Direct Access to 4,8-Functionalized Benzo[1,2-b:4,5-b']dithiophenes with deep low-lying HOMO levels and high mobilities

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1. Materials and Characterization

1.1 Materials

All commercially available chemicals and reagents were purchased from Sigma-Aldrich or Acros Chemical Co. and used without further purification. The purity of trifluoromethanesulfonic anhydride was 98%. THF and diethyl ether was dried over sodium/benzophenone and freshly distilled prior to use. DMF and dichloromethane were distilled from CaH_2 under nitrogen. N,N-Diethylthiophene-3-carboxamide[S1], 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)-thiophene[S2], 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(octyl)-thiophene[S2], 2-(5-hexylthien-[3,2-b]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S3], 2-(2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S3] and 4,8-dihydroxybenzo[1,2-b:4,5-b']dithiophene (**2**)[S4] were synthesized by following the reported procedures.

1.2 Characterization

^1H NMR and ^{13}C NMR spectra were characterized on Bruker AVANCE 500-MHz (Bio-Spin Corporation, Europe) spectrometer with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were obtained by Bruker ultrafleXtreme MALDI TOF/TOF. High-resolution EI mass spectra were recorded by the EPSRC National Mass Spectrometry Service at Swansea (UK) by using a Finnigan MAT 95 XP spectrometer. Gel permeation chromatography (GPC) analysis was measured with on a Waters 717-2410 instrument with polystyrene as the standard and THF as eluent (flow rate 1.0 mL/min). Ultraviolet–visible (UV-vis) absorption spectra were recorded on a UV-vis instrument Evolution 220. The electrochemical cyclic voltammetry was conducted on an electrochemical workstation (CHI660D, Chenhua Shanghai) with Pt plate as working electrode, Pt slice as counter electrode, and saturated calomel electrode (SCE) as reference electrode in tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) acetonitrile solutions at a scan rate of 50 mV/s. Melting points were determined on a WRS-1B Digital Melting Point apparatus. X-ray diffraction studies were performed on PAN-alytical X'PERT PRO system using Cu-Ka source in air. Atomic force microscopy (AFM) was recorded on a Dimension Icon AFM in tapping mode.

1.3 Synthetic procedures

4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (1). N,N-Diethylthiophene-3-carboxamide (36.6 g, 200 mmol) was put into a well-dried flask with THF (200 mL) under an inert atmosphere. The solution was cooled down with an ice-water bath, and *n*-butyllithium (70 mL, 2.4 M) was added into the flask dropwise within 30 min. The reaction was then stirred at ambient temperature for 30 min. The reaction mixture was poured into ice water (500 mL) and stirred for

several hours. The mixture was filtrated, and the yellow precipitate was washed with water (200 mL), methanol (50 mL) and hexane (50 mL) successively. The *title* compound **1** was obtained as a yellow powder (17.6 g, yield 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* =5.0 Hz, 2H), 7.64 (d, *J* = 5.0 Hz, 2H).

4,8-Dihydroxybenzo[1,2-b:4,5-b']dithiophene (2). To a stirred suspension of **1** (13.95 g, 63 mmol) in ethanol (200 ml) was added with $NaBH_4$ (5.27 g, 139 mmol) in one portion under ice/water bath cooling. The reaction mixture was stirred for at 85^{o}C 12 h before quenched by pouring it into HCl (50 mL, 1 M) solution. The crude product was filtered, washed with water, and dried under vacuum at 70^{o}C. The *title* compound **2** was obtained as a green solid (13.90 g, yield 99%) and used for next step without further purification. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.81 (s, 2H), 7.60 (d, *J* = 5.5 Hz, 2H), 7.54 (d, *J* = 5.5 Hz, 2H).

4,8-Bis(trifluoromethanesulfonyloxy)benzo[1,2-b:4,5-b']dithiophene (3). To a suspension of **2** (6 g, 27 mmol) and dry pyridine (6.6 mL) in dichloromethane (150 mL) was slowly added trifluoromethanesulfonic anhydride (13.6 mL, 80 mmol) at 0^{o}C. After the mixture was stirred at 0^{o}C for 12 h, water (100 mL) and hydrochloric acid (100 mL, 1 M) were added. The resulting mixture was extracted with dichloromethane (3×80 mL), and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified with column chromatography on silica gel eluted with petroleum ether/ethyl acetate (19:1) to give pure *title* compound as a white solid (9 g, yield 70%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ = 8.22 (d, *J* = 5.5 Hz, 2H), 7.57 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 135.70, 132.95, 132.52, 130.41, 119.52, 118.55 ($J_{C\text{-}F}$ = 319 Hz, CF_3); HRMS (EI): m/z = 485.8799 $[M]^+$, calcd for $C_{12}H_4O_6S_4F_6$: 485.8795.

General synthetic procedure for 4,8-diarylbenzo[1,2-b:4,5-b']dithiophene via Suzuki cross-coupling

The bistriflate **3** (200 mg, 0.41 mmol), arylboronic acids or esters (1.2 mmol) and palladium[0]-tetrakis(triphenylphosphine) (23 mg, 0.02 mmol) were placed in a round-bottomed flask. Tetrahydrofuran (20 mL, degassed with nitrogen) and aqueous sodium carbonate (5 mL, 1.0 M, degassed with nitrogen) were added via a septum. The mixture was heated at 85^{o}C for 16 h then poured onto aqueous hydrochloric acid. The aqueous phase was extracted with dichloromethane, washed with water, dried and evaporated under vacuum. The product was obtained by column chromatography on silica gel using petroleum ether.

4,8-Di(thien-2'-yl)-benzo[1,2-b:4,5-b']dithiophene (4). Following the above procedure, Suzuki coupling between **3** (200 mg, 0.41 mmol) and thiophen-2-boronic acid (154 mg, 1.2 mmol) afforded the *title* compound as a yellow solid (114 mg, yield 80%). m.p. 207-210^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ = 7.87-7.86 (4H), 7.57-7.56 (2H), 7.55-7.54 (2H), 7.36-7.34 (2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 139.59, 139.24, 136.71, 128.04, 127.77, 127.42, 126.39, 123.85, 123.21. MALDI-TOF/TOF-MS (positive ion mode): m/z= 353.9660 $[M]^+$, calcd for $C_{18}H_{10}S_4$: 353.9660.

4,8-Di(5-trimethylsiyl-thien-2'-yl)-benzo[1,2-b:4,5-b']dithiophene (5). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)-thiophene[S3] (338 mg, 1.2 mmol) afforded the *title* compound as a yellow solid (143 mg, yield 70%). m.p. 232-234^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.65 (d, *J* = 5.5 Hz, 2H), 7.57 (d, *J* = 3.5 Hz, 2H), 7.47 (d, *J* = 5.5 Hz, 2H), 7.37 (d, *J* = 3.5 Hz, 2H), 0.41 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ= 144.89, 141.68, 138.90, 136.47, 134.27, 129.25, 127.55, 123.98, 123.42, 0.04. MALDI-TOF/TOF-MS (positive ion mode): m/z= 498.0450 $[M]^+$, calcd for $C_{24}H_{26}S_4Si_2$: 498.0450.

4,8-Di(5-octyl-thien-2'-yl)-benzo [1,2-b:4,5-b']dithiophene (6). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(octyl)-thiophene[S3] (380 mg, 1.2 mmol) afforded the *title* compound as a yellow liquid (161 mg, yield 68%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.64 (d, *J* = 5.5 Hz, 2H), 7.55 (d, *J* = 5.5 Hz, 2H), 7.29 (d, *J* = 3.5 Hz, 2H,), 6.89 (d, *J* = 3.5 Hz, 2H), 2.86 (d, *J* = 6.5 Hz, 4H), 1.70-1.65 (m, 2H), 1.45-1.33 (br, 16H), 0.96-0.90 (br, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ= 145.69, 138.96, 137.19, 136.47, 127.67, 127.43, 125.35, 124.65, 123.40, 41.44, 34.23, 32.46, 28.90, 25.69, 23.01, 14.15, 10.90. MALDI-TOF/TOF-MS (positive ion mode): m/z = 578.2164 $[M]^+$, calcd for $C_{34}H_{42}S_4$: 578.2164.

4,8-Di(dodecylthio-thien-2'-yl)-benzo[1,2-b:4,5-b']dithiophene (7). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and 5-(dodecylthio)-thiophen-2-ylboronic acid[S3] (120 mg, 1.2 mmol) afforded the *title* compound as a yellow solid (180 mg, yield 69%). m.p. 43-45^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.61 (d, *J* = 5.5 Hz, 2H), 7.48 (d, *J* = 5.5 Hz, 2H), 7.33 (d, *J* = 3.5 Hz, 2H), 7.22 (d, *J* = 3.5Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 4H), 1.72 (m, 4H), 1.45 - 1.44 (m, 4H), 1.30 -1.25 (br, 32H), 0.88 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 142.45, 139.02, 136.72, 136.54, 132.96, 128.40, 127.88, 123.65,

123.14, 38.88, 31.91, 29.64, 29.51, 29.34, 29.17, 28.49, 22.68, 14.09. MALDI-TOF/TOF-MS (positive ion mode): m/z = 754.2857[M]$^+$, calcd for $C_{42}H_{58}S_6$: 754.2857.

4,8-Di(5-hexylthieno[3,2-b]thiophen-2-yl-benzo[1,2-b:4,5-b']dithiophene (8). Following the similar procedure as for **4,** Suzuki coupling of **3** (200 mg, 0.41 mmol) with 2-(5-hexylthien-[3,2-*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S3] (430 mg, 1.2 mmol) afforded the *title* compound as a yellow solid (137 mg, yield 55%). m.p. 198-200^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.67 (d, *J* = 5.5 Hz, 2H), 7.57 (s, 2H), 7.48 (d, *J* = 5.5 Hz, 2H), 7.05 (s, 2H), 2.95 (t, *J* = 7.5 Hz, 4H), 1.85-1.75 (4H), 1.47-1.44 (4H), 1.37-1.34 (br, 8H), 0.92 (t, 6H, *J* = 7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 149.08, 139.50, 139.43, 139.36, 137.34, 136.80, 127.92, 124.27, 123.30, 120.43, 116.38, 31.62, 31.26, 28.80, 22.60, 14.10. MALDI-TOF/TOF-MS (positive ion mode): m/z = 634.0979 [M]$^+$, calcd for $C_{34}H_{42}S_6$: 634.0979.

4,8-Di(bithienyl)-benzo[1,2-b:4,5-b']dithiophene (9). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and 2-(2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (350 mg, 1.2 mmol) afforded the *title* compound as a yellow solid (127 mg, yield 60%). m.p. 230-232^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.70 (d, *J* = 5.5 Hz, 2H), 7.51 (d, *J* = 5.5 Hz, 2H), 7.41 (d, *J* = 3.5 Hz, 2H), 7.32 (d, *J* = 3.5 Hz, 2H), 7.28 (s, 2H), 7.27 (s, 2H), 7.07 (t, *J* = 3.5 Hz, 5Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 139.16, 138.51, 138.43, 137.07, 136.65, 128.93, 127.93, 124.79, 124.09, 124.01, 123.58, 123.25. MALDI-TOF/TOF-MS (positive ion mode): m/z = 517.9414 [M]$^+$, calcd for $C_{26}H_{14}S_6$: 517.9414 .

4,8-Di(bithienyl)-benzo[1,2-b:4,5-b']dithiophene (10). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and furan-2-ylboronic acid (134 mg, 1.2 mmol) afforded the *title* compound as a yellow solid (108 mg, yield 81%). m.p. >250^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.96 (d, *J* = 5.5 Hz, 2H), 7.70 (s, 2H), 7.56 (d, *J* = 5.5 Hz, 2H), 7.09 (d, *J* = 3.0 Hz, 2H), 6.69 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 151.90, 142.41, 136.49, 134.97, 127.66, 123.62, 119.96, 111.66, 110.74. MALDI-TOF/TOF-MS (positive ion mode): m/z = 322.0125 [M]$^+$, calcd for $C_{18}H_{10}O_2S_6$: 322.0117 .

4,8-Di(phenyl)-benzo[1,2-b:4,5-b']dithiophene (11). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and phenylboronic acid (146 mg, 1.2 mmol) afforded the *title* compound as a white solid (127 mg, yield 90%). m.p. 234-236^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.74 (d, *J* = 7.0 Hz, 4H), 7.59 (t, *J* = 7.0 Hz, 7.5 Hz, 4H), 7.51 (t, *J* = 6.5 Hz, 7.5 Hz, 2H), 7.41 (d, *J* = 5.5 Hz, 2H), 7.35 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$,

ppm): δ = 139.31, 138.15, 136.13, 130.45, 129.38, 128.81, 128.15, 127.26, 122.87. MALDI-TOF/TOF-MS (positive ion mode): m/z = 342.0531 $[M]^+$, calcd for $C_{22}H_{14}S_2$: 342.0531.

4,8-Di(4-fluoro-phenyl)-benzo[1,2-b:4,5-b']dithiophene (12). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and 4-fluorophenylboronic acid (168 mg, 1.2 mmol) afforded the *title* compound as a white solid (126 mg, yield 81%). m.p. 230-232°C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.67 (s, 4H), 7.42-7.41 (2H), 7.28-7.27 (6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 163.58, 161.61, 138.27, 136.20, 135.11, 131.13, 131.07, 129.51, 127.52, 122.67, 115.98, 115.81. MALDI-TOF/TOF-MS (positive ion mode): m/z = 378.0348 $[M]^+$, calcd for $C_{22}H_{12}F_2S_2$: 378.0343.

4,8-Di(4-trifluoromethyl-phenyl)-benzo[1,2-b:4,5-b']dithiophene (13). Following the similar procedure as for **4,** Suzuki coupling between **3** (200 mg, 0.41 mmol) and 4-(trifluoromethyl)phenylboronic acid (228 mg, 1.2 mmol) afforded the *title* compound as white solid (160 mg, yield 82%). m.p. 237-239°C; ^{1}H NMR (500 MHz $CDCl_3$, ppm): δ = 7.86 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 5.5 Hz, 2H), 7.28 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 142.65, 138.07, 136.07, 129.78, 129.44, 128.05, 125.95, 122.64. MALDI-TOF/TOF-MS (positive ion mode): m/z = 478.0279 $[M]^+$, calcd for $C_{24}H_{12}F_6S_2$: 478.0279.

General Procedure for the palladium-catalyzed Sonogashira coupling of bistriflate 3 with terminal alkynes

The bistriflate **3** (200 mg, 0.41 mmol), terminal alkyne (2.5 mmol) and $Pd(PPh_3)_2Cl_2$ (57 mg, 0.04 mmol, 10 mol %), CuI (30 mg, 0.08 mmol, 20 mol% equiv.) were placed in a round-bottomed flask (25 mL), fitted with a condenser, under nitrogen. DMF (7 mL) and diisopropylamine (7 mL) was added via a septum. The mixture was stirred for 12 h at 100°C then poured onto aqueous hydrochloric acid (1 mL, 1 M). The resulting mixture was extracted with dichloromethane (3×5 mL), and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluted with hexane to give solid.

4,8-Di(ethynyl)-benzo[1,2-b:4,5-b']dithiophene (14). Following the above procedure, Sonogashira coupling between **3** (200 mg, 0.41 mmol) and trimethylsilylacetylene (0.17 mL, 1.2 mmol) afforded the *title* compound as a yellow solid (57 mg, yield 55%). m.p. 55-57°C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.63 (d, *J* = 5.5 Hz, 2H), 7.59 (d, *J* = 5.5 Hz, 2H), 3.86 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 140.83, 138.91, 128.58, 122.96, 111.30, 86.84, 79.63. MALDI-TOF/TOF-MS (positive ion mode): m/z = 237.9906 $[M]^+$, $C_{14}H_6S_2$: 237.9905.

4,8-Di(decyn-1-yl)-benzo[1,2-b:4,5-b']dithiophene (15). Following the similar procedure as for 1**4,** Sonogashira coupling between **3** (200 mg, 0.41 mmol) and 1-decyne (0.22 mL, 1.2 mmol) afforded the *title* compound as a yellow solid (165 mg, yield 90%). m.p. 45-47^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.57 (d, 2H, *J* = 5.5 Hz), 7.49 (d, 2H, *J* = 5.5 Hz), 2.62 (t, 4H, *J* = 7.0 Hz), 1.75-1.69 (m, 4H), 1.49-1.26 (br, 20H), 0.87-0.85 (6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 140.21, 138.24, 127.51, 123.23, 112.21, 100.41, 31.86, 29.23, 29.14, 28.92, 28.81, 22.67, 19.94, 14.10. MALDI-TOF/TOF-MS (positive ion mode): m/z = 462.2409 $[M]^+$; calcd for $C_{30}H_{38}S_2$: 462.2409.

4,8-Di(4-methyl-phenylethynyl)-benzo[1,2-b:4,5-b']dithiophene (16). Following the similar procedure as for **14**, Sonogashira coupling between **3** (200 mg, 0.41 mmol) and 4-tolylacetylene (0.15 mL, 1.2 mmol) afforded the *title* compound as a yellow solid (150 mg, yield 88%). m.p. >250^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.71 (d, *J* = 5.5 Hz, 2H), 7.59-7.57 (br, 6H), 7.23 (d, *J* = 8.0 Hz, 4H), 2.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 140.29, 139.10, 138.19, 131.68, 129.26, 128.00, 123.27, 119.85, 112.09, 99.45, 85.13, 21.60. MALDI-TOF/TOF-MS (positive ion mode): m/z = 418.0844 $[M]^+$, calcd for $C_{28}H_{18}S_2$: 418.0844.

