

## Supporting Information

### End-Group Engineering of Low-Bandgap Compounds for High-Detectivity Solution-Processed Small-Molecule Photodetectors

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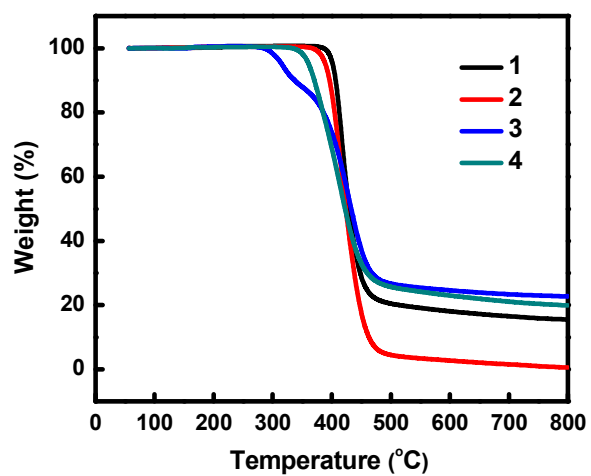
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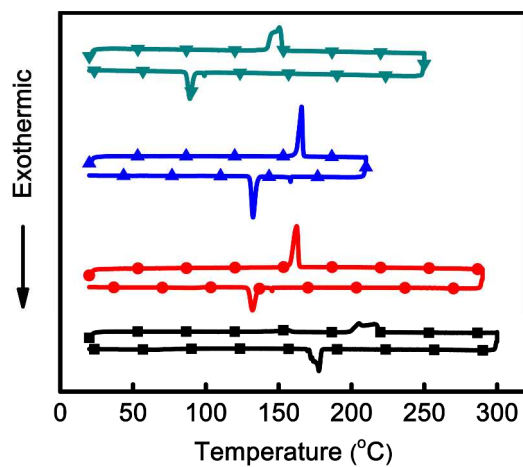
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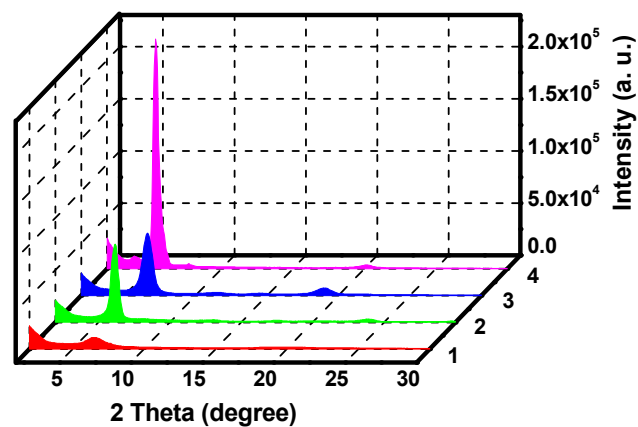
\*E-mail: wayne\_wang@carleton.ca (Z. Y. W.), wqqiao@ciac.ac.cn (W. Q.)



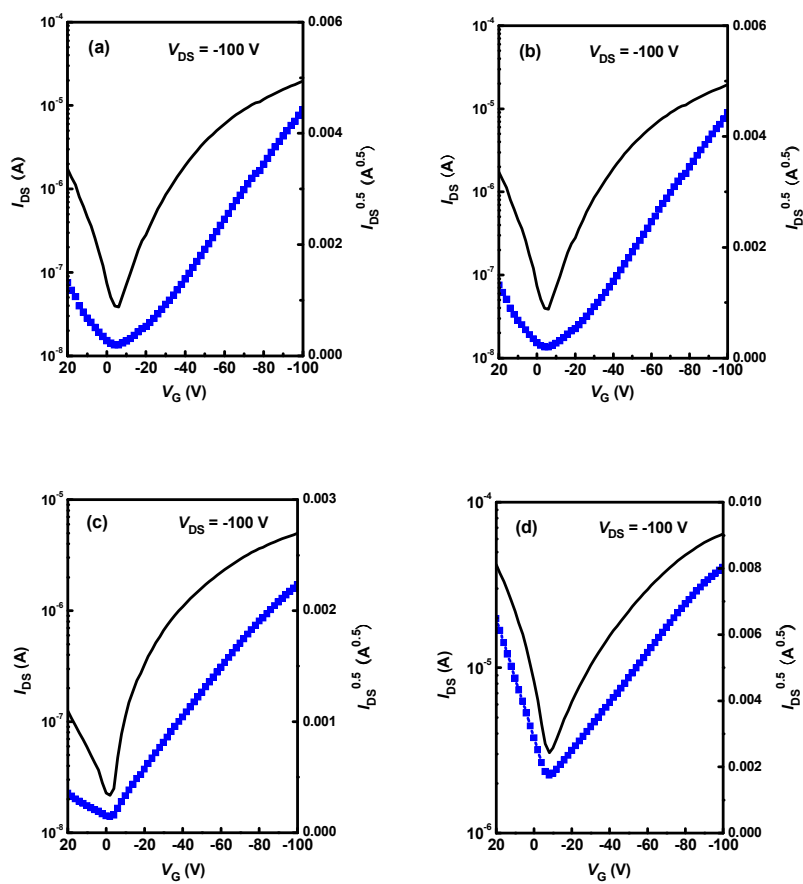
**Figure S1.** TGA traces of the compounds under nitrogen atmosphere.



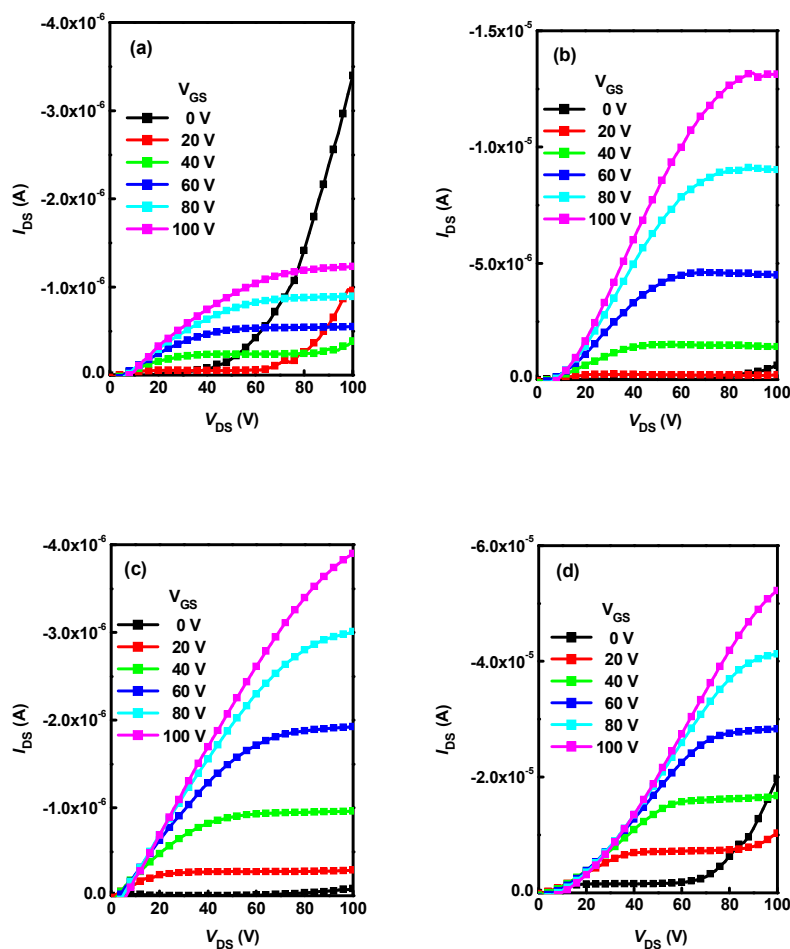
**Figure S2.** The second heating DSC scans of the compounds under nitrogen atmosphere (black square: **1**; red circle: **2**; blue up triangle: **3**; green down triangle: **4**).



