolyte. Atomic force microscopy (AFM) measurement was performed using Agilent 5400 scanning probe microscope in tapping-mode with MikroMasch NSC-15 AFM tips. Transmission electron microscopy (TEM) measurement was performed by using a HITACHI H-7650 electron microscope with an acceleration voltage of 100 kV.

2. Device Fabrication and Testing

Photovoltaic devices were fabricated with a conventional device structure of ITO/PEDOT:PSS/active layer /PFN/Al. The ITO-coated glass substrates were cleaned successively with detergent, deionized water, acetone and isopropanol, and dried with N_2 flow. And then, the PEDOT:PSS layer was spin-coated onto the ITO from different weight ratios of donor and $PC_{71}BM$ blends in *o*-dichlorobenzene solution with different spin-coating speeds. The concentration of P1/acceptor blend solutions are 15 mg/mL, and the concentration of P2/acceptor blend solutions are 25 mg/mL. The solutions were stirred overnight at room temperature before spin-coating. Then PFN solution (in CH_3OH) was spin-coating as electron transfer layer. Finally, aluminum (100 nm) was evaporated onto the active layer at a vacuum of ~2×10^{-4} Pa to form the top electrode. The effective area of the device is 0.1 cm^2. The current-voltage (*J-V*) characteristics

were measured with a Keithley 2420 source measurement unit. The PSCs were measured under an irradiation intensity of 100 mW/cm^2 (AM 1.5 G) by a Newport solar simulator. The EQE spectra were analyzed using a certified Newport IPCE measurement system. The hole and electron mobilities were calculated using the space charge limited current (SCLC) model with a device configuration of ITO/PEDOT:PSS/active layer/MoO_3/Al and ITO/ZnO/active layer/PFN/Al, respectively, where the current density is calculated by:

$$J = 9\varepsilon\mu V^2/(8L^3)$$

where ε represents the dielectric constant of the metal, and μ is the carrier mobility, V is the voltage drop across the device ($V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage to the device, V_{bi} is the built-in voltage due to the difference in work function of the two electrodes), L is the thickness of the active layer .

3. TGA curves

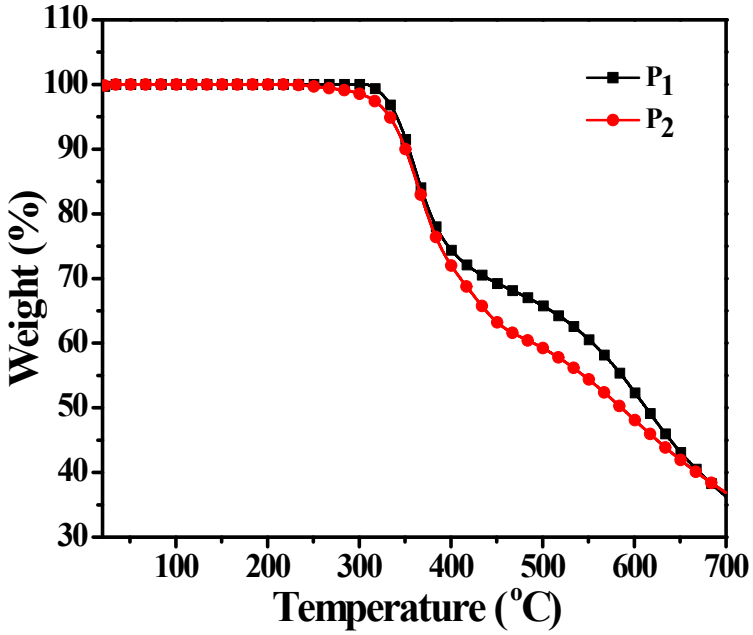

Fig. S1 Thermogravimetric analysis (TGA) of the polymers.

