Electronic Supplementary Information

Benzodithiophene with multiple side-chains for efficient wide-bandgap D-A copolymers

Zhijian Li, Yunlong Ma and Qingdong Zheng[*]

Reagents and instruments

All commercial reagents were used without any further treatment unless specifically stated. Y6 was purchased from Solarmer Materials Inc. Compounds 6 and 7 were purchased from SunaTech Inc. The other reagents were purchased from Adamas-Beta Ltd., Sigma-Aldrich Inc., J&K Scientific Ltd., and Aladdin-Reagent Inc. ^{1}H NMR spectra were obtained using a Bruker AVANCE-400 spectrometer. Photoluminescence spectra were taken on an Edinburgh Instrument FLS 920. UV-vis absorption spectra were obtained on a Lambda 365 spectrophotometer. The AFM images of the active layers were acquired by a Dimension Icon AFM. The thickness of films was measured by a Bruker Dektak XT surface profilometer. Cyclic voltammetry was performed in a solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in acetonitrile on a CHI 604E electrochemical workstation with a three-electrode system at a scan rate of 100 mV s^{-1}. The polymer donors were deposited on a Pt plate electrode by dipping the electrode into the corresponding solutions and then dried under the ambient condition. Pt wire and Ag/AgNO$_3$ were used as the counter electrode and reference electrode, respectively.

Synthesis

Compounds **1** and **3** were prepared according to the reported procedures.[S1, S2]

Synthesis of compound 2
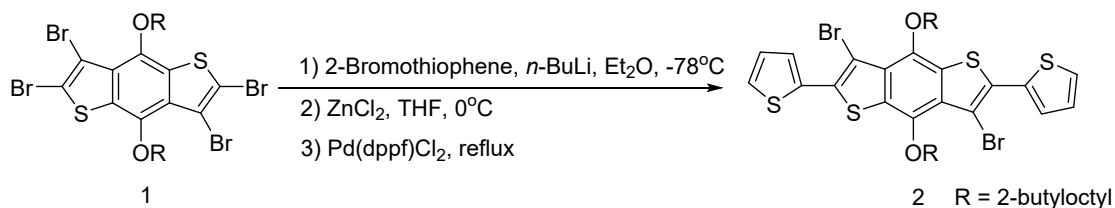
To the diethyl ether solution of 2-bromothiophene (0.75 g, 4.57 mmol) was added *n*-BuLi (2.1 mL, 5.03 mmol) dropwise at -78 °C under N_2 atmosphere, and then the temperature was maintained for 1 h. $ZnCl_2$ solution (5.1 mL, 5.03 mmol) was subsequently added, followed by stirring at 0 °C for another 1 h. After that, compound 1 (0.5 g, 0.57 mmol) and dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) (0.042 g, 0.057 mmol) were added and then the mixture was heated to reflux for 12 h. Finally, saturated aqueous NH_4Cl solution was used to quench the reaction. The organic layer was then extracted by water and diethyl ether, washed by brine, dried over anhydrous $MgSO_4$ and filtrated. By using column chromatography on silica gel (petroleum ether as eluent), compound 2 was successfully obtained as a yellow solid (0.37 g, 73%). ^1H NMR (400 MHz, CDCl$_3$): δ 7.68 - 7.63 (m, 2H), 7.55 - 7.49 (m, 2H), 7.21 - 7.17 (m, 2H), 4.10 (d, *J* = 6.4 Hz, 4H), 2.10 - 1.98 (m, 2H), 1.56 - 1.52 (m, 2H), 1.47 - 1.19 (m, 30H), 1.00 - 0.89 (m, 12H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 144.19, 134.75, 133.38, 130.58, 129.89, 128.73, 127.66, 127.16, 100.15, 79.18, 38.89, 31.98, 31.05, 30.74, 29.86, 29.08, 26.82, 23.20, 22.75, 14.21, 14.17. HRMS (MALDI) m/z: calcd. for $C_{42}H_{56}O_2Br_2S_4$, 878.1524; found, 878.1517.

Synthesis of compound 4
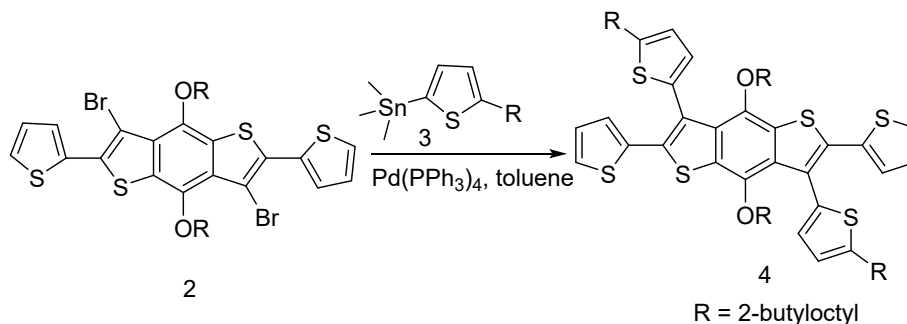
Under N_2 atmosphere, compound 3 (0.57 g, 1.36 mmol) and Pd(PPh$_3$)$_4$ (0.04 g, 0.034 mmol) were added to the mixture of toluene (10 mL) and compound 2 (0.3 g, 0.34