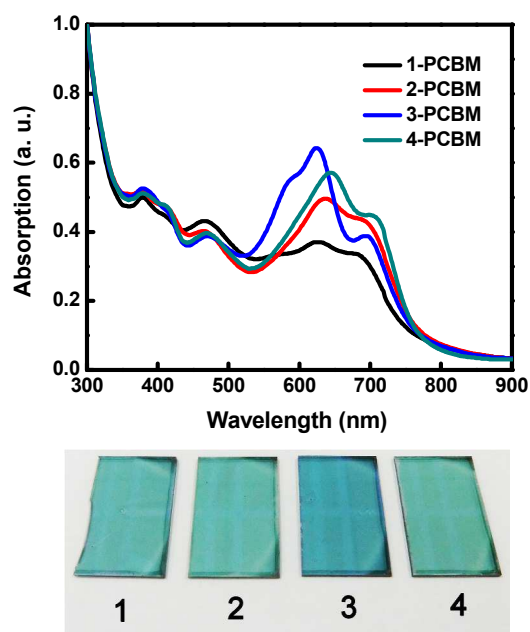
**Figure S3.** Out-of-plane grazing incidence X-ray diffraction (GIXRD) diagrams of pristine molecular films on quartz.



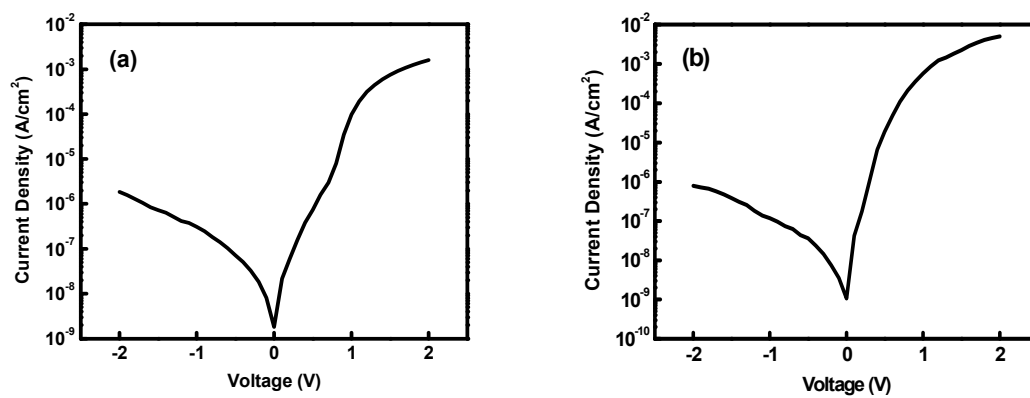
**Figure S4.** Transfer characteristics of the OFETs based on the four compounds (a-d correspond to compounds **1-4**, respectively).

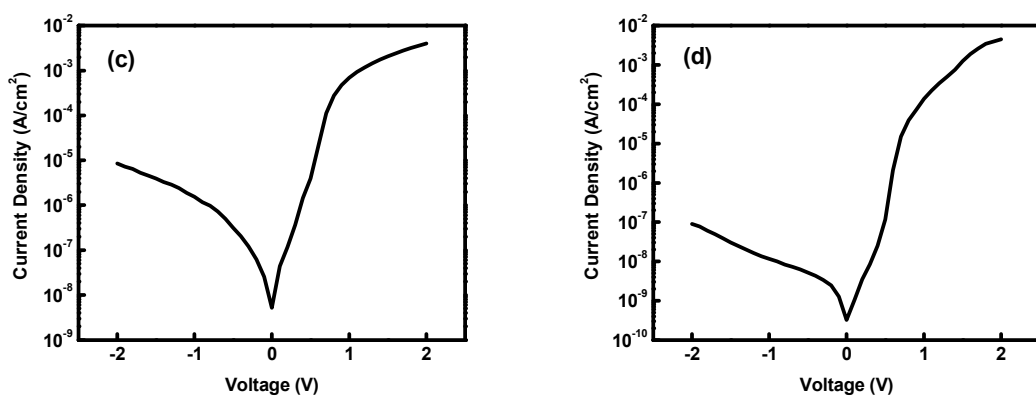


**Figure S5.** Output characteristics of the OFETs based on the four compounds (a-d correspond to compounds **1-4**, respectively).

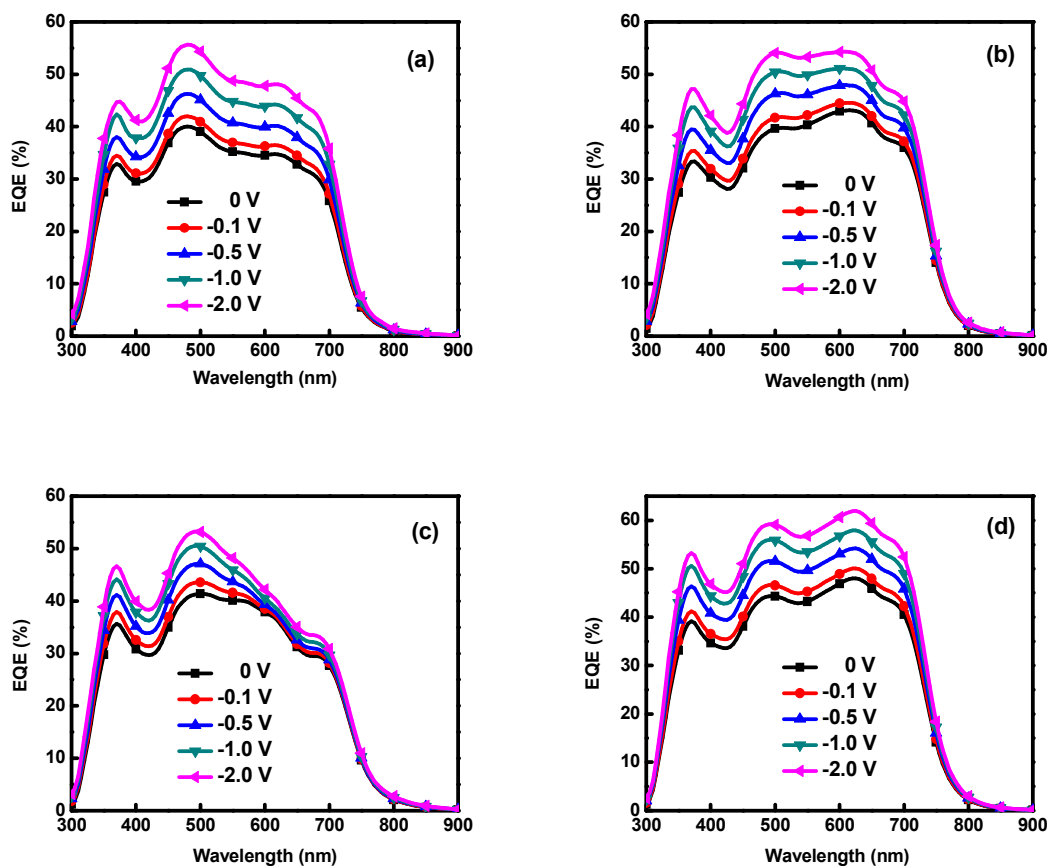


**Figure S6.** Absorption spectra of the active films spin-coated on glass/ITO/PEDOT:PSS. The photographs of the films are shown below.