General procedure for the palladium-catalyzed coupling of triflates 3 with aryl thiols or alkyl thiols

A mixture of bistriflate **3** (200 mg, 0.41 mmol), *i*-Pr_2Net (0.16 mL, 0.947 mmol), and dry toluene (8 mL) was added into a Shlenk tube, which was then evacuated and filled with nitrogen (three cycles). Catalyst $Pd_2(dba)_3$ (11.1 mg, 0.0012 mmol), Xantphos (14.0 mg, 0.024 mmol) and aryl thiols or alkyl thiols (1.2 mmol) were added and the mixture was degassed twice more. The mixture was heated to reflux overnight and TLC confirmed completion of the reaction. The reaction was cooled, filtered and concentrated. The crude product was purified by column chromatography (silica gel, hexane) to afford the desired product.

4,8-Di(octylthio)-benzo[1,2-b:4,5-b']dithiophene (17). Following the above procedure, palladium-catalyzed coupling between bistriflate **3** (200 mg, 0.41mmol) and 1-mercaptooctane (0.21ml, 1.2 mmol) afforded the *title* compound as a yellow liquid (178 mg, yield 90%). m.p. 33-34^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.75 (d, *J* = 5.5 Hz, 2H), 7.53 (d, *J* = 5.5 Hz, 2H), 2.99 (t, *J* = 7 Hz, 4H), 1.57 - 1.51 (4H), 1.39 - 1.37 (4H),1.27 - 1.20 (br, 12H), 0.86 (t, *J* = 7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 144.97, 140.59, 128.27, 123.94, 123.06, 35.81, 31.73, 30.21, 29.11, 29.05, 28.62, 22.59, 14.06. MALDI-TOF/TOF-MS (positive ion mode): m/z= 478.1851 $[M]^+$, calcd for $C_{26}H_{38}S_4$: 478.1851.

4,8-Di(dodecylthio)-benzo[1,2-b:4,5-b']dithiophene (18). Following the similar procedure as for **17,** palladium-catalyzed coupling between bistriflate **3** (200 mg, 0.41mmol) and 1-dodecanethiol (0.3 mL, 1.2 mmol) afforded the *title* compound as a yellow solid (221 mg, yield 91%). m.p. 39-41^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.75 (d, *J* = 5.5 Hz, 2H), 7.53 (d, *J* = 5.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 4H), 1.26-1.20 (br, 40H), 0.88 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 144.99, 140.62, 128.28, 123.96, 123.12, 35.84, 34.06, 31.91, 30.23, 29.61, 29.34, 29.10, 28.64, 22.68, 14.10; MALDI-TOF/TOF-MS (positive ion mode): m/z= 590.3103 $[M]^+$, calcd for $C_{34}H_{54}S_4$: 590.3103.

4,8-Di(4-methyl-phenylthio)-benzo[1,2-b:4,5-b']dithiophene (19). Following the similar procedure as for **17,** palladium-catalyzed coupling between bistriflate **3** (200 mg, 0.41mmol) and 4-methylbenzenethiol (153mg, 1.2 mmol) afforded the *title* compound as a yellow solid **19** (159 mg, yield 90%). m.p. 147-149^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ= 7.64 (d, *J* = 5.6 Hz, 2H), 7.47 (d, 2H, *J* = 5.6 Hz, 2H), 7.10 (d, *J* = 8.5Hz, 4H), 7.01 (d, *J* = 8.5Hz, 2H), 2.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ= 144.88, 140.69, 136.42, 131.83, 129.87, 129.01, 128.66, 123.64, 121.93, 20.98. MALDI-TOF/TOF-MS (positive ion mode): m/z = 434.0286 $[M]^+$, calcd for $C_{24}H_{18}S_4$: 434.0286.

Poly(9,9-dioctylfluorene-2,7-diyl-alt-dithieno[2,3-b:5,6-b']phenylene-1,4-diyl). A 2-necked round bottom flask equipped with a condenser was charged with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (264 mg, 0.41 mmol) and the corresponding bistriflate **3** (200 mg, 0.41 mmol). Toluene (4 mL) and Na_2CO_3 (4 mL, 1 M) were added to the flask and the heterogeneous reaction mixture was degassed by passing a flow of nitrogen through the solution for 30 min. Then $Pd(PPh_3)_4$ (22 mg, 5% eq.) was added and the reaction mixture was heated at 85°C for 3 days under vigorous stirring. The reaction mixture was cooled to room temperature, poured into MeOH (120 mL) and stirred for 1 h. The precipitate was filtered, washed with MeOH and dried in vacuum. The precipitated material was collected and was Soxhlet-extracted in order with methanol, acetone and then with chloroform. The chloroform solution was concentrated to a small volume, and the polymer was precipitated by pouring this solution into methanol. Finally, the gray polymer **P1** was collected by filtration and dried under vacuum at 40°C overnight (120 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 8.03-8.01 (d, 2H), 7.83 (s, 2H), 7.79-7.77 (d, 2H), 7.48 (4H), 2.12-2.10 (4H), 1.65-1.63 (4H), 1.18-1.15 (20H), 0.88-0.86 (6H); M_w = 21.4 kDa, M_w/M_n = 1.81.

2. ^{1}H-NMR and ^{13}C-NMR Spectra

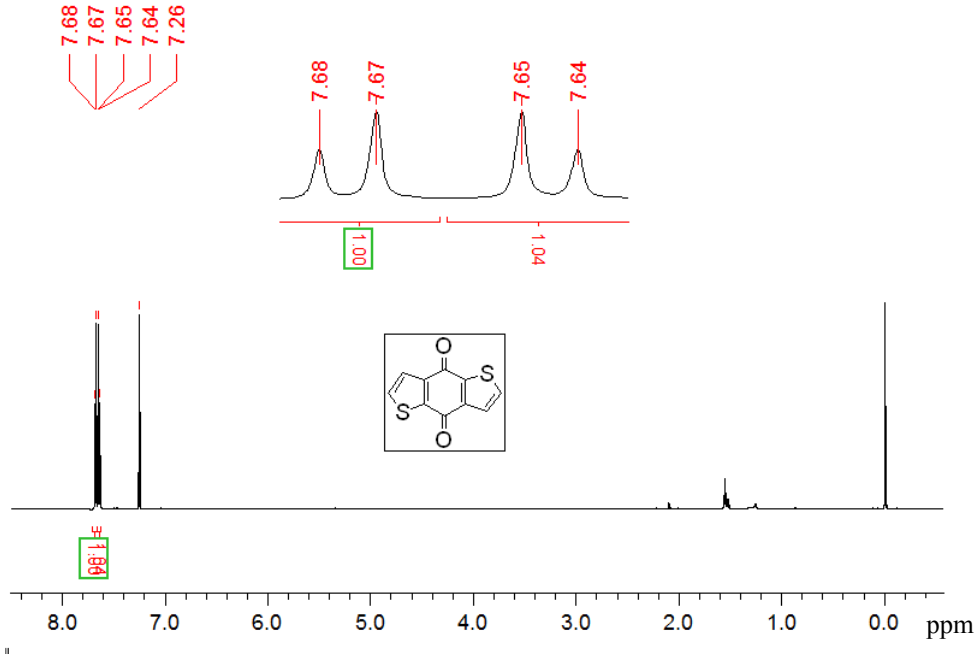

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ solution.

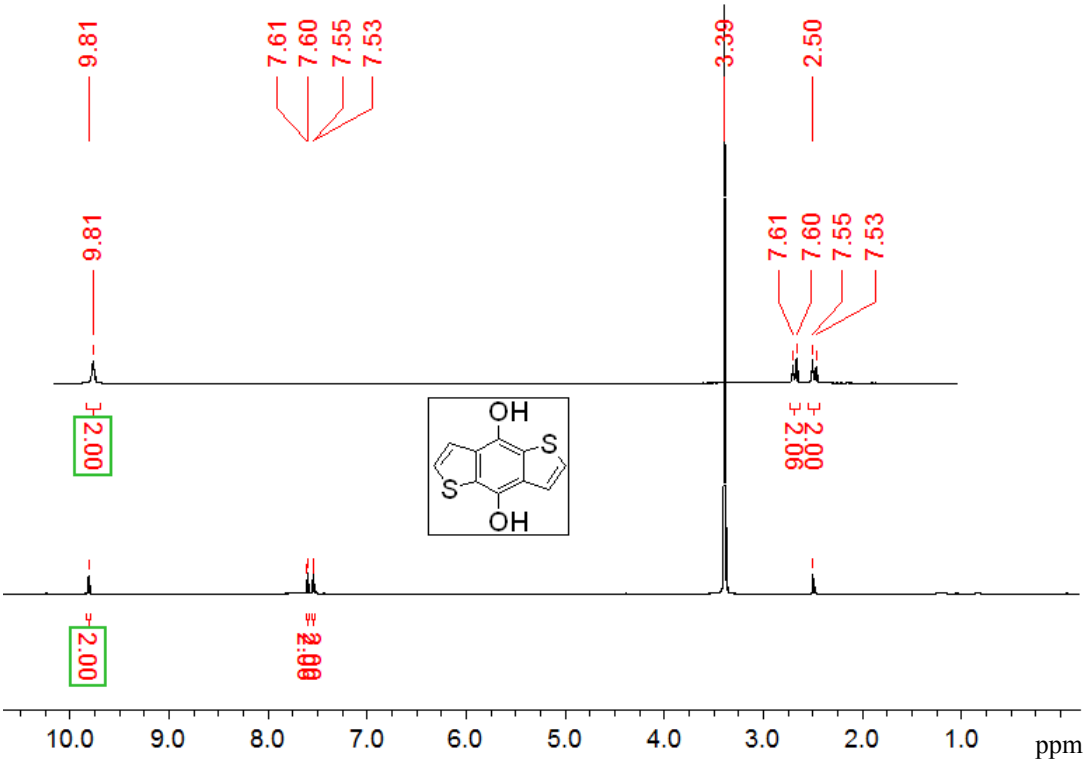

Figure S2. ^{1}H NMR spectrum of **2** in DMSO-d_6 solution.

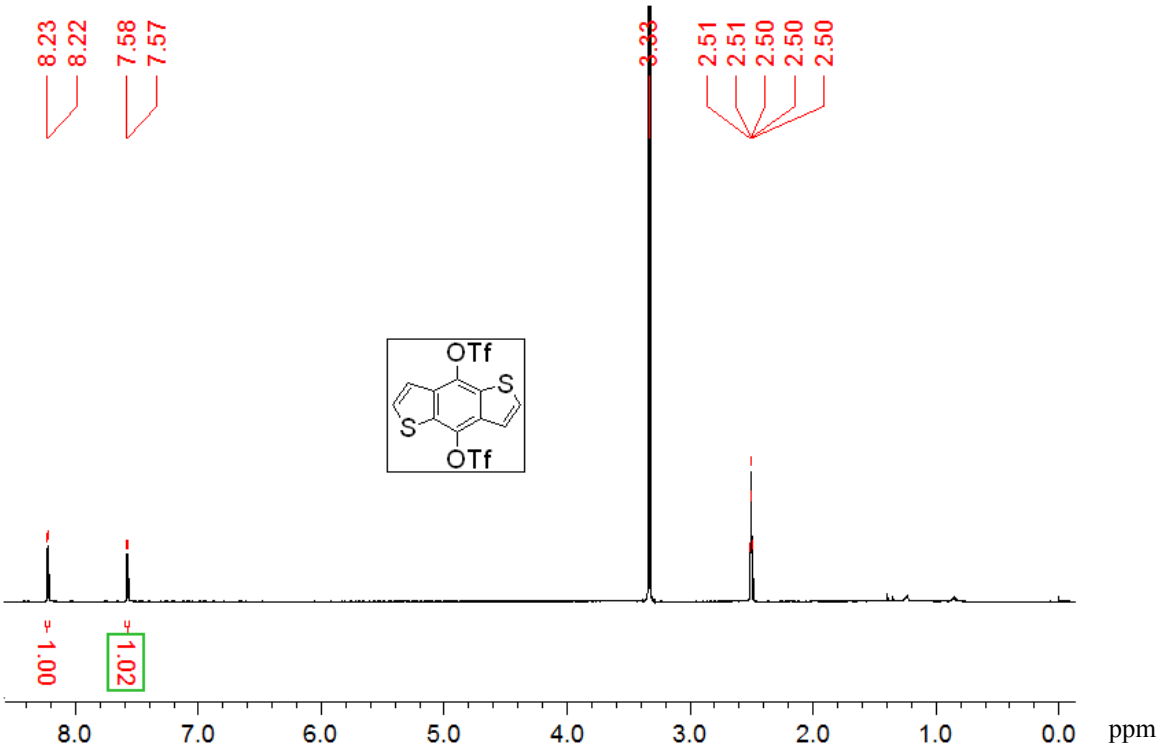

Figure S3. ^{1}H NMR spectrum of **3** in DMSO-d_6 solution.

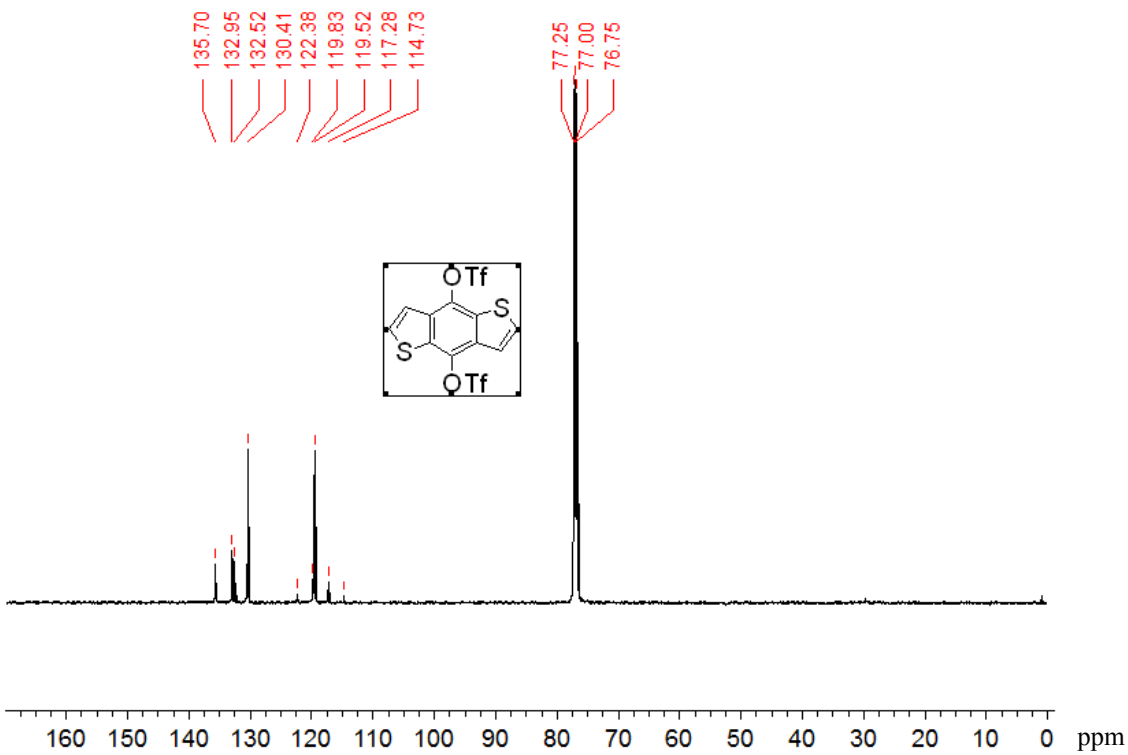

Figure S4. ^{13}C NMR spectrum of **3** in $CDCl_3$ solution.