mmol), followed by refluxing for 12 h. The crude product was then extracted by water and CH$_2$Cl$_2$, washed by brine, dried over anhydrous MgSO$_4$ and filtrated. By using column chromatography on silica gel (CH$_2$Cl$_2$: petroleum ether = 1:30 as eluent), compound 4 was successfully obtained as a yellow solid (0.41 g, 98%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.25 - 7.20 (m, 4H), 6.99 - 6.94 (m, 4H), 6.81 (d, J = 3.6 Hz, 2H), 3.67 (d, J = 6.3 Hz, 4H), 2.84 (d, J = 6.6 Hz, 4H), 1.75 - 1.66 (m, 2H), 1.44 - 1.17 (m, 66H), 0.99 - 0.87 (m, 24H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.50, 144.93, 136.69, 136.31, 133.58, 132.36, 130.40, 128.99, 127.34, 127.21, 126.44, 125.17, 123.80, 78.55, 39.99, 38.33, 34.59, 33.23, 32.87, 32.05, 31.97, 30.82, 30.50, 29.96, 29.81, 28.94, 28.89, 26.69, 26.65, 23.26, 23.13, 22.79, 22.74, 14.24, 14.22, 14.19, 14.14. HRMS (MALDI) m/z: calcd. for C$_{74}$H$_{110}$O$_2$S$_6$, 1222.6825; found, 1222.6816.

Synthesis of compound 5
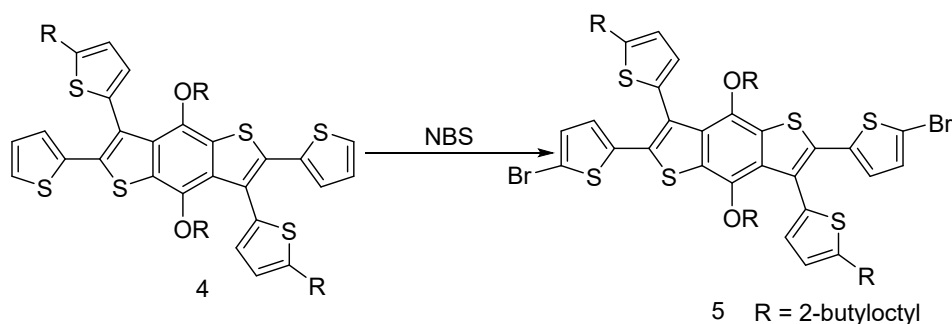
To the mixture of compound 4 (0.1 g, 0.082 mmol) and anhydrous tetrahydrofuran (10 mL) was added NBS (0.1 g, 0.56 mmol) at 0 °C in the dark. After the mixture was stirred at room temperature for 12 h, saturated aqueous Na$_2$SO$_3$ solution was injected to the mixture to quench the reaction. The organic layer was then extracted by water and CH$_2$Cl$_2$, washed by brine, dried over anhydrous MgSO$_4$ and filtrated. By using column chromatography on silica gel (CH$_2$Cl$_2$: petroleum ether = 1:50 as eluent), compound 5 was successfully obtained as a yellow solid (0.08 g, 71%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.02 (m, 2H), 6.96 (m, 2H), 6.93 (m, 2H), 6.83 (d, J = 3.1 Hz, 2H), 3.66 (d, J = 5.82 Hz, 4H), 2.87 (d, J = 6.5 Hz, 4H), 1.78 - 1.66 (m, 2H), 1.56 - 1.07 (m, 66H), 1.04 - 0.76 (m, 24H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 147.06, 145.04, 137.77, 136.20, 132.94, 132.44, 130.22, 129.35, 129.09, 127.13, 125.44, 124.17, 115.25, 78.61,

39.83, 38.35, 34.49, 33.11, 32.77, 32.07, 32.04, 30.83, 30.51, 29.97, 29.80, 28.98, 28.85, 26.72, 26.61, 23.26, 23.14, 22.81, 22.76, 14.29, 14.26, 14.22, 14.18. HRMS (MALDI) m/z: calcd. for $C_{74}H_{108}O_2Br_2S_6$, 1378.5035; found, 1378.5033.

