Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2015

Electronic Supplementary Information (ESI)

Correlation of Structure and Photovoltaic Performance of Benzo[1,2-b:4,5-b']dithiophene Copolymers Alternating with Different Acceptors

Jiangsheng Yu,[a] Baofeng Zhao,[b] Xuemei Nie,[a] Baojin Zhou,[a] Yang Li,[a] Jiefeng Hai,[a] Enwei Zhu,[a] Linyi Bian,[a] Hongbin Wu,*[,b] Weihua Tang*[,a]

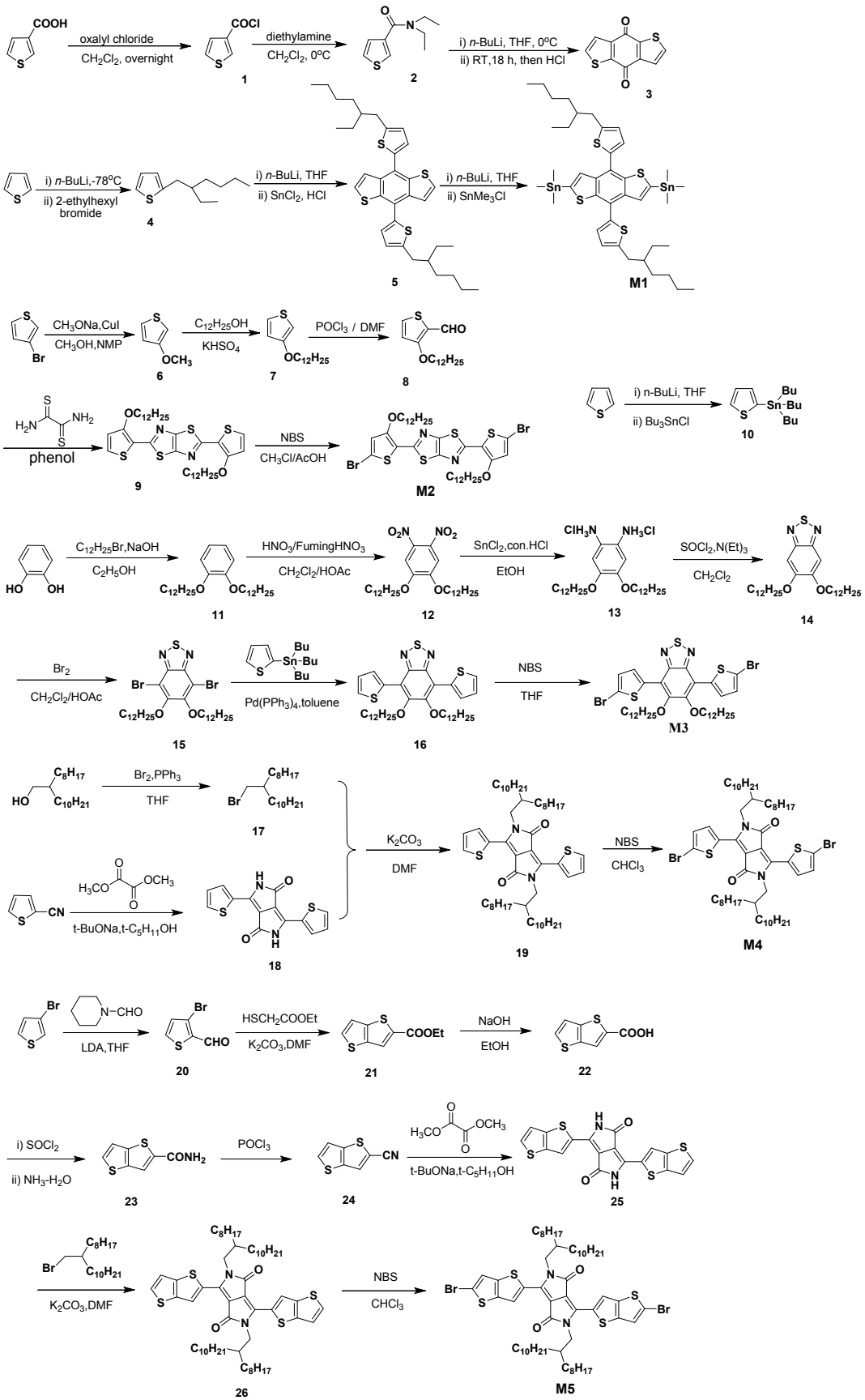
[a] *Key Laboratory of Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China.*
[b] *Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, People's Republic of China.*

Table of Contents

1. Synthesis of monomers

The synthetic routes for the monomers were outlined in Scheme S1. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**M1**)[1], 2,5-bis(5-bromo-3-dodecyloxythiophen-2yl)thiazolo[5,4-*d*]thiazole (**M2**)[2], 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole (**M3**)[3, 4], 2,5-bis(2-octyldodecyl)-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (**M4**)[5] and 3,6-bis(2-bromothieno[3,2-b]thiophen-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**M5**)[6,7] were synthesized according to the similar procedure in the literature. The detailed synthetic procedures are as follows.

Thiophene-3-carbonyl chloride (1). Thiophene-3-carboxylic acid (15.00 g, 117.05 mmol) was dissolved in 100 mL of anhydrous CH_2Cl_2. The mixture was cooled by ice-water bath, and then oxalyl chloride (29.71 g, 234.10 mmol) was added dropwise. The reactant was stirred overnight at room temperature (RT). After removing unreacted oxalyl chloride and the solvent by rotary evaporation, 15.56 g of compound **1** was obtained as colorless solid (106.14mmol, 91%) and used for the next step directly without further purification. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.37 (dd, J = 3.0, 1.2 Hz, 1H), 7.57 (dd, J = 5.2, 1.2 Hz, 1H), 7.39 (dd, J = 5.1, 3.1 Hz, 1H).



Scheme S1. Synthetic routes of the monomers.

N,N-Diethylthiophene-3-carboxamide (2). In a 500 mL flask in ice-water bath, 21.9 mL of diethylamine (15.53 g, 212.29 mmol) and 75 mL of anhydrous CH_2Cl_2 was mixed. Compound **1** (15.56 g, 106.14 mmol) was dissolved in 60 mL of anhydrous CH_2Cl_2 then the solution was dropped into the flask slowly. After adding compound **1**, the ice bath was removed, and the reactant was stirred at room temperature overnight. Then, the reactant was washed by water several times and extracted by CH_2Cl_2. The organic layer was dried with anhydrous $MgSO_4$, filtered, concentrated via rotary evaporation. The crude product was purified by distillation under vacuum, and 17.20 g of compound **2** (93.85 mmol, 79%) was obtained as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.47 (dd, J = 2.9, 1.2 Hz, 1H), 7.32 (dd, J = 4.9, 3.0 Hz, 1H), 7.18 (dd, J = 5.0, 1.3 Hz, 1H), 3.44 (d, J = 61.6 Hz, 4H), 1.20 (s, 6H).

4,8-Dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-dione (3). Compound **2** (17.20 g, 93.85 mmol) was dissolved in 150 mL of anhydrous THF under nitrogen atmosphere. The solution was cooled down to -30 ^{o}C, and 41.1 mL of n-butyllithium (98.54 mmol, 2.4 M) was dropped slowly. After all of the solution was added, the reactant was stirred at ambient temperature for 6 h. Then, the reactant was poured into 300mL of ice water and stirred for several hours. The mixture was filtrated, and the yellow precipitate was washed by 200 mL of water, and 50 mL of cool methanol successively. 8.0 g of compound **3** was obtained as a yellow powder (36.32mmol, 77%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.68 (d, J = 5.0 Hz, 2H), 7.65 (d, J = 5.0 Hz, 2H).

2-(2-Ethyl-hexyl)thiophene (4). Thiophene (5.00 g, 59.43 mmol) was dissolved in

100 mL of anhydrous THF under nitrogen atmosphere. The solution was cooled down to -78 ° C and 26.0 mL of n-butyllithium (62.4 mmol, 2.4 M) was added dropwise. After being stirred at -78°C for 1 h, then, 12.05 ml of 2-ethylhexyl bromide (62.4 mmol) was added in one portion and the mixture was stirred at -78°C for another 1 h,then warmed up to RT overnight. The mixture was quenched by 20 mL of cool water and extracted by diethyl ether three times. The organic layer was dried with anhydrous $MgSO_4$. After removing solvent under vacuum, the residue was purified by vacuum distilled to yield the compound **4** as colorless oil (10.00 g, 50.93 mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.12 (d, *J* = 5.1 Hz, 1H), 6.93 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.78 (d, *J* = 3.3 Hz, 1H), 2.79 (d, *J* = 6.8 Hz, 2H), 1.63-1.54 (m, 1H), 1.42-1.32 (br, 8H), 0.96-0.91 (m, 6H).

4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (5). 7.7 mL of n-Butyllithium (18.39 mmol, 2.4 M) was added dropwise to the solution of compound **4** (3.57 g, 18.16 mmol) in 50 mL of anhydrous THF at -30°C under nitrogen atmosphere. The mixture was heated up to 50°C for 2 h. Then the solvent was cooled in ice-water bath, subsequently, compound **3** (1.00 g, 4.54 mmol) was added one portion, and the mixture was heated at 50°C for another 2 h. After cooling the mixture down to RT, a mixture of $SnCl_2{\cdot}2H_2O$ (8.20 g, 36.32 mmol) in 20 mL of aqueous HCl (10%) was added, and the mixture was stirred overnight. The organic layer was washed with water and brine, dried with $MgSO_4$, filtered, concentrated via rotary evaporation. Further purification was carried out by column chromatography on silica gel eluting with petroleum ether to obtain pure compound **5** as a yellow

liquid (2.00 g, 3.45 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.65 (d, *J* = 5.7 Hz, 2H), 7.46 (d, *J* = 5.7 Hz, 2H), 7.30 (d, *J* = 3.5 Hz, 2H), 6.90 (d, *J* = 3.5 Hz, 2H), 2.87 (d, *J* = 6.8 Hz, 4H), 1.72-1.67 (m, 2H), 1.49-1.33 (br, 16H), 0.97-0.91 (m, 12H).

2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (M1). Compound **5** (1.00 g, 1.73 mmol) and 50 mL of anhydrous THF were added into a flask under nitrogen atmosphere. The solution was cooled to 0 °C and 1.8 mL of n-butyllithium (4.32 mmol, 2.4 M) was added dropwise. The reaction mixture was then stirred for 2 h at room temperature, then the reaction mixture was cooled to 0 °C and 4.4 ml of trimethyltin chloride (4.40 mmol, 1.0 M in hexane) was added in one portion and the mixture was stirred at RT overnight. The mixture was quenched by addition of 20 mL of water and extracted by diethyl ether three times. The combined organic phase was dried with $MgSO_4$, filtered, concentrated via rotary evaporation. The residue was recrystallized by isopropanol to obtain compound **M1** as pale yellow solid (1.20 g, 1.33 mmol, 77%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.69 (s, 2H), 7.32 (d, *J* = 3.5 Hz, 2H), 6.91 (d, *J* = 3.5 Hz, 2H), 2.89-2.86 (m, 4H), 1.72-1.68 (m, 2H), 1.46-1.35 (br, 16H), 0.98-0.86 (m, 12H), 0.40 (s, 18H).

3-Methoxythiophene (6). In a 100 mL flask under nitrogen atmosphere, to a stirred solution of sodium methanolate (3.24 g, 60 mmol) in methanol (12 ml) were added with N-methyl pyrrolidone (30 ml) and 3-bromothiophene (8.15 g, 50 mmol). The mixture was heated to 110 °C to remove surplus methanol, then CuI (1.23 g, 6.46 mmol) was added in one portion and kept reflux overnight. The reaction was cooled

to room temperature. The crude product was extracted with dichloromethane and the combined organic layers were washed with saturated aqueous NH_4Cl, dried with anhydrous $MgSO_4$, filtered, and concentrated via rotary evaporation. The residue was further distilled under reduced pressure to obtain the compound **6** as a colorless liquid (5.00 g, 43.8mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.18 (dd, *J* = 5.2, 3.1 Hz, 1H), 6.76 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.26 (dd, *J* = 3.1, 1.6 Hz, 1H), 3.82 (s, 3H).

3-Dodecyloxythiophene (7). A mixture of compound **6** (5.00 g, 43.80 mmol), 1-dodecanol (16.32g, 87.59 mmol), potassium bisulfate (1.19 g, 8.76 mmol, 0.2 eq) and 60 mL toluene was heated in a 100 °C bath for 15 hours under nitrogen atmosphere. After dichloromethane/water extraction, the combined organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was purified by column chromatography on silica gel eluting with petroleum ether to obtain pure compound **7** as a colorless liquid (7.00 g, 26.07mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.17 (dd, *J* = 5.2, 3.1 Hz, 1H), 6.75 (dd, *J* = 5.2, 1.5 Hz, 1H), 6.22 (dd, *J* = 3.1, 1.5 Hz, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.81-1.70 (m, 2H), 1.47-1.39 (m, 2H), 1.32-1.25 (br, 16H), 0.88 (t, *J* = 6.9 Hz, 3H).

2-Formyl-3-dodecyloxythiophene (8). To the stirred solution of anhydrous DMF (40 mL) at 0 °C in 100 mL flask under nitrogen atmosphere, $POCl_3$ (3.43g, 22.35 mmol) was added dropwise for 15 minutes. The reaction mixture was stirred for 3 hour. Then compound **7** (5.00 g, 18.62 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at 70°C for 12h. The reaction was cooled to room temperature and poured it into ice water carefully, then slowly neutralized with 10%

NaOH solution (80 mL). The aqueous layer was extracted with dichloromethane (3 × 100 mL), followed by drying over anhydrous $MgSO_4$. After the removal of solvents, the crude mixture was chromatographed on silica gel eluting with petroleum ether/ethyl acetate (8:1) to give compound **8** as colorless oil. (4.20 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.81 (s, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 6.90 (d, *J* = 3.7 Hz, 1H), 2.86 (t, *J* = 7.6 Hz, 2H), 1.75-1.66 (m, 2H), 1.35-1.24 (br, 18H), 0.88 (t, *J* = 6.9 Hz, 3H).

2,5-Bis(3-dodecyloxythiophen-2yl)thiazolo[5,4-*d*]thiazole (9). In a round-bottom flask combined dithiooxamide (0.41 g, 3.37 mmol), 1.5 g of phenol, and compound **8** (2.00 g, 6.75 mmol) were heated at 150 °C for 2 h under nitrogen atmosphere. The crude product was purified by column chromatography on silica gel using petroleum ether/chloroform (1:1) to give pure product **9** as a brownish yellow solid (1.26g, 1.87mmol, 28%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.32 (d, *J* = 5.5 Hz, 2H), 6.88 (d, *J* = 5.5 Hz, 2H), 4.23 (t, *J* = 6.1 Hz, 4H), 1.95-1.85 (m, 4H), 1.57 (m, 4H), 1.39-1.25 (br, 32H), 0.87 (t, *J* = 6.9 Hz, 6H).

2,5-Bis(5-bromo-3-dodecyloxythiophen-2yl)thiazolo[5,4-*d*]thiazole (M2). Under nitrogen atmosphere, compound **9** (0.50 g, 0.74 mmol) was dissolved in $CHCl_3$/AcOH (20/10 mL). NBS (0.29 g, 1.63 mmol) was added one portion and stirred at 0 °C for 2 hours under dark. Then the reaction solution was stirred at room temperature for 24 hours. The reaction solution was washed with water, and the combined organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, the crude product was purified by column chromatography on silica gel eluting with petroleum ether/

chloroform (2:1) to give compound **M2** as a yellow solid. (0.53 g, 0.64mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.89 (s, 2H), 4.18 (t, *J* = 6.2 Hz, 4H), 1.92-1.85 (m, 4H), 1.58-1.52 (m, 4H), 1.39-1.25 (br, 32H), 0.87 (t, *J* = 6.9 Hz, 6H).

2-(Tributylstanny)thiophene (10). Thiophene (5.00 g, 59.43 mmol) was dissolved in 100 mL of anhydrous THF under nitrogen atmosphere. The solution was cooled down to -78 ° C and 26.0 mL of n-butyllithium (62.4 mmol, 2.4 M) was added dropwise over 1 h. After being stirred at -78 ^{o}C for 1 h, tributyltin chloride (21.28 g, 65.37 mmol) was added dropwise within 30 minutes. After the addition the resulting mixture was stirred at -78 °C for another 1 h and was allowed to warm to RT overnight. The mixture was then poured into 100 mL of water and extracted with diethyl ether. The reaction solution was washed with saturated NH_4C1, and the combined organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, the crude product was purified by column chromatography on silica gel eluting with petroleum ether to give compound **10** as yellow oil (24 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.66 (dd, *J* = 4.7, 0.5 Hz, 1H), 7.28 (dd, *J* = 4.6, 3.2 Hz, 1H), 7.21 (dd, *J* = 3.2, 0.5 Hz, 1H), 1.61-1.53 (m, 6H), 1.39-1.32 (m, 6H), 1.14-1.12 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H).

1,2-Bis(dodecyloxy)benzene (11). Sodium hydroxide (9.08 g, 227.04 mmol) was added to a solution catechol (10 g, 90.82 mmol) in ethanol (100 mL). After stirring at 60 °C for 30 minutes, 1-bromododecane (56.59 g, 227.04 mmol) was added dropwise into the reaction mixture and the reaction mixture was stirred at 60 °C for 40 h. After cooling down to room temperature, ethanol was removed on a rotary evaporator and

the residue was extracted with dichloromethane and water. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was recrystallized using MeOH to afford **11** as a white solid (30.55 g, 68.38mmol, 75%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.89 (s, 4H), 3.99 (t, *J* = 6.7 Hz, 4H), 1.84-1.78 (m, 4H), 1.49-1.44 (m, 4H), 1.36-1.26 (br, 32H), 0.88 (t, *J* = 6.9 Hz, 6H).