4. Temperature-dependent UV-vis absorption spectra

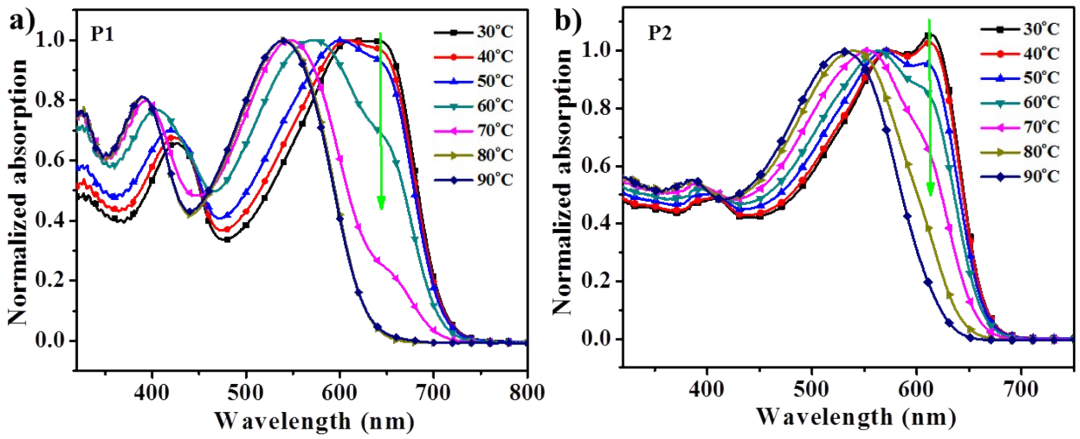

Fig. S2 The temperature-dependent UV-vis absorption spectra of P1 and P2 in *o*-DCB dilute solutions.

5. Photovoltaic performance

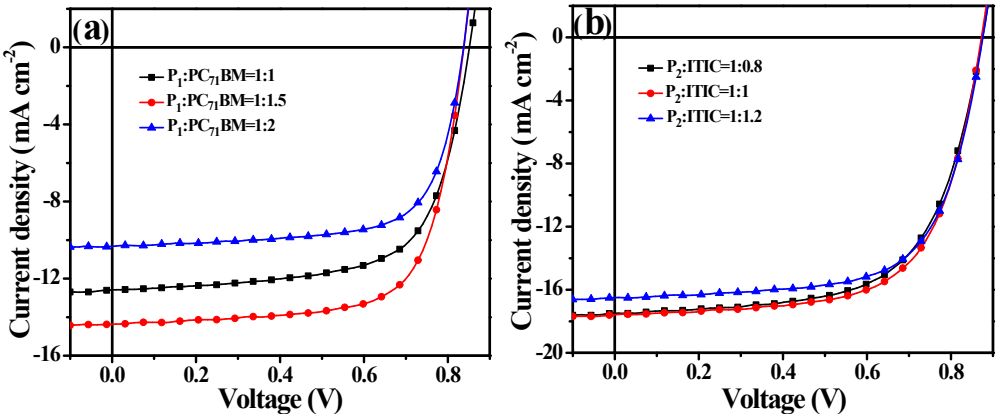

Fig. S3 (a) *J-V* curves of the PSCs based on $P_1/PC_{71}BM$ with different donor/acceptor ratios (1:1, 1:1.5, 1:2); (b) *J-V* curves of the PSCs based on P_2/ITIC (thermal annealing) with different donor/acceptor ratios (1:0.8, 1:1,1:1.2).

Table S1. The optimized details and the corresponding photovoltaic parameters of the PSCs

Active layer	D/A *w/w*	DIO v/v%	Annealing °C	V_{OC} V	J_{SC} mA cm^{-2}	FF %	PCE[a] %
P_1:$PC_{71}BM$	1:1	0	no	0.851	12.61	66.82	7.17(6.95)
	1:1.5	0	no	0.838	14.35	70.27	8.45(8.29)
	1:1.5	0.5	no	0.826	12.42	69.85	7.17(6.82)
	1:1.5	0	110	0.846	14.91	65.40	8.24(7.93)