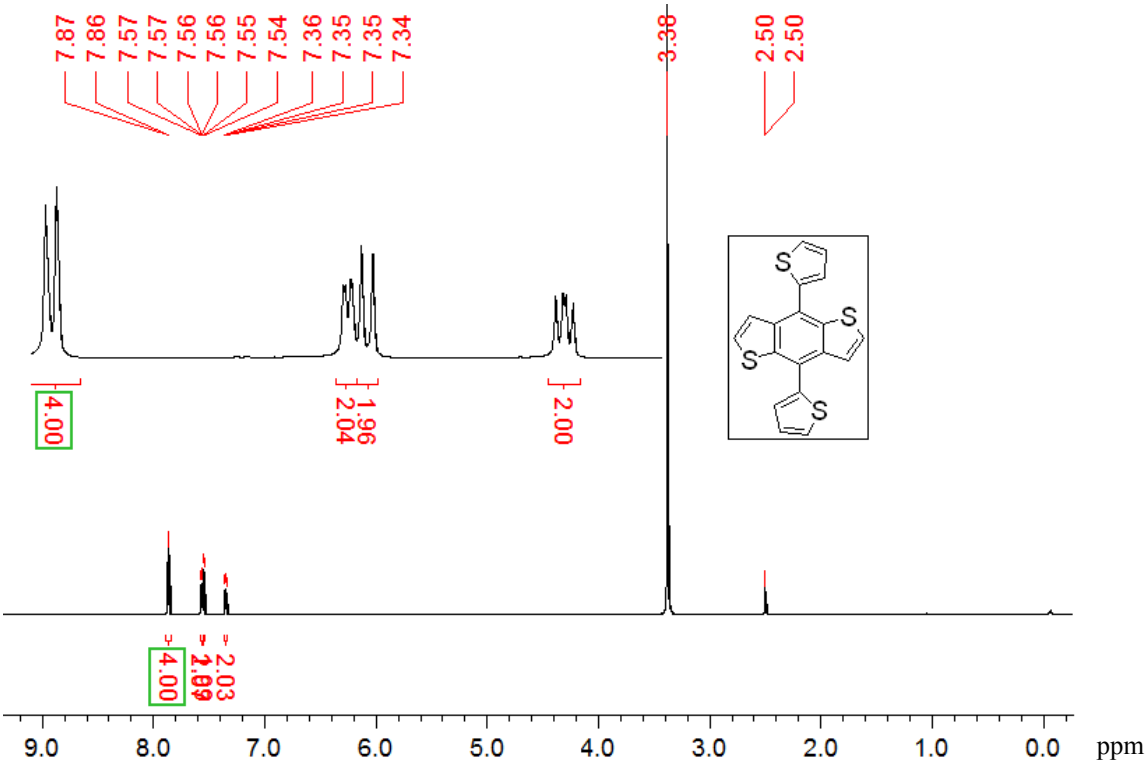

Figure S5. ^{1}H NMR spectrum of **4** in DMSO-d_6 solution.

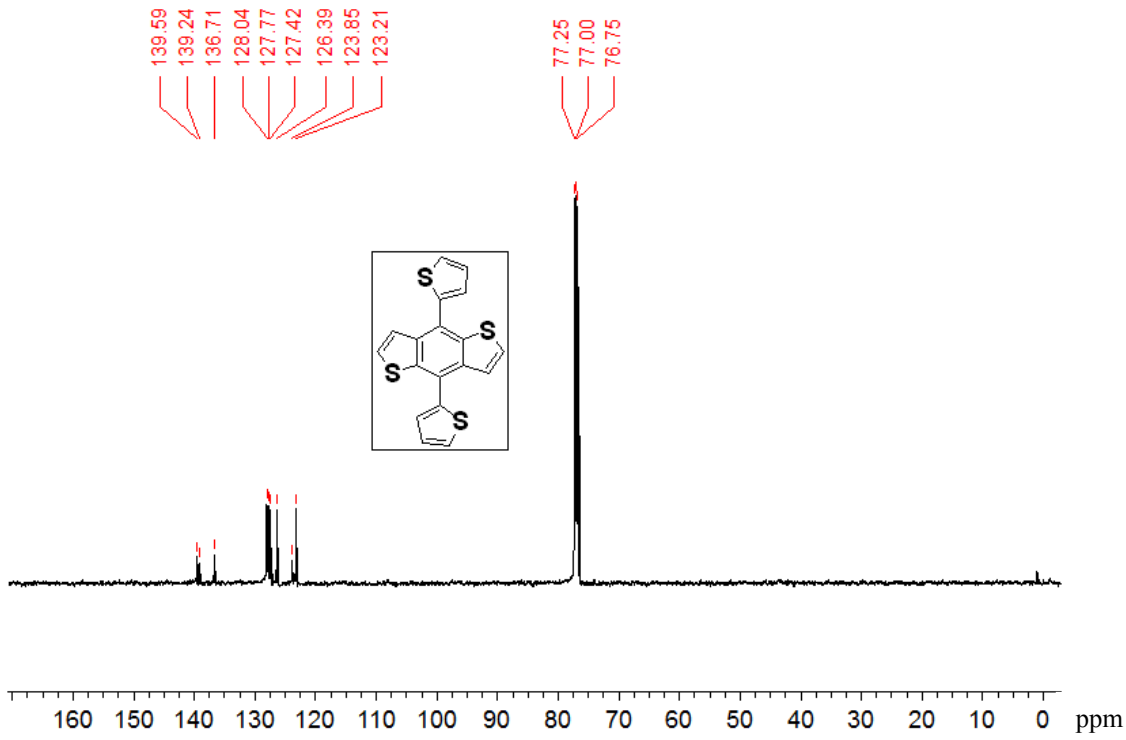

Figure S6. ^{13}C NMR spectrum of **4** in $CDCl_3$ solution.

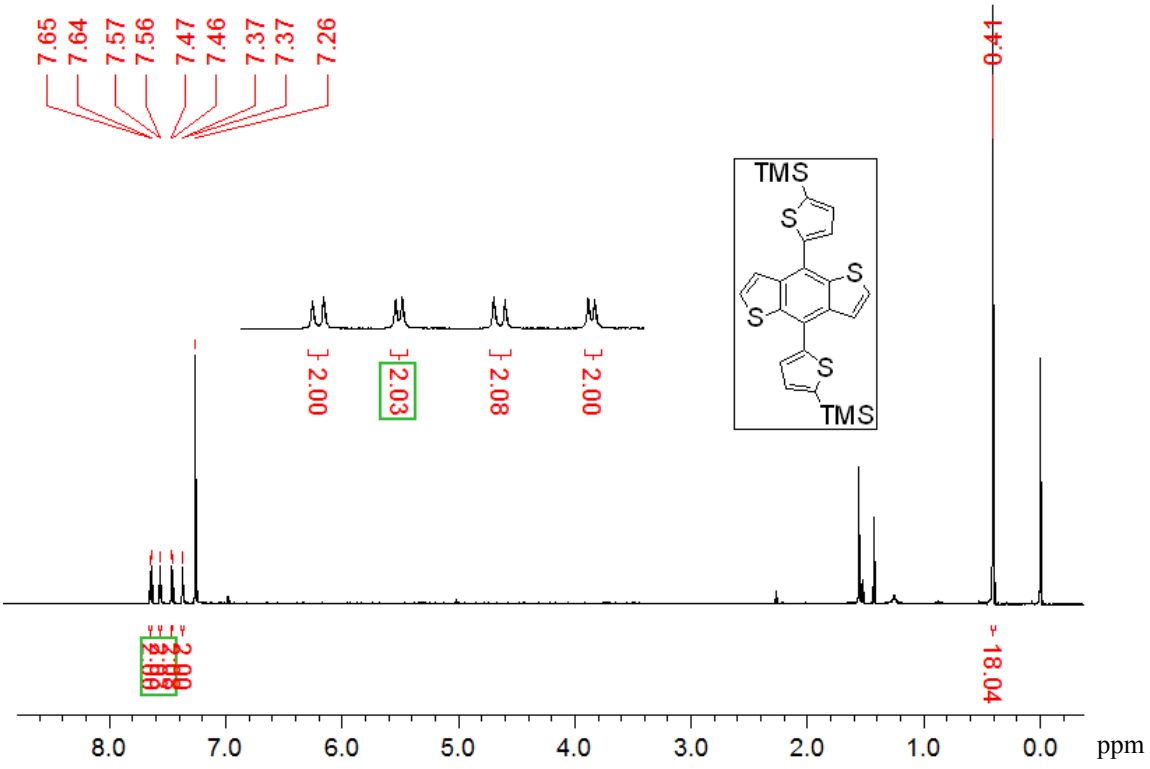

Figure S7. ^{1}H NMR spectrum of **5** in $CDCl_3$ solution.

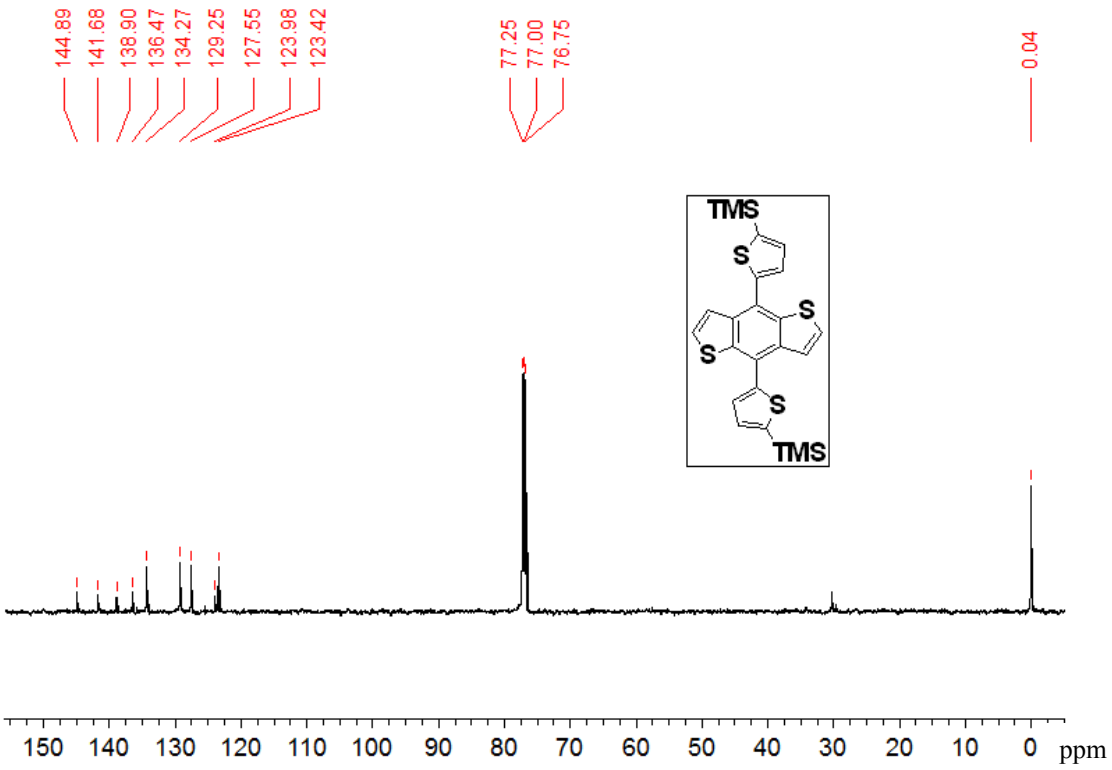

Figure S8. ^{13}C NMR spectrum of **5** in $CDCl_3$ solution.

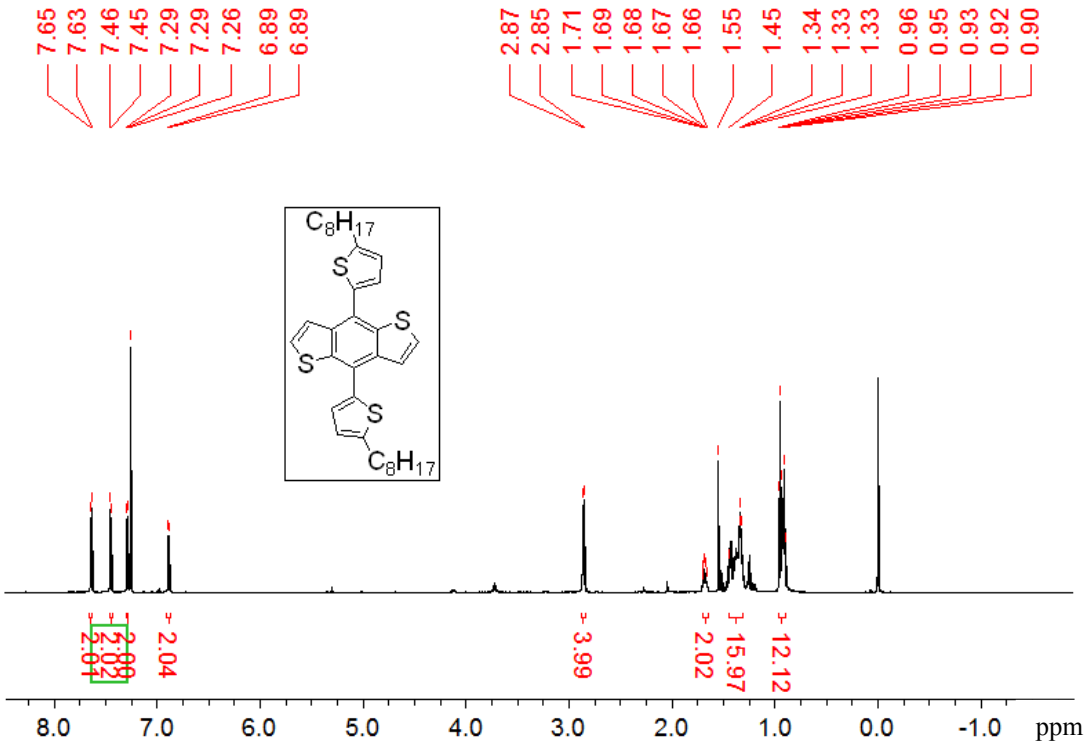

Figure S9. ^{1}H NMR spectrum of **6** in $CDCl_3$ solution.

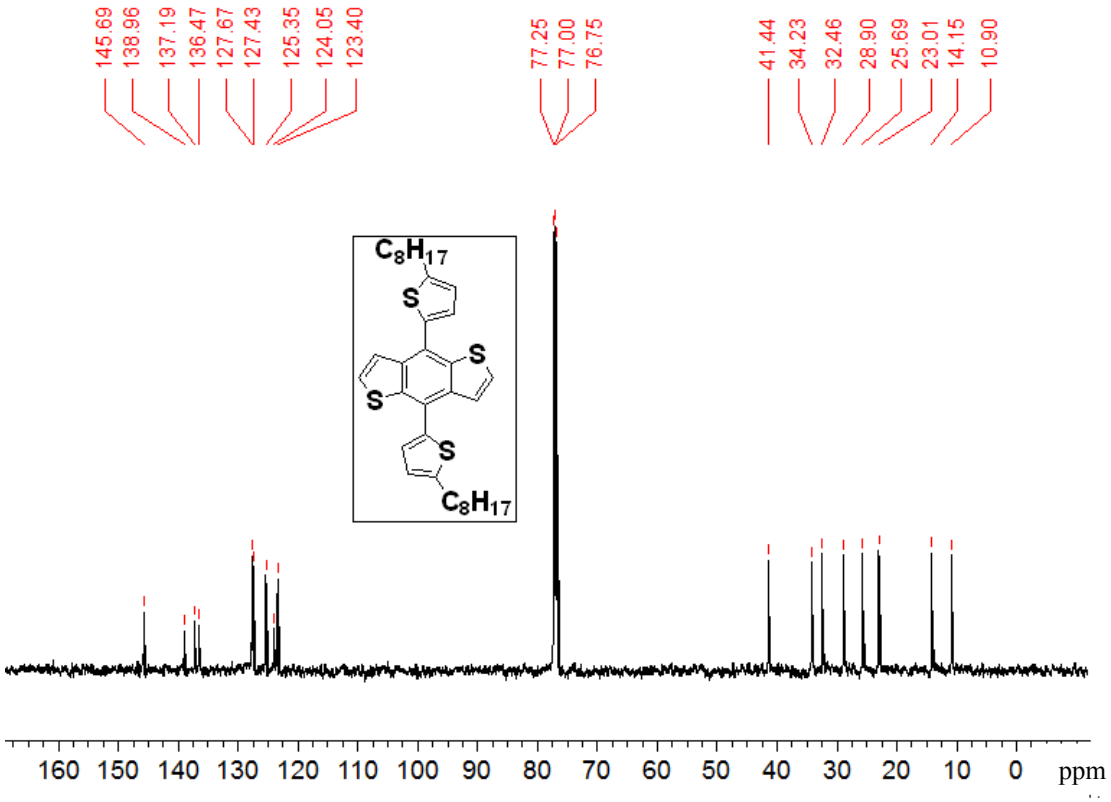

Figure S10. ^{13}C NMR spectrum of **6** in $CDCl_3$ solution.

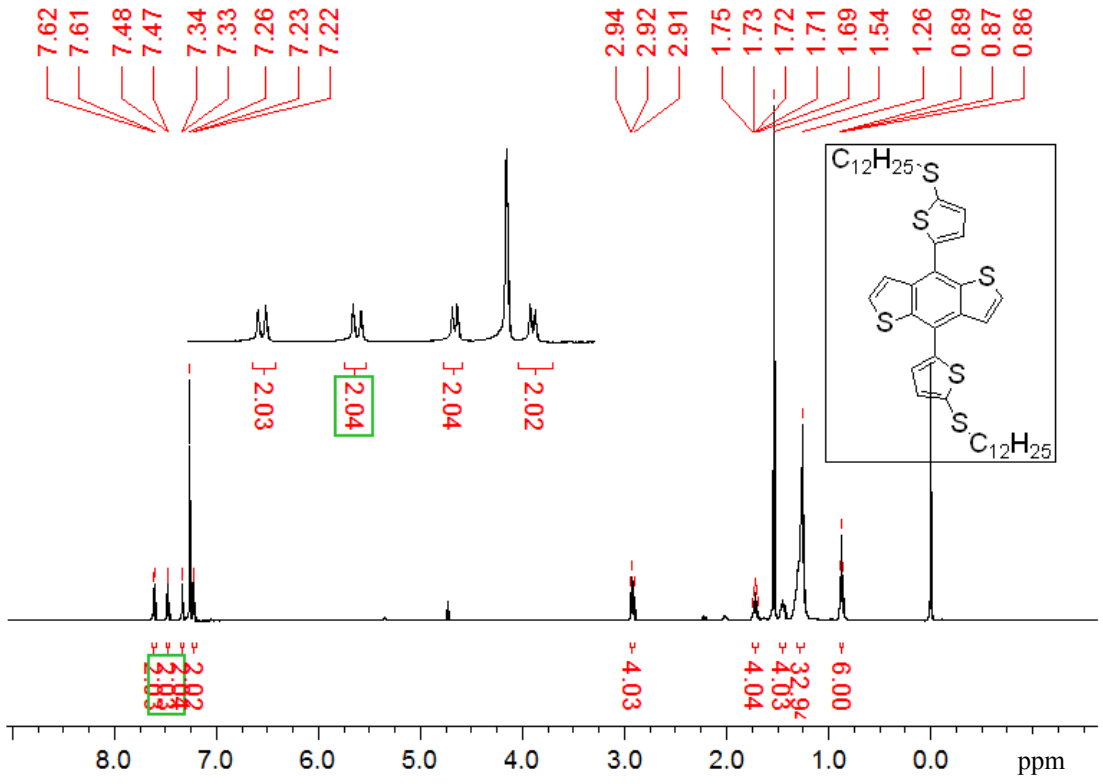

Figure S11. ^{1}H NMR spectrum of **7** in $CDCl_3$ solution.