1,2-Bis(dodecyloxy)-4,5-dinitrobenzene (12). Compound **11** (10.00 g, 22.38 mmol) was dissolved in CH_2Cl_2/AcOH (70/70mL). 20 mL of 65% nitric acid was added dropwise. After stirred for 30 minutes, 50mL of fuming nitric acid was slowly added at 10 °C. Then the mixture was allowed to warm to room temperature and the mixture was stirred for 40 h. The reaction mixture was then poured over an ice-water mixture. After dichloromethane/water extraction, the combined organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was recrystallized using EtOH to afford **12** as a yellow solid (10.20 g, 19.00mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.29 (s, 2H), 4.10 (t, *J* = 6.5 Hz, 4H), 1.89-1.84 (m, 4H), 1.50-1.45 (m, 4H), 1.37-1.26 (br, 32H), 0.88 (t, *J* = 6.9 Hz, 6H).

4,5-Bis(dodecyloxy)benzene-1,2-diaminium chloride (13). A mixture of compound **12**(5.00 g, 9.32 mmol) in ethanol (100 mL) was added $Sn(II)Cl_2{\cdot}2H_2O$ (17.87 g, 79.18mmol) in conc. HCl (50 mL) under nitrogen atmosphere. Then the mixture was heated to 80 °C overnight. After cooled to room temperature, the residue was filtered and washed with water and methanol to obtain compound **13** as a white solid (unstable, 4.38 g, 7.97 mmol, 86%).

5,6-Bis(octyloxy)benzo[c][1,2,5]thiadiazole (14). To a mixture of compound **13**

(4.38 g, 7.97 mmol) and triethylamine (11 mL 79.68 mmol) in 100 mL dichloromethane was slowly added a solution of thionyl chloride (4.63 mL, 63.74mmol) in 40 mL dichloromethane at 0 °C. After addition, the mixture was heated to reflux overnight under nitrogen atmosphere. The cooled solution was concentrated in vacuum. The residue was filtered and purified on a silica gel column eluting with petroleum ether/ethyl acetate (40:1) to afford compound **14** as a off-white solid (3.15g, 6.24mmol 78%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.13 (s, 2H), 4.09 (t, *J* = 6.5 Hz, 4H), 1.95-1.87 (m, 4H), 1.56 – 1.49 (m, 4H), 1.40-1.25 (br, 32H), 0.88 (t, *J* = 6.9 Hz, 6H).

4,7-Dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (15). To a solution of compound **14** (3.15 g, 6.24 mmol) in a mixture of dichloromethane (100 mL) and acetic acid (65mL), was added bromine (2.6 mL, 49.92 mmol). The resulting mixture was stirred for 48 h at room temperature. 45 mL of saturated Na_2SO_3 (aq) was added to the mixture, extracted with dichloromethane, and the solvents are evaporated under reduced pressure. The crude product was recrystallized using EtOH to afford compound **15** as a white needle solid (3.85 g, 5.81mmol, 93%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.16 (t, *J* = 6.7 Hz, 4H), 1.91-1.85 (m, 4H), 1.56-1.50 (m, 4H), 1.42-1.25 (br, 32H), 0.88 (t, *J* = 6.9 Hz, 6H).

5,6-Bis(dodecyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (16). To a solution of compound **15** (2.0 g, 3.02 mmol), Pd(PPh3)4 (0.35 g, 0.30 mmol) in dry toluene (100 mL) was added 2-(tributylstannyl)thiophene (3.38 g, 9.06 mmol), and the reaction mixture was heated to at 110 °C for 48 h under nitrogen atmosphere. The

reaction mixture was cooled to room temperature, extracted with chloroform and water. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated The residue was chromatographically purified on a silica gel column eluting with petroleum ether/dichloromethane (20:1) to give compound **16** as a yellow-green oil (1.86 g, 2.78mmol, 92%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.47 (dd, *J* = 3.8, 1.1 Hz, 2H), 7.50 (dd, *J* = 5.2, 1.1 Hz, 2H), 7.23 (dd, *J* = 5.1, 3.8 Hz, 2H), 4.11 (t, *J* = 7.1 Hz, 4H), 1.95-1.89 (m, 4H), 1.48-1.40 (m, 4H), 1.35-1.23 (br, 32H), 0.90 (d, *J* = 6.8 Hz, 6H).

4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole (M3). Compound **16** (1.86 g, 2.78 mmol) was dissolved in THF (50 mL) in ice-bath. Then NBS (1.24 g, 6.95 mmol) was added in dark. The reaction mixture was stirred at room temperature for 18 h. After dichloromethane/water extraction, the combined organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was purified by column chromatography on silica gel eluting with petroleum ether/dichloromethane (20:1) to obtain pure compound **M3** as a reddish orange solid (1.97 g, 2.38mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.36 (d, *J* = 4.1 Hz, 2H), 7.17 (d, *J* = 4.1 Hz, 2H), 4.12 (t, *J* = 7.2 Hz, 4H), 1.97-1.91 (m, 4H), 1.47-1.42 (m, 4H), 1.37-1.25 (br, 32H), 0.88 (t, *J* = 7.0 Hz, 6H).

1-Bromo-2-octyldodecane (17). A mixture of 2-octyl-1-dodecanol (10.00 g, 35.50 mmol) and triphenylphosphine (35.14 g, 133.98 mmol) was dissolved in 200 mL THF. Bromine (6.9 mL, 133.98 mmol) was added slowly and the solution was stirred at room temperature overnight. The solvent was removed. Then the residue was

suspended in 200mL hexane. After evaporation of the solvent from the filtrate, the obtained oil is purified by column chromatography on silica gel eluting with petroleum ether to obtain compound **17** as a colourless oil (11.50g, 31.83mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.44 (s, 2H), 1.62-1.56 (m, 1H), 1.47-1.12 (br,32H), 0.88 (t, *J* = 6.9 Hz, 6H).

3,6-Di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (18). In a 500mL round-bottom flask combined sodium tert-butoxide (10.57 g, 110 mmol), 200mL tert-amyl alcohol was heated at 80 °C for 1 h. After all the sodium tert-butoxide was dissolved, 2-cyanothiophene (10.00 g, 91.62 mmol) was added to the reaction. One hour later, dimethyl succinate (3.61 g, 30.54mmol) in 20mL tert-amyl alcohol was added dropwise to the reaction mixture. The reaction were stirred at 105 °C for 16 h. Then the reaction mixture was cooled to 50 °C, and 20 mL MeOH and 10 mL conc. HCl was added. The reaction mixture was filtered. The residue was washed several times with hot methanol and water. The resultant solid was dried in vacuum to obtained compound **18** as a dark red solid (8.00 g, 26.64mmol, 87%), which was used in subsequent reactions without further purification. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 11.24 (s, 2H), 8.21 (d, *J* = 2.5 Hz, 2H), 7.96 (d, *J* = 4.3 Hz, 2H), 7.30 (d, *J* = 3.7 Hz, 2H).

2,5-Bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (19). Compound **18** (8.00 g, 26.64mmol) and potassium carbonate (14.72 g, 106.54 mmol) were dissolved in freshly distilled DMF (200 mL), stirred and heated at 120 °C for 2h under nitrogen atmosphere. Then compound **17** (28.88g 138.32mmol)

was added. After addition the reaction was stirred and heated at 130 °C for 40 h. The reaction mixture was cooled to room temperature, and was poured into distilled water (300 mL). The organic phases was extracted with dichloromethane, washed with brine and dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was purified by column chromatography on silica gel eluting with petroleum ether/dichloromethane (4:1) to obtain pure compound **19** as a red solid (3.9 g, 4.53 mmol, 17%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.87 (dd, J = 3.9, 1.0 Hz, 2H), 7.62 (dd, J = 5.0, 1.0 Hz, 2H), 7.27 (d, J = 5.8 Hz, 2H), 4.01 (d, J = 7.7 Hz, 4H), 1.95-1.89 (m, 2H), 1.29-1.21 (br, 64H), 0.90-0.84 (m, 12H).

2,5-Bis(2-octyldodecyl)-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (M4). Compound **19** (1.80 g, 2.09 mmol) was dissolved into chloroform (30 mL) in ice-bath under nitrogen atmosphere. Then NBS (0.78 g, 4.39 mmol) was added in dark. After 48 h, the mixture was washed with distilled water, and the organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was purified by column chromatography on silica gel eluting with petroleum ether/dichloromethane (4:1) to obtained pure compound **M4** as a purple-black solid (1.32 g, 1.41mmol, 67%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.62 (d, J = 4.2 Hz, 2H), 7.22 (d, J = 4.2 Hz, 2H), 3.92 (d, J = 7.8 Hz, 4H), 1.90-1.85 (m, 2H), 1.34-1.26 (br, 64H), 0.90-0.86 (m, 12H).

3-Bromo-2-formylthiophene (20). 3-Bromothiophene (10.00 g, 61.34 mmol) was dissolved in THF (50 mL) in ice-bath under nitrogen atmosphere. 33mL lithium diisopropylamide (LDA, 64.37mmol, 1M) was added dropwise and then stirred for 1

h at room temperature. Following that 1-formylpiperidin (8.33 g, 73.56 mmol) was added. After 12 h, the reaction mixture was stopped with saturated solution of NH_4Cl (10 mL). For purification it was extracted three times with diethyl ether and the combined organic phases was subsequently dried over anhydrous $MgSO_4$. After filtration the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1) to obtained pure compound **20** as a colorless liquid (10.07 g, 52.71mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.98 (s, 1H), 7.71 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.15 (dd, *J* = 5.1, 1.5 Hz, 1H).

Ethyl thieno[3,2-*b*]thiophene-2-carboxylate (21). To a 500mL round-bottom flask, compound **20** (30.00g, 157.03mmol), potassium carbonate (43.40g, 314.06g), dimethylformaldehyde (200mL) were added and stirred at room temperature for 1 h. Then to this mixture ethyl mercaptoacetate (22.64 g, 188.44 mmol) was added and stirred for another 36 h. After completion of the reaction, 200 mL of water was added and extracted with ethyl acetate. The combined organic phases was dried over anhydrous MgSO4. After evaporating the solvent, the brownish crude target was obtained and was purified by flash chromatography on silica gel eluting with ethyl acetate to obtained pure compound **21** as a light yellow liquid (23.36g, 110.04mmol, 70%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.99 (s, 1H), 7.58 (d, *J* = 5.3 Hz, 1H), 7.28 (d, *J* = 5.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

Thieno[3,2-*b*]thiophene-2-carboxylic acid (22). Compound **21** (10.00 g, 47.11 mmol) was dissolved into a mixture of ethyl alcohol (200 mL) and NaOH (5.65g,

141.32 mmol). This mixture was refluxed overnight. The mixture was then poured into water and conc.hydrochloric acid (100mL) was added dropwise. The precipitate was filtered off, washed with water. The crude product was recrystallized using n-hexane to afford compound **22** as a light-yellow solid (7.70 g, 41.79mmol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.10 (s), 7.65 (d, J = 5.3 Hz), 7.32 (d, J = 5.3 Hz).

Thieno[3,2-*b*]thiophene-2-carboxamide (23). Compound **22** (6.00 g, 32.75 mmol) was dissolved in thionyl chloride (100 mL). The mixture was refluxed for 3 h. After removing unreacted thionyl chloride by rotary evaporation, the brown solid was dissolved in dichloromethane (100 mL). Then ammonium hydroxide (100 mL) in dichloromethane (100mL) was added dropwise in ice-bath. Milky solids were separated out. After 1 h, the precipitate was filtered off, washed with dichloromethane, and dried to obtained compound **23** as a white powder solid (5.50 g, 30.01mmol, 92%). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.07 (s, 2H), 7.83 (d, J = 5.3 Hz, 1H), 7.48 (d, J = 5.2 Hz, 2H).

Thieno[3,2-*b*]thiophene-2-carbonitrile (24). Compound **23** (4.00 g, 21.83 mmol) was mixed with 30 mL of $POCl_3$ and the mixture was heated to reflux for 3 h. Then the mixture was poured into 200 mL of ice water and extracted with dichloromethane. The organic layer was dried over anhydrous MgSO4 before the solvent was removed. The brown oil obtained was passed through a short column of silica gel with dichloromethane as eluent. After removal of the solvent, a yellow needle was obtained (3.00g, 18.16mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.79 (s, 1H), 7.71 (d, J = 5.3 Hz, 1H), 7.29 (d, J = 5.3 Hz, 1H).

3,6-Di(thieno[3,2-*b*]thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (25)

In a 100mL round-bottom flask combined sodium tert-butoxide (2.26 g, 27.23 mmol), 20mL tert-amyl alcohol was heated at 80 °C for 1 h. After all the sodium tert-butoxide was dissolved, compound **24** (3.00 g, 18.16 mmol) was added to the reaction. One hour later, dimethyl succinate (1.33 g, 9.08mmol) in 10 mL tert-amyl alcohol was added dropwise to the reaction mixture. The reaction was stirred at 105 °C overnight. Then the reaction mixture was cooled to room temperature, 20 mL glacial acetic acid was added. The reaction mixture was filtered. The residue was washed several times with hot methanol and water. The resultant solid was dried in vacuum to obtained compound **25** as a dark blue solid (2.40 g, 5.82mmol, 64%), which was used in subsequent reactions without further purification. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 11.24 (s, 2H), 8.21 (s, 2H), 7.96 (d, J = 4.3 Hz, 2H), 7.30 (d, J = 3.7 Hz, 2H).

2,5-Bis(2-octyldodecyl)-3,6-di(thieno[3,2-*b*]thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (26). Compound **25** (2.40 g, 5.82mmol) and potassium carbonate (3.22 g, 23.27mmol) were dissolved in freshly distilled DMF (100mL), stirred and heated at 120 °C for 2h under nitrogen atmosphere. Then compound **17** (6.31 g 17.45mmol) was added. After addition the reaction was stirred and heated at 130 °C for 40 h. The reaction mixture was cooled to room temperature and was poured into distilled water (200 mL). The organic phases was extracted with dichloromethane, washed with brine and dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was purified by column chromatography on silica gel eluting with petroleum ether/dichloromethane (1:1) to obtain pure compound **26** as a dark red

solid (1.10 g, 1.13mmol, 19%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.28 (d, *J* = 0.5 Hz, 2H), 7.60 (d, *J* = 5.2 Hz, 2H), 7.31 (dd, *J* = 5.2, 0.6 Hz, 2H), 4.07 (d, *J* = 7.8 Hz, 4H), 2.00-1.95 (m, 2H), 1.33-1.20 (br, 64H), 0.88-0.82 (m, 12H).

3,6-Bis(2-bromothieno[3,2-*b*]thiophen-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (M_5). Compound **26** (1.10 g, 1.13 mmol) was dissolved into chloroform (50 mL) in ice-bath under nitrogen atmosphere. Then NBS (0.50 g, 2.82 mmol) was added in dark. After 48 h, the mixture was washed with distilled water, and the organic layer was dried over anhydrous $MgSO_4$. After solvent evaporation, the residue was purified by column chromatography to afford compound **M5** as a dark violet solid (1.16 g, 1.03mmol, 91%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.18 (s, 2H), 7.30 (s, 2H), 4.03 (d, *J* = 7.7 Hz, 4H), 2.00-1.85 (m, 2H), 1.39-1.20 (br, 64H), 0.88-0.83 (m, 12H).