	1:2	0	no	0.837	10.31	70.09	6.05(5.79)
P_1:ITIC	1:0.8	0	no	0.748	9.67	50.85	3.68(3.65)
	1:1	0	no	0.772	15.20	54.02	6.35(6.10)
	1:1	0.5	no	0.770	11.83	49.40	4.52(4.37)
	1:1	0	150	0.732	14.10	51.35	5.30(5.18)
	1:1.5	0	no	0.784	14.98	53.36	6.22(6.03)
P_2:$PC_{71}BM$	1:1	0	no	0.807	9.16	61.81	4.57(4.52)
	1:2	0	no	0.842	7.94	69.44	4.64(4.50)
	1:2	0.5	no	0.833	7.73	69.14	4.45(4.35)
	1:2	0	110	0.840	8.20	66.20	4.55(4.24)
	1:2.5	0	no	0.853	6.55	68.82	3.85(3.58)
P_2:ITIC	1:0.8	0	0	0.891	17.63	58.27	9.16(8.85)
	1:0.8	0	110	0.870	17.29	63.65	9.58(9.45)
	1:1	0	0	0.903	17.35	61.81	9.68(9.32)
	1:1	0	110	0.873	17.60	65.37	10.04(9.88)
	1:1	0.5	110	0.892	16.14	65.06	9.40(9.22)
	1:1.2	0	0	0.901	16.07	61.85	8.96(8.73)
	1:1.2	0	110	0.876	16.13	65.27	9.22(8.98)

[a] values were provided in optimal (average) results based on more than 10 devices for each case.

6. Mobilities based on SCLC measurement

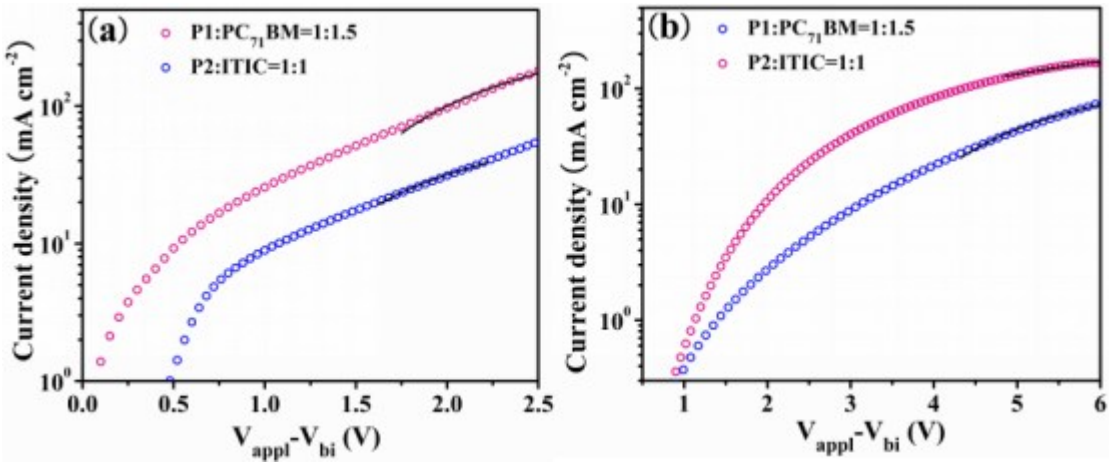

Fig. S4 Plots obtained from the a) hole-only and b) electron-only devices. (The symbols are experimental data for transport of hole, and the black lines are fitted according to the space-charge-limited-current model).