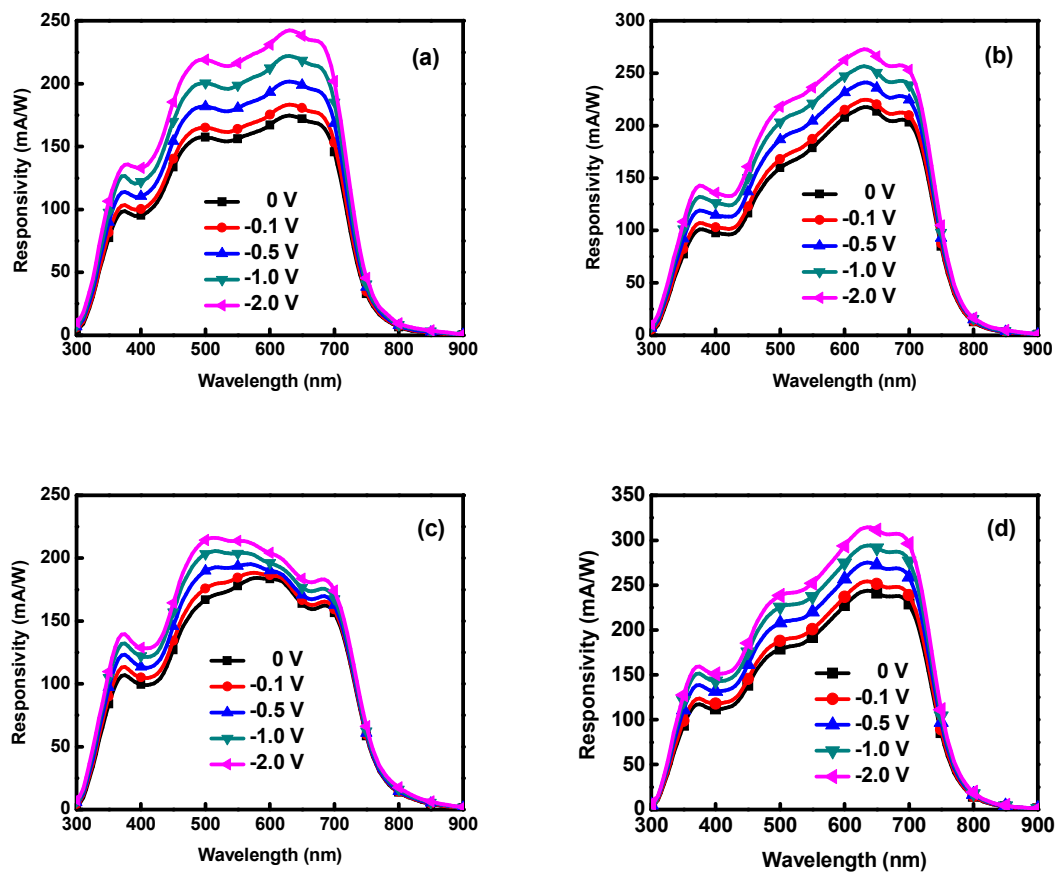


**Figure S7.** Current density-voltage ( $J$ - $V$ ) characteristics of the photodetectors based on the four compounds in the dark (a-d correspond to SMPD-1 to SMPD-4, respectively).

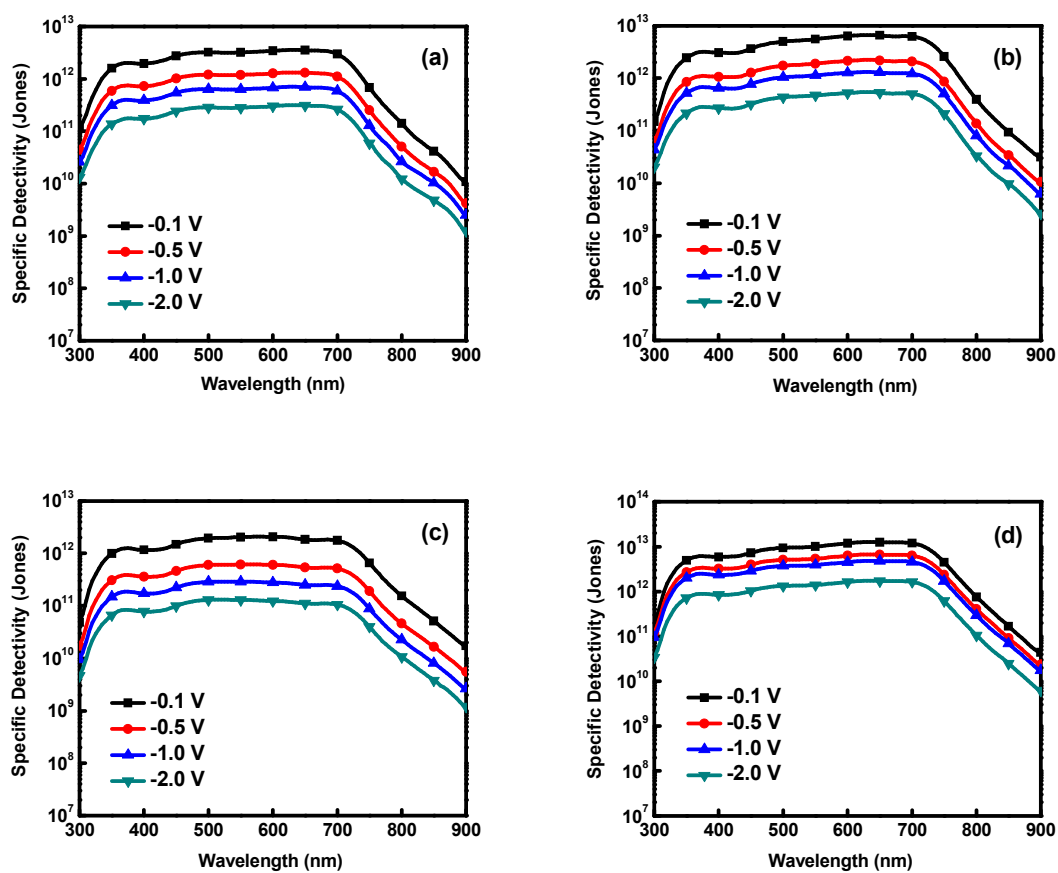


**Figure S8.** EQE of the photodetectors based on the four compounds at different biases (a-d

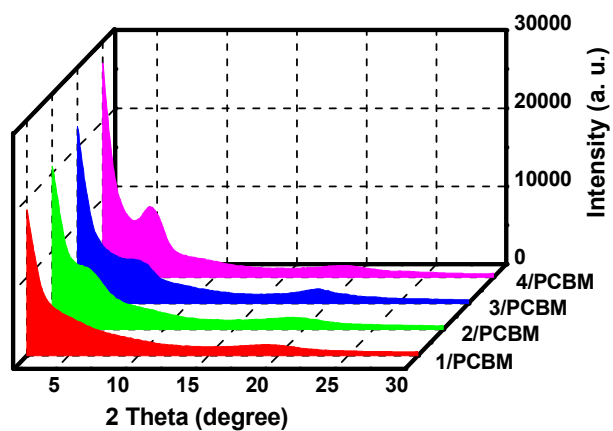
correspond to SMPD-1 to SMPD-4, respectively).