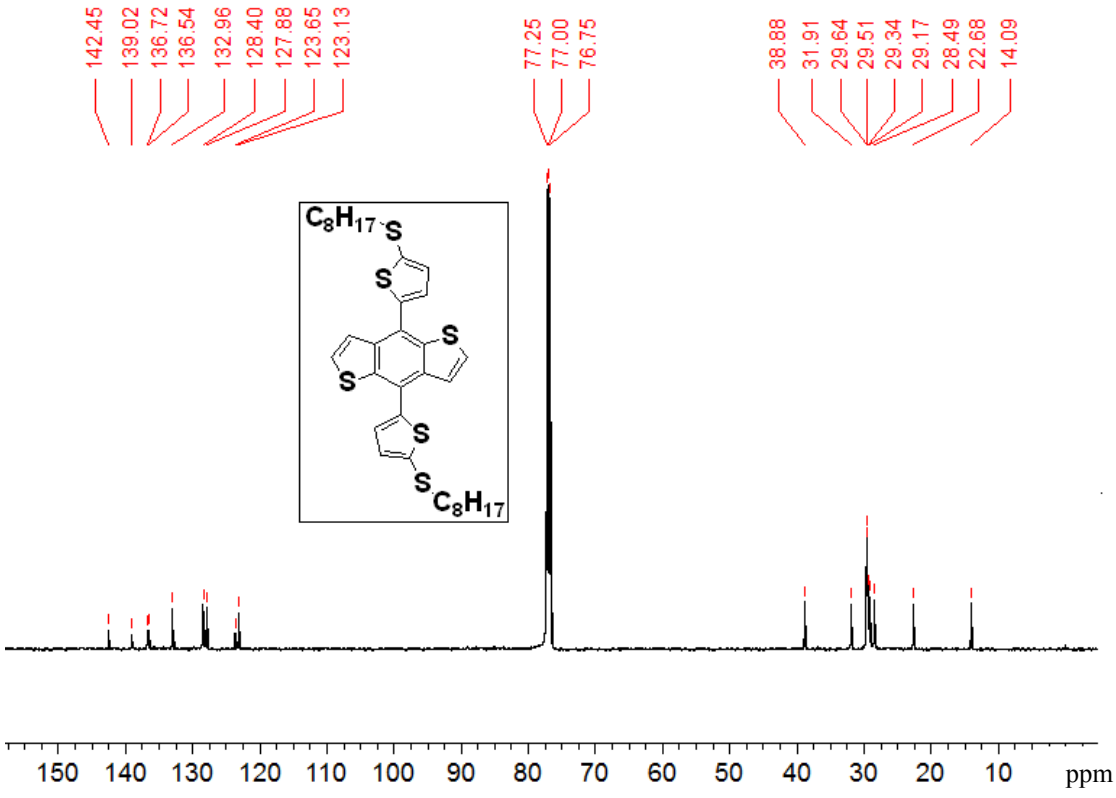

Figure S12. ^{13}C NMR spectrum of **7** in $CDCl_3$ solution.

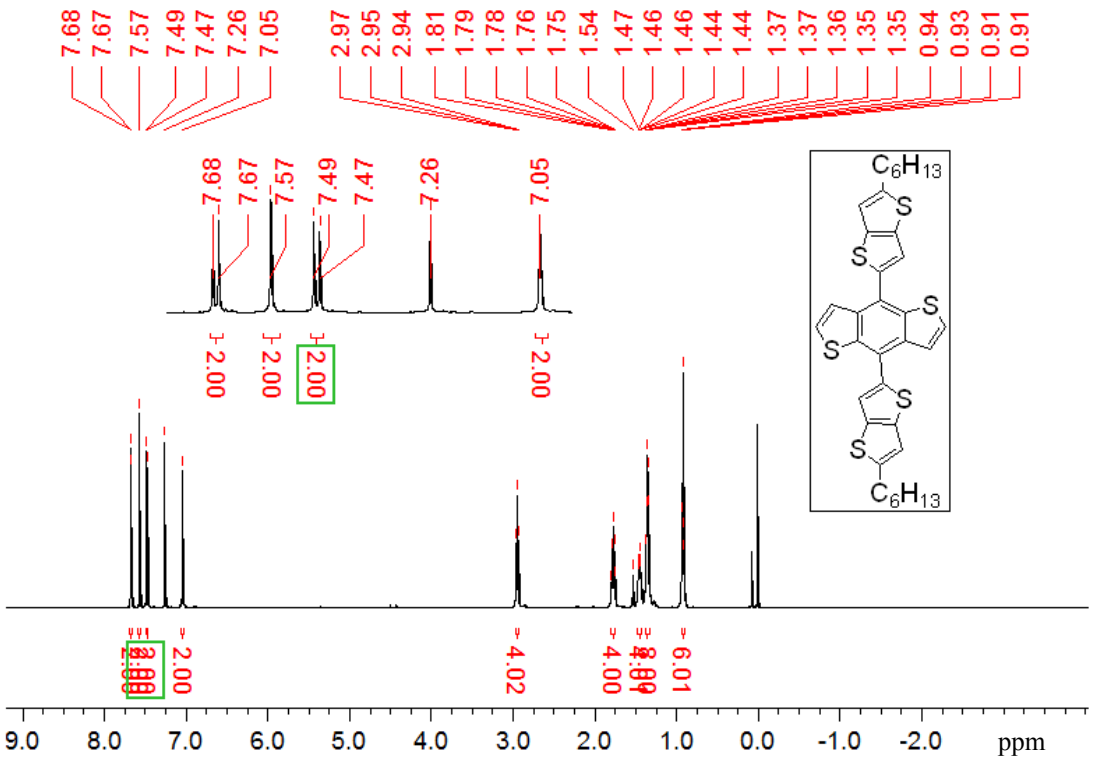

Figure S13. ^{1}H NMR spectrum of **8** in $CDCl_3$ solution.

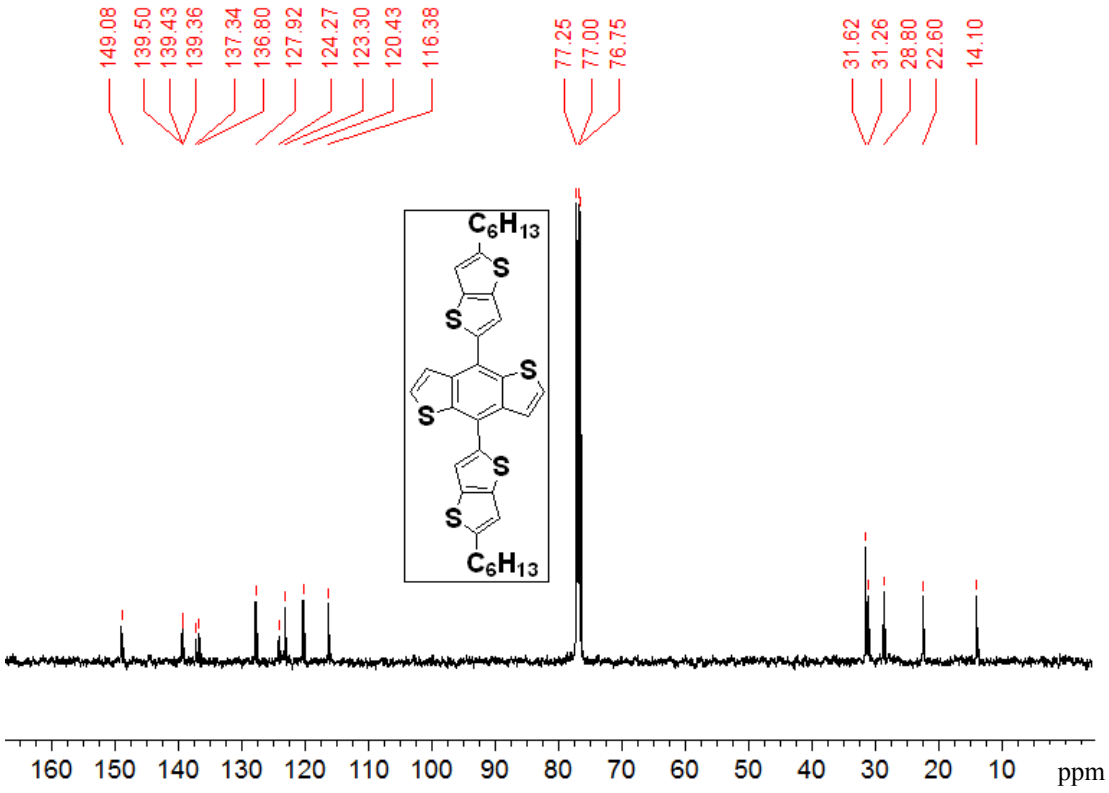

Figure S14. ^{13}C NMR spectrum of **8** in $CDCl_3$ solution.

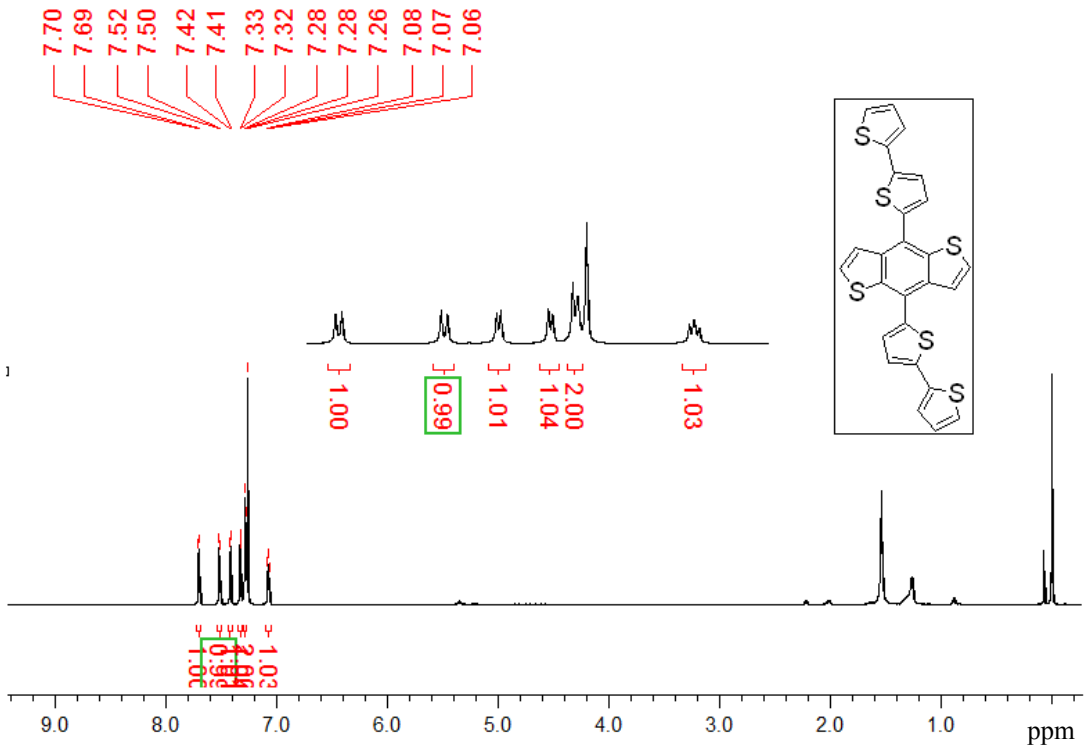

Figure S15. ^{1}H NMR spectrum of **9** in $CDCl_3$ solution.

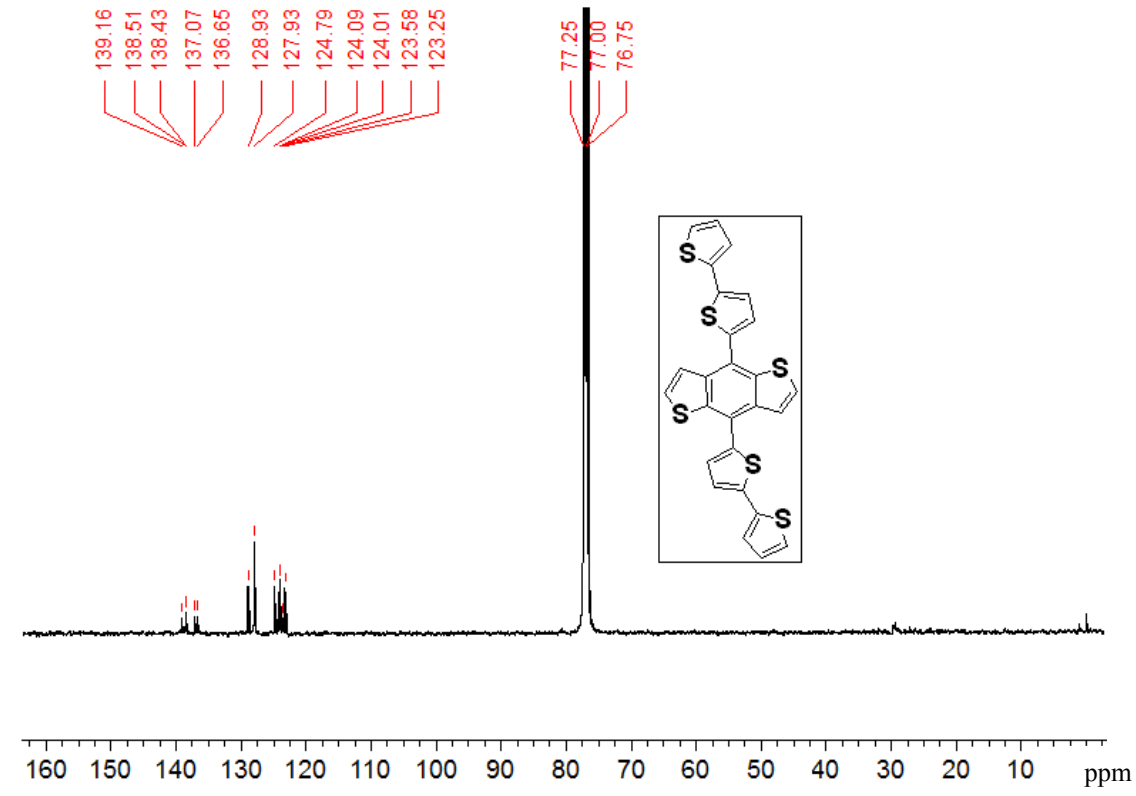

Figure S16. ^{13}C NMR spectrum of **9** in $CDCl_3$ solution.

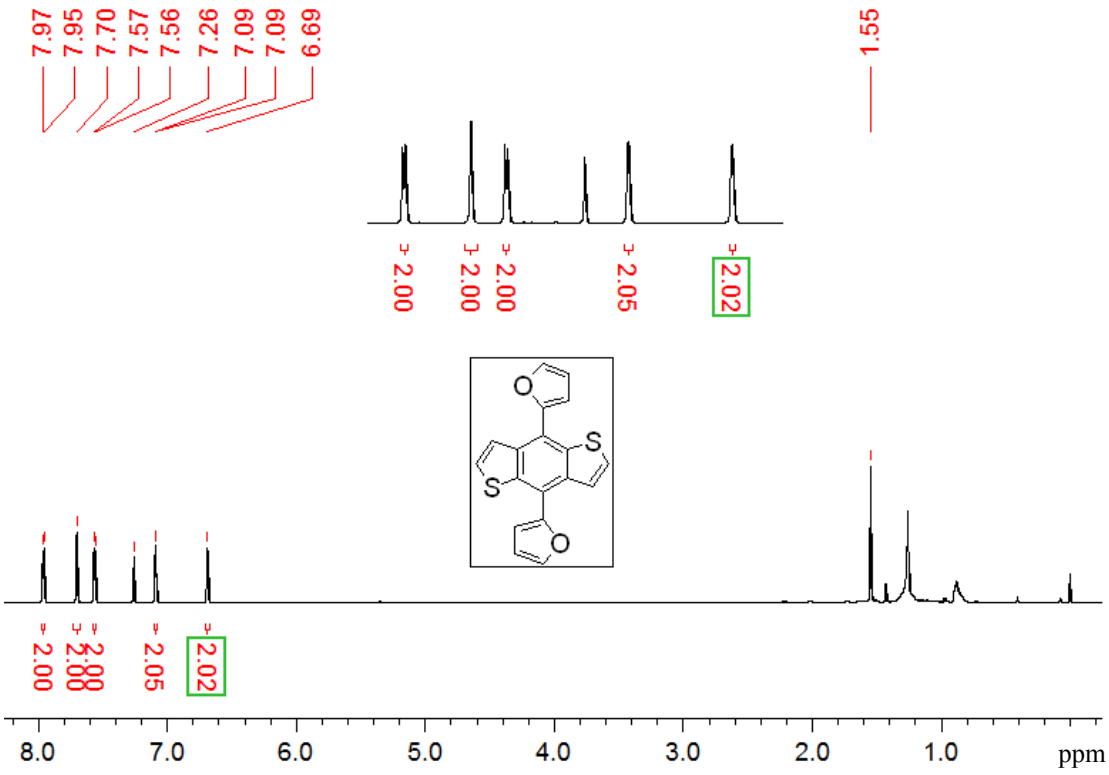

Figure S17. ^{1}H NMR spectrum of **10** in $CDCl_3$ solution.