2. NMR Spectra of intermediates

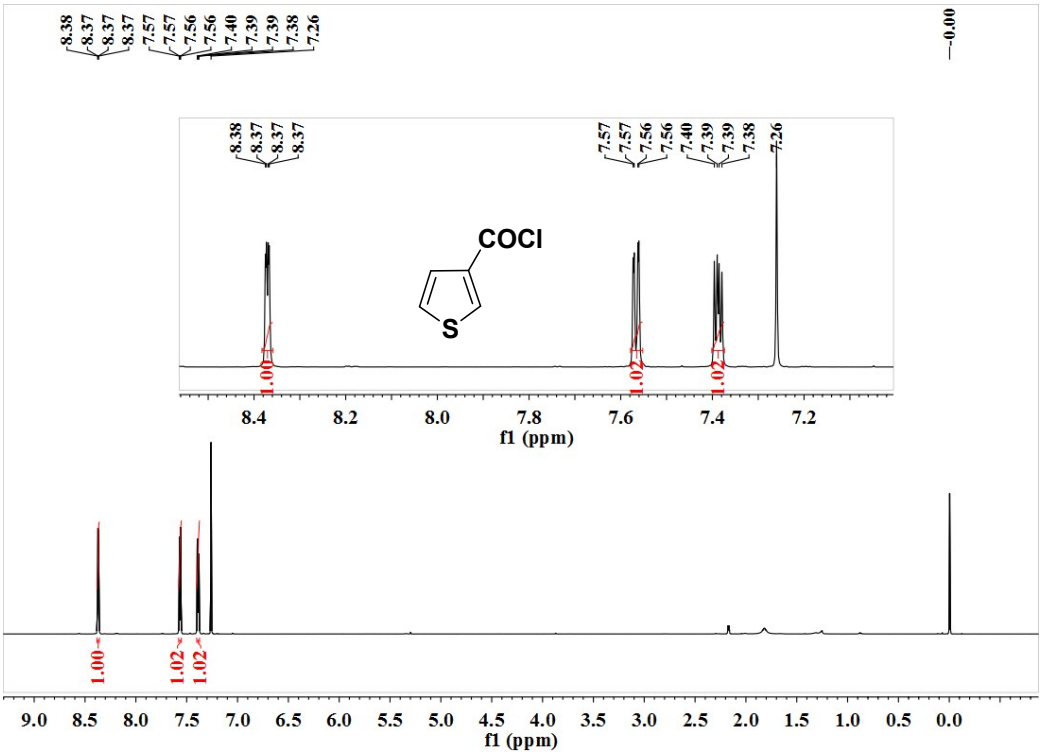


Figure S1. ^{1}H NMR spectrum of **1.**

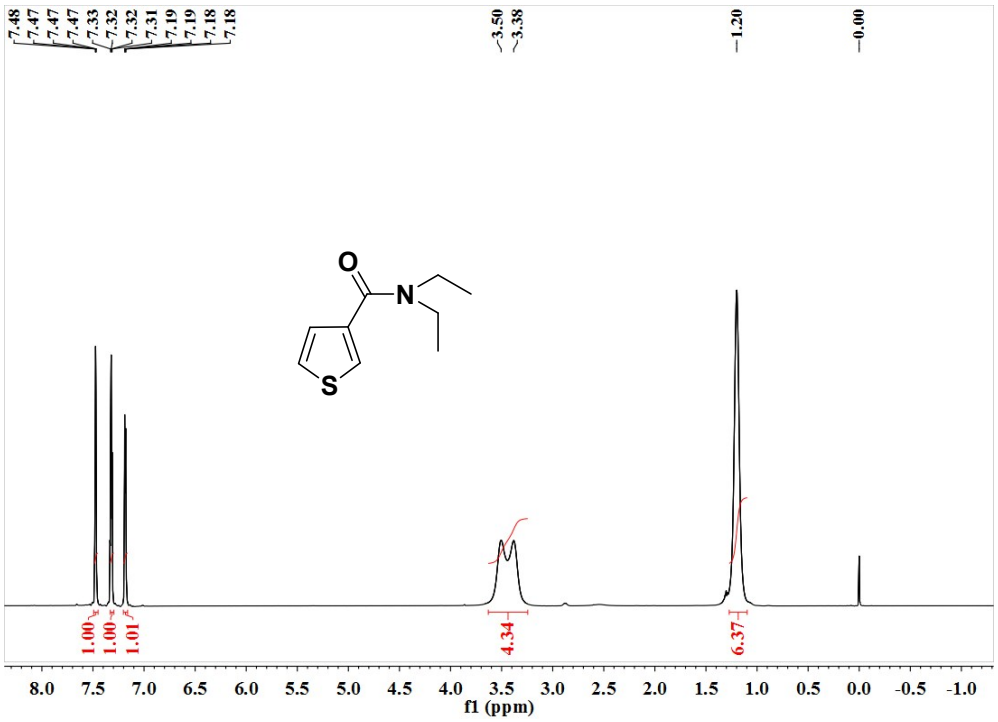


Figure S2. ^{1}H NMR spectrum of **2.**

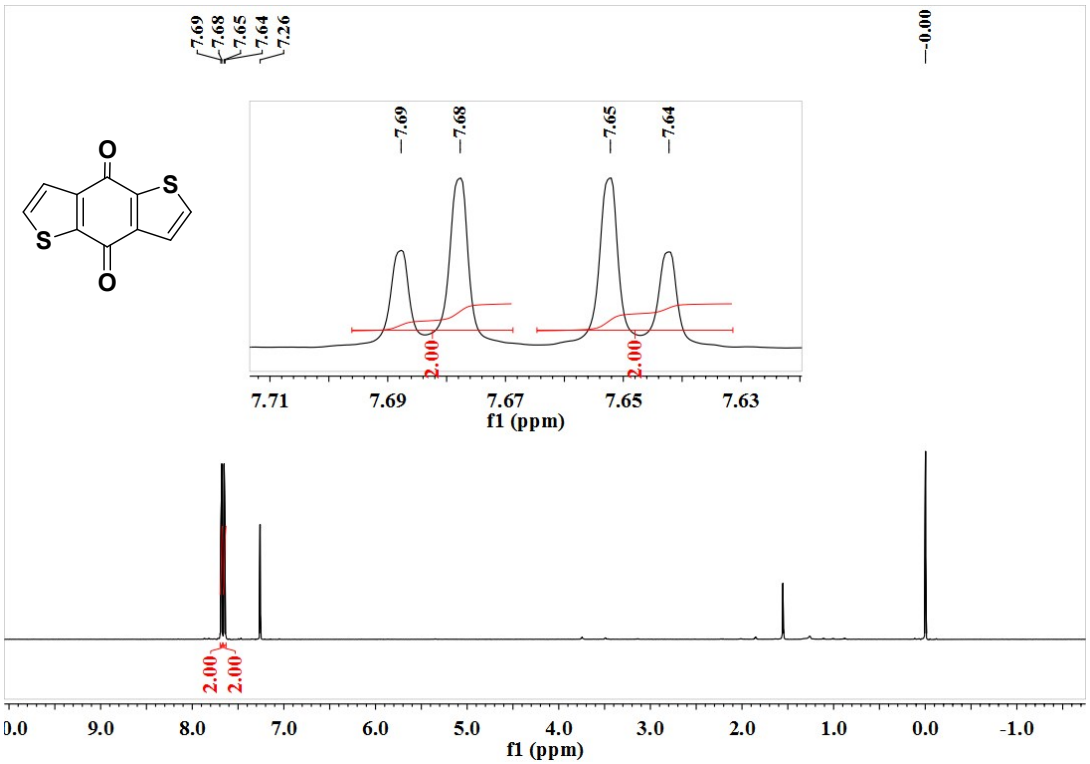


Figure S3. ^{1}H NMR spectrum of **3.**

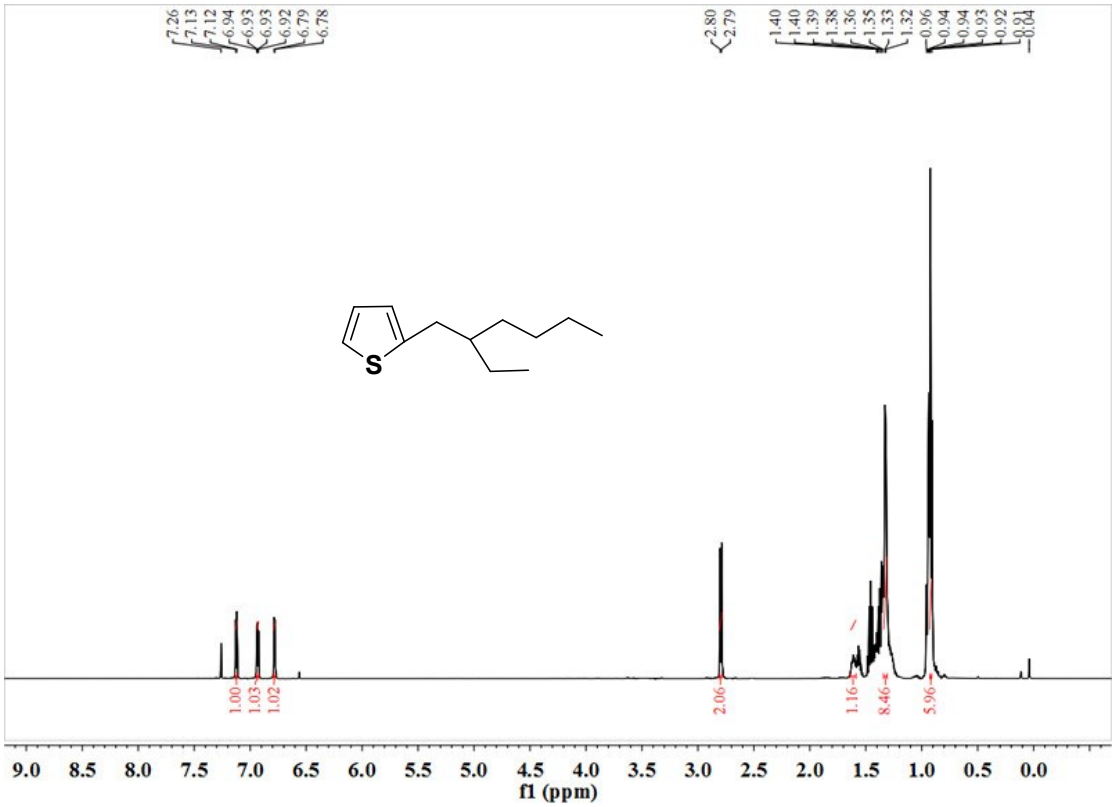


Figure S4. ^{1}H NMR spectrum of **4.**

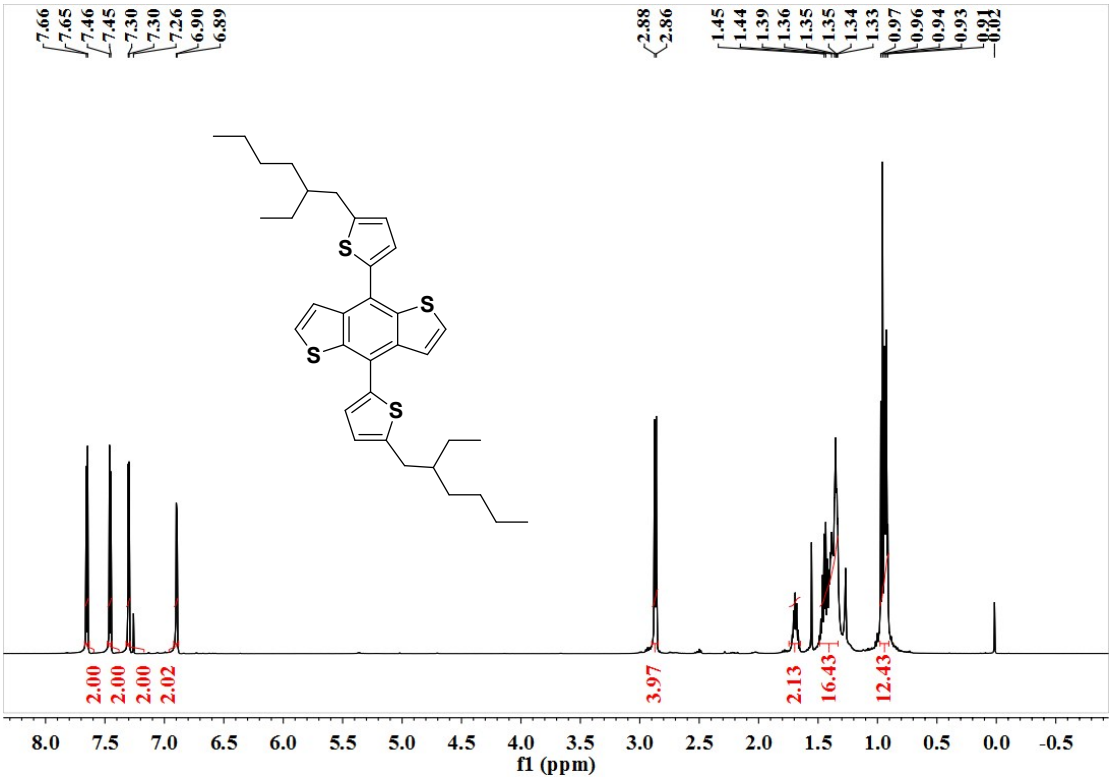


Figure S5. ^{1}H NMR spectrum of **5.**

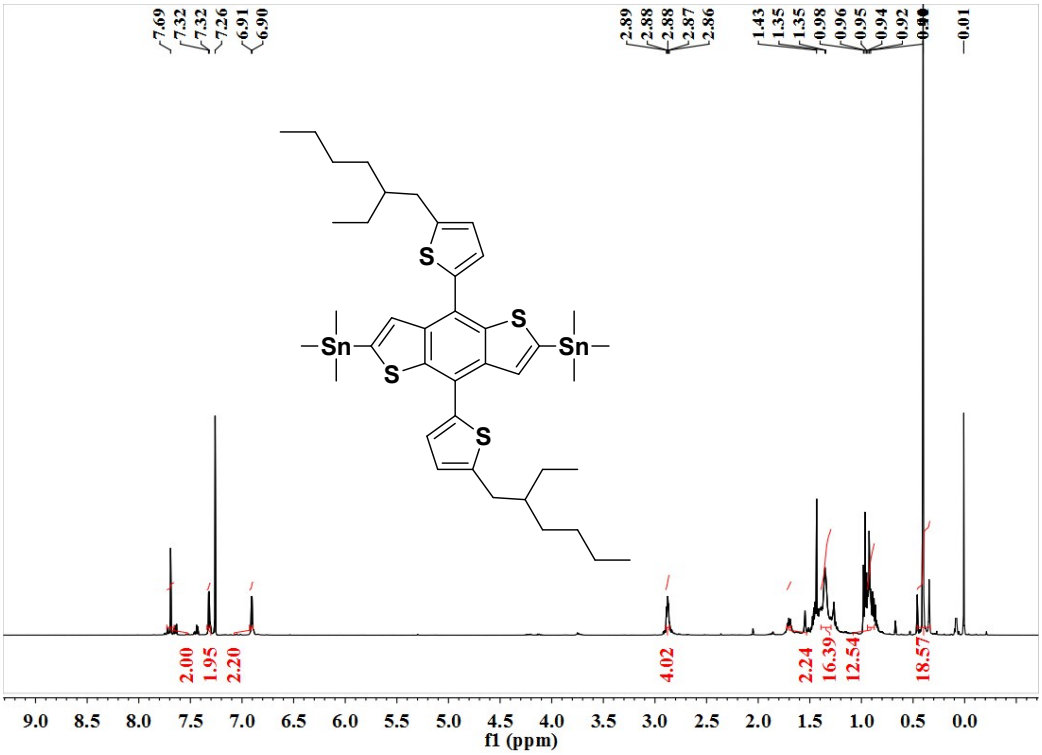


Figure S6. ^{1}H NMR spectrum of **M1**

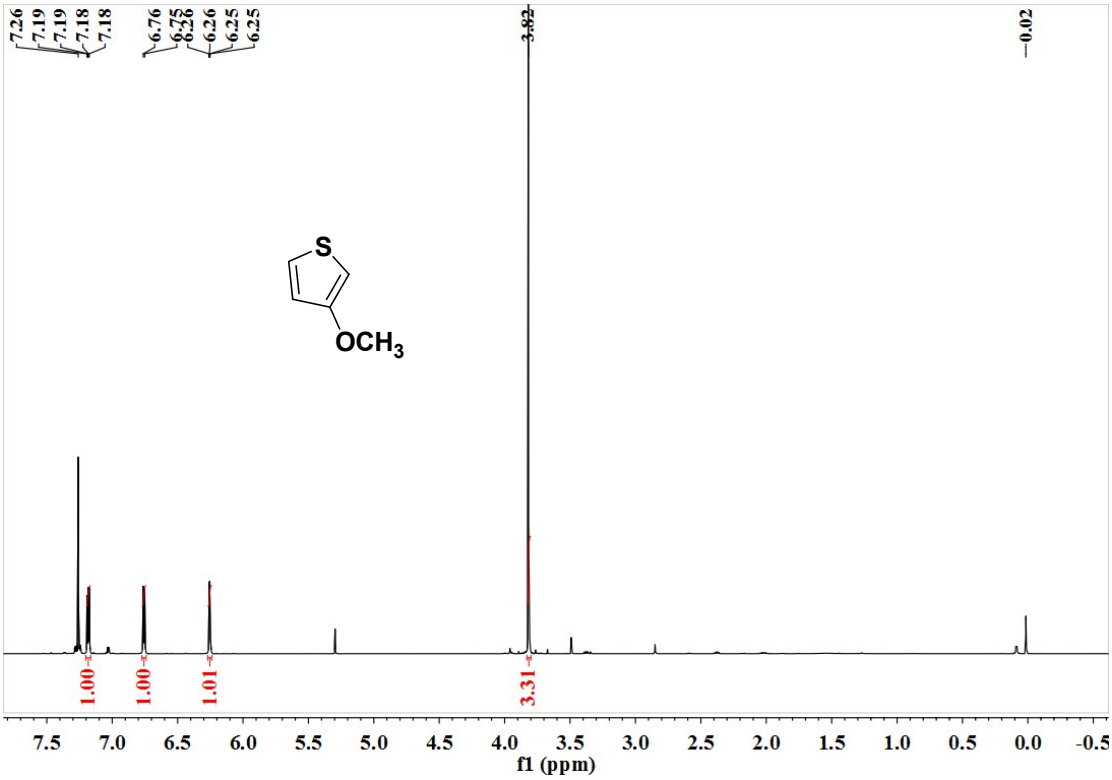