7. Photoluminescence emission spectra

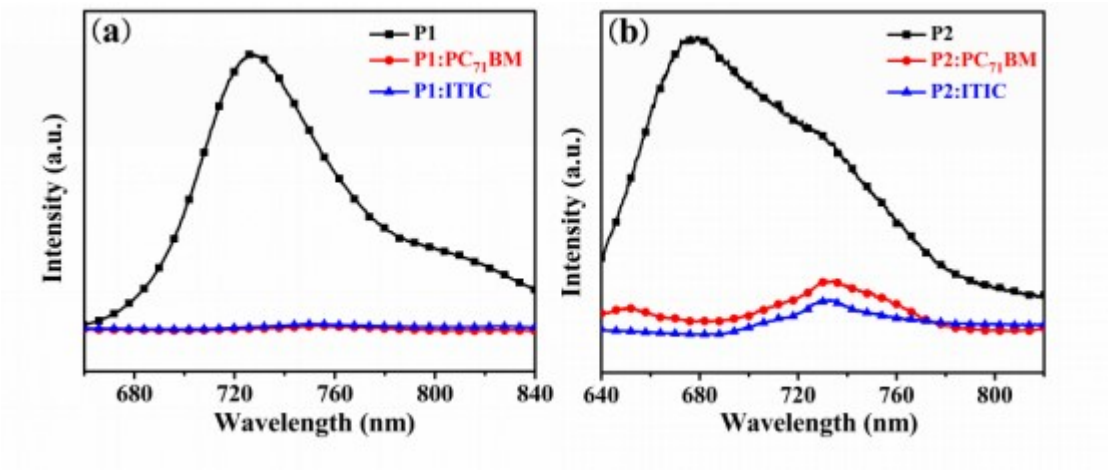

Fig. S5 PL emission spectra of pure polymers P1, P2 and blend films.

8. NMR Spectra

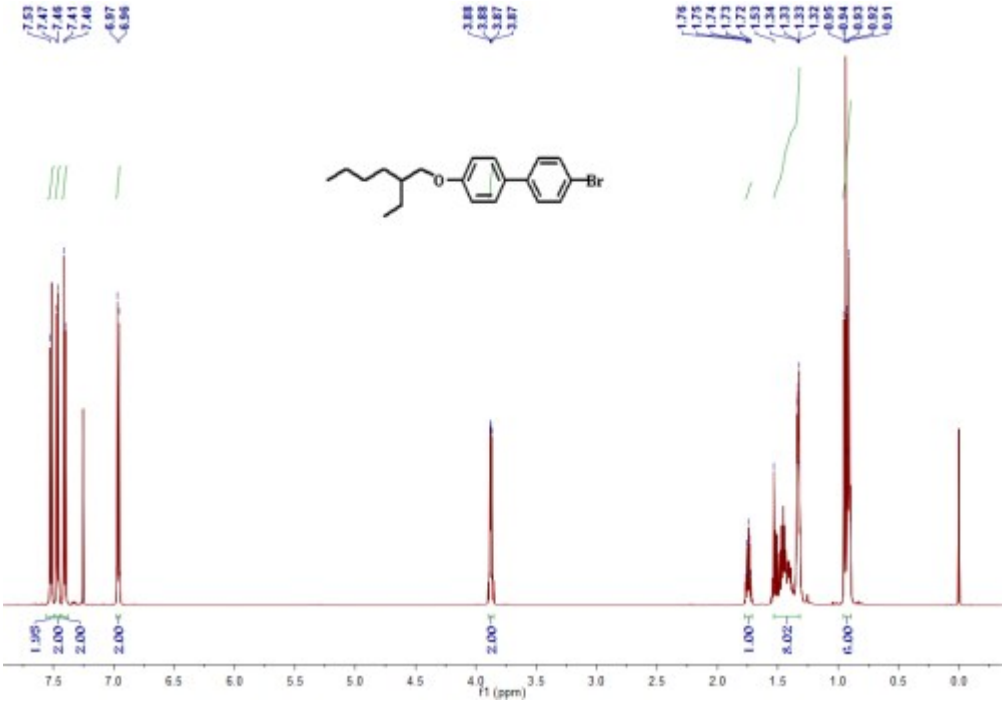

Fig. S6 ^{1}H NMR spectrum of compound **2**.