**Figure S9.** Spectral responsivity of the photodetectors based on the four compounds at different biases (a-d correspond to SMPD-1 to SMPD-4, respectively).

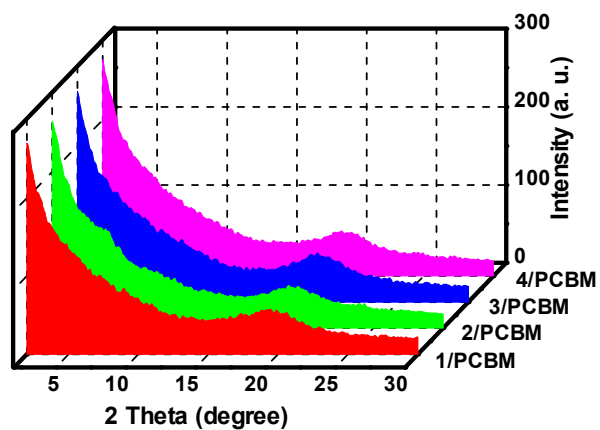


**Figure S10.** Spectral specific detectivity of the photodetectors based on the four compounds at different biases (a-d correspond to SMPD-1 to SMPD-4, respectively).

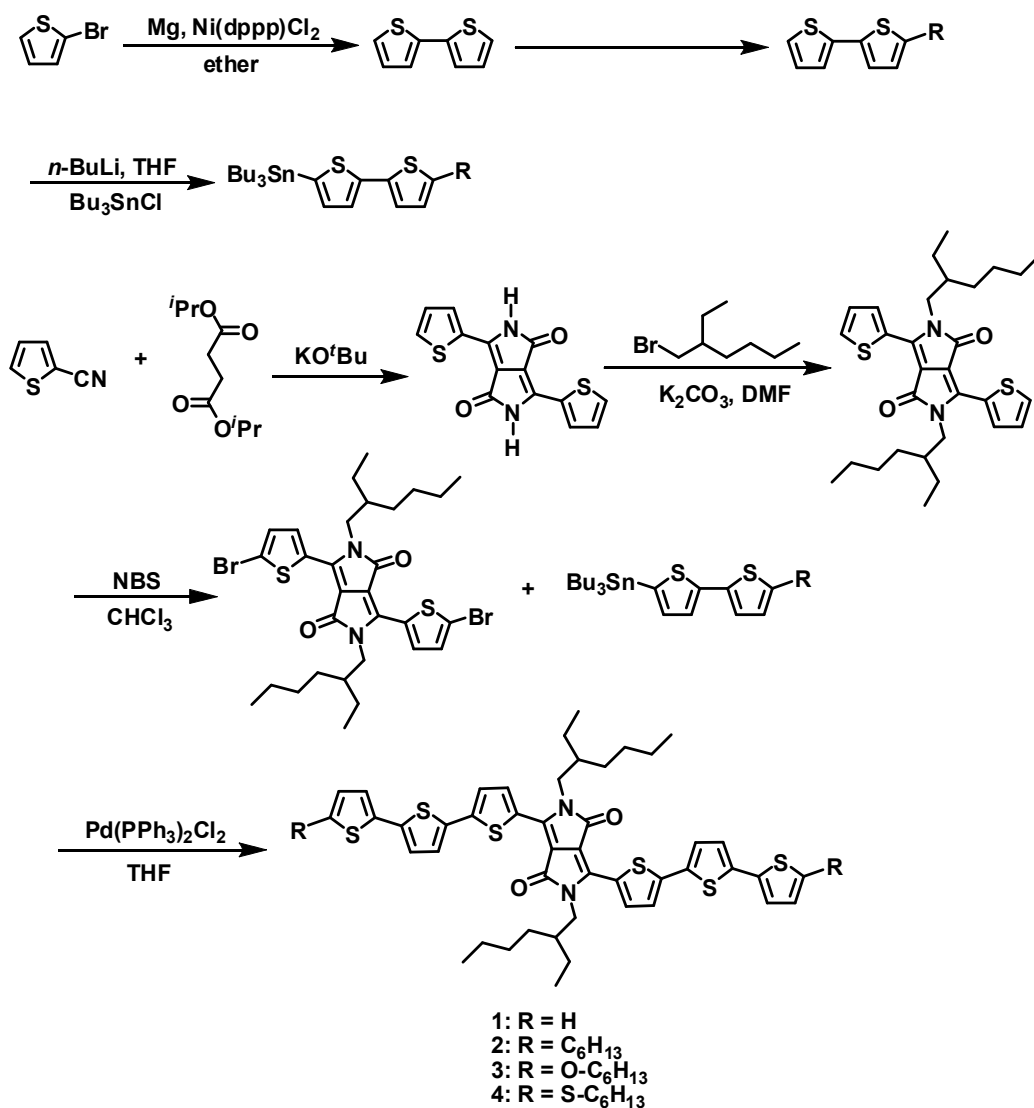




**Figure S11.** Out-of-plane grazing incidence X-ray diffraction (GIXRD) diagrams of the active films spin-coated on glass/ITO/PEDOT:PSS.



**Figure S12.** In-plane grazing incidence X-ray diffraction (GIXRD) diagrams of the active films spin-coated on glass/ITO/PEDOT:PSS.



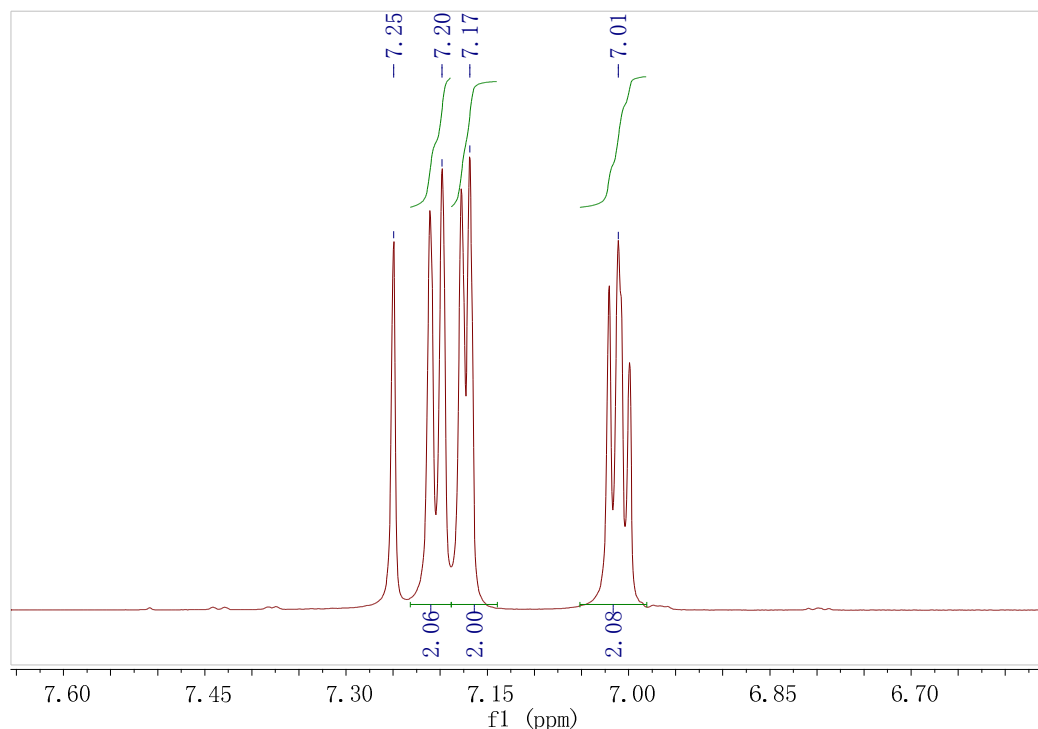
**Scheme S1. Synthesis of Compounds 1-4.**