Figure S7. ^{1}H NMR spectrum of **6.**

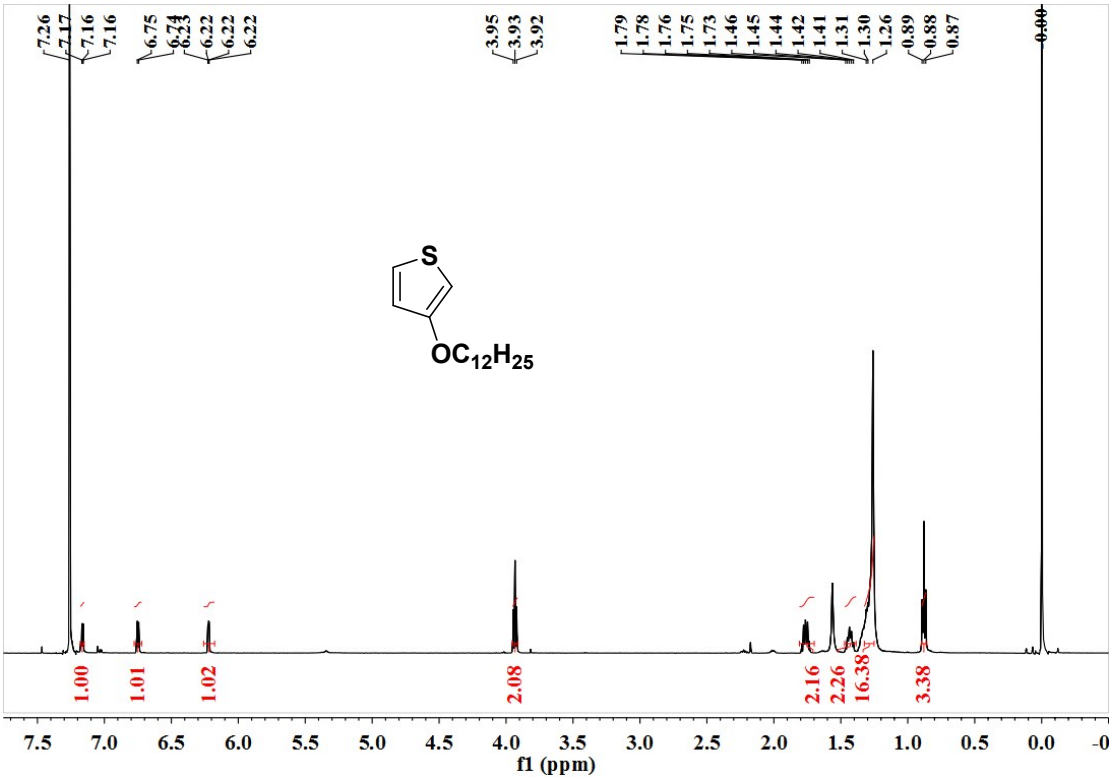


Figure S8. ^{1}H NMR spectrum of **7.**

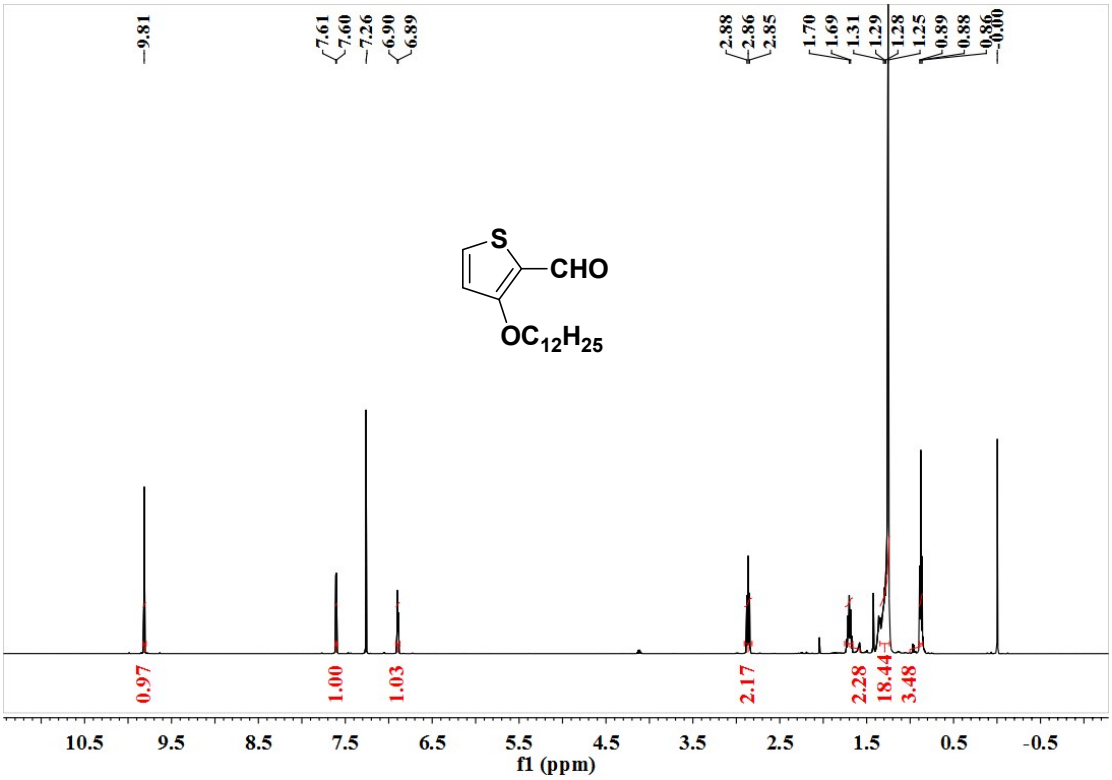


Figure S9. ^{1}H NMR spectrum of **8.**

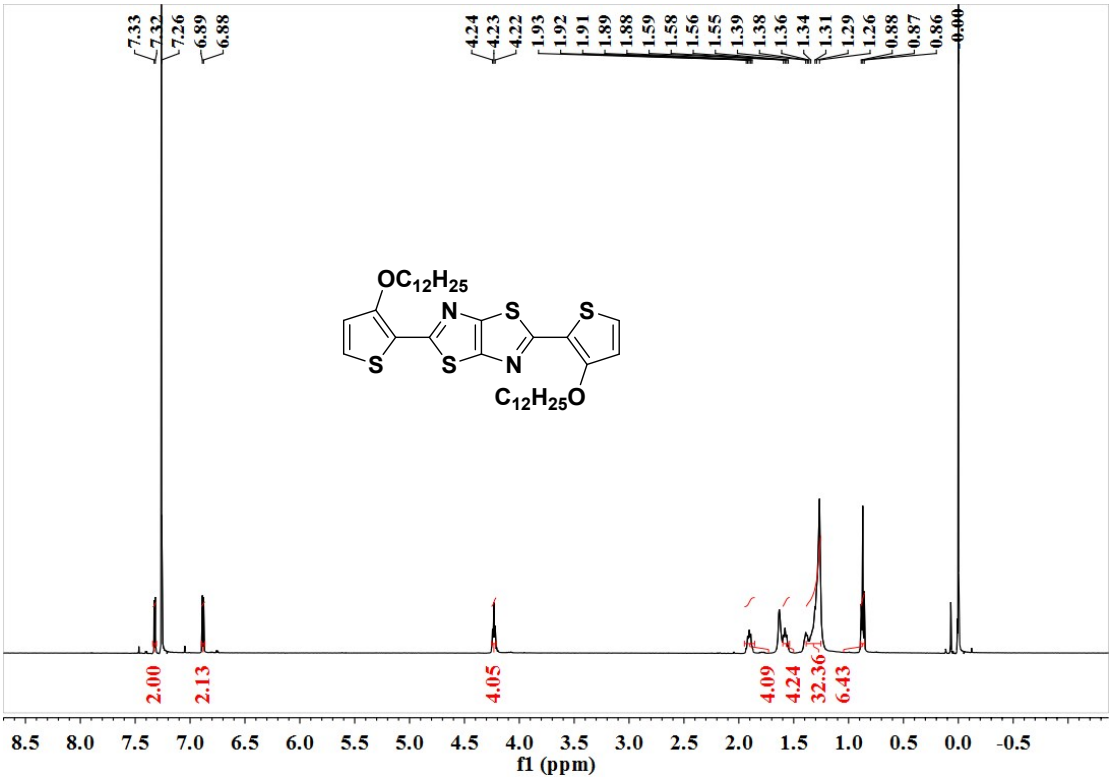


Figure S10. ^{1}H NMR spectrum of **9.**

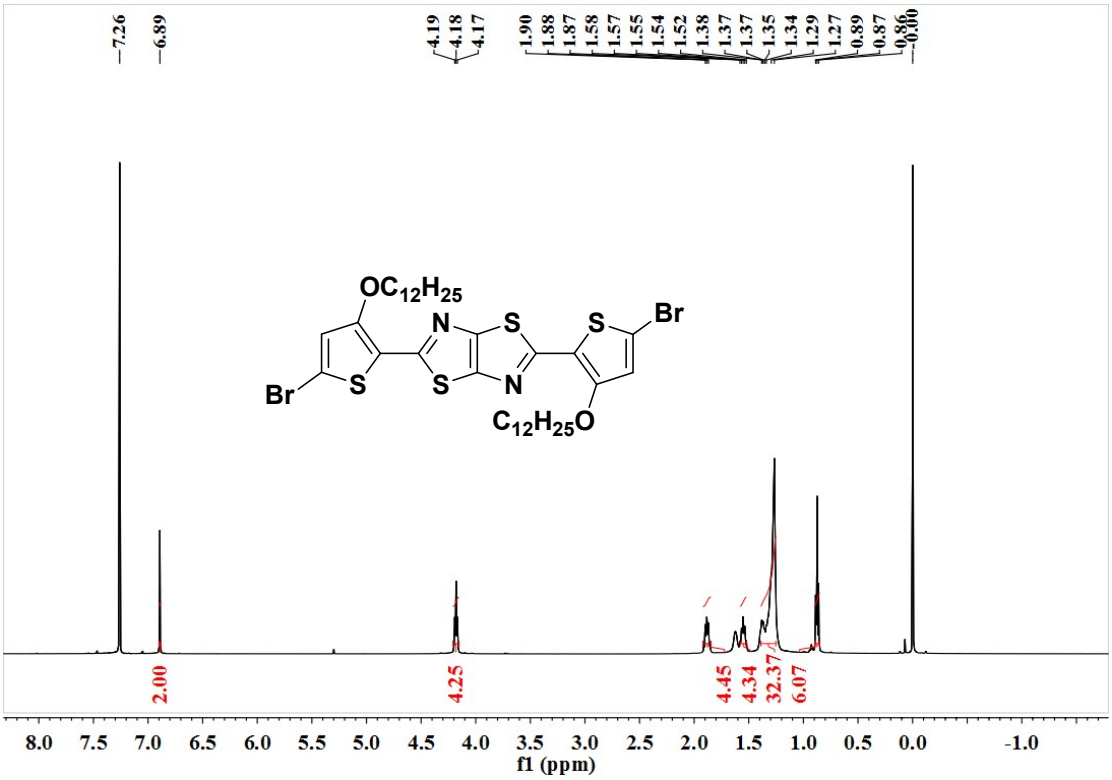


Figure S11. ^{1}H NMR spectrum of **M2.**

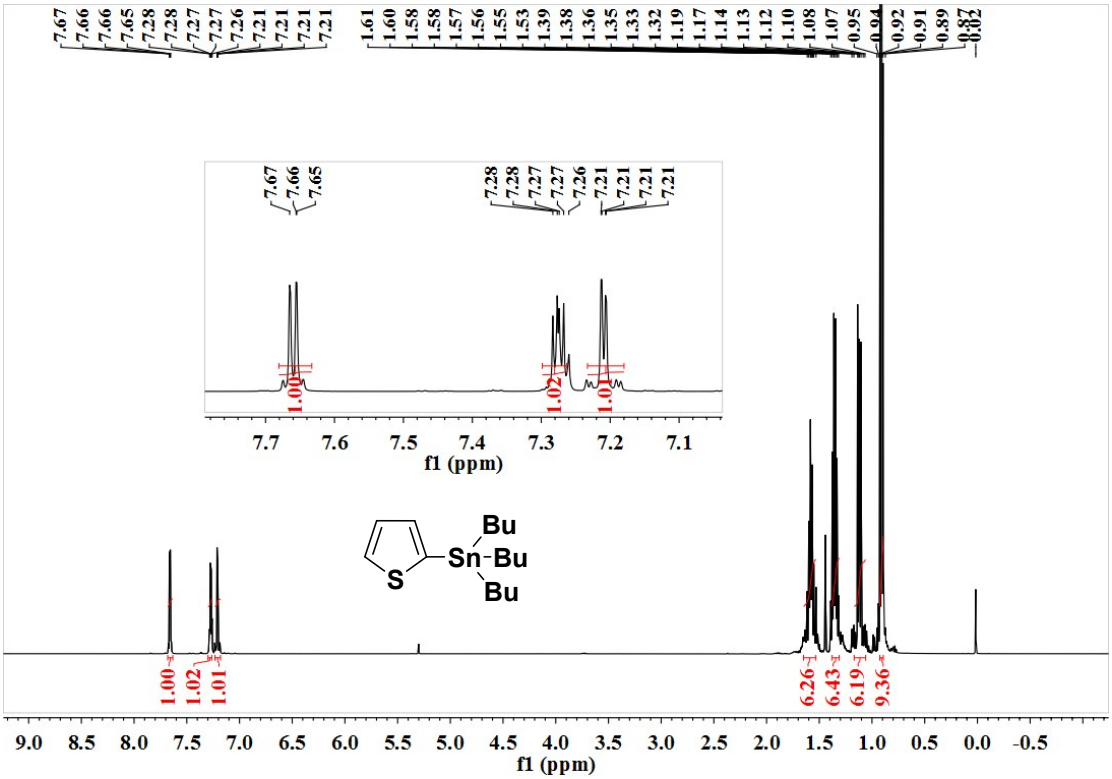


Figure S12. ^{1}H NMR spectrum of **10.**

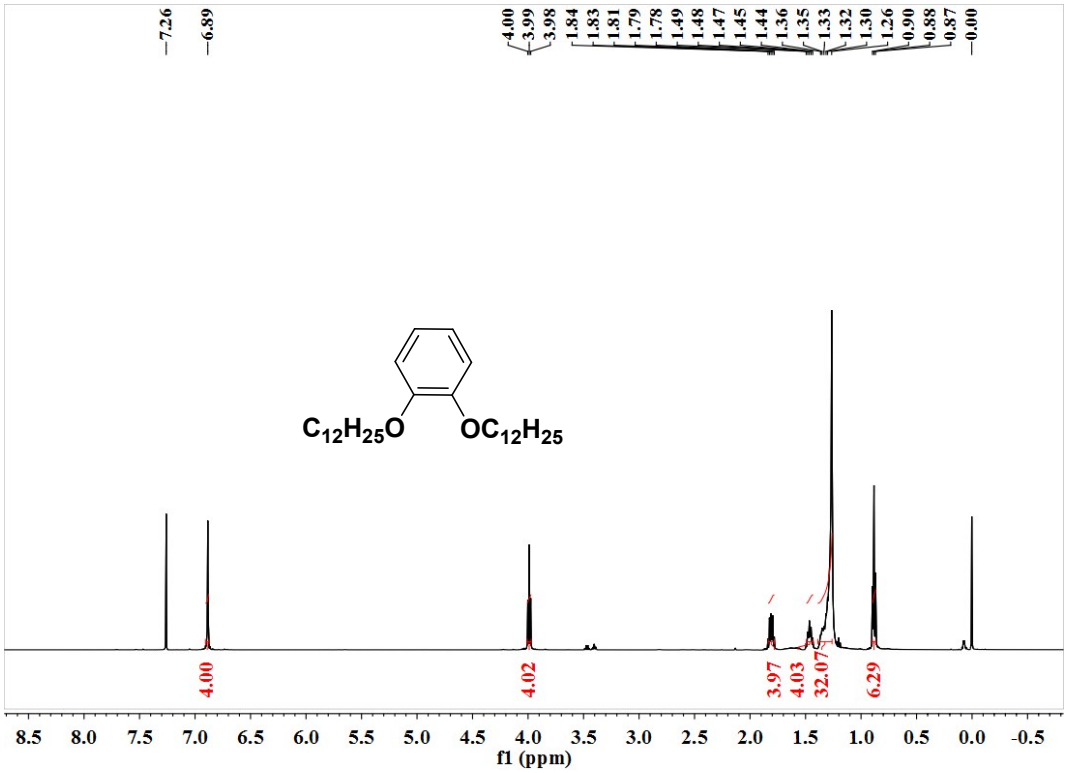


Figure S13. ^{1}H NMR spectrum of **11.**

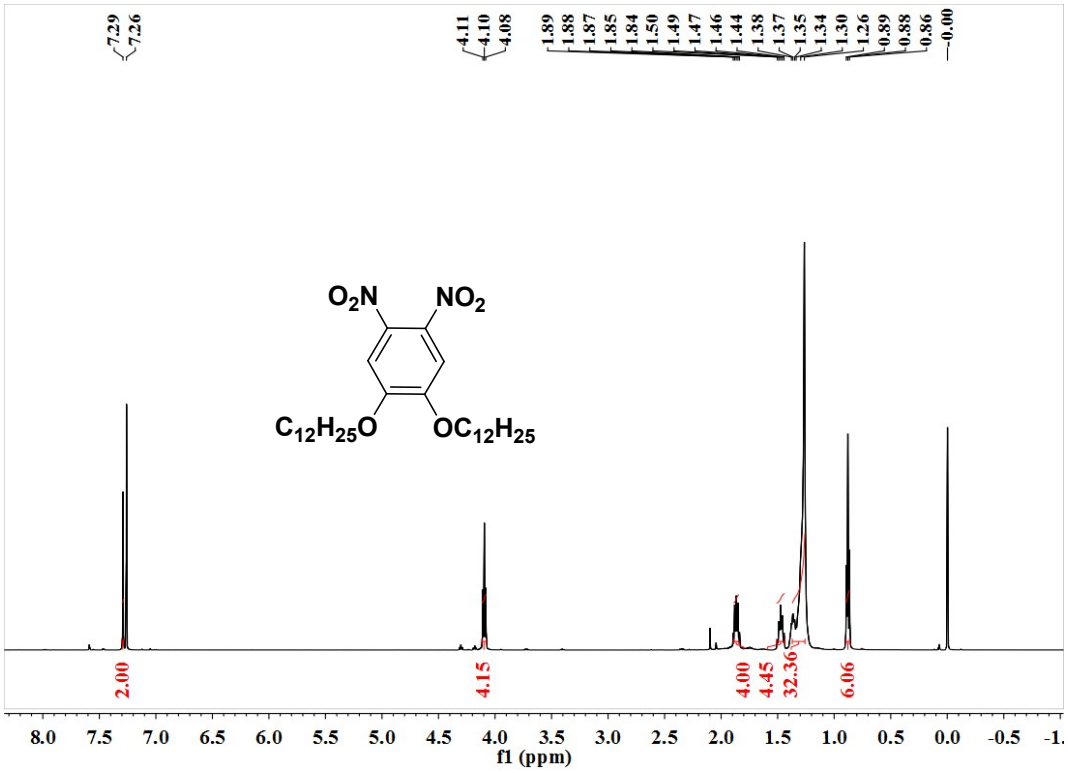