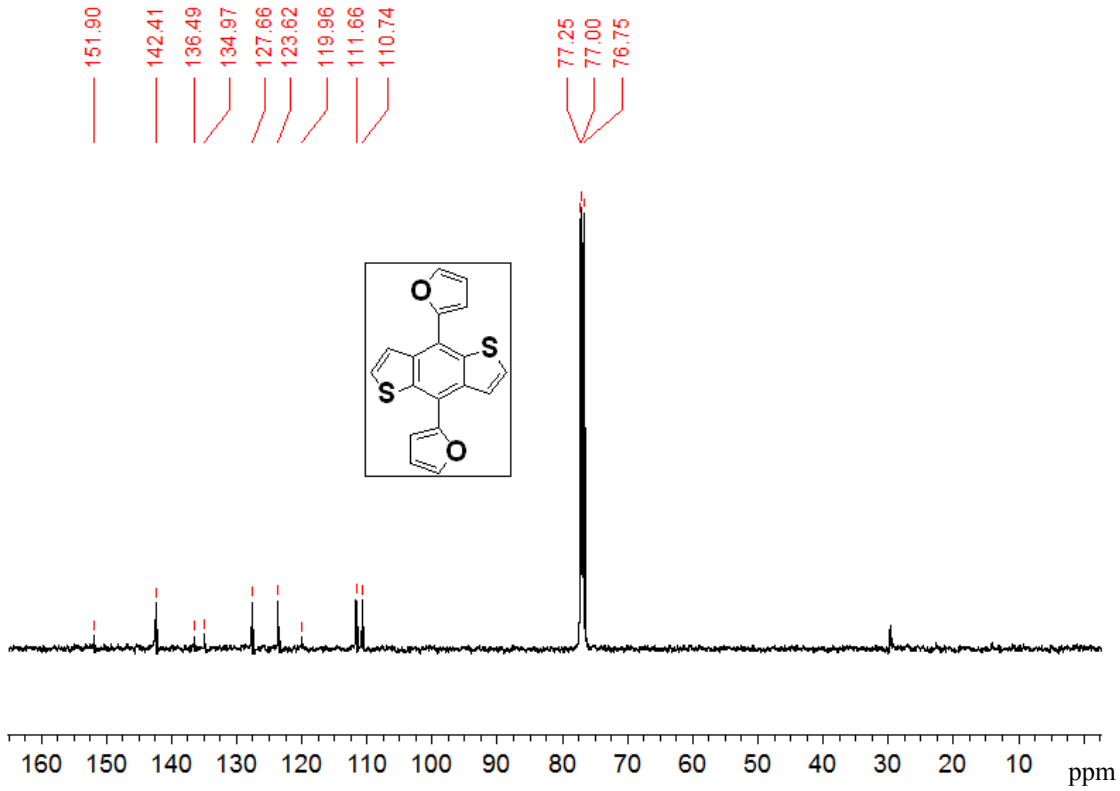

Figure S18. ^{13}C NMR spectrum of **10** in $CDCl_3$ solution.

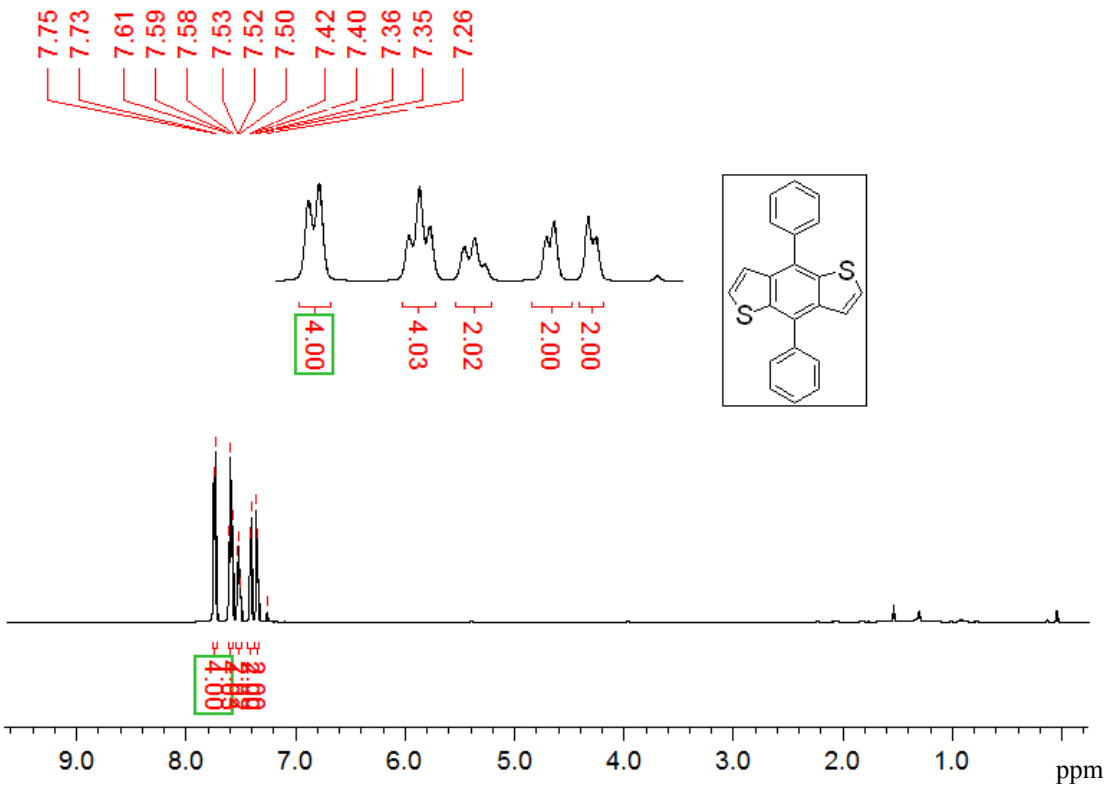

Figure S19. ^{1}H NMR spectrum of **11** in $CDCl_3$ solution.

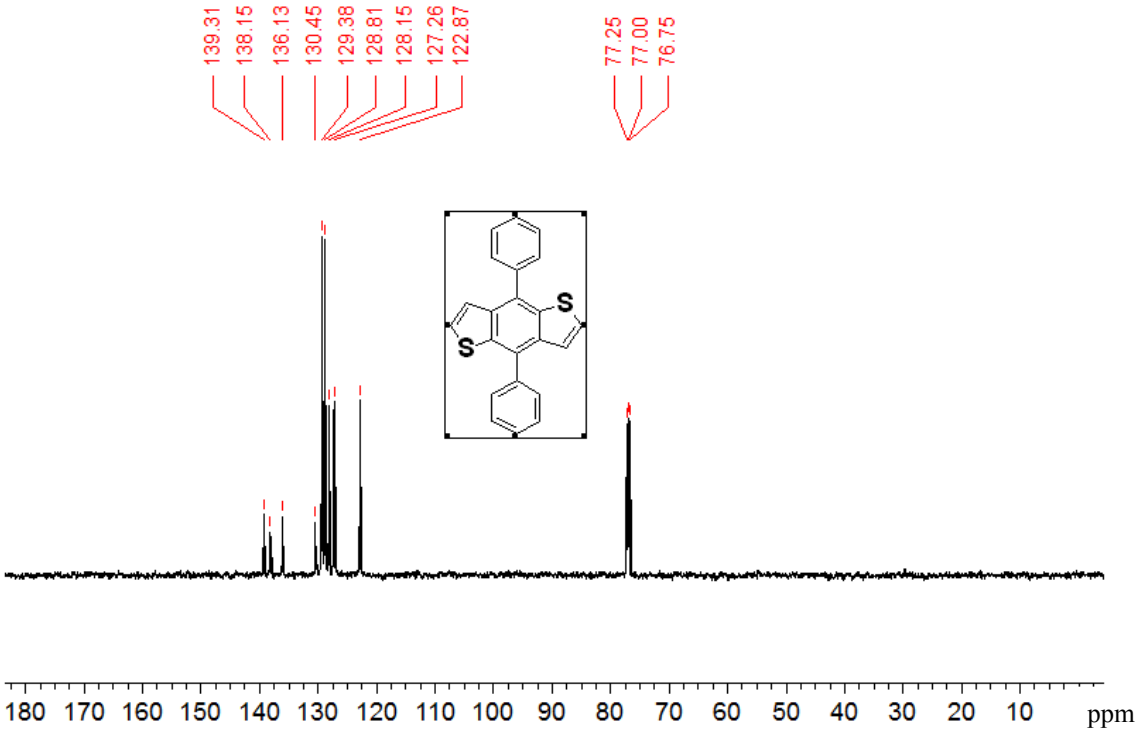

Figure S20. ^{13}C NMR spectrum of **11** in $CDCl_3$ solution.

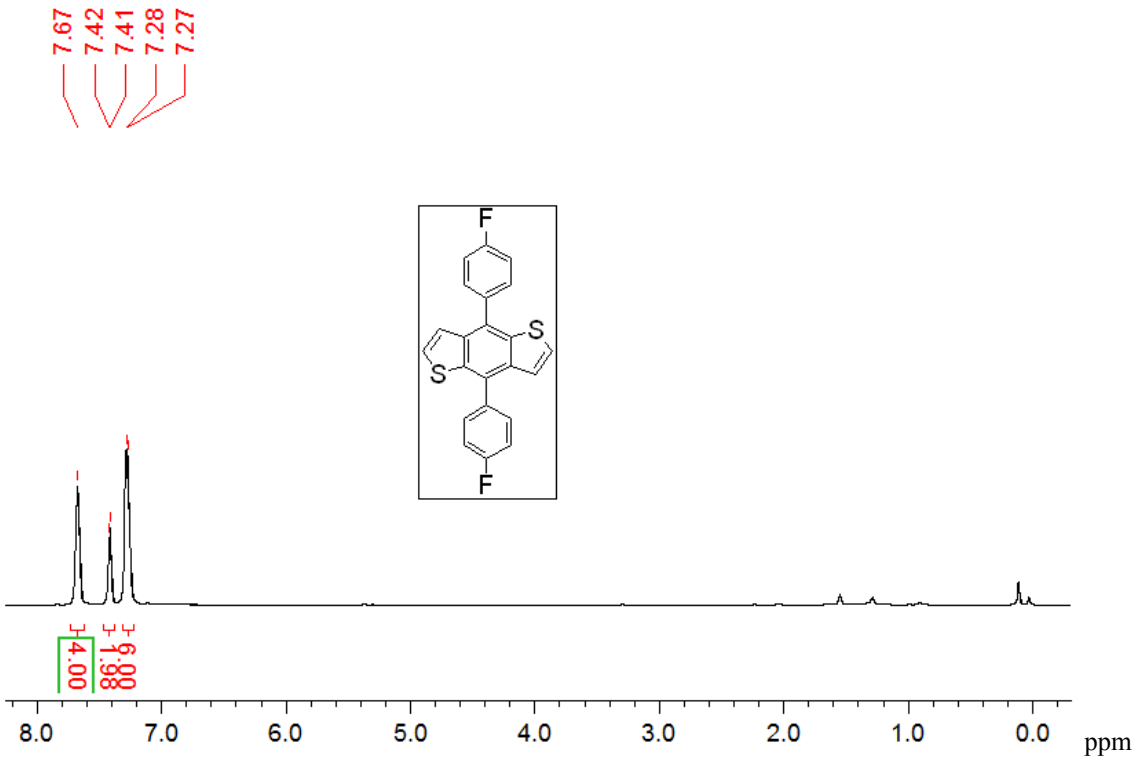

Figure S21. ^{1}H NMR spectrum of **12** in $CDCl_3$ solution.

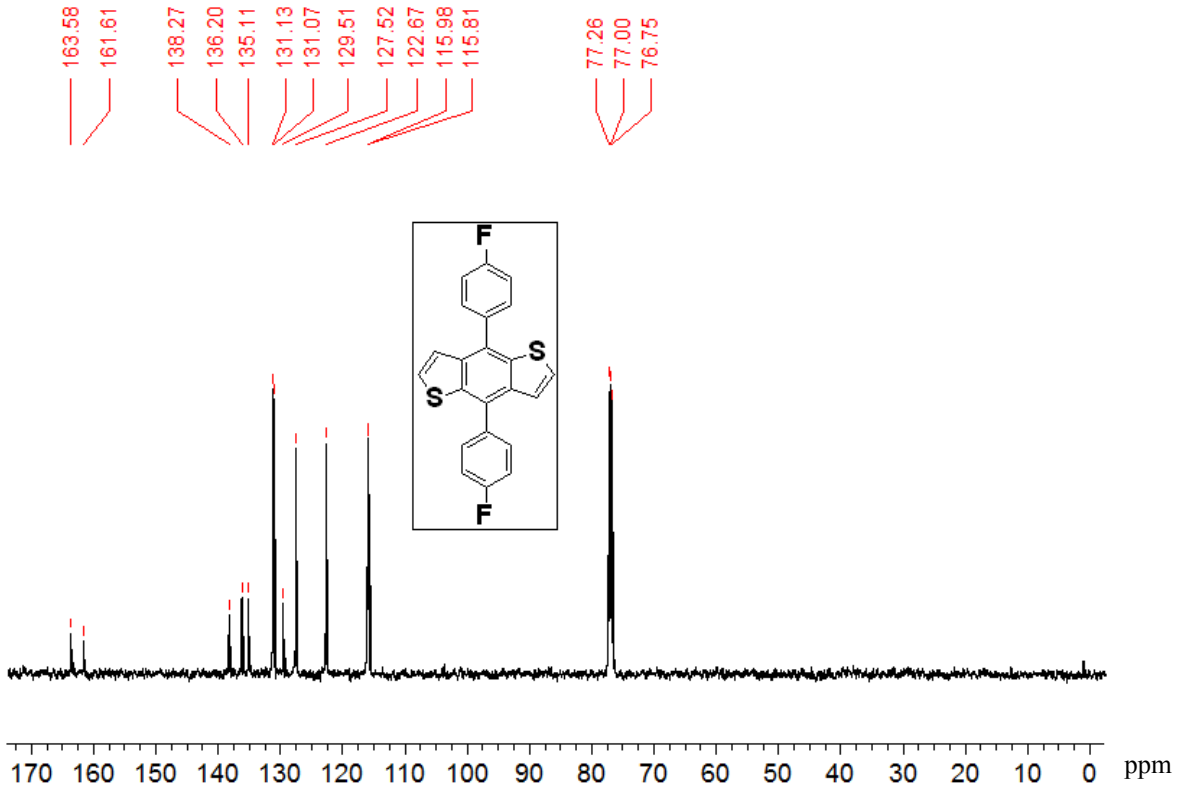

Figure S22. ^{13}C NMR spectrum of **12** in $CDCl_3$ solution.

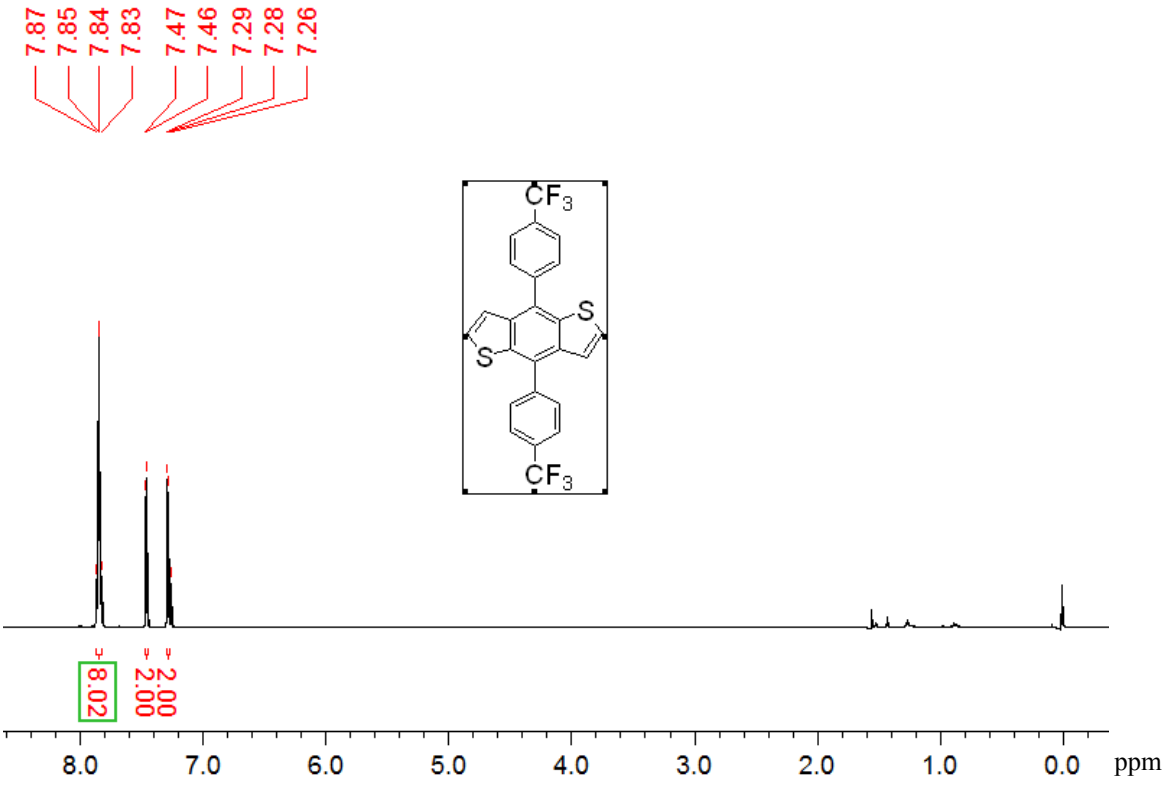

Figure S23. ^{1}H NMR spectrum of **13** in $CDCl_3$ solution.