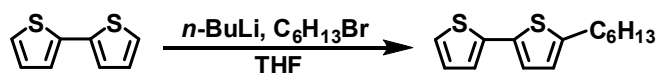
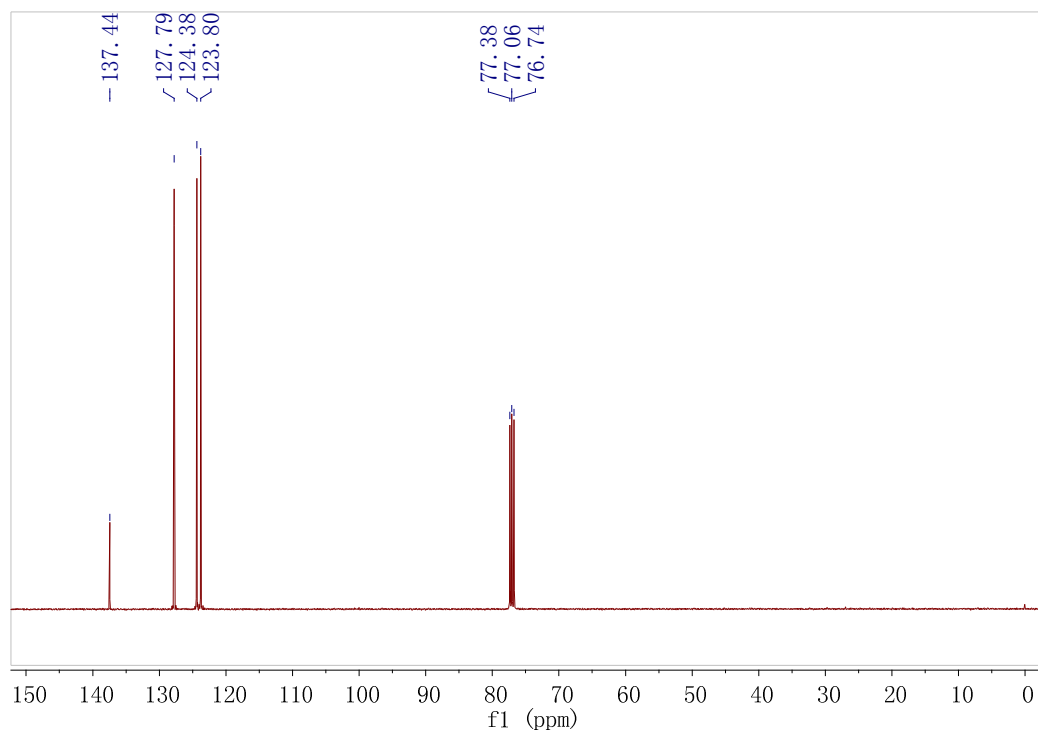
### Syntheses and characterizations:



**2,2'-Bithiophene.** To a mixture of magnesium turnings (3.28 g, 0.135 mol) and a small amount of iodine in anhydrous ether (30 mL) in a 250 mL three-neck flask, a solution of 2-

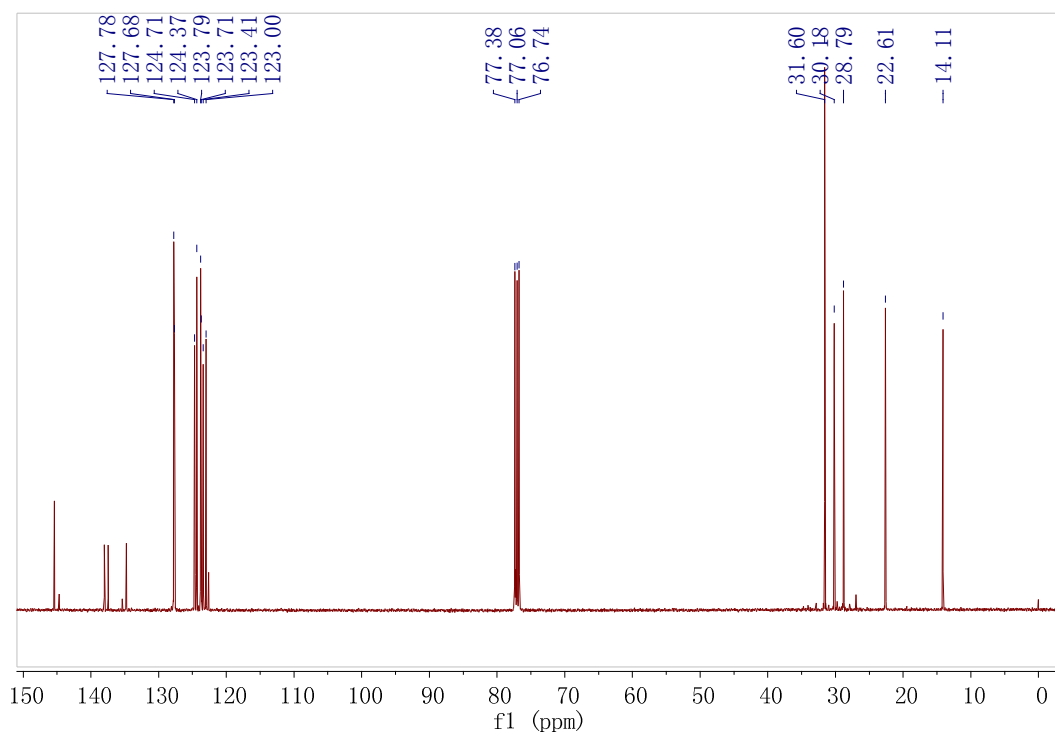
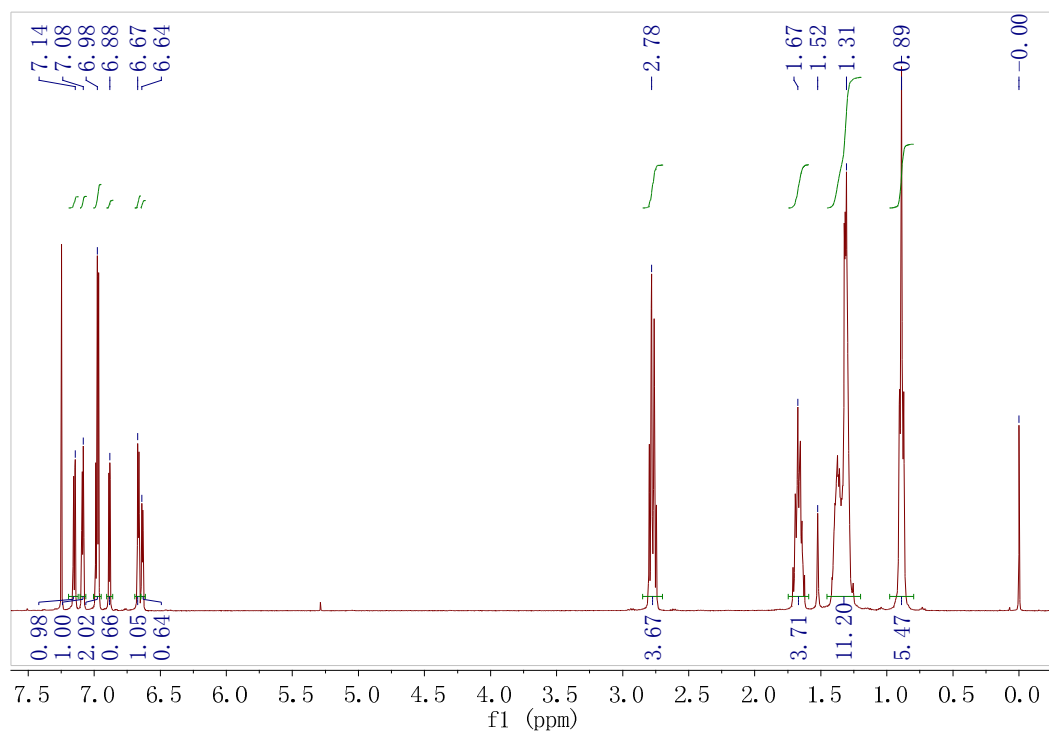
bromothiophene (21.2 g, 0.13 mol) in anhydrous ether (45 mL) was added slowly at room temperature under argon atmosphere. After completion, the mixture was heated and refluxed for 2 h, then the solution was cooled down by a mixture of ice and water, Ni(dppp)Cl<sub>2</sub> (0.54 g, 1 mmol) suspended in ether was added to the solution. Then 2-bromothiophene (19.56 g, 0.12 mol) and anhydrous ether (40 mL) was added slowly. After stirred at room temperature overnight, cold HCl aq. (1.5 M) was poured into the mixture. The product was extracted with hexane and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was further purified by column chromatography using hexane as the eluent to give a colorless crystal (17.56 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 7.20 (d, 2H), 7.17 (d, 2H), 7.01 (t, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 137.44, 127.79, 124.38, 123.80.