Figure S14. ^{1}H N MR spectrum of **12.**

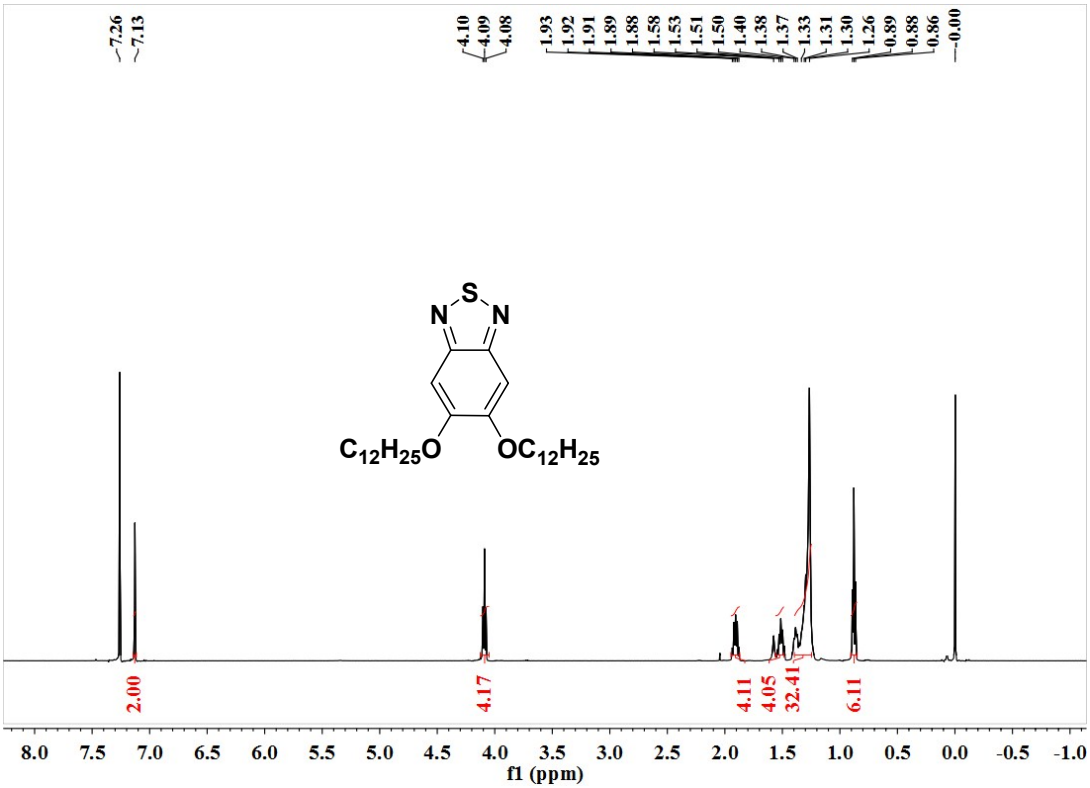


Figure S15. [1] H NMR spectrum of **14.**

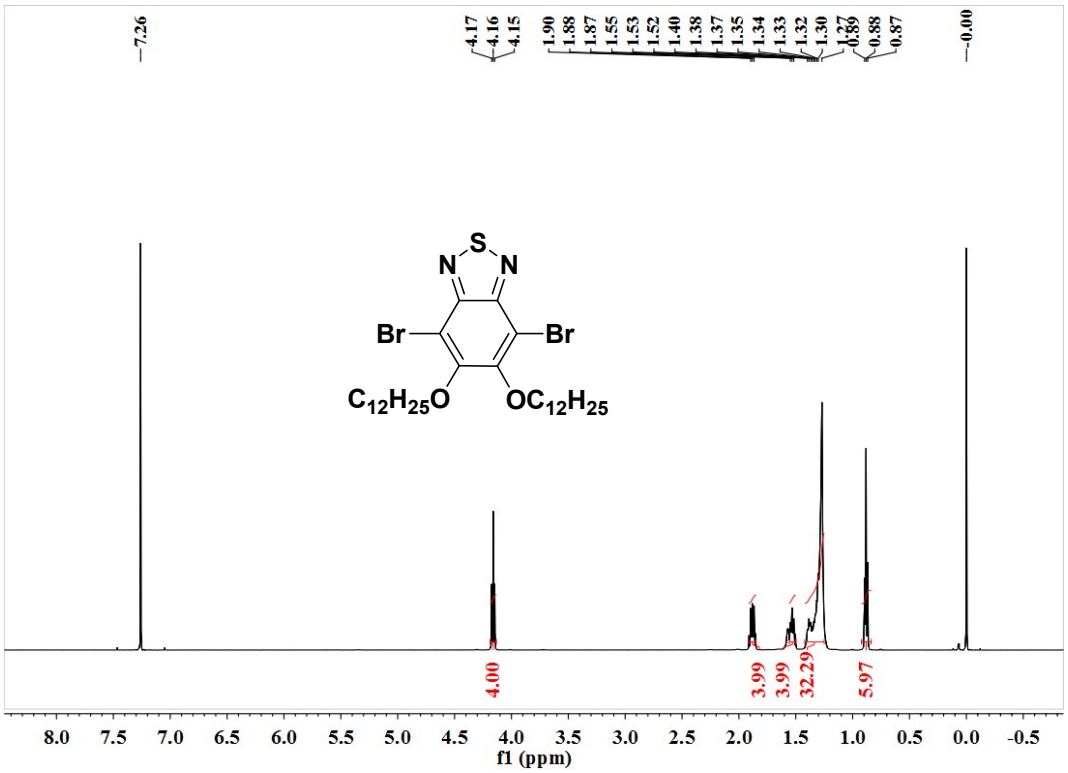


Figure S16. [1] H NMR spectrum of **15.**

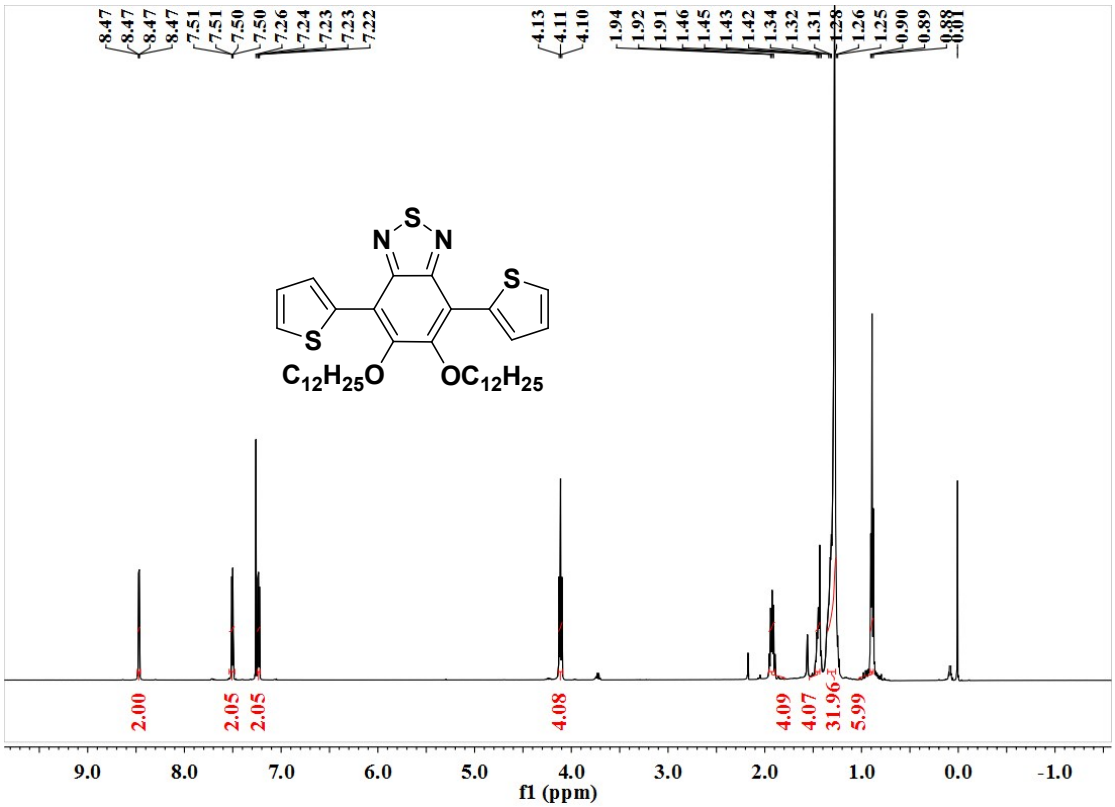


Figure S17. ^{1}H NMR spectrum of **16.**

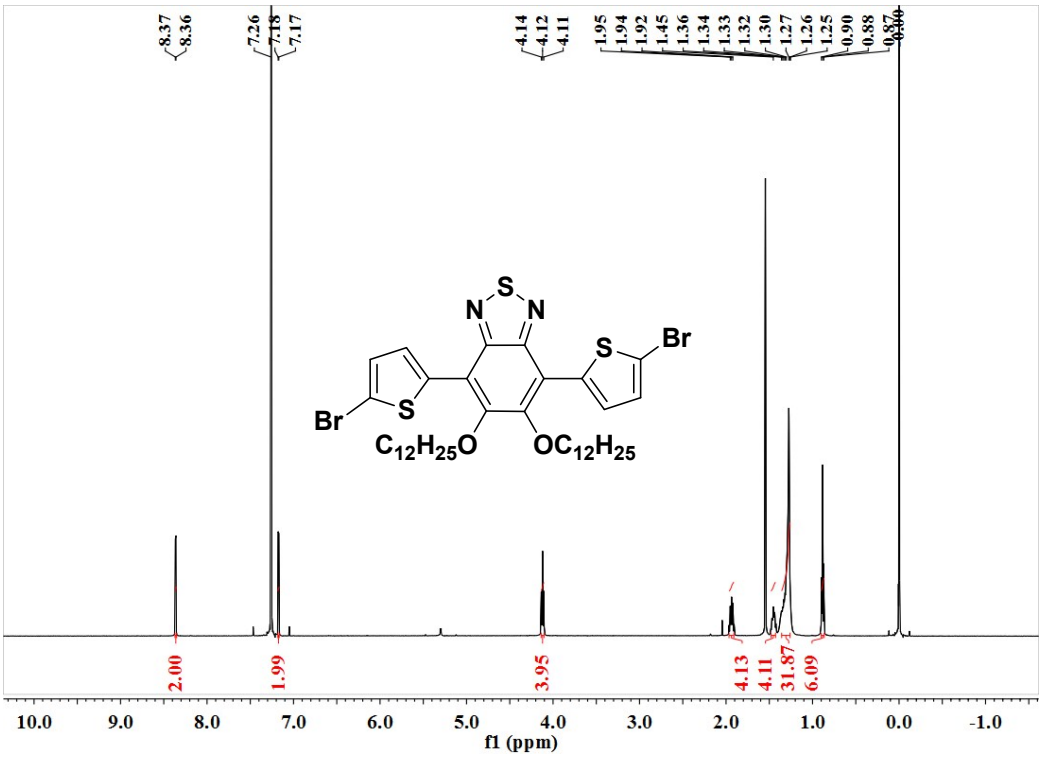


Figure S18. ^{1}H NMR spectrum of **M3.**

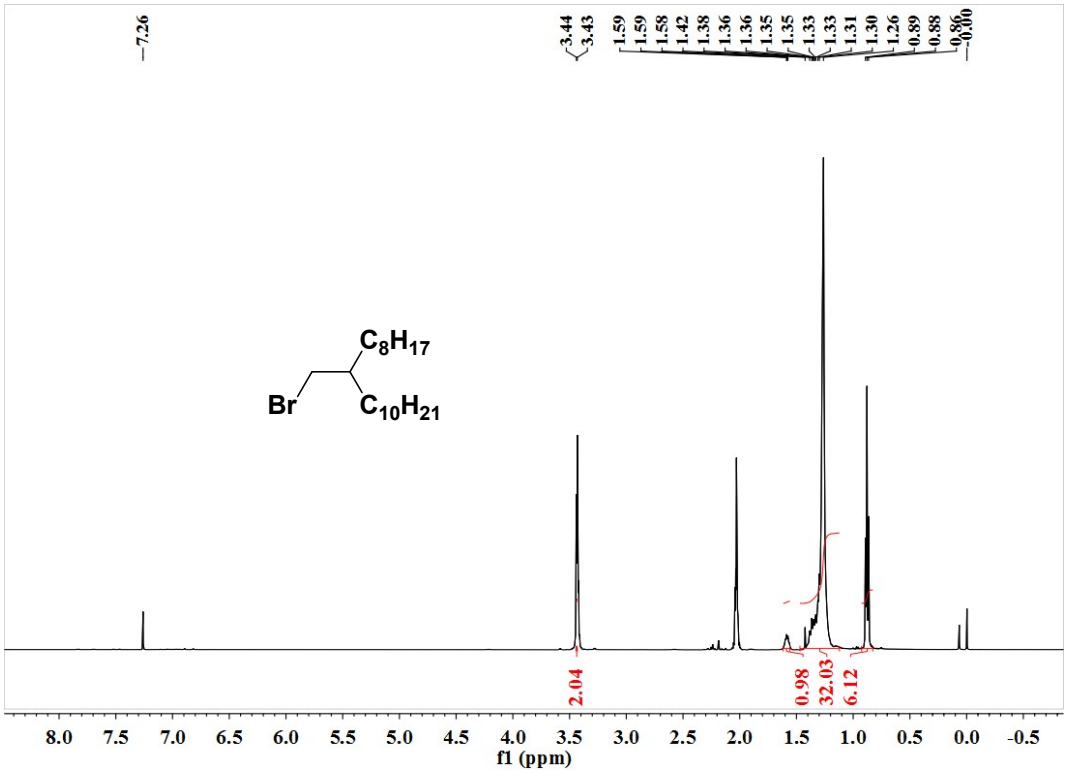


Figure S19. ^{1}H NMR spectrum of **17.**

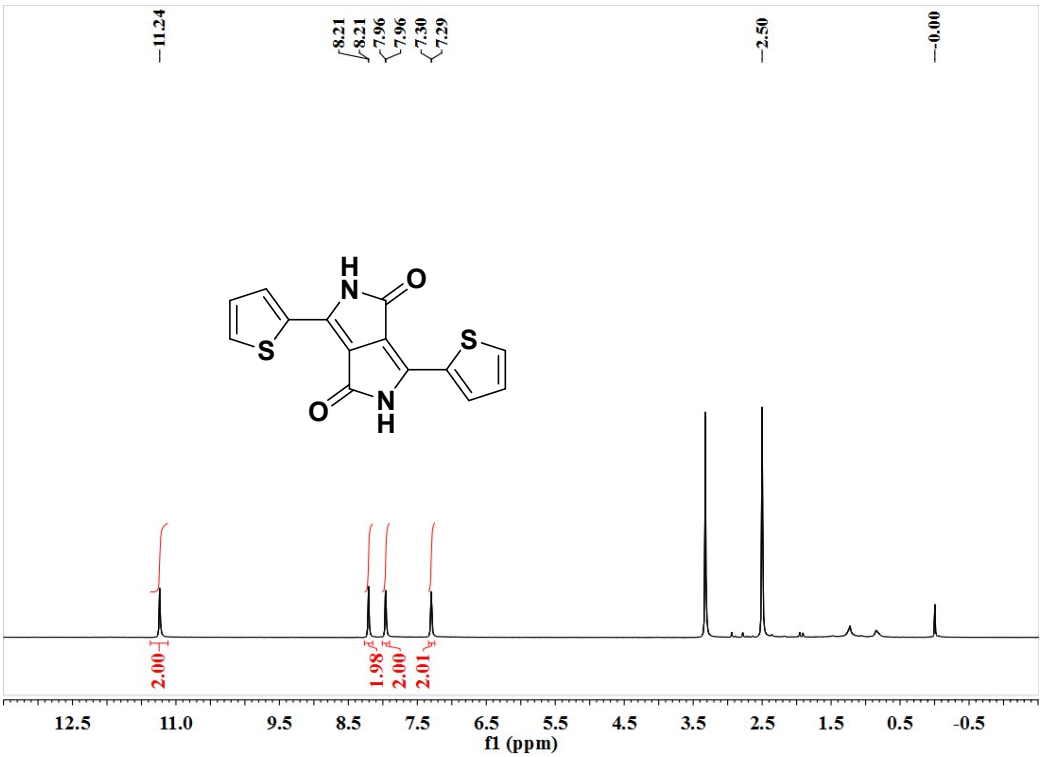


Figure S20. ^{1}H NMR spectrum of **18.**