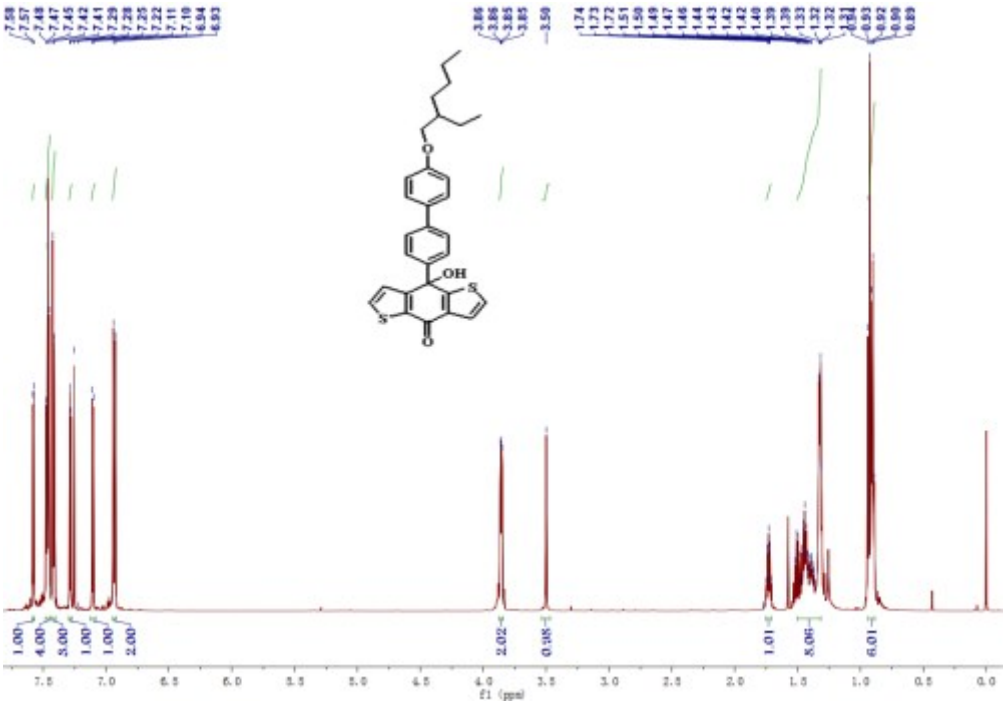

Fig. S7 ^{1}H NMR spectrum of compound 3.