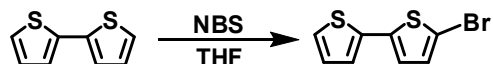




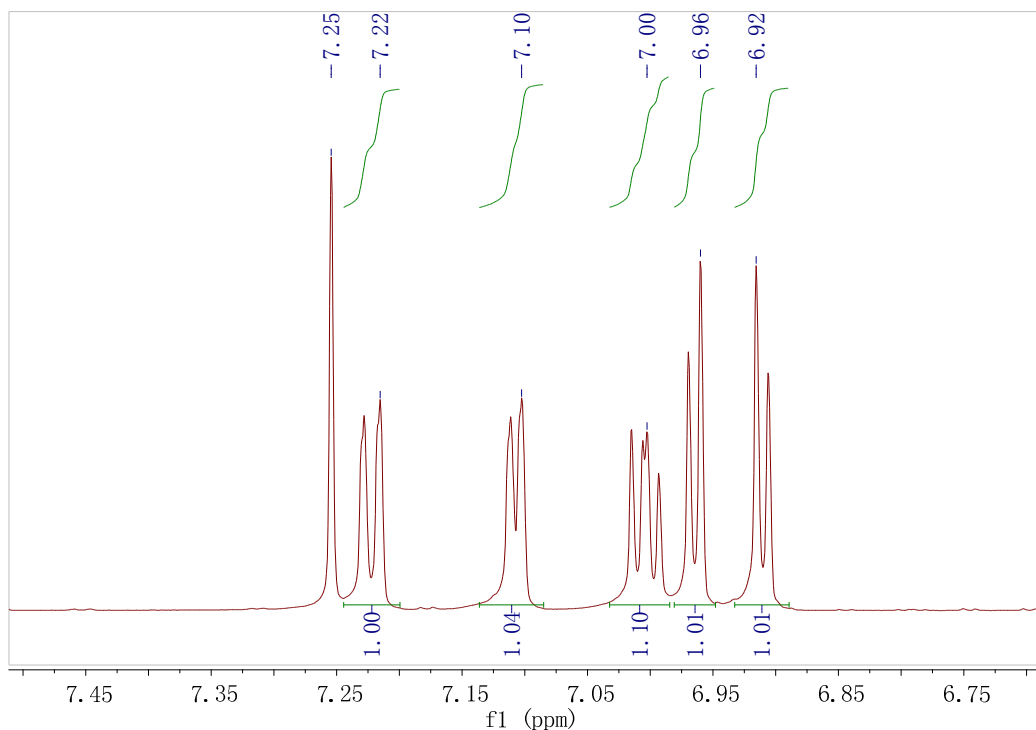
**5-Hexyl-2,2'-bithiophene.** 2,2'-Bithiophene (3.33 g, 20 mmol) in anhydrous THF (40 mL) was cooled with dry ice-acetone to  $-78\text{ }^{\circ}\text{C}$ , a solution of *n*-BuLi in hexane (2.5 M, 8 mL, 20 mmol) was added dropwise. After stirring at this temperature for 3 h, 1-bromohexane (3.3 g, 20 mmol) was added. The mixture was slowly warmed to room temperature and stirred overnight. Then water was added and the mixture was extracted with diethyl ether three times. The combined organic phase was dried over  $\text{MgSO}_4$  and concentrated in vacuum. The product was purified by silica chromatography (hexane as the eluent) to give a colorless liquid (4.06 g, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ )  $\delta$  (ppm): 7.14 (d, 1H), 7.08 (d, 1H), 6.98 (t, 2H), 6.67 (d, 1H), 2.78 (t, 2H), 1.67 (m, 2H), 1.22-1.43 (br, 6H), 0.89 (t, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ )  $\delta$  (ppm): 127.78, 127.68, 124.71, 124.37, 123.79, 123.71, 123.41, 123.00, 31.60 (two peaks overlapped),

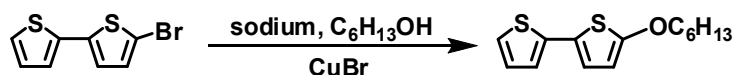
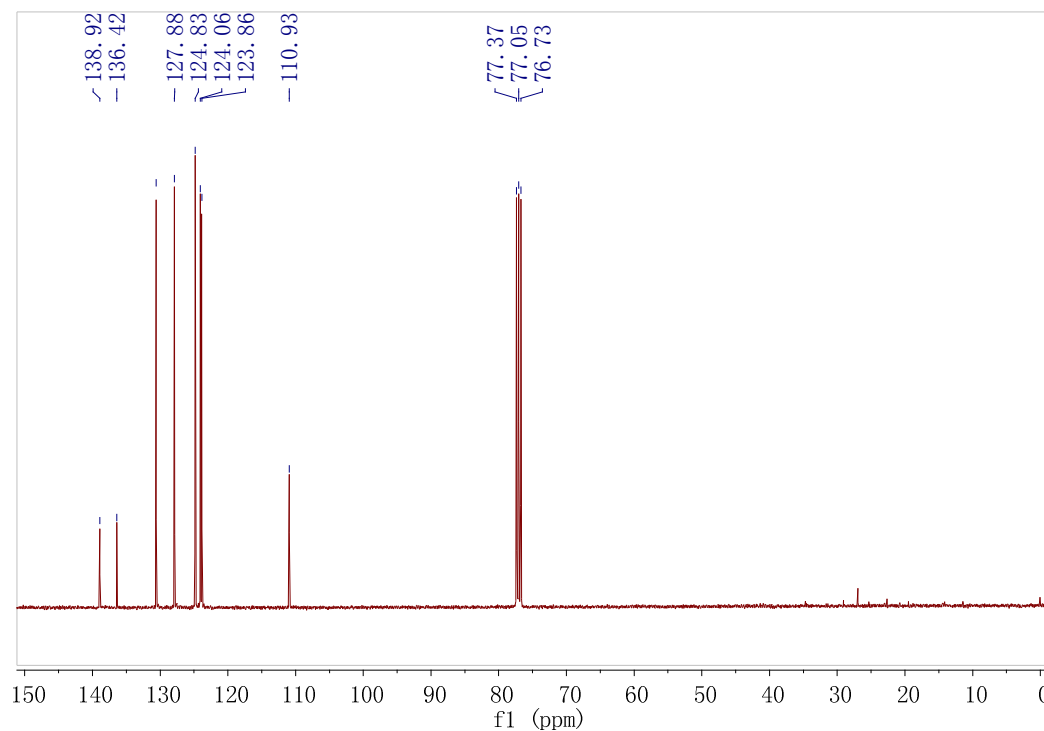
30.18, 28.79, 22.61, 14.11.