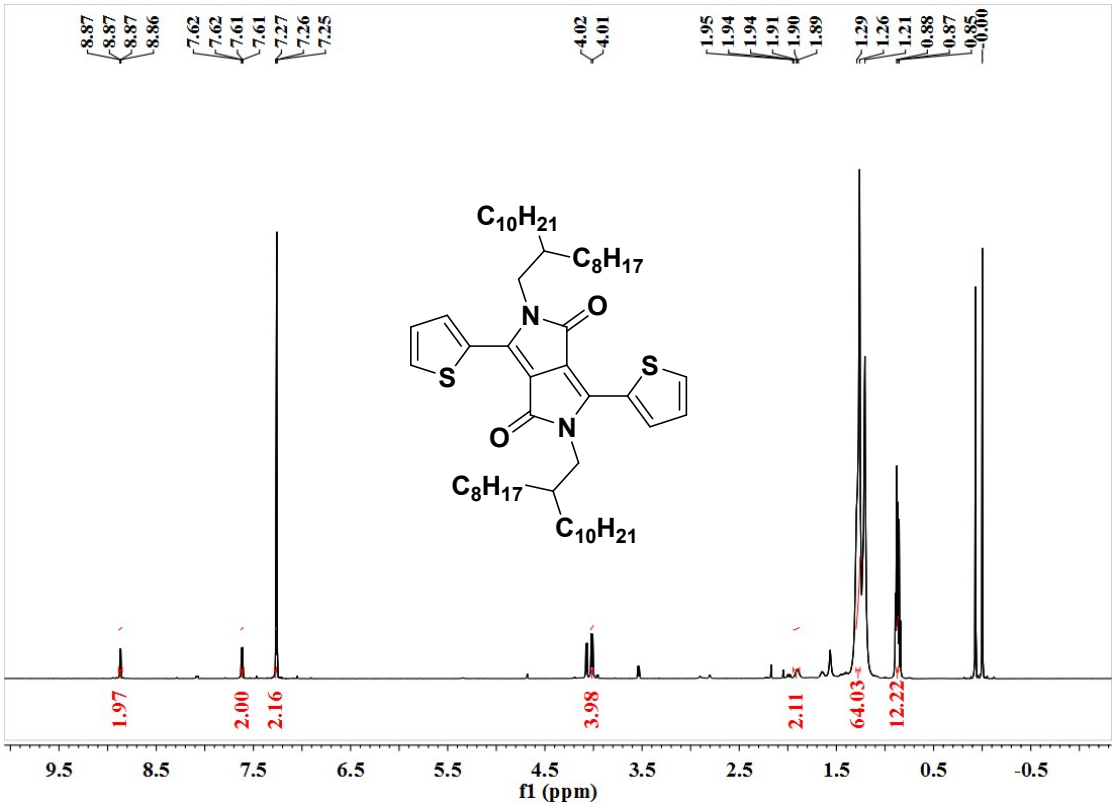


Figure S21. ^{1}H NMR spectrum of **19.**

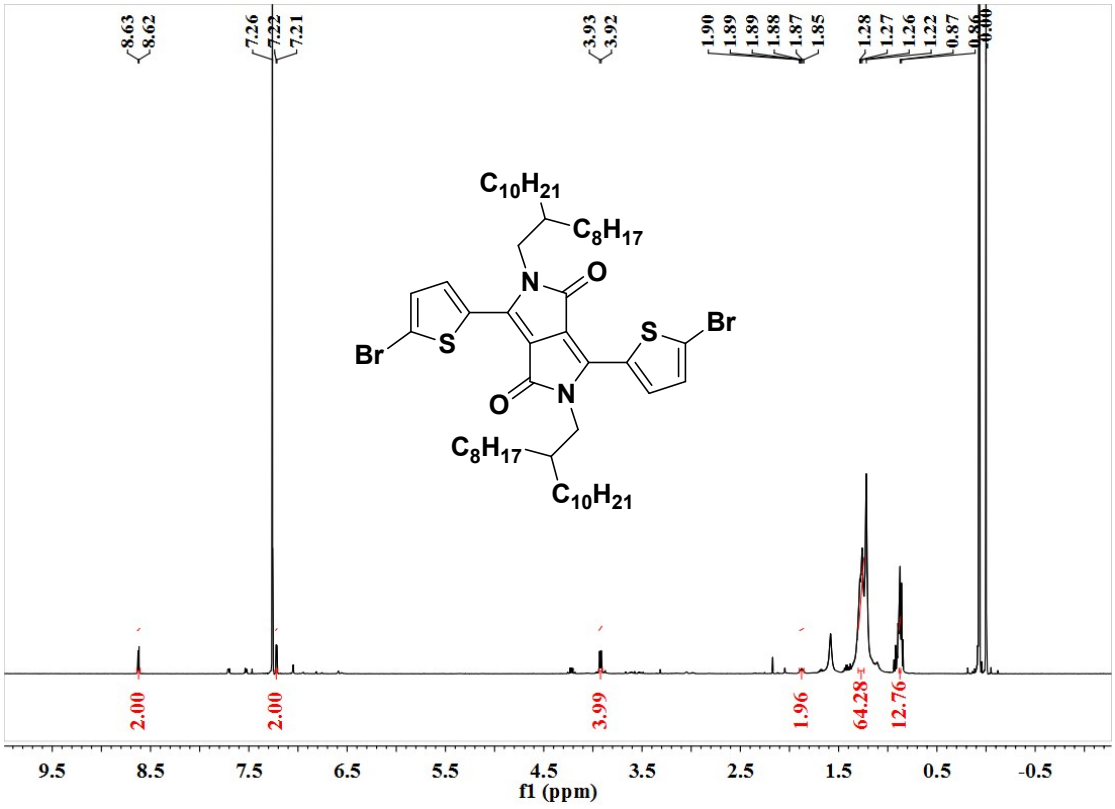


Figure S22. ^{1}H NMR spectrum of **M4.**

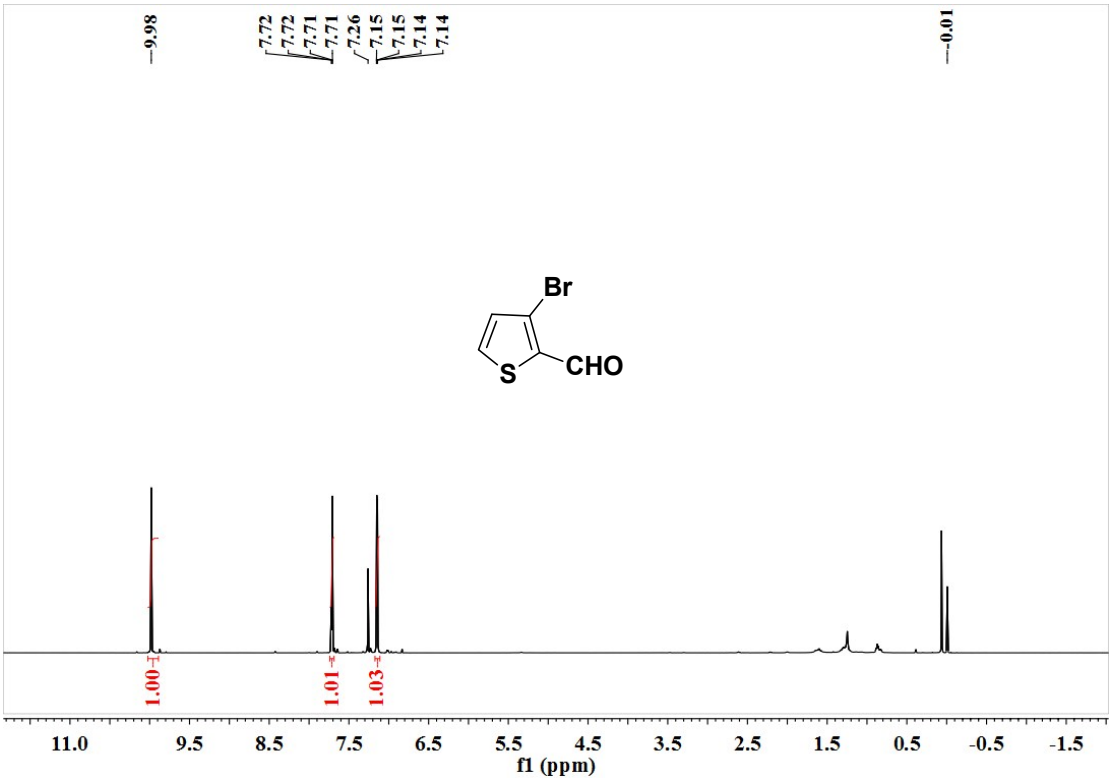


Figure S23. ^{1}H NMR spectrum of **20.**

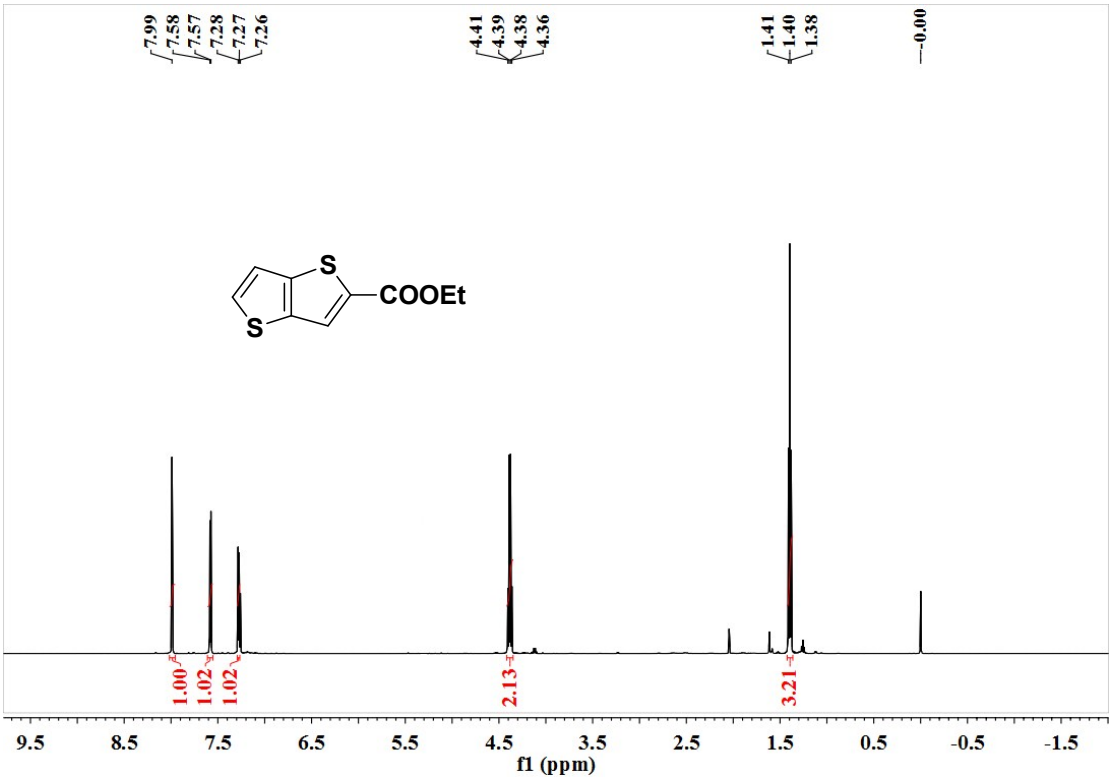


Figure S24. ^{1}H NMR spectrum of **21**

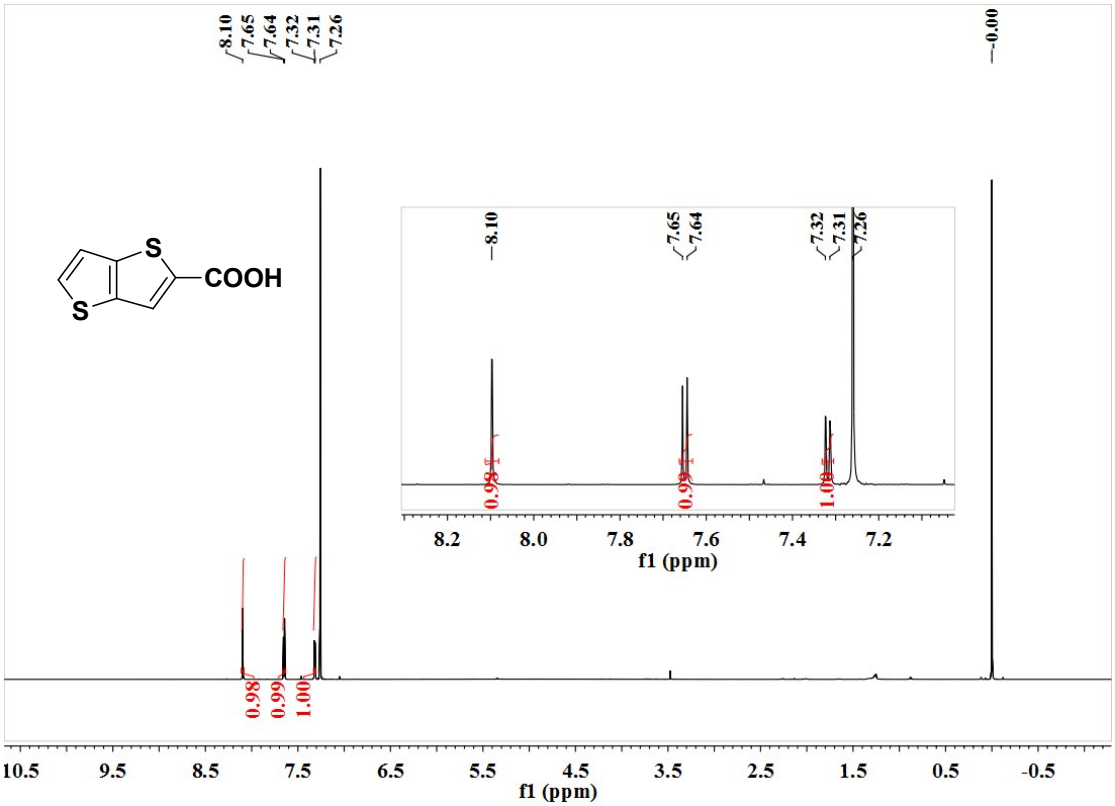


Figure S25. ^{1}H NMR spectrum of **22.**

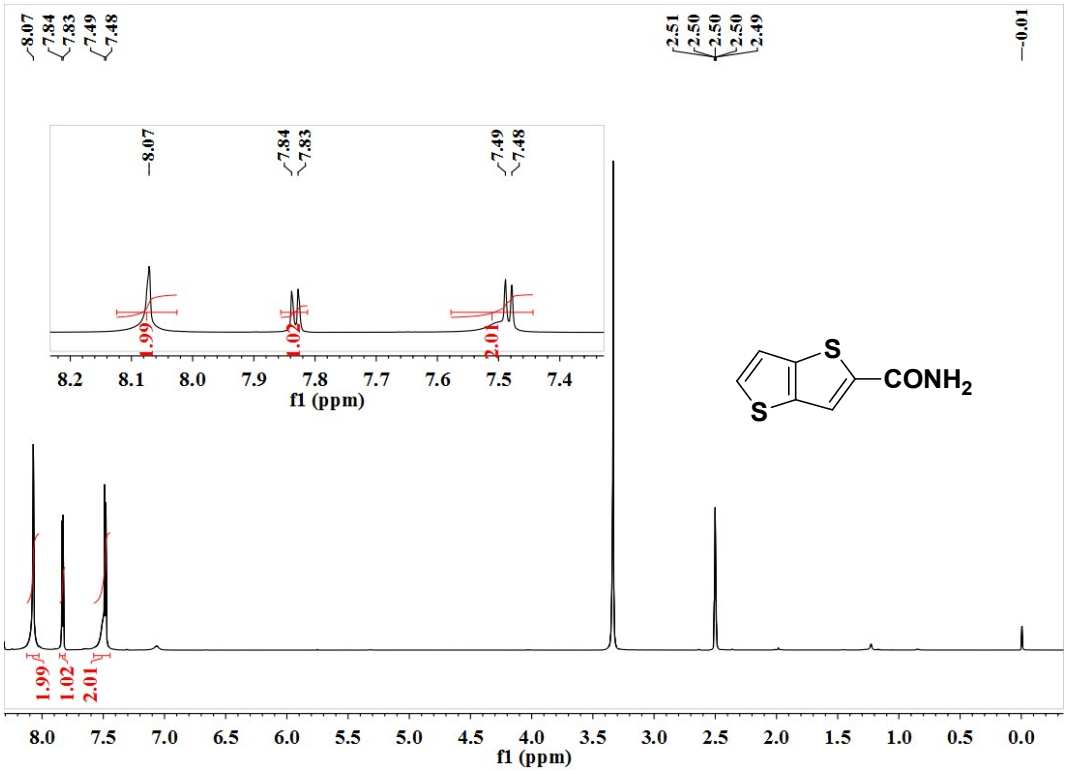


Figure S26. ^{1}H NMR spectrum of **23.**

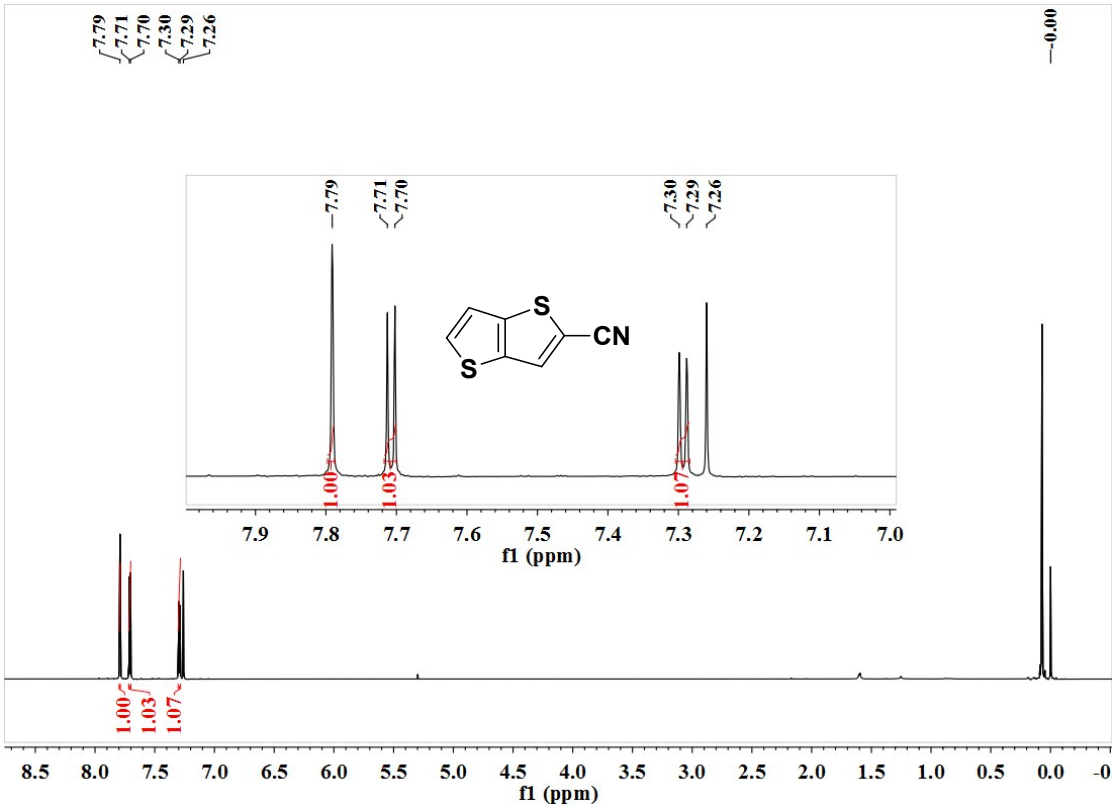


Figure S27. ^{1}H NMR spectrum of **24.**