Synthesis of PL4
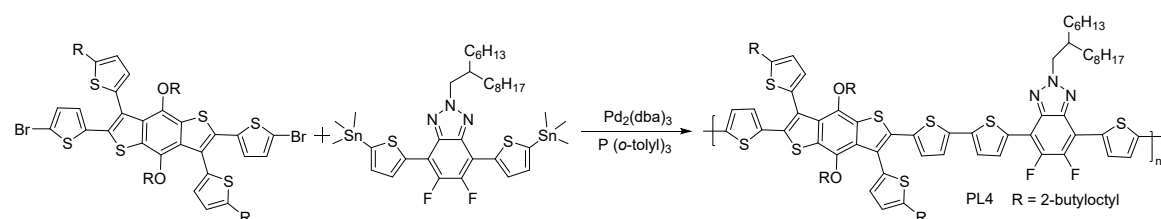
Under N_2 atmosphere, compound 5 (0.1 g, 0.0724 mmol) and compound 6 (0.063 g, 0.0724 mmol) were added to 9 mL of toluene, followed by bubbling for 15 min. Subsequently, $Pd_2(dba)_3$ (0.003 g, 0.004 mmol) and $P(o\text{-tol})_3$ (0.002 g, 0.08 mmol) were added to the mixture. After the mixture was heated to reflux for 78 h, 100 mL of methanol was added to precipitate the polymer donor and then filtered, followed by Soxhlet extraction with methanol, acetone, n-hexane, and dichloromethane. Finally, the excess solvent was removed by rotary evaporation to afford PL4 as a red solid (0.111 g, 76% yield, M_n = 55.1 KDa, PDI = 2.17). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16-8.00 (m, 4H), 6.87-6.83 (m, 8H), 4.86-4.65 (m, 2H), 3.68-3.61 (m, 4H), 2.88-2.86 (m, 4H), 2.27-2.26 (m, 1H), 1.76-1.74 (m, 2H), 1.30-1.28 (m, 90H), 0.85-0.83 (m, 30H).

Synthesis of PL5
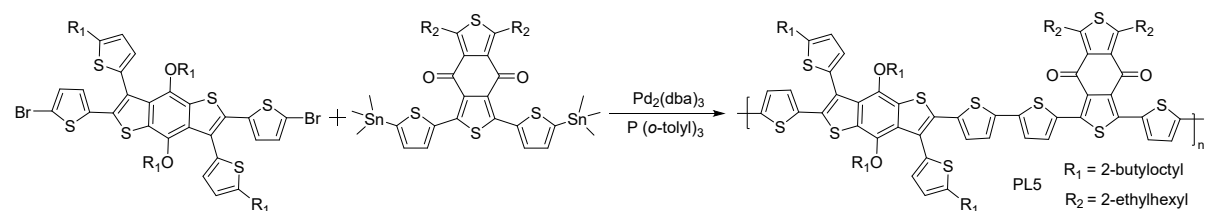
The preparation of PL5 was similar to that of PL4. PL5 was obtained as a red solid (70% yield, M_n = 64.3 KDa, PDI = 2.41). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.10-6.78 (br, 12H), 3.77-3.48 (m, 4H), 3.37-3.26 (m, 4H), 2.89-2.82 (m, 4H), 1.76-1.73 (m, 2H), 1.38-1.27 (m, 84H), 0.95-0.88 (m, 36H).

OSC device fabrication and characterization

OSCs were fabricated with a conventional device architecture of ITO/PEDOT:PSS/active layer/PDIN/Ag. ITO glass was ultrasonically cleaned with detergent, deionized water, acetone and isopropanol for 15 min each, then dried overnight in an oven, and subsequently subjected to UV-O$_3$ treatment for 15 min prior to use. To get the PEDOT:PSS film on ITO glass, a filtered PEDOT:PSS solution (Baytron PVP AI 4083 from H. C. Starck) was spin-coated onto the cleaned ITO substrates at 3500 rpm, followed by baking at 140 ^{o}C for 15 min in air. Subsequently, the PEDOT:PSS-coated ITO glass substrates were transferred into a N$_2$-filled glovebox. The overall concentration of polymer donor:Y6 is fixed at 20 mg mL^{-1} in chloroform which was subsequently spin-coated (3500 rpm, 30 s) on the PEDOT:PSS layer to form the active layer (~110 nm). Then the active layer was annealed at 85 °C for 5 min. Subsequently, 10 nm of PDIN layer was spin-coated (3300 rpm, 30 s) from the PDIN methanol solution (2.0 mg/mL and 0.3% *v/v* CH$_3$COOH). Finally, 100 nm of Ag layer was deposited onto the active layer by shadow masks. The active area for the devices was fixed at 4 mm^2. Device characterization was performed under AM 1.5G irradiation (100 mW cm^{-2}) using a solar simulator with the model of SS-X50 (EnliTech). The *J-V* curves were obtained by using a Keithley 2440 source measurement unit. EQE spectra were measured on a Newport EQE measuring system.