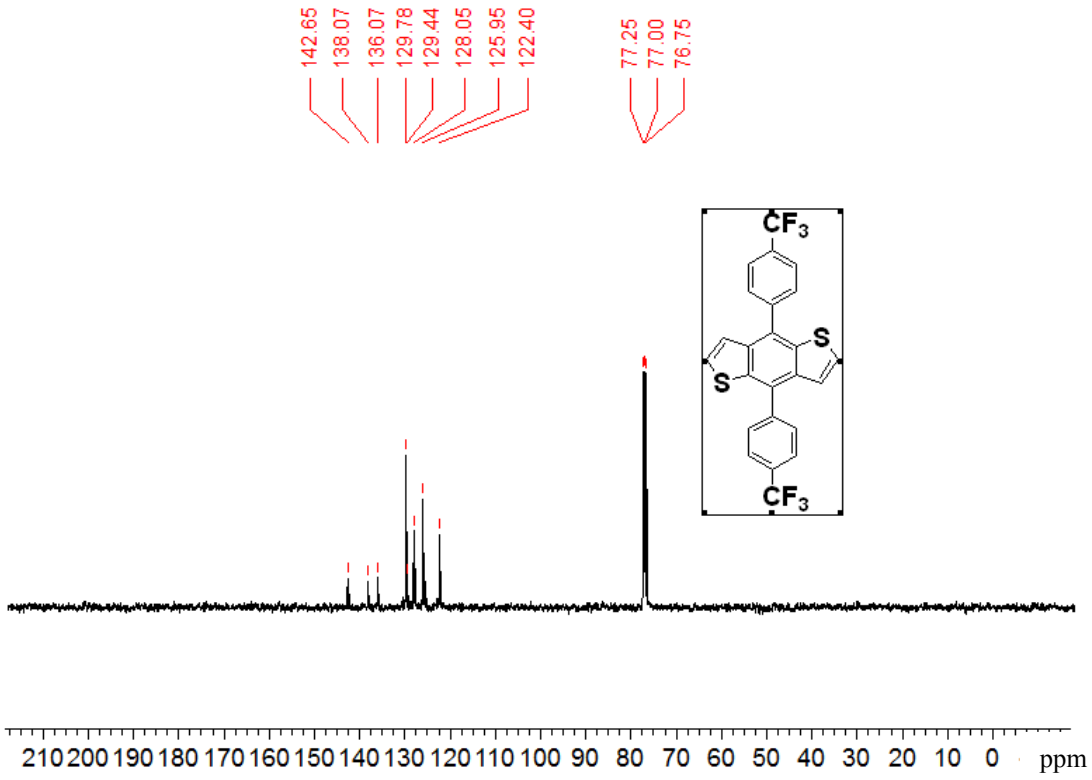

Figure S24. ^{13}C NMR spectrum of **13** in $CDCl_3$ solution.

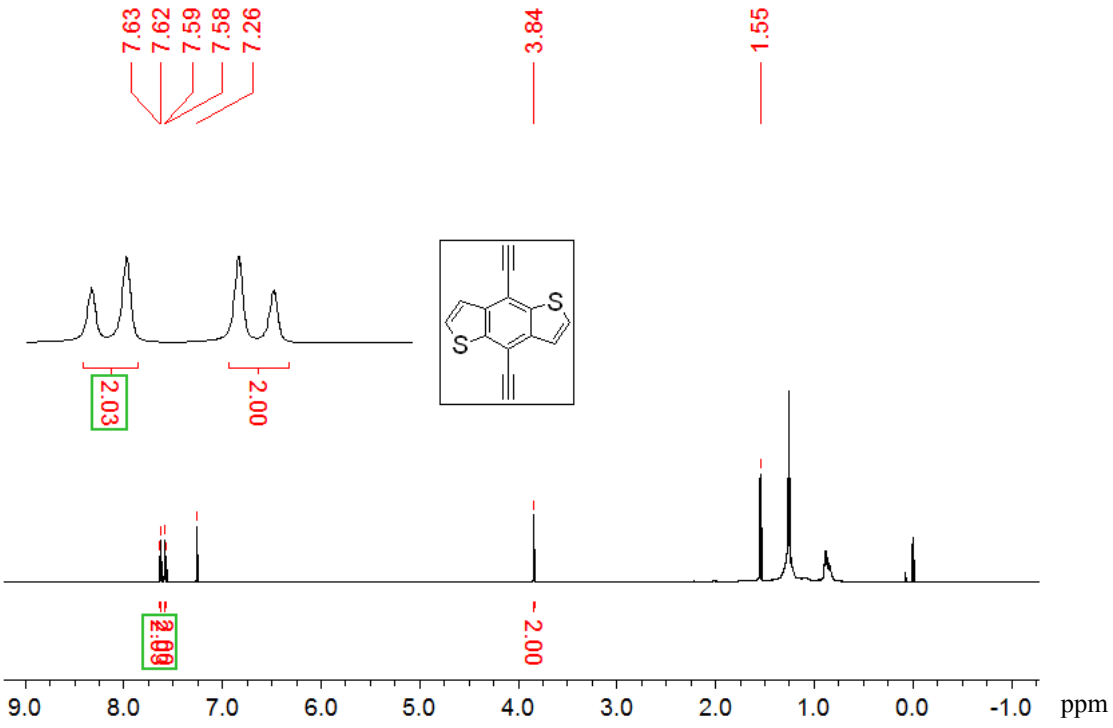

Figure S25. ^{1}H NMR spectrum of **14** in $CDCl_3$ solution.

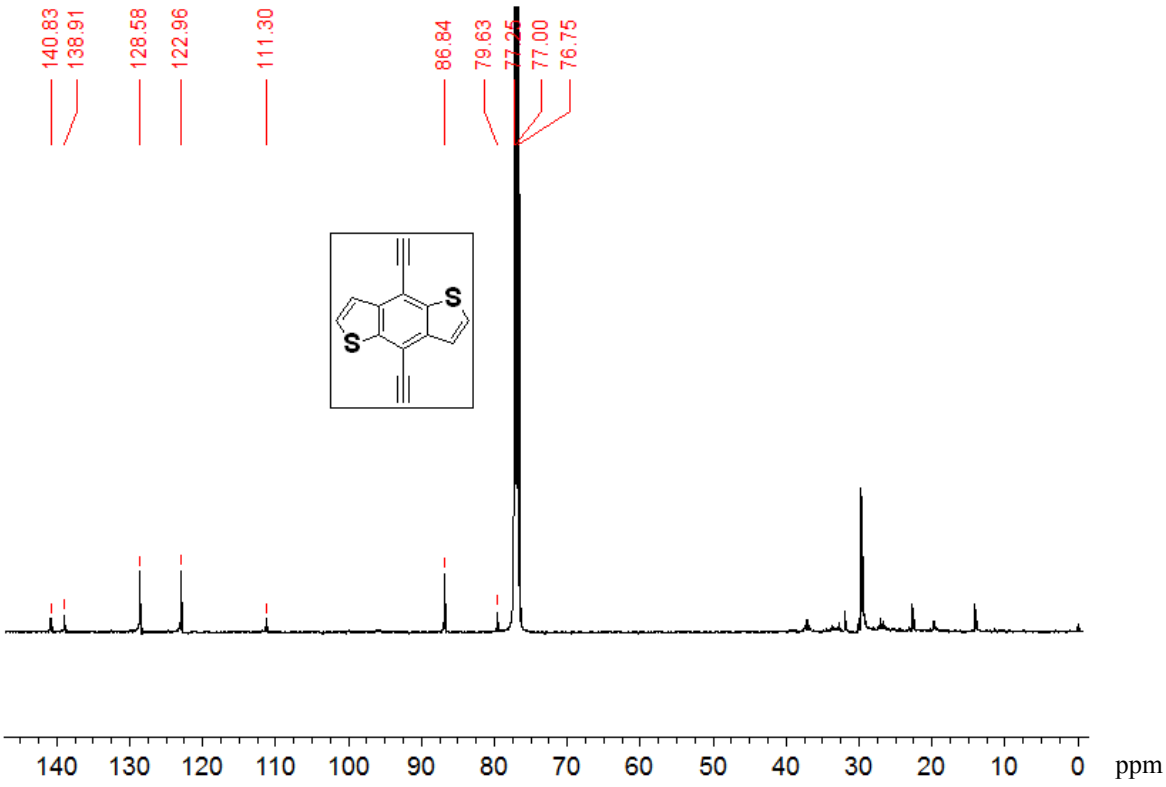

Figure S26. ^{13}C NMR spectrum of **14** in $CDCl_3$ solution.

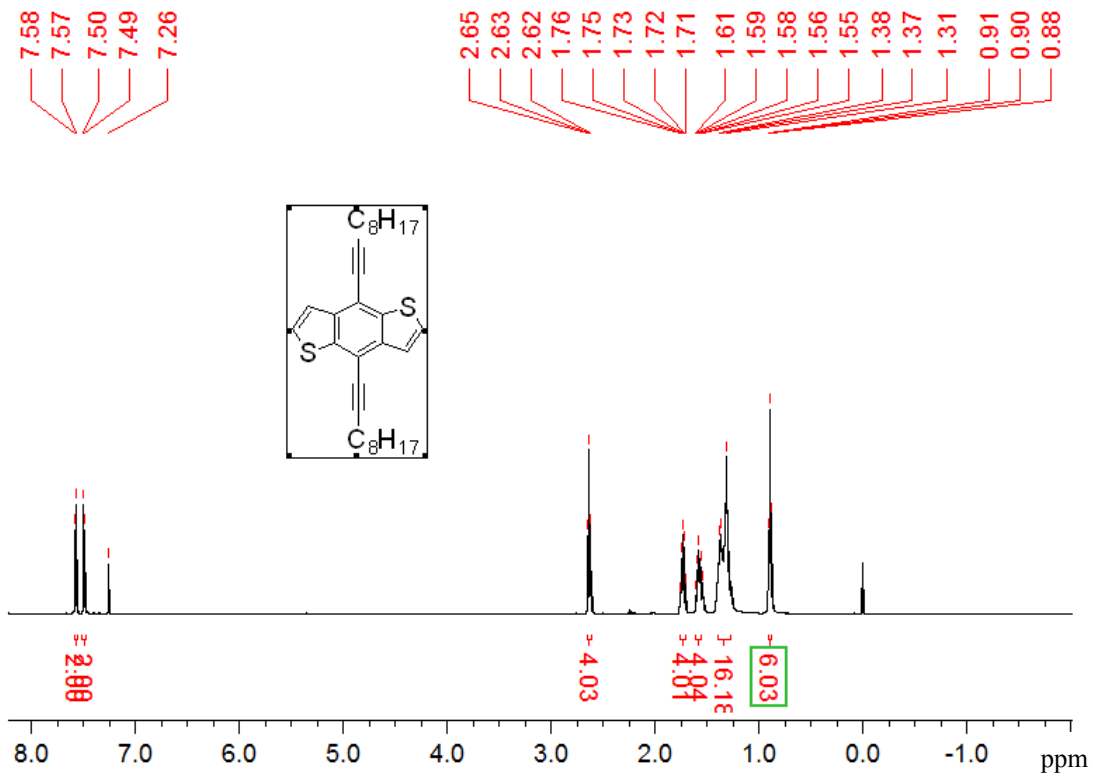

Figure S27. ^{1}H NMR spectrum of **15** in $CDCl_3$ solution.

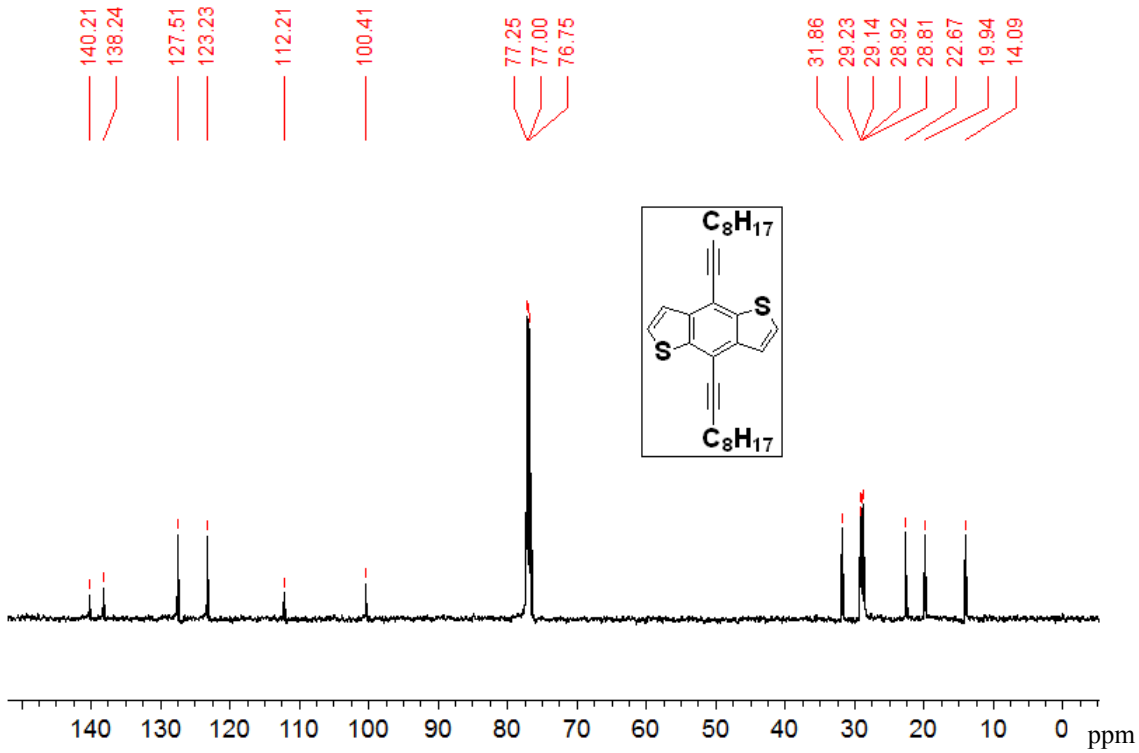

Figure S28. ^{13}C NMR spectrum of **15** in $CDCl_3$ solution.

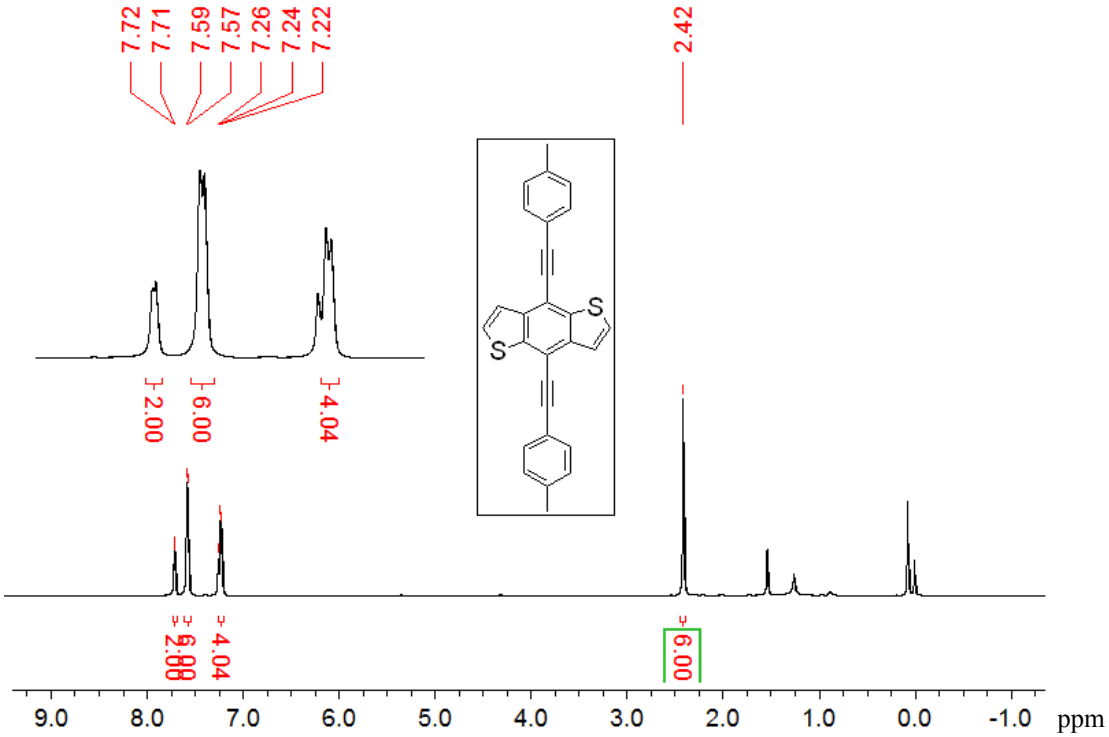

Figure S29. ^{1}H NMR spectrum of **16** in $CDCl_3$ solution.