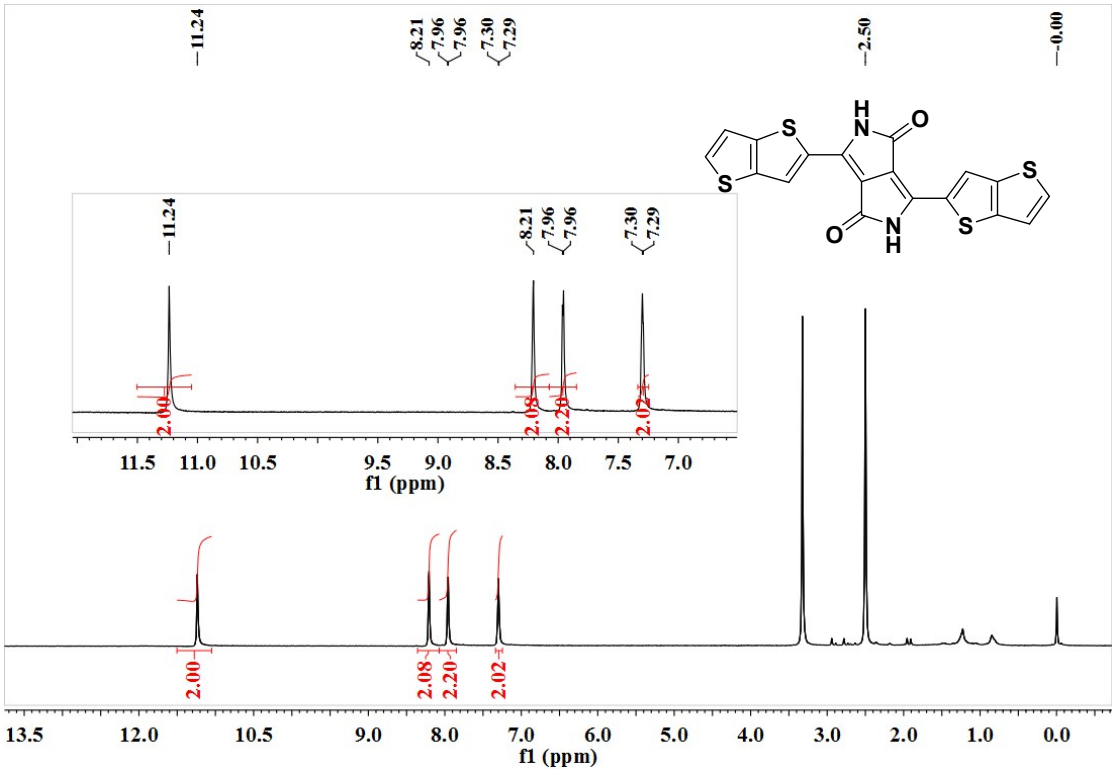


Figure S28. ^{1}H NMR spectrum of **25.**

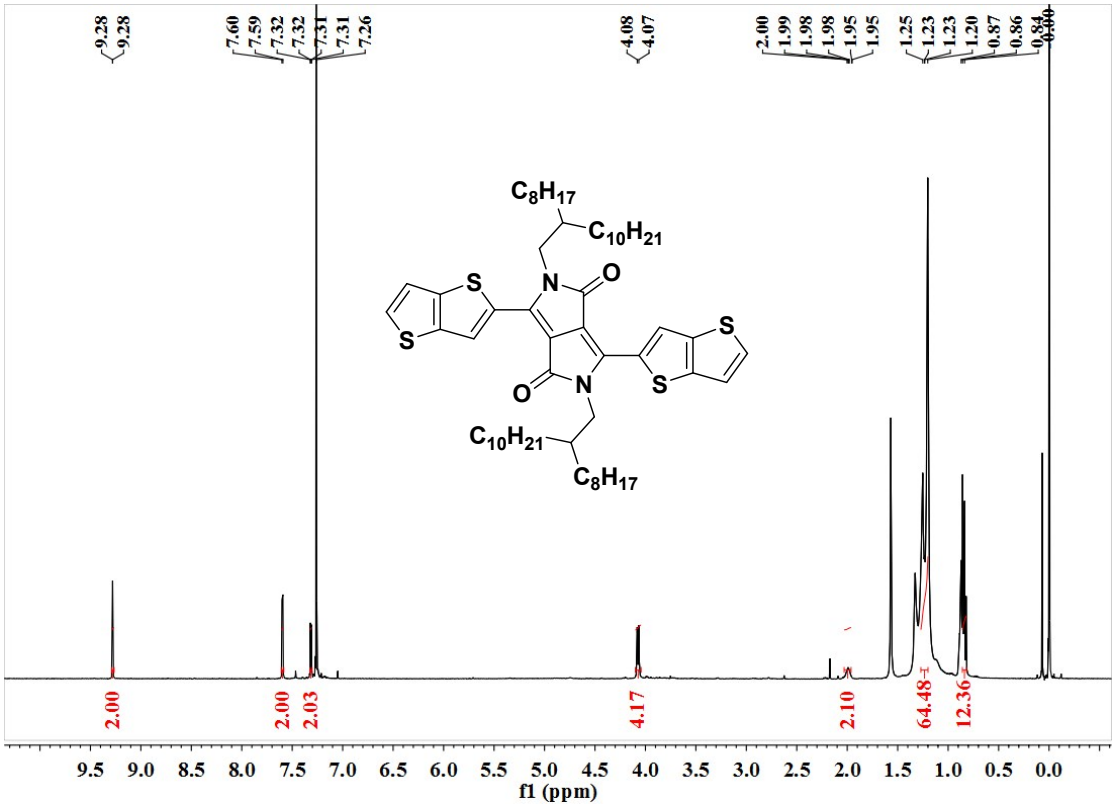


Figure S29. ^{1}H NMR spectrum of **26.**

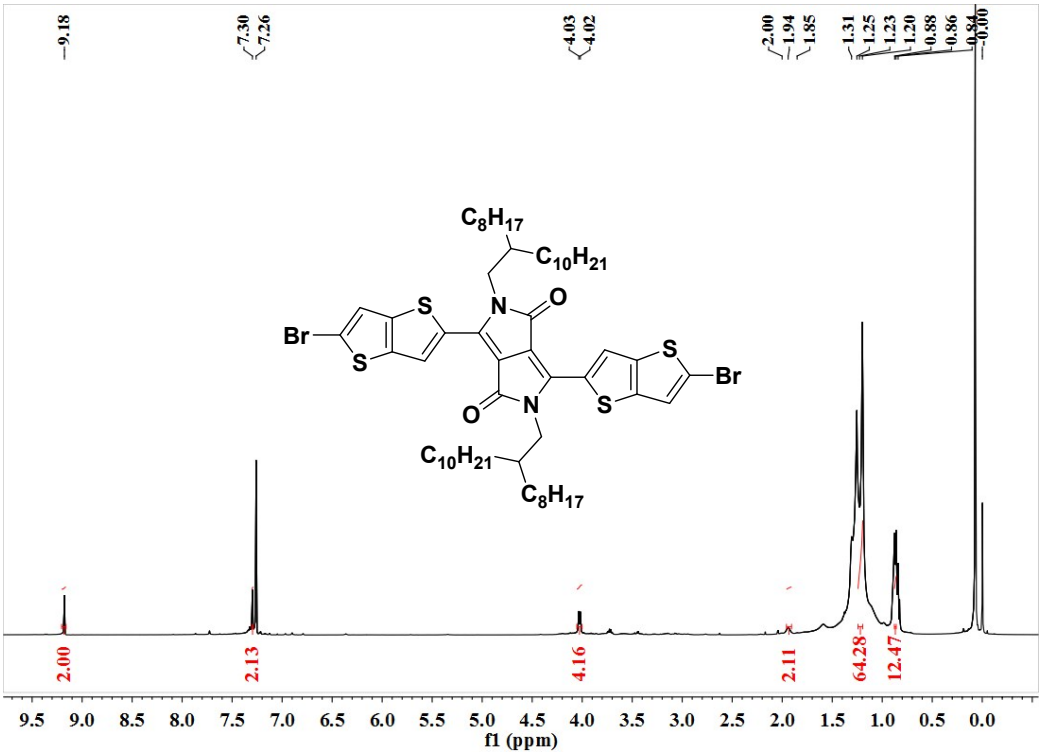


Figure S30. ^{1}H NMR spectrum of **M5.**

3. NMR Spectra of copolymers

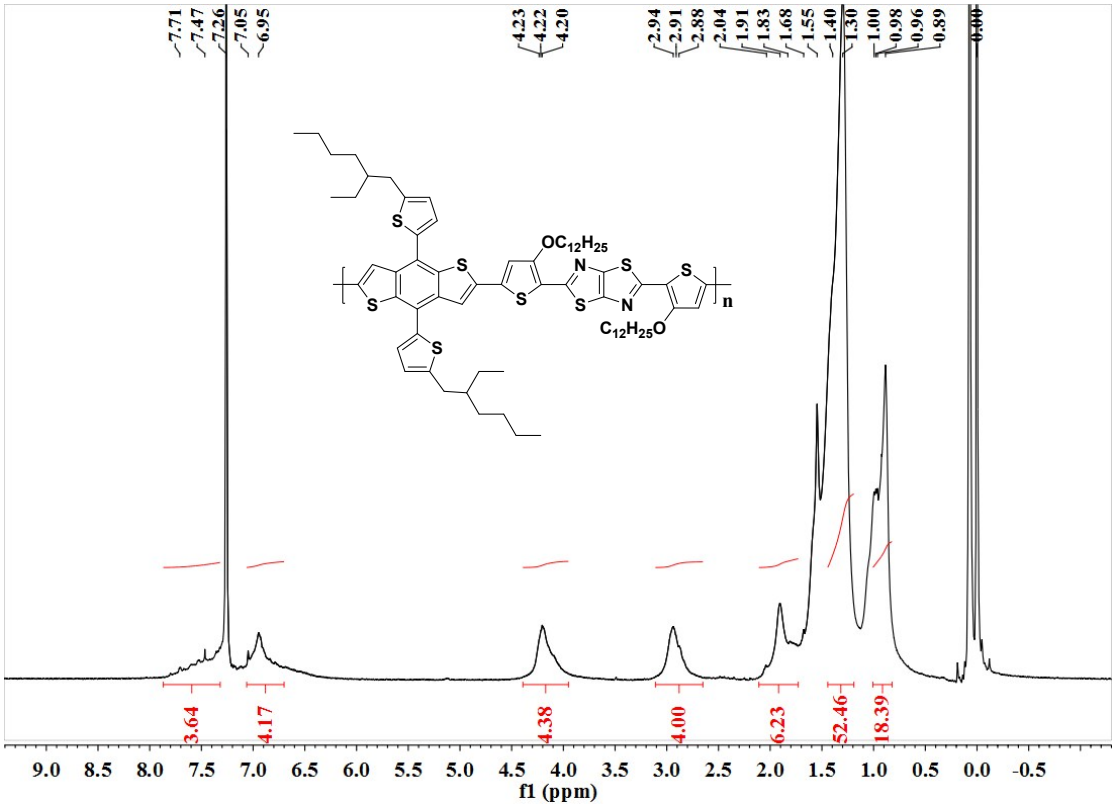


Figure S31. ^{1}H NMR spectrum of **PBDTT-TTz**.

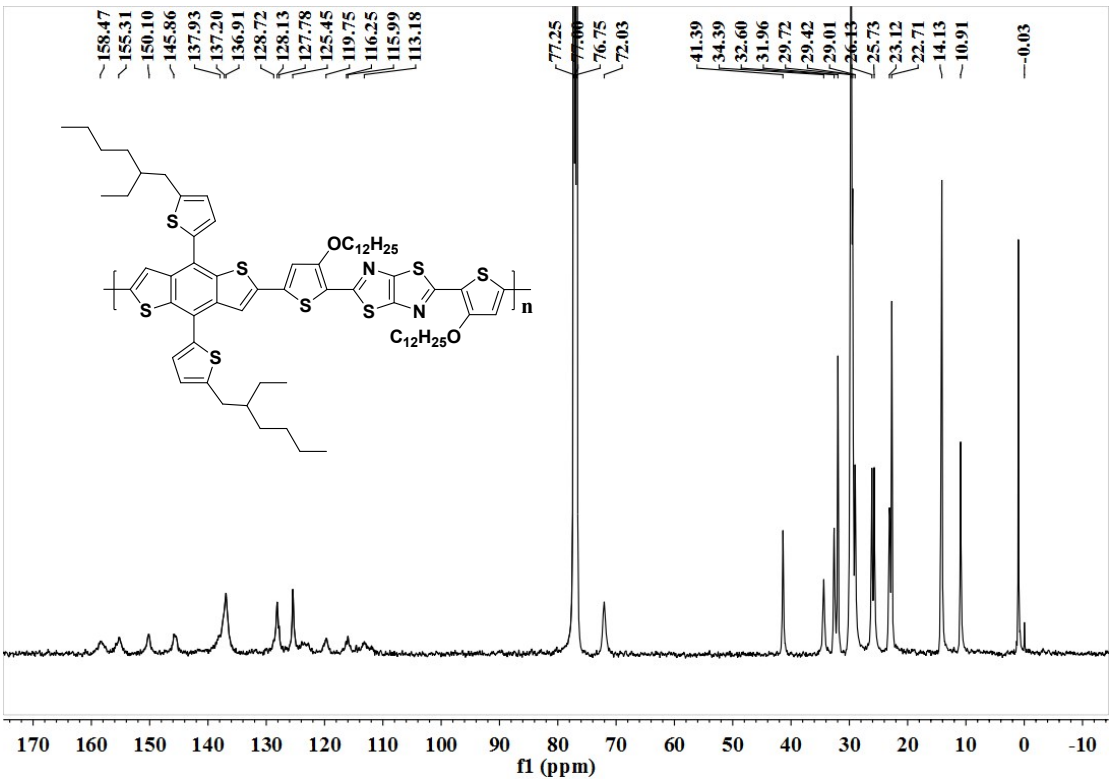


Figure S32. ^{13}C NMR spectrum of **PBDTT-TTz**.

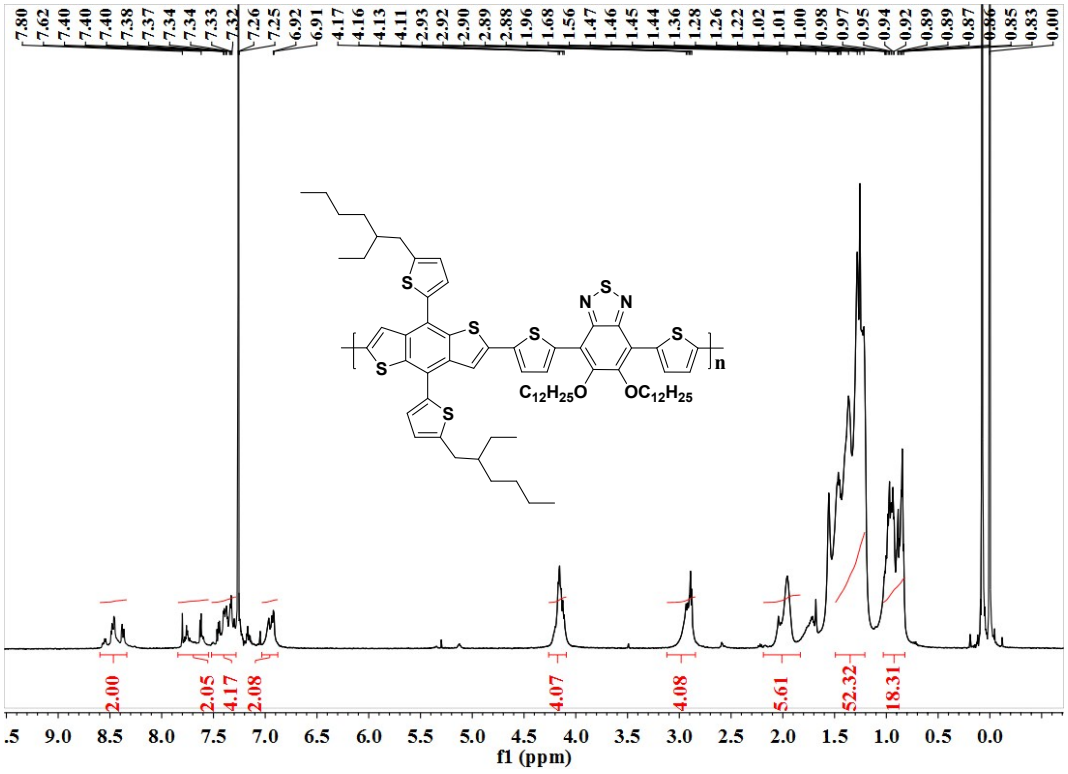


Figure S33. [1]H NMR spectrum of **PBDTT-DTBT**.