Fabrication and characterization of hole- and electron-only devices

Hole- and electron- mobilities were measured by using the space charge limited current (SCLC) method. Hole-only devices were fabricated with an architecture of ITO/PEDOT:PSS/active layer/MoO$_3$/Ag, while electron-only devices were constructed with an architecture of ITO/ZnO/active layer/Ca/Al. The active layers were prepared using the same method as that used for the best-performance PSCs. Device areas were fixed at 4 mm^2. The current density (*J*) was measured by a Keithley 2440 source measurement unit. The SCLC hole- and electron-mobilities were calculated according to the following equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

Where J is the current density (A m^{-2}), ε_0 is the free-space permittivity (8.85×10^{-12} F m^{-1}), ε_r is the relative dielectric constant of the active layer material, usually 2-4 for organic semiconductors (herein we used a relative dielectric constant of 3), μ is the hole- or electron-mobility, V is the voltage drop across the SCLC device ($V = V_{appl}-V_{bi}$, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage. Due to the difference in the work function of two electrodes in the hole- and electron-only devices, the V_{bi} values are 0.5 and 0.7 V, respectively), and L is the thickness of active layer. The thickness of film was determined by a Bruker Dektak XT surface profilometer. The hole- or electron-mobility can be calculated from the slope of the $J^{1/2}$-V curves.

GIWAXS characterization

All samples for the GIWAXS measurements were prepared on the PEDOT:PSS-coated Si substrates. The 2D GIWAXS patterns were acquired using a XEUSS SAXS/WAXS system at the National Center for Nanoscience and Technology (NCNST, Beijing). The wavelength of the X-ray beam is 1.54 Å, and the incident angle was set as 0.2˚. Scattered X-rays were detected by using a Dectris Pilatus 300 K photon counting detector. The coherence length (*CCL*) was estimated by the Scherrer equation: *CCL*= $2\pi k$/FWHM, where FWHM is the full width at half-maximum of the peak and k is a shape factor (0.9 was used here).

Table S1. Photovoltaic parameters of PSCs based on PL5:Y6 under the illumination of AM

1.5G (100 mW/cm^2).

DIO (vol %)	Annealing temperature [°C]	Annealing time [min]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [c] [%]
0.7	85	5	0.80	24.25	63.98	12.34 (12.11 ± 0.11)
1.0	85	5	0.81	26.86	70.01	15.27 (14.82 ± 0.24)
1.0 [a]	85	5	0.82	26.63	70.81	15.50 (15.30 ± 0.13)
1.0 [b]	85	5	0.82	26.60	72.47	15.77 (15.45 ± 0.19)
1.5	85	5	0.80	22.69	63.67	11.52 (11.21 ± 0.23)
0.5	90	5	0.79	20.39	65.05	10.46 (10.17 ± 0.17)
0.5	95	5	0.79	20.96	62.57	10.39 (10.14 ± 0.17)
0.5	85	3	0.84	19.40	63.42	10.31 (10.10 ± 0.18)
0.5	85	7	0.84	20.44	63.24	10.82 (10.46 ± 0.29)

The PL5:Y6 blend with the weight ratio of 1:1.2 [a] and 1:1.4 [b], respectively, was dissolved in chloroform with an overall concentration of 20 mg mL^{-1}; [c] In parentheses are averaged values with standard deviations based on 10 devices.

Table S2. Summarized parameters of the ordered structures based on pure donor films and two blends.

Samples	π-π stacking		Lamellar stacking	
	d_π (Å)[a]	CCL (Å) [b] (FWHM (Å^{-1}))	d_l (Å)[c]	CCL (Å)[b] (FWHM (Å^{-1}))
PL4	3.81	15.53 (0.364)	21.59	81.45 (0.069)
PL5	3.76	10.83 (0.522)	21.16	53.89 (0.105)
PL4:Y6	3.70	12.83 (0.082)	21.23	58.60 (0.097)
PL5:Y6	3.65	14.45 (0.391)	20.81	63.05 (0.090)