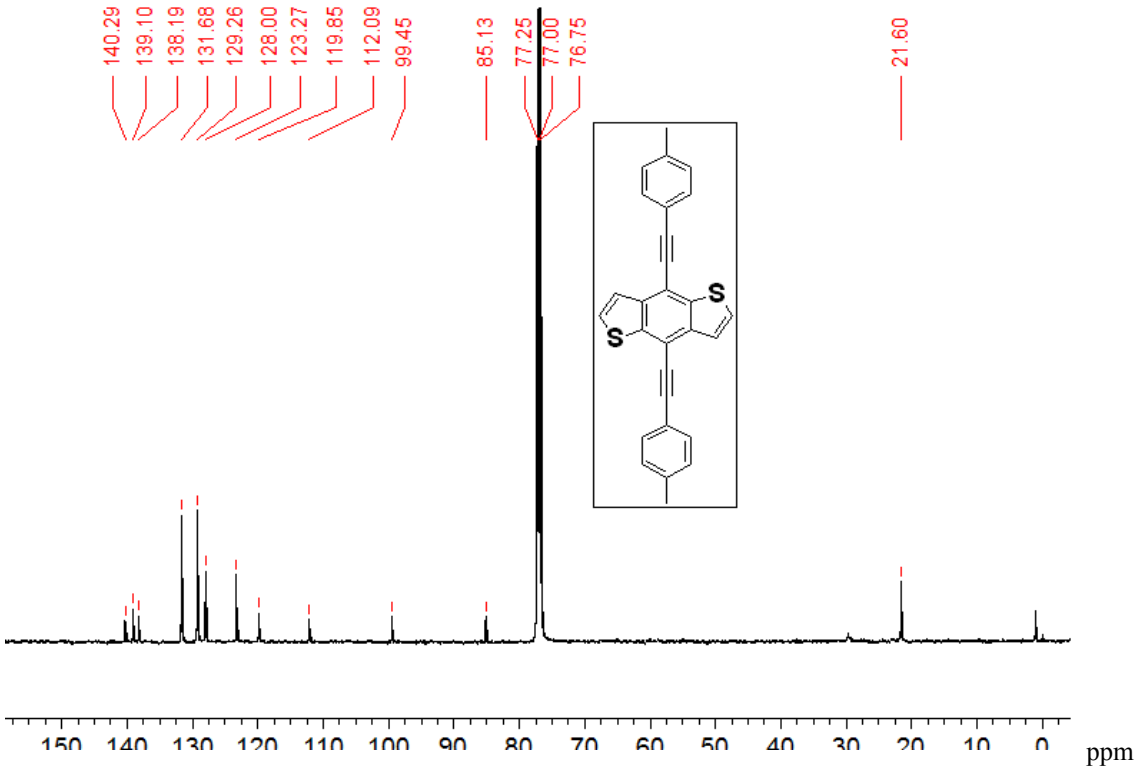

Figure S30. ^{13}C NMR spectrum of **16** in $CDCl_3$ solution.

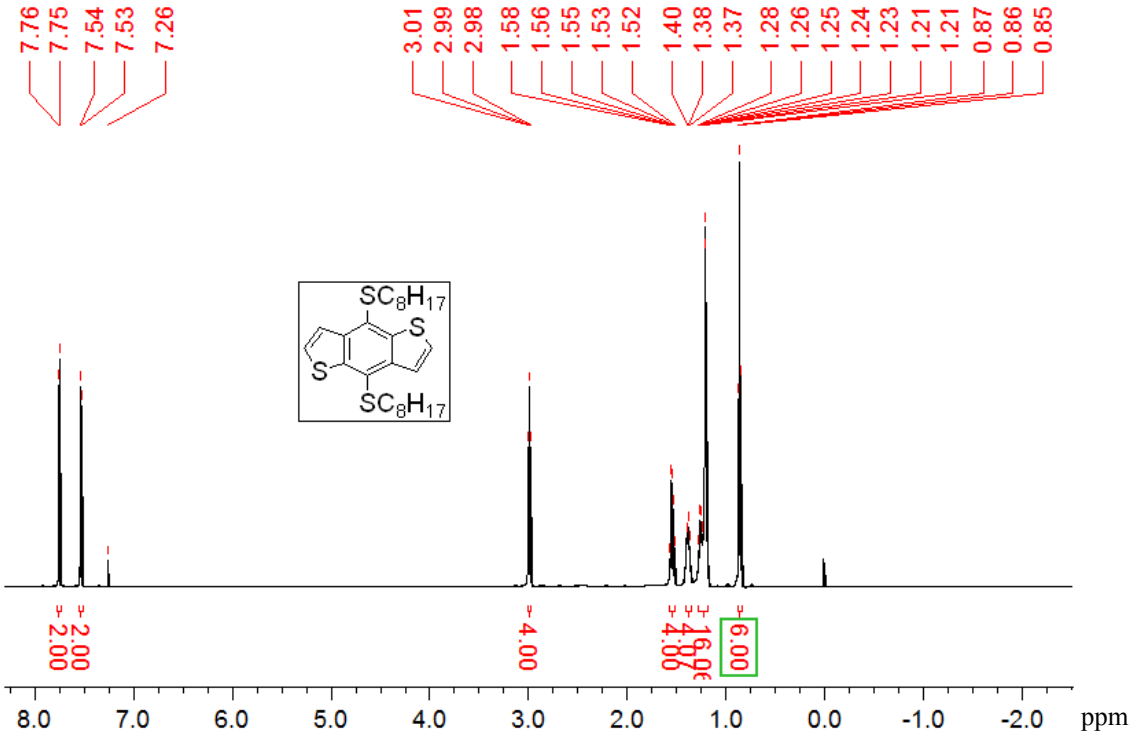

Figure S31. ^{1}H NMR spectrum of **17** in $CDCl_3$ solution.

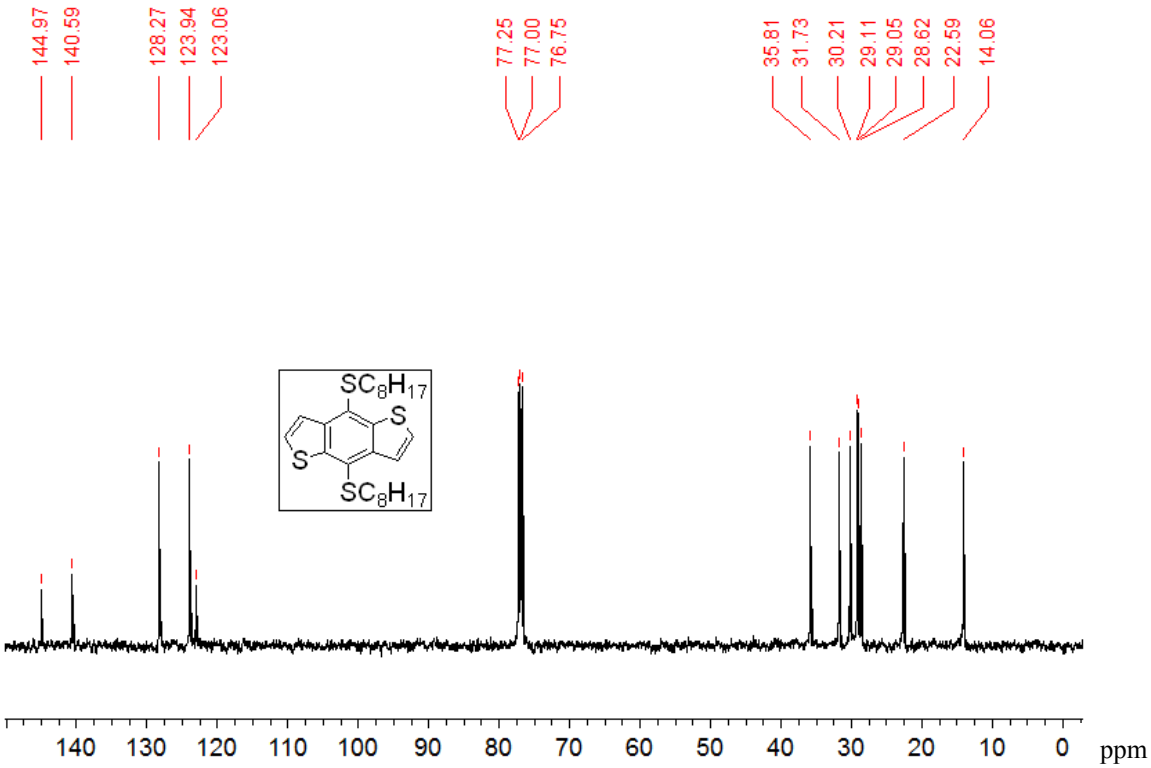

Figure S32. ^{13}C NMR spectrum of **17** in $CDCl_3$ solution.

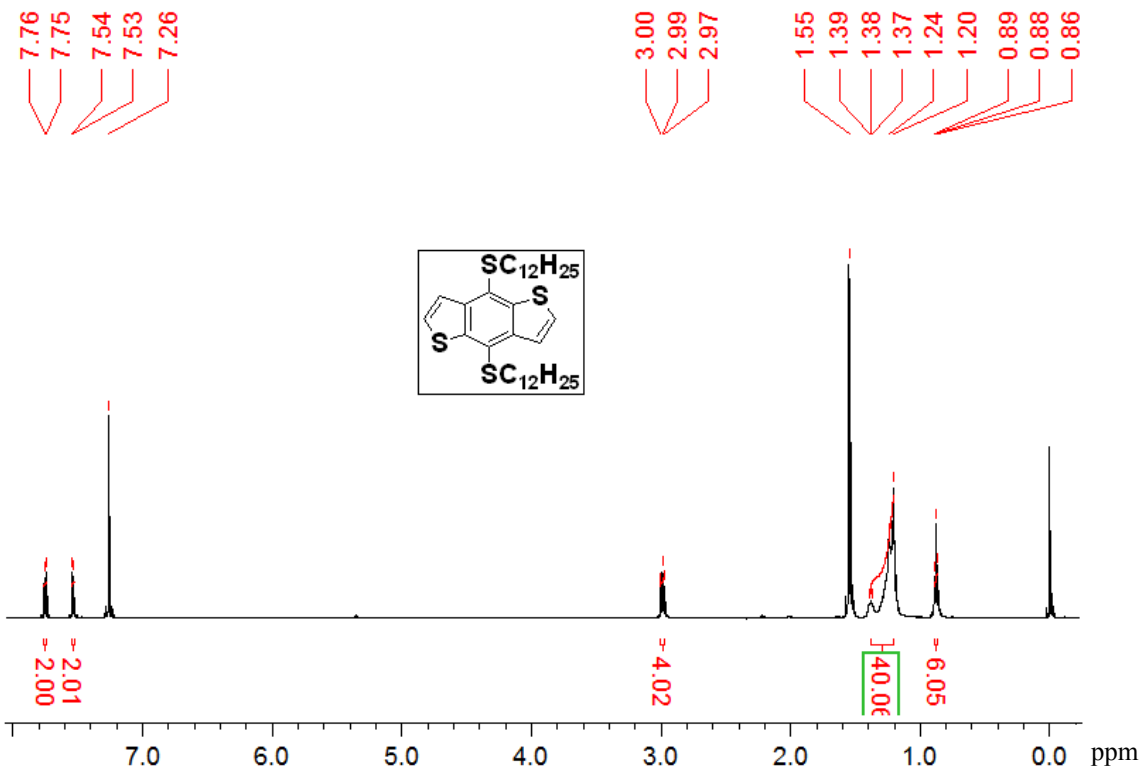

Figure S33. ^{1}H NMR spectrum of **18** in $CDCl_3$ solution.

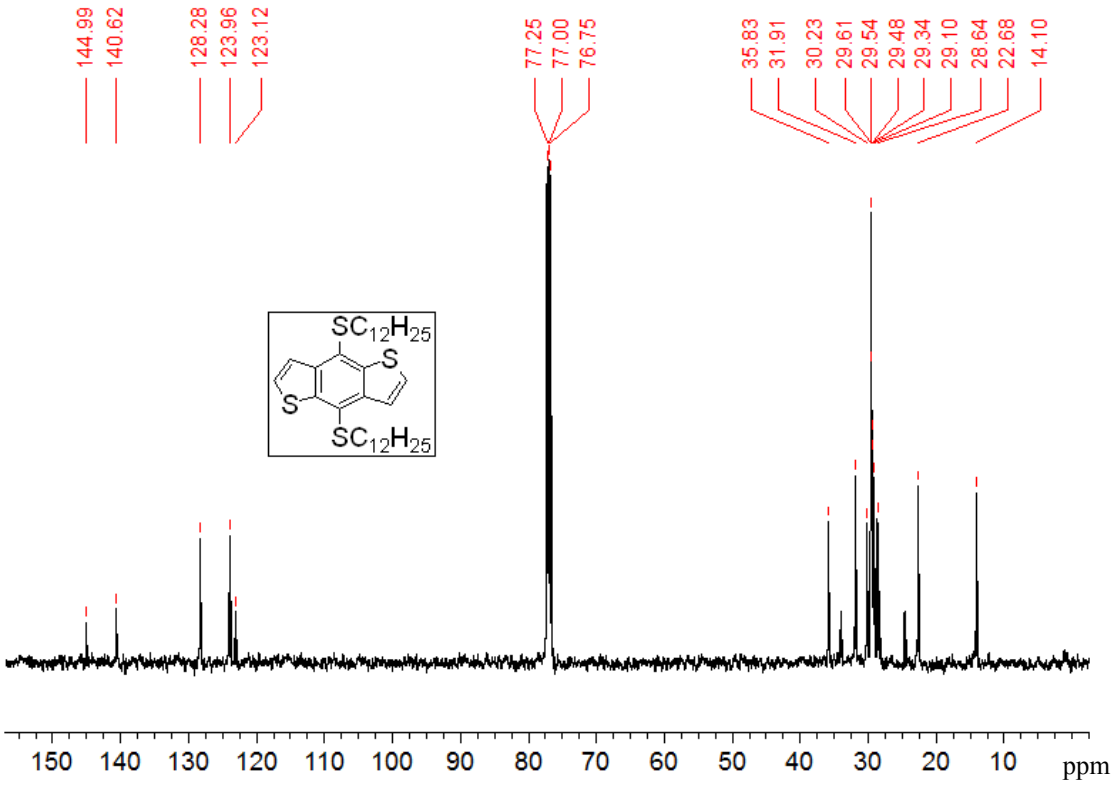

Figure S34. ^{13}C NMR spectrum of **18** in $CDCl_3$ solution.

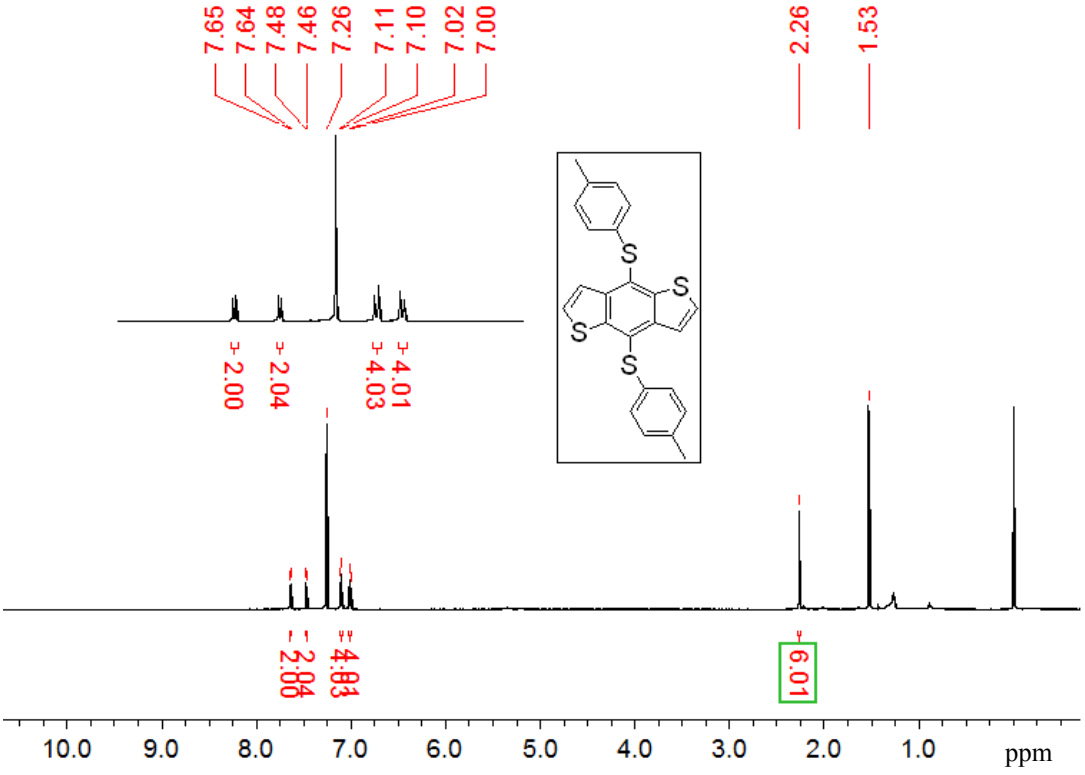

Figure S35. ^{1}H NMR spectrum of **19** in $CDCl_3$ solution.