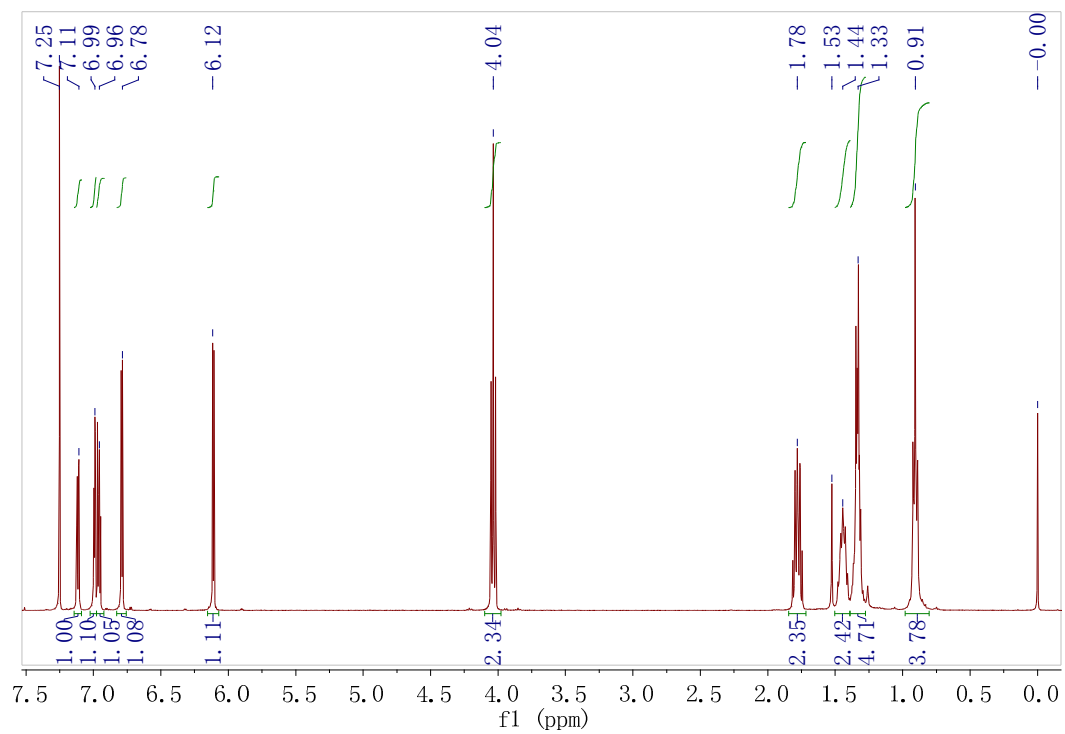
**5-Bromo-2,2'-bithiophene.** *N*-bromosuccinimide (5.34 g, 30 mmol) was added to a solution of 2,2'-bithiophene (4.99 g, 30 mmol) in THF (70 mL) in portions in absence of light, and the mixture was stirred at room temperature overnight. The organic fraction was quenched with aq. NaHCO<sub>3</sub> solution, extracted with hexane, and dried over anhydrous MgSO<sub>4</sub>. The product was purified by silica chromatography (hexane as the eluent) to give a transparent oil (6.69 g, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 7.22 (d, 1H), 7.10 (d, 1H), 7.00 (m, 1H), 6.95 (d, 1H), 6.92 (d, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 138.92, 136.42, 130.60, 127.88, 124.83, 124.06, 123.86, 110.93.



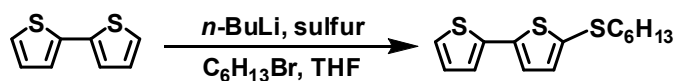
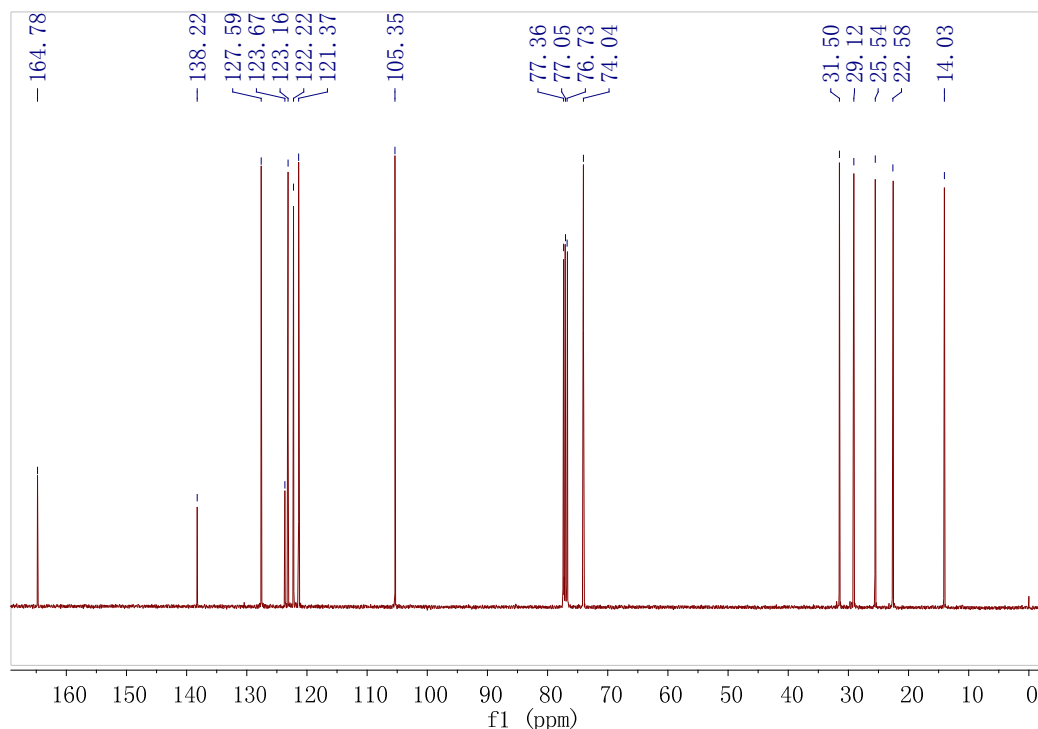