[a] d_π was calculated from the (010) diffraction peak along the q_z axis; [b] CCL was estimated from the Scherrer equation (CCL=2πk/FWHM), in which k is the Scherrer factor and FWHM is the full-width at the half-maximum of the peak; [c] d_l was calculated from (100) diffraction peak along the q_{xy} axis.
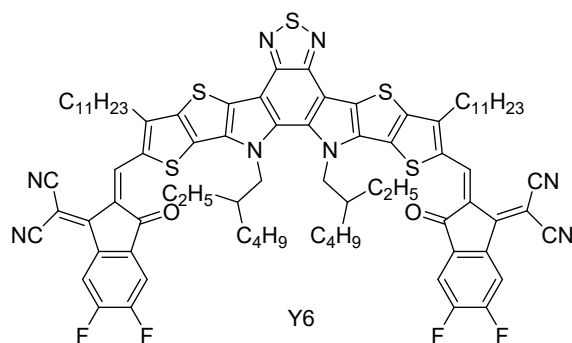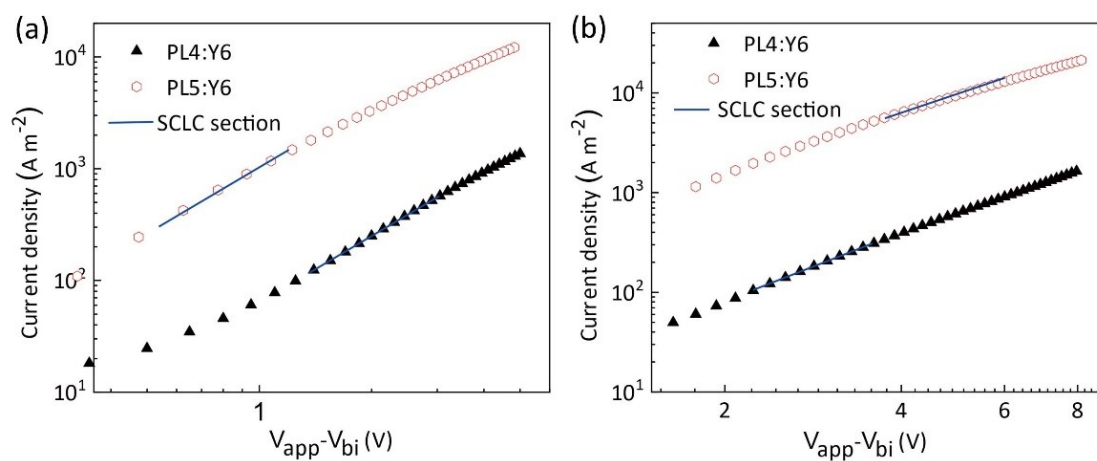
Fig S1. Chemical structure of Y6.

Fig S2. (a) *J-V* plots for hole-only and (b) electron-only devices based on PL4:Y6 and PL5:Y6.
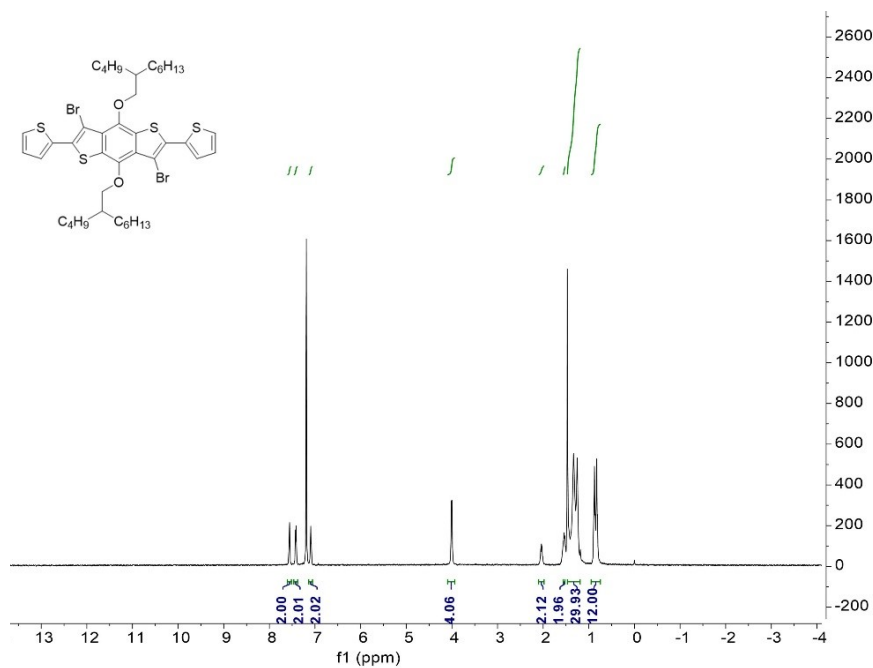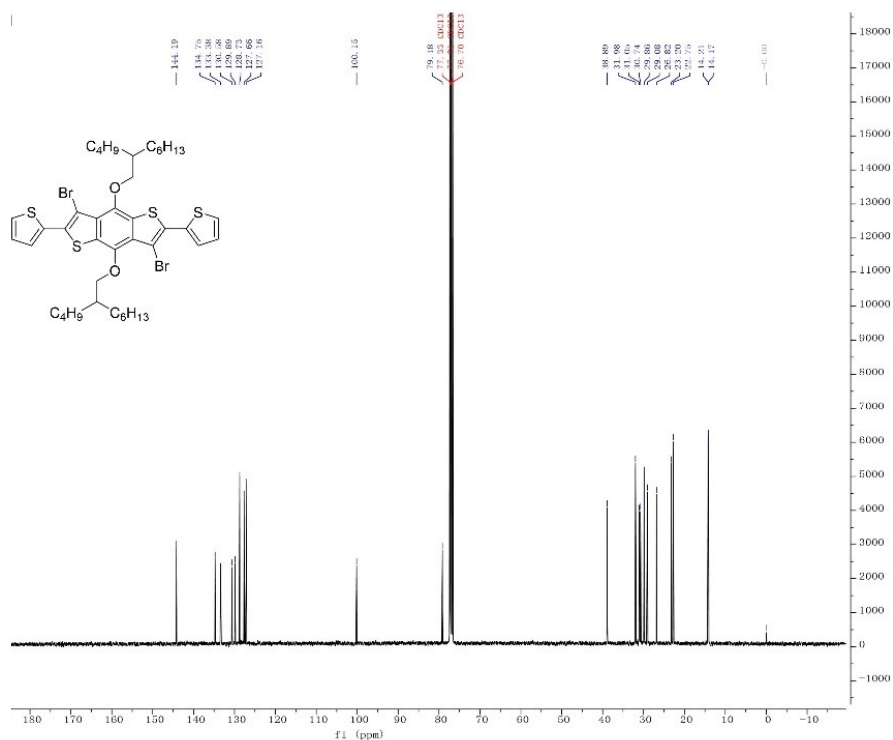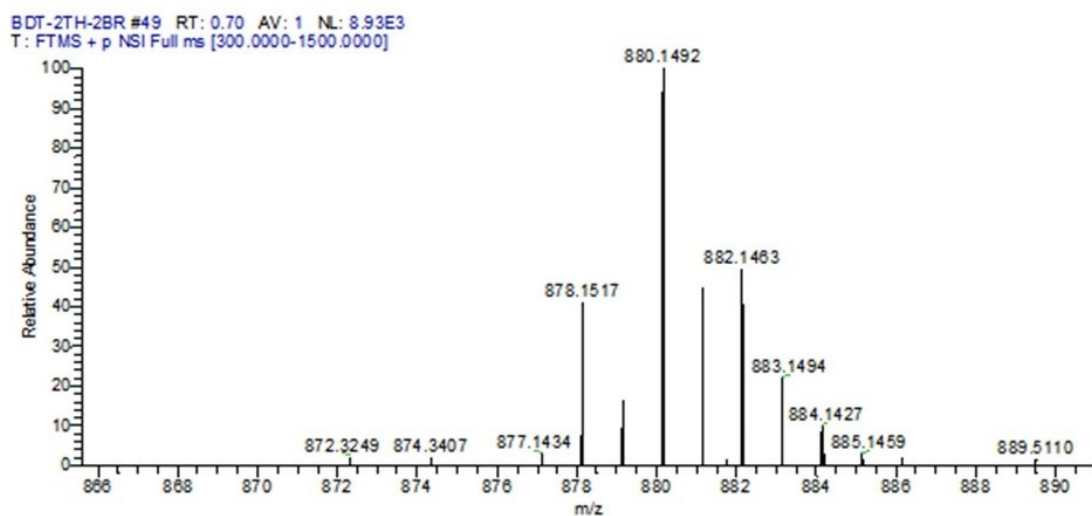