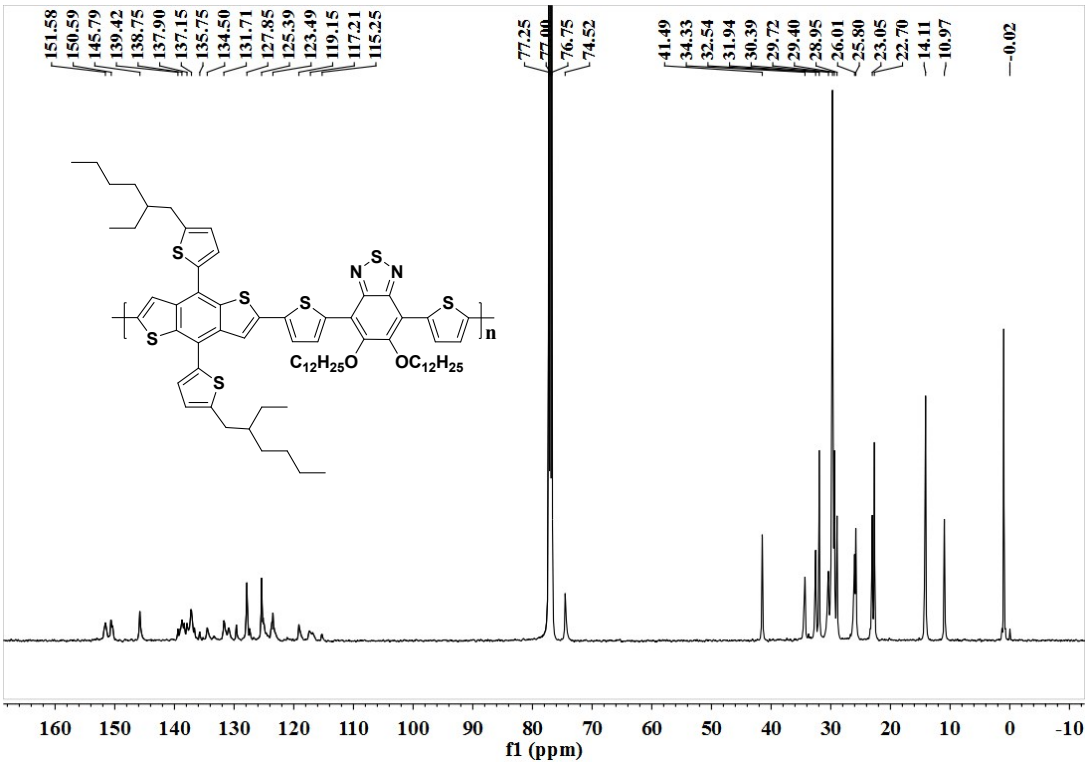


Figure S34. [13]C NMR spectrum of **PBDTT-DTBT**.

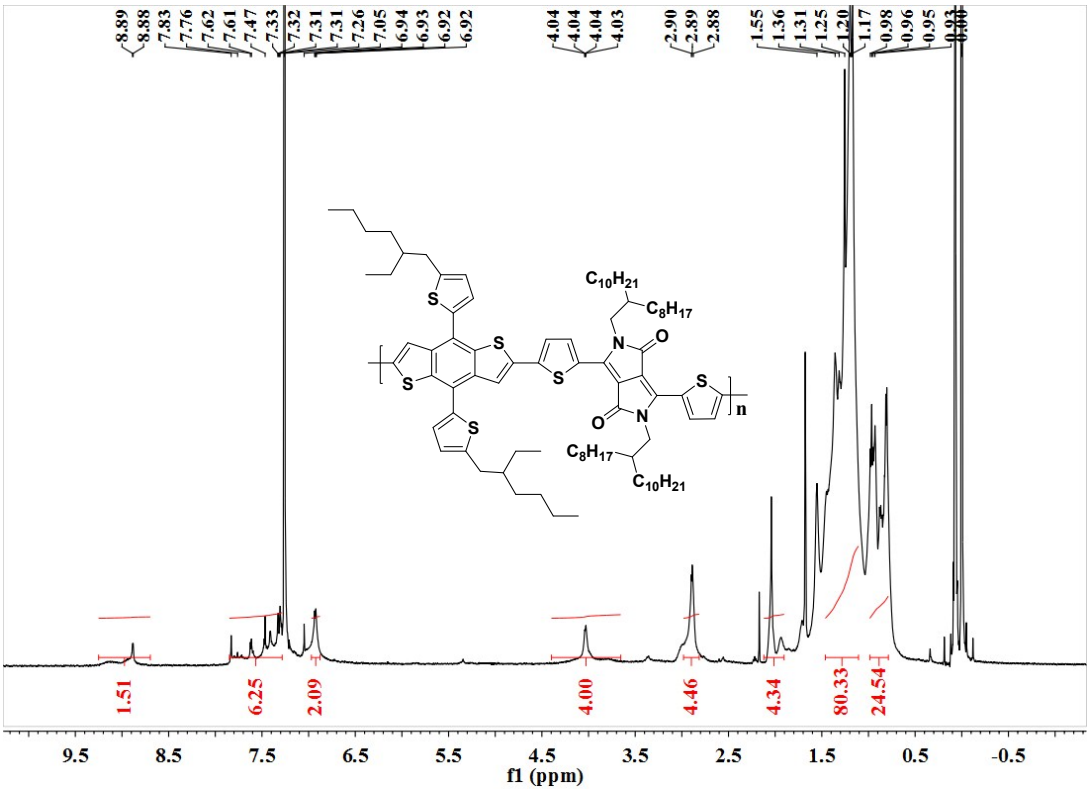


Figure S35. ^{1}H NMR spectrum of **PBDTT-DPP**.

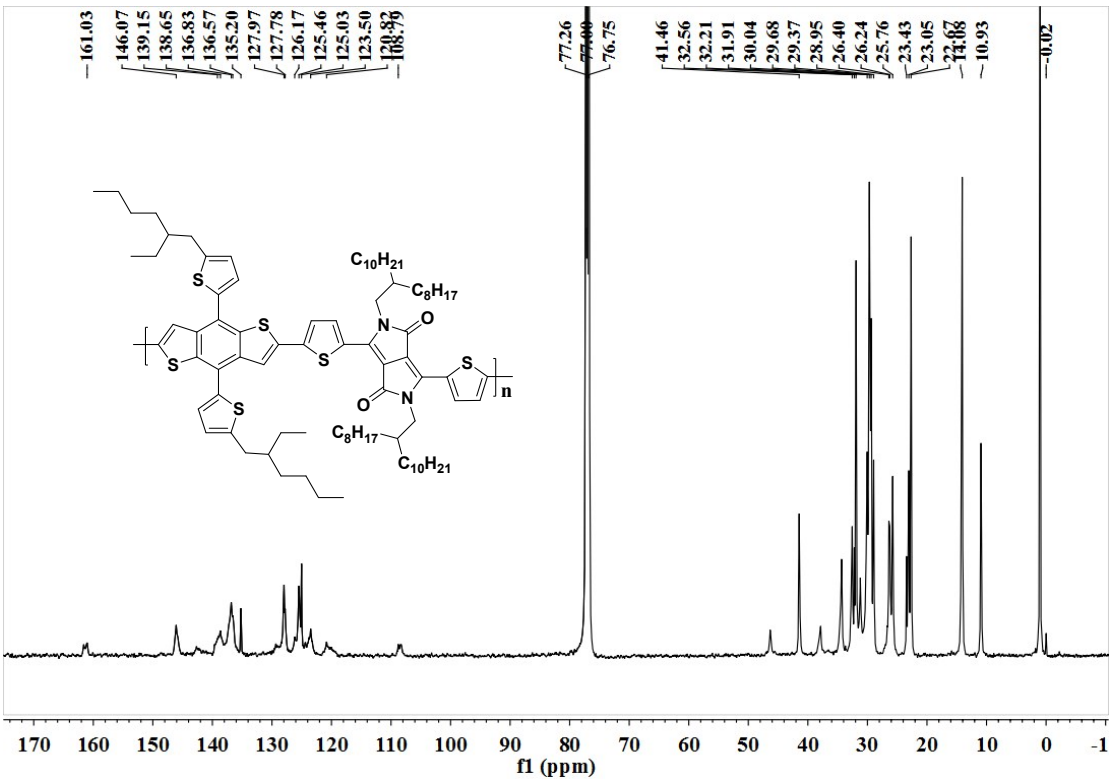


Figure S36. ^{13}C NMR spectrum of **PBDTT-DPP**.

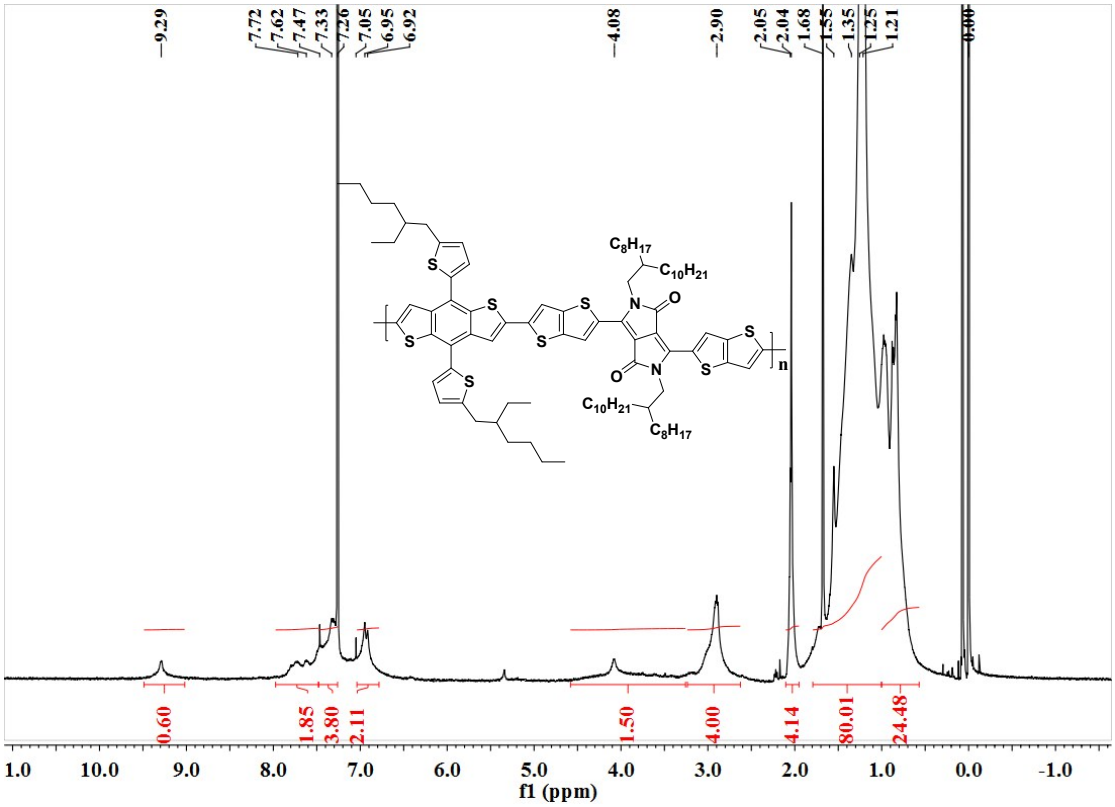


Figure S37. ^{1}H NMR spectrum of **PBDTT-TTDPP**.

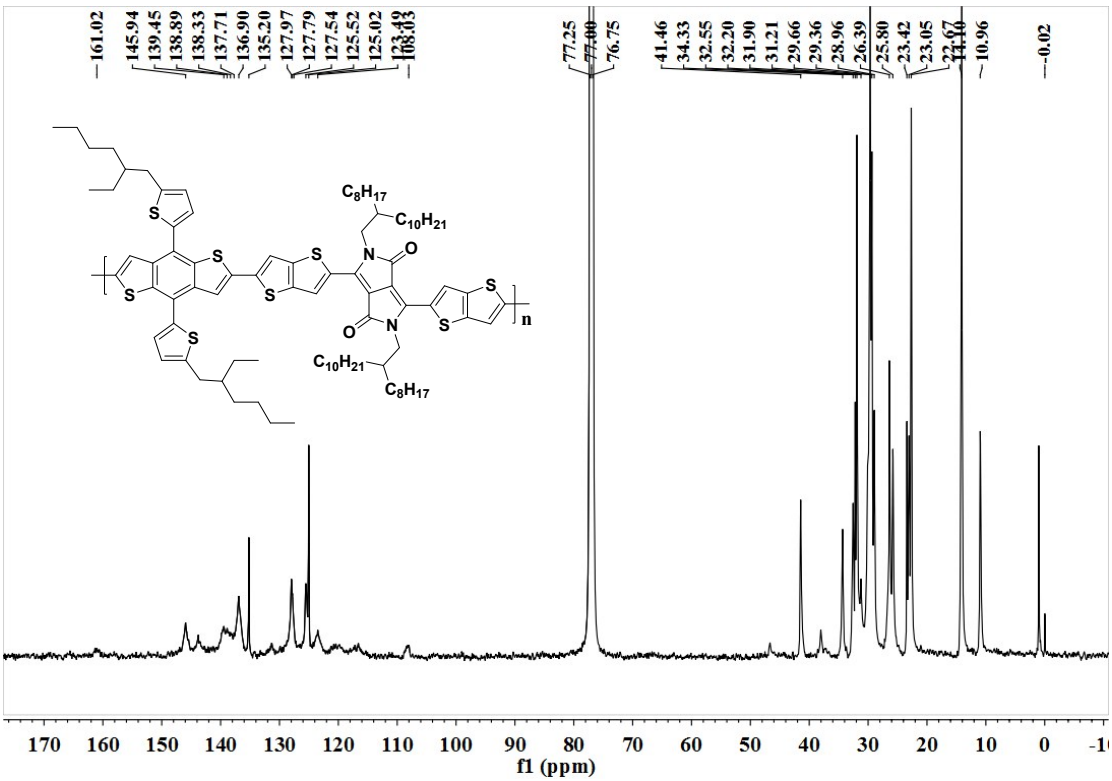


Figure S38. ^{13}C NMR spectrum of **PBDTT-TTDPP**.

4. Photovoltaic properties of PBDTT-DPP and PBDTT-TTDPP

Different PBDTT-DPP or PBDTT-TTDPP/$PC_{61}BM$ weight ratios, such as 1:1, 1:2 and 1:3 have been investigated to optimize the photovoltaic properties. The typical device structure was ITO/PEDOT:PSS/polymer:$PC_{61}BM$/PFN/Al. The active layers were thermally annealed at 90°C for 10 min during device fabrication. The corresponding photovoltaic parameters of devices were summarized in Table S1.

Table S1. Photovoltaic properties of polymer solar cells based **PBDTT-DPP** or **PBDTT-TTDPP**:$PC_{61}BM$ blend films after annealed at 90°C

Polymer	D/A	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PBDTT-DPP	1:1	0.64	1.41	31.7	0.28
PBDTT-DPP	1:2	0.52	1.87	29.8	0.30
PBDTT-DPP	1:3	0.56	1.32	30.2	0.22
PBDTT-TTDPP	1:1	0.62	1.31	23.7	0.19
PBDTT-TTDPP	1:2	0.64	1.33	24.7	0.21
PBDTT-TTDPP	1:3	0.64	1.31	24.7	0.21

References

[1] L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li, J. Hou, *Angewandte Chemie* **2011**, *50*, 9697.

[2] S. Subramaniyan, H. Xin, F. S. Kim, S. Shoaee, J. R. Durrant, S. A. Jenekhe, *Adv. Energy Mater.* **2011**, *1*, 854.

[3] Z. B. Lim, B. Xue, S. Bomma, H. Li, S. Sun, Y. M. Lam, W. J. Belcher, P. C. Dastoor, A. C. Grimsdale, *J. Polym.Sci. Part A: Polym. Chem.* **2011**, *49*, 4387.

[4] P. Ding, C.-C. Chu, Y. Zou, D. Xiao, C. Pan, C.-S. Hsu, *J. Appl.Polym. Sci.***2012**, *123*, 99.

[5] L. Huo, J. Hou, H.-Y. Chen, S. Zhang, Y. Jiang, T. L. Chen, Y. Yang, *Macromolecules* **2009**, *42*, 6564.

[6] H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. Shakya Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney, I. McCulloch, *J. Am. Chem. Soc.***2011**, *133*, 3272.

[7] I. Meager, R. S. Ashraf, S. Rossbauer, H. Bronstein, J. E. Donaghey, J. Marshall, B. C. Schroeder, M. Heeney, T. D. Anthopoulos, I. McCulloch, *Macromolecules* **2013**, *46*, 5961.