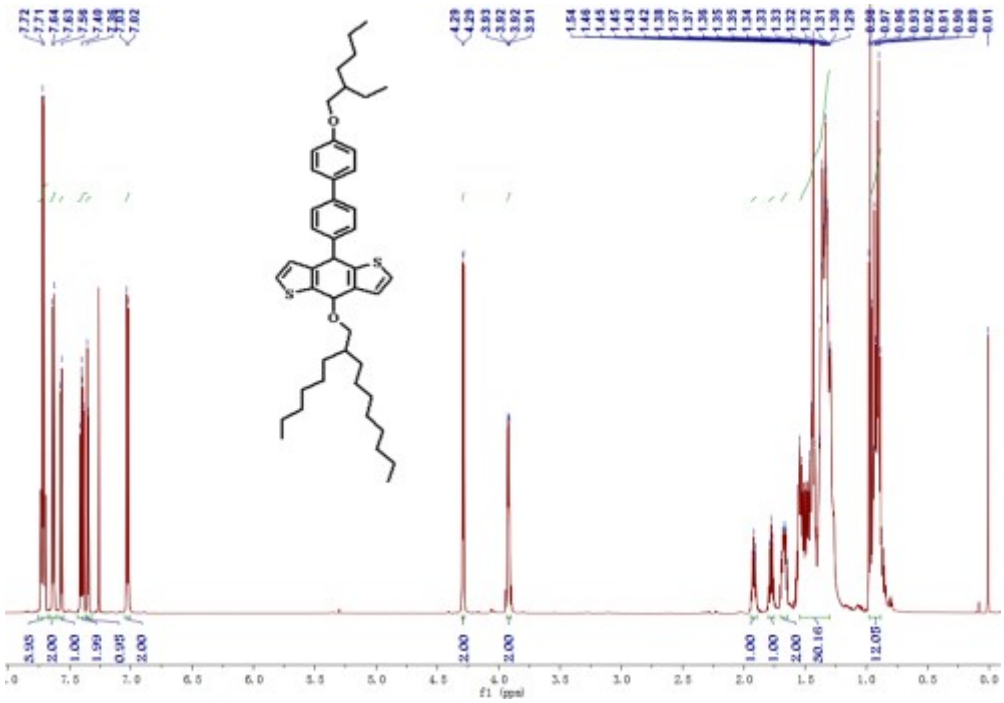

Fig. S8 ^{1}H NMR spectrum of compound 4.

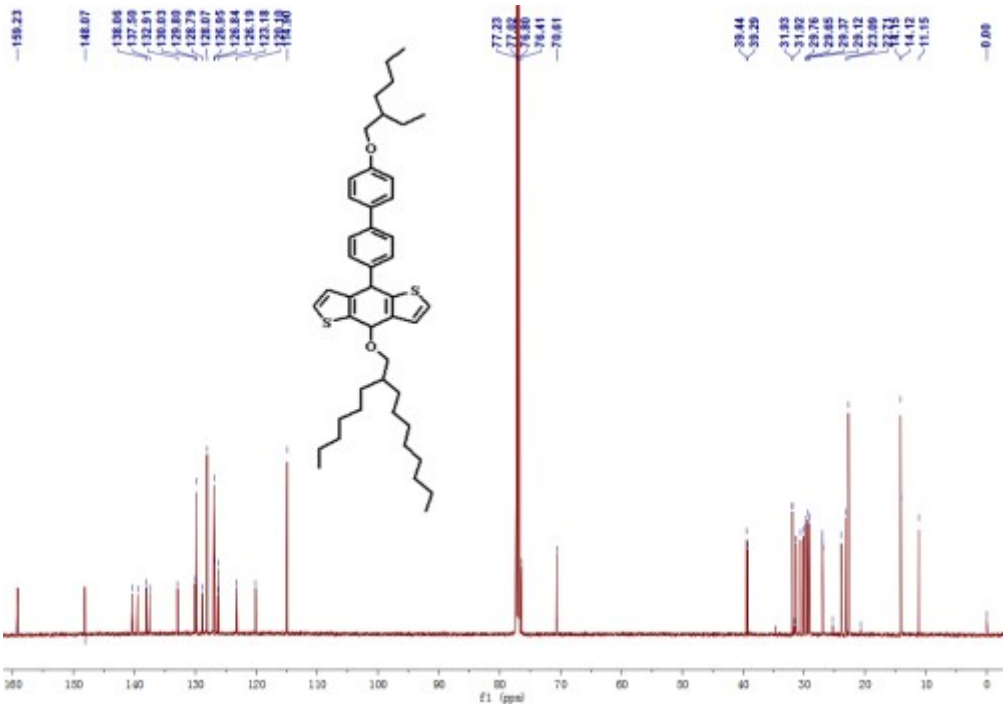

Fig. S9 ^{13}C NMR spectrum of compound 4.