Fig S3. ^{1}H NMR spectrum of compound 2.

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

BDT-2TH-2BR #49 RT: 0.70 AV: 1 NL: 8.93E3
T: FTMS + p NSI Full ms [300.0000-1500.0000]

Elemental composition search on mass 878.1517

m/z= 873.1517-883.1517

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
878.1517	878.1524	-0.81	14.0	$C_{42} H_{56} O_2 Br_2 S_4$

Fig S5. HRMS spectrum of compound 2.
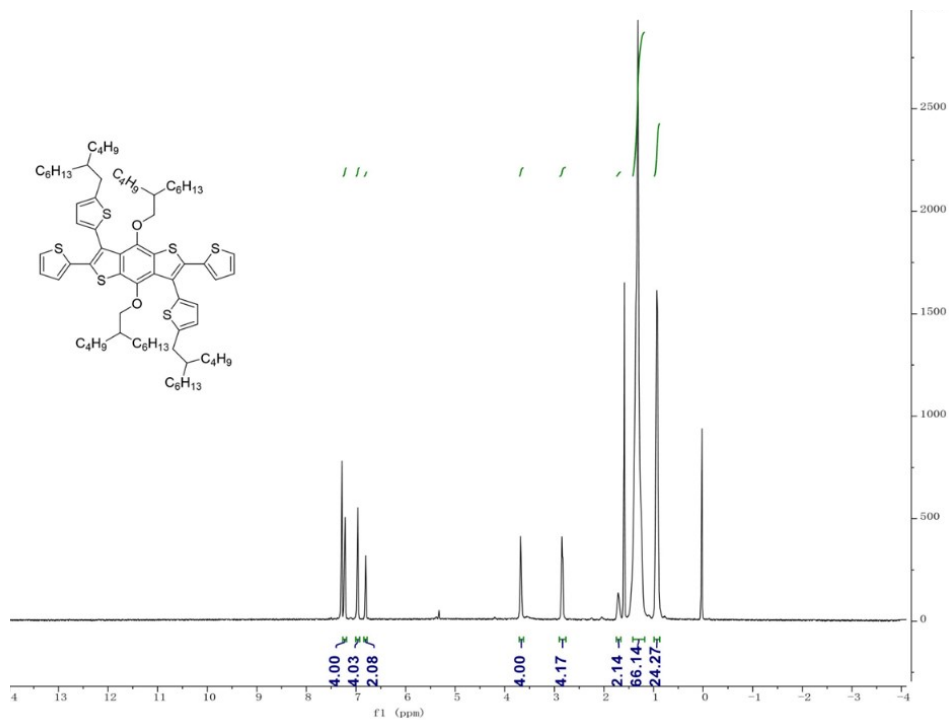
Fig S6. ^{1}H NMR spectrum of compound 4.