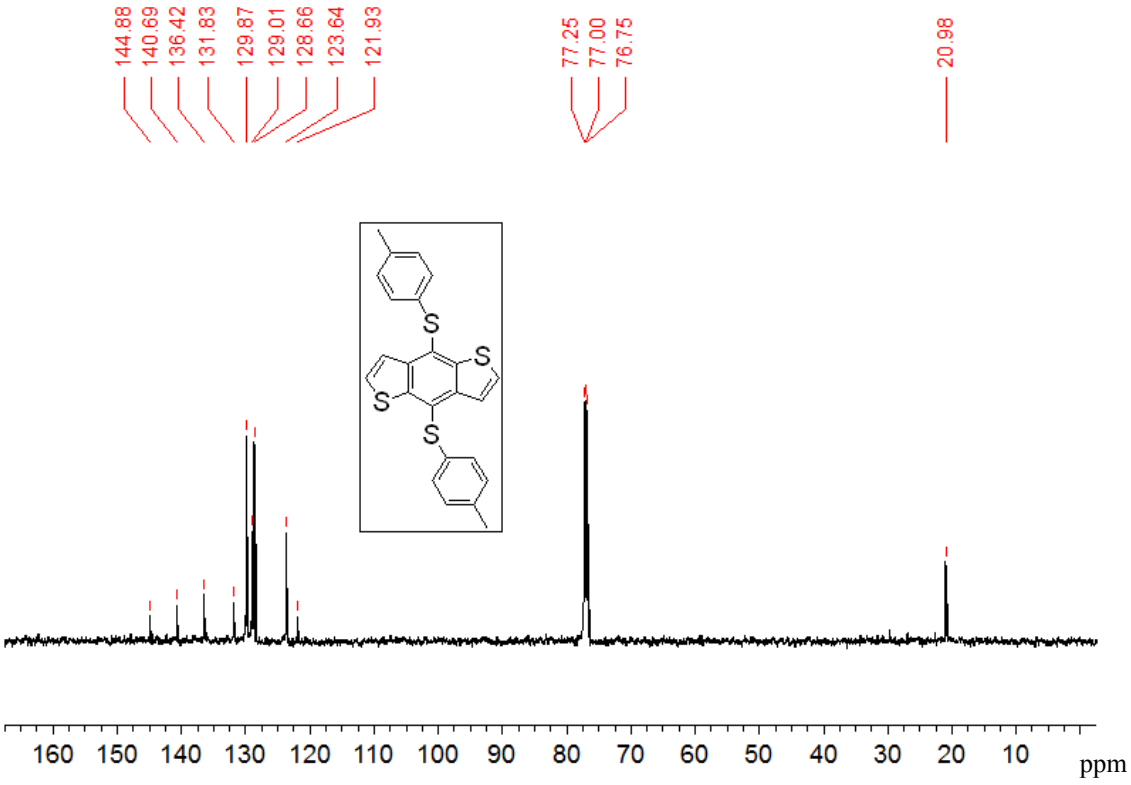

Figure S36. ^{13}C NMR spectrum of **19** in $CDCl_3$ solution.

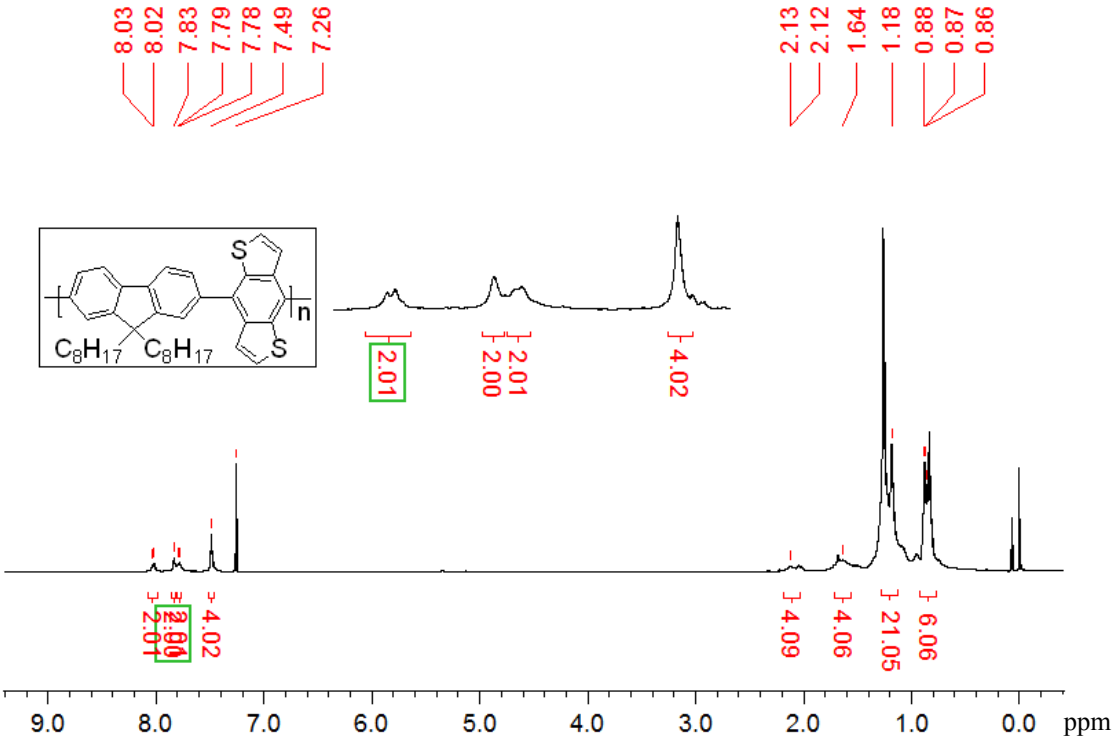

Figure S37. ^{1}H NMR spectrum of polymer **P1** in $CDCl_3$ solution.

3. Electrochemical characterization of BDT oligomers

The highest occupied molecular orbital (HOMO) of the BDT were determined by electrochemical cyclic voltammetry (CV). **Figure S38** shows the CV traces of **4-19** films on Pt electrode in acetonitrile solution containing 0.1 M Bu_4NPF_6 at a scan rate of 50 mV/s. The potential of ferrocene 0.40 V vs SCE is used as internal standard.

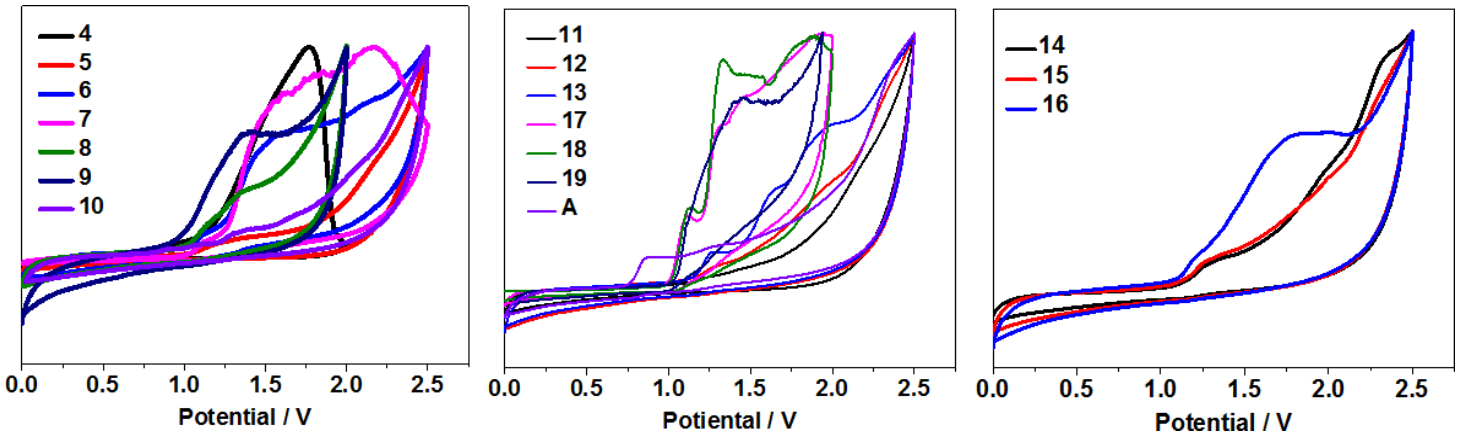

Figure S38. Cyclic voltammograms of as-prepared BDT oligomers and 4,8-didodeoxyl BDT.

On the basis of 4.8 eV below vacuum for the energy level of Fc/Fc+, the HOMO level of the BDT is calculated from the onset oxidation potentials (E_{ox}^{onset}) and the LUMO levels are calculated using HOMO and E_g^{opt} according to the following equations:[S3]

$$\text{HOMO} = -e\,(E_{ox}^{onset} + 4.4)\ (\text{eV})$$

$$\text{LUMO} = (\text{HOMO} + E_g^{opt})\ (\text{eV})$$

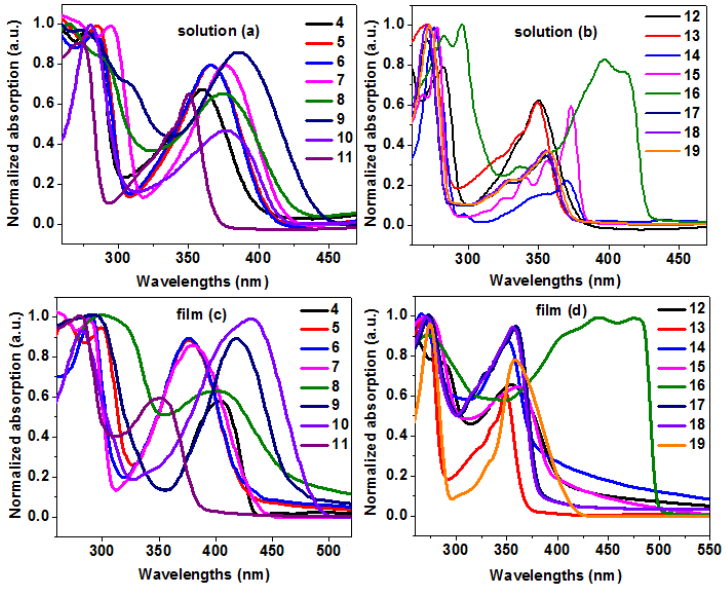

Figure S39. UV−vis absorption spectra of BDT oligomers in $CHCl_3$ solutions and thin films.

The absorption maximum (λ_{max}) in both solution and thin films as well as the HOMO and LUMO energy levels of BDT oligomers are summarized in Table S1.

Table S1. Optical and electrochemical data of BDT oligomers

Oligomer	λ_{max} (nm) solution	λ_{max} (nm) film	E_g^{opt} [a] (eV)	E_{ox}^{onset} (V)	HOMO (eV)	LUMO[b] (eV)	λ_{edge} (nm)
4	360	404	2.87	1.01	-5.41	-2.54	431
5	366	378	2.87	1.06	-5.45	-2.59	432
6	366	377	2.87	1.03	-5.43	-2.56	432
7	376	380	2.83	1.02	-5.42	-2.59	437
8	375	402	2.67	1.03	-5.43	-2.76	463
9	386	430	2.55	0.98	-5.38	-2.83	485
10	377	432	2.53	1.02	-5.42	-2.89	490
11	350	351	3.22	1.15	-5.55	-2.33	384
12	350	350	3.34	1.16	-5.56	-2.22	371
13	350	355	3.10	1.18	-5.58	-2.48	400
14	370	367	3.26	1.07	-5.47	-2.21	380
15	373	350	3.22	1.08	-5.48	-2.26	384
16	397, 412	476	2.48	1.11	-5.51	-3.03	500
17	354	358	3.23	1.01	-5.41	-2.18	383
18	355	359	3.27	1.01	-5.41	-2.15	379
19	355	360	3.07	1.02	-5.42	-2.35	405
BDT-O-$C_{12}H_{25}$	350	351	3.33	0.78	-5.18	-1.85	372

[a]The optical band gap was obtained from the equation $E_g^{opt} = 1240/\lambda_{onset}$ (eV), where λ_{onset} is the onset value of absorption spectrum in long wavelength direction, [b]estimated using empirical equation $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

4.Fabrication and characterization of TFT devices

Top-contact, bottom-gate TFT test devices were prepared under N_2 on highly n-doped Si substrates (gate electrode) with 300 nm of thermally grown SiO_2 (insulating layer). FET substrates surfaces were treated with octyltrichlorosilane (OTS) or spin-coated by polymethyl methacrylate (PMMA). Thin films of oligomers as the active layer were vacuum-deposited on the Si/SiO_2 at a rate of 1Hz/s under the 2×10^{-4}Pa. Transistor source and drain gold electrodes were deposited on a SiO_2 layer through a shadow mask to offer FET devices with a channel length of 0.1mm and channel width of 2 mm. Characteristics of the FET devices were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. The mobility of the devices was calculated on the saturated region according to the expression $I_{DS} = (W/2L)\mu C_i(V_G-V_{Th})^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, and C_i is the capacitance. V_G and V_{th} are the gate voltage and threshold voltage, respectively. The FET data for all prepared oligomers are listed as in Table S2.

Table S2. FET characteristics of the as-prepared oligomers

Monomers	μ ($\times10^{-2}$ $cm^2V^{-1}s^{-1}$)[c]	on/off ratio	V_{th} (V)
4[a]	1.13 (1.25)	10^5-10^6	-27.58
5[a]	1.32 (1.59)	10^5-10^6	-25.60
5[b]	4.54 (6.11)	10^4-10^5	-37.01
6[a]	1.06 (1.12)	10^5-10^6	-28.10
7[a]	0.53 (0.6)	10^6-10^7	-40.32
8[a]	1.26 (1.52)	10^5-10^6	-26.93
9[a]	1.15 (1.38)	10^5-10^6	-27.16
10[a]	1.08 (1.15)	10^5-10^6	-27.84
11[a]	0.86 (1.05)	10^5-10^6	-39.12
12[a]	0.91 (1.07)	10^5-10^6	-36.45
13[a]	0.82 (1.04)	10^5-10^6	-37.69
14[a]	0.05 (0.06)	10^7-10^8	-43.68
15[a]	0.03 (0.04)	10^7-10^8	-46.12
16[a]	0.07 (0.09)	10^7-10^8	-41.25
17[b]	1.63 (2.52)	10^4-10^6	-40.68
18[a]	0.94 (1.02)	10^5-10^6	-46.51
19[a]	1.46 (1.78)	10^5-10^6	-42.85

[a]PMMA-modified Si/SiO_2 substrate, [b]OTS-treated Si/SiO_2 substrate, [c]the average mobility and the maximum in parenthesis out of six samples

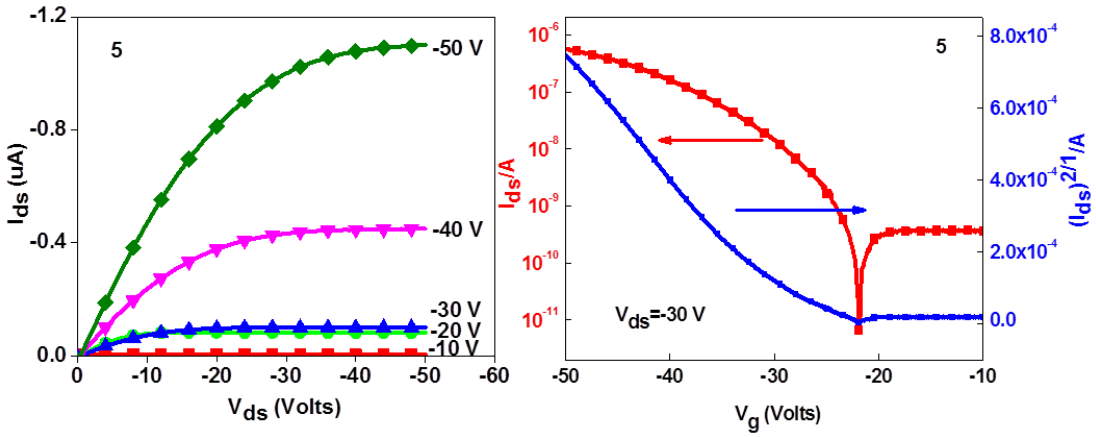

Figure S40. The Output (left) and Transfer (right) curves of **5** FETs with PMMA modified Si/SiO_2 substrate.

5. References

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