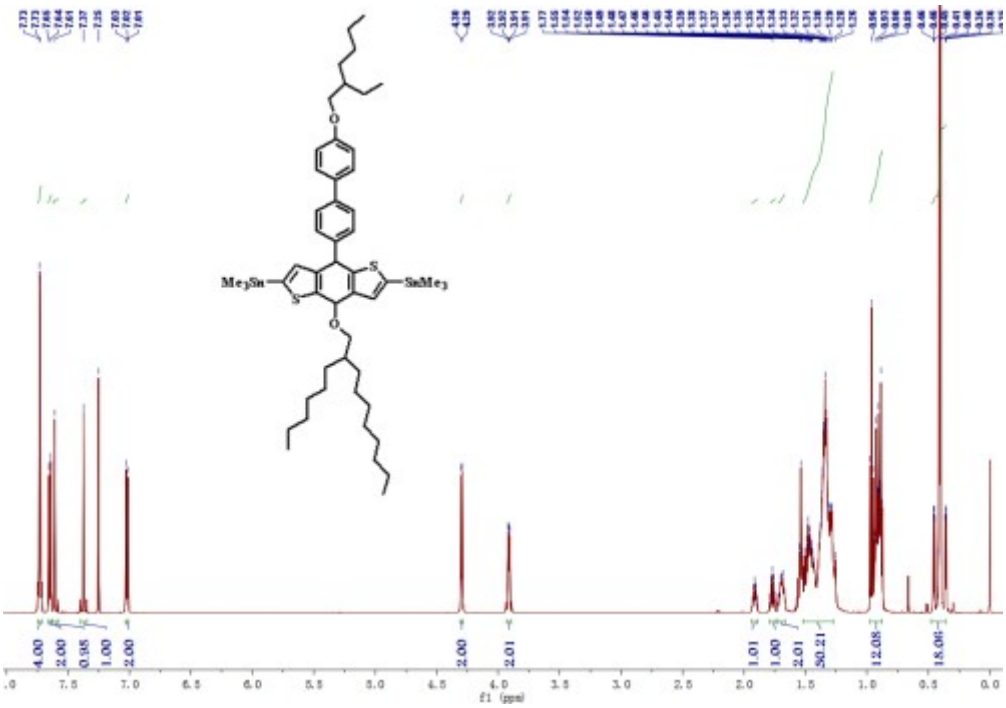

Fig. S10 ^{1}H NMR spectrum of compound asy-BDTBP.

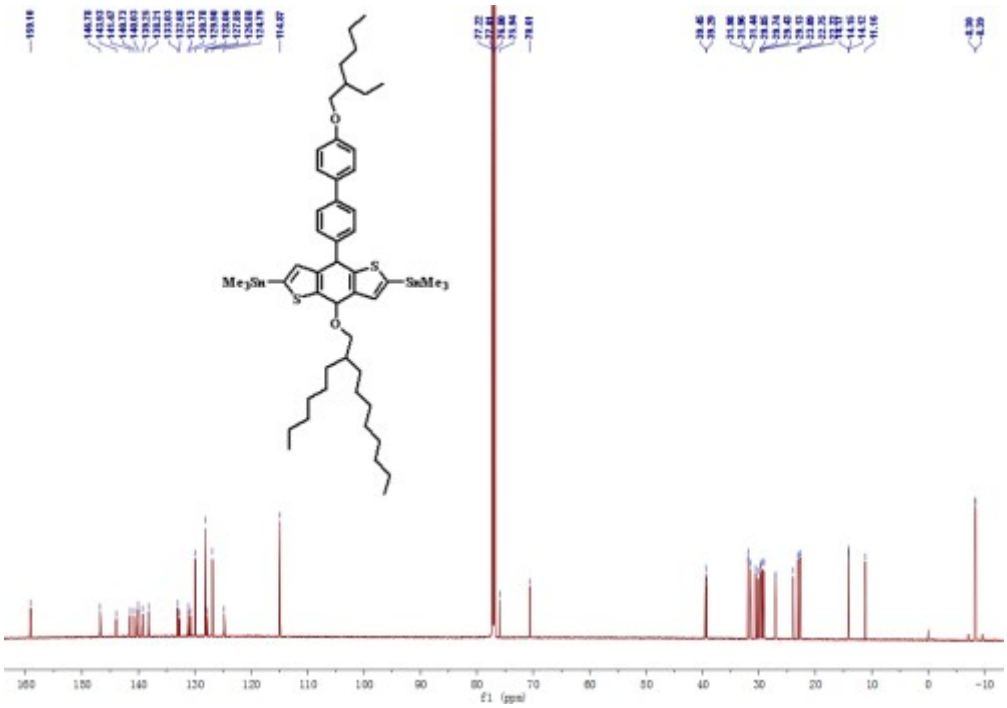

Fig. S11 ^{13}C NMR spectrum of compound asy-BDTBP.