Fig S7. ^{13}C NMR spectrum of compound 4.

Fig S8. HRMS spectrum of compound 4.
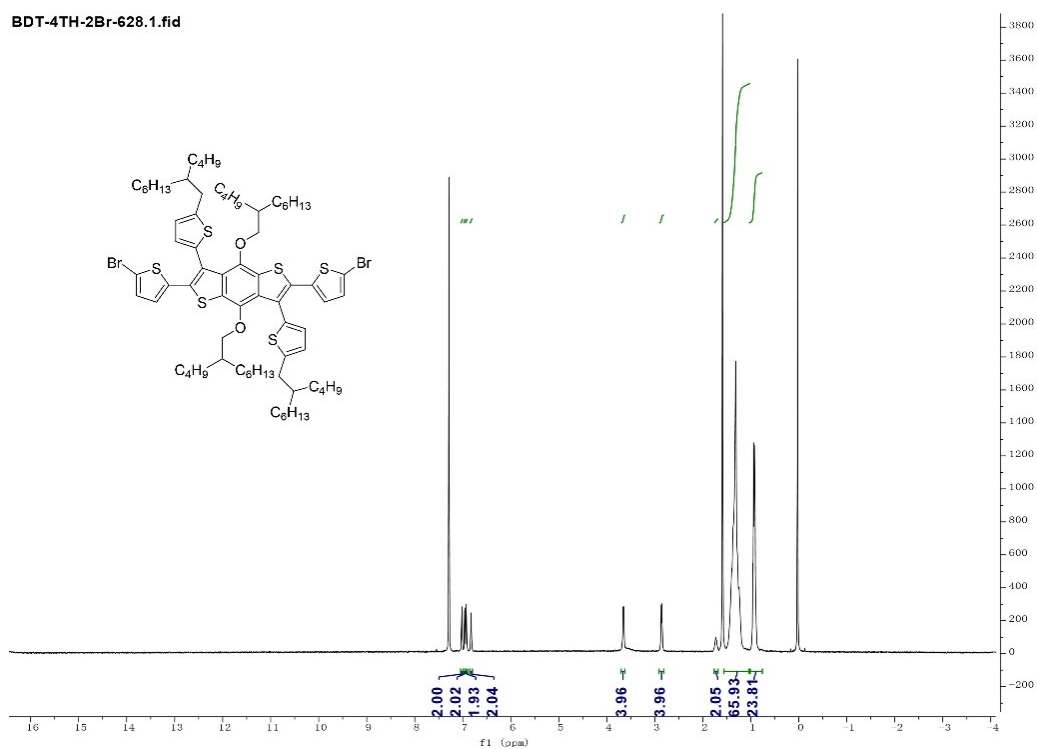
Fig S9. ^{1}H NMR spectrum of compound 5.
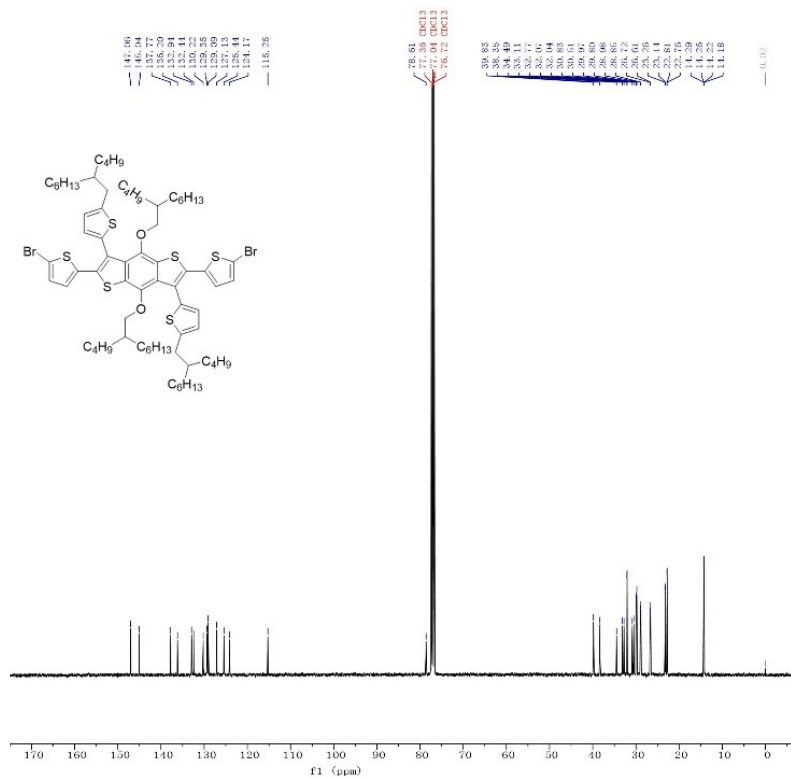
Fig S10. ^{13}C NMR spectrum of compound 5.

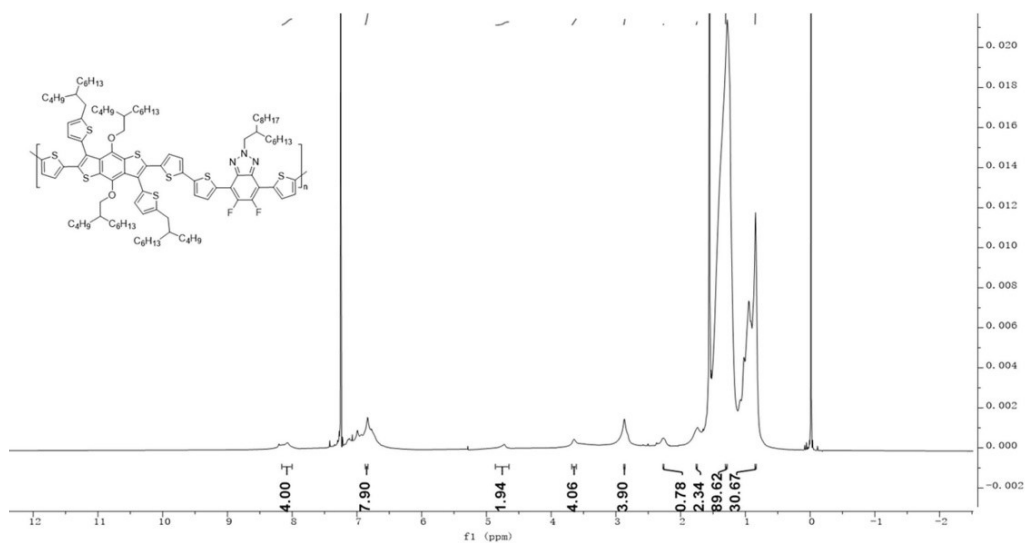**Fig S11**. HRMS spectrum of compound 5.

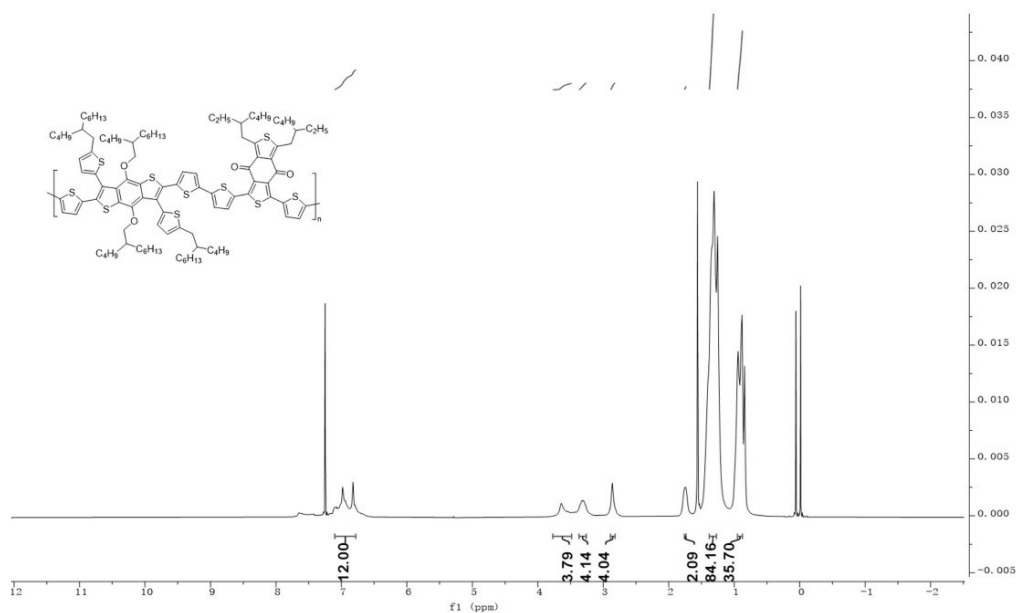**Fig S12.** ^{1}H NMR spectrum of PL4.

Fig S13. ^{1}H NMR spectrum of PL5.

References

S1. H. J. Son, W. Wang, T. Xu, Y. Liang, Y. Wu, G. Li and L. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 1885-1894.

S2. P.-Y. Gu, J. Zhang, G. Long, Z. Wang and Q. Zhang, *J. Mater. Chem. C*, 2016, **4**, 3809-3814.