**5-(Hexyloxy)-2,2'-bithiophene.** Sodium (0.46 g, 20 mmol) was added to *n*-hexyl alcohol (7.8 g, 60 mmol) and stirred at room temperature until the sodium completely disappeared (about 1 h), then 5-bromo-2,2'-bithiophene (4.90 g, 20 mmol) was added into the mixture under argon. After 5 min, cuprous bromide (0.58 g, 4 mmol) was added to the reaction mixture and stirred at 120 °C for 24 h. When the reaction temperature was cooled to room temperature, water was added and the mixture was extracted with hexane several times. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the removal of solvent, purification was carried out by silica gel column chromatography using hexane as eluent to give the product as a colorless oil (3.3 g, yield 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 7.11 (m, 1H), 6.99 (m, 1H), 6.96 (m, 1H), 6.78 (d, 1H), 6.12 (d, 1H), 4.04 (t, 2H), 1.78 (m, 2H), 1.44 (m, 2H), 1.28-1.39 (m, 4H), 0.91 (t,

3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm): 164.78, 138.22, 127.59, 123.67, 123.16, 122.22, 121.37, 105.35, 74.04, 31.50, 29.12, 25.54, 22.58, 14.03.

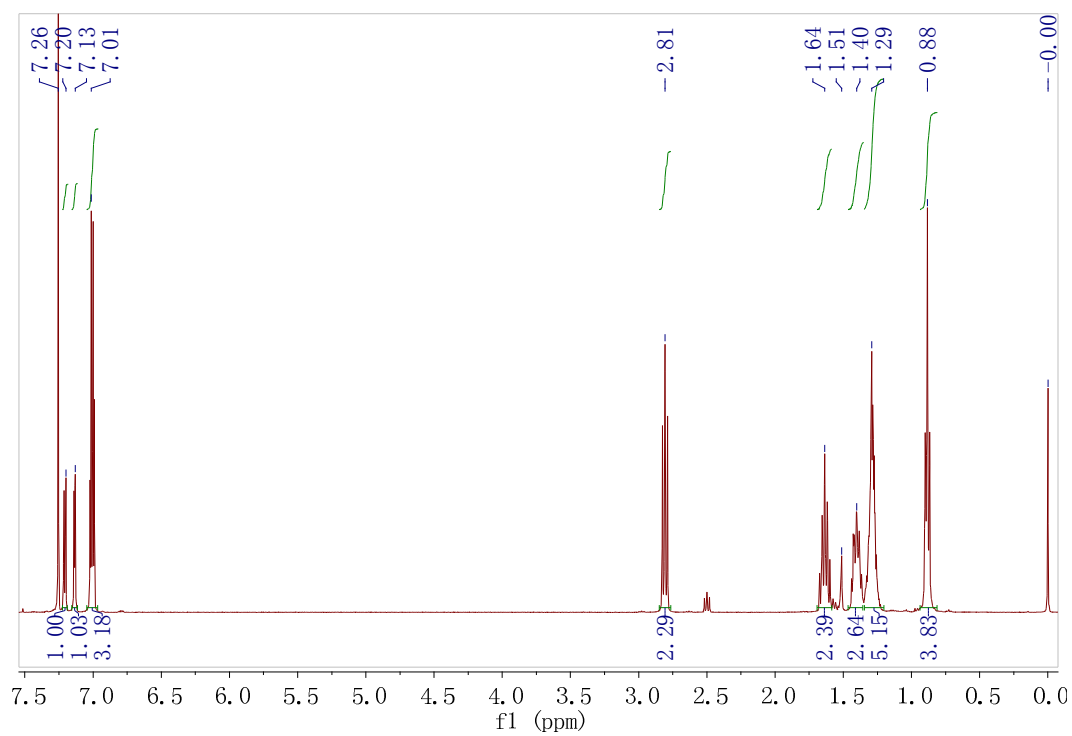


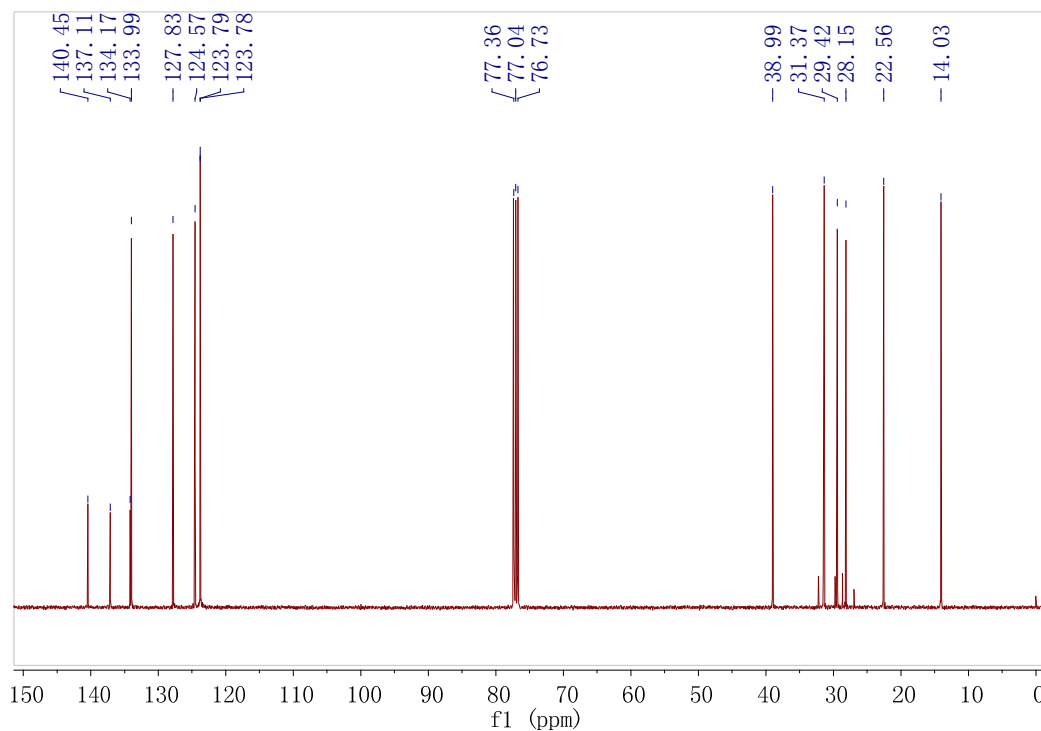




**5-(Hexylthio)-2,2'-bithiophene.** *n*-Butyllithium (8 mL, 20 mmol, 2.5 M in hexane) was added dropwise into 2,2'-bithiophene (3.33 g, 20 mmol) and 40 mL of dry THF at -78 °C under argon atmosphere. After stirred at this temperature for 2 h, sulfur powder (0.64 g, 20 mmol) was added in one portion, and the resulting suspension was stirred for 2 h. Subsequently, 1-bromohexane (3.3 g, 20 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred overnight. Then ice-water containing NH<sub>4</sub>Cl was added, and the mixture was extracted with diethyl ether, washed with water, and dried over MgSO<sub>4</sub>. After the removal of solvent, the product was purified by silica gel column chromatography using hexane as the eluent to give a colorless oil (4.86 g, yield 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 7.20 (d, 1H), 7.13 (d, 1H), 6.98-7.04 (m, 3H), 2.81 (t, 2H), 1.64 (m, 2H), 1.40 (m, 2H), 1.29 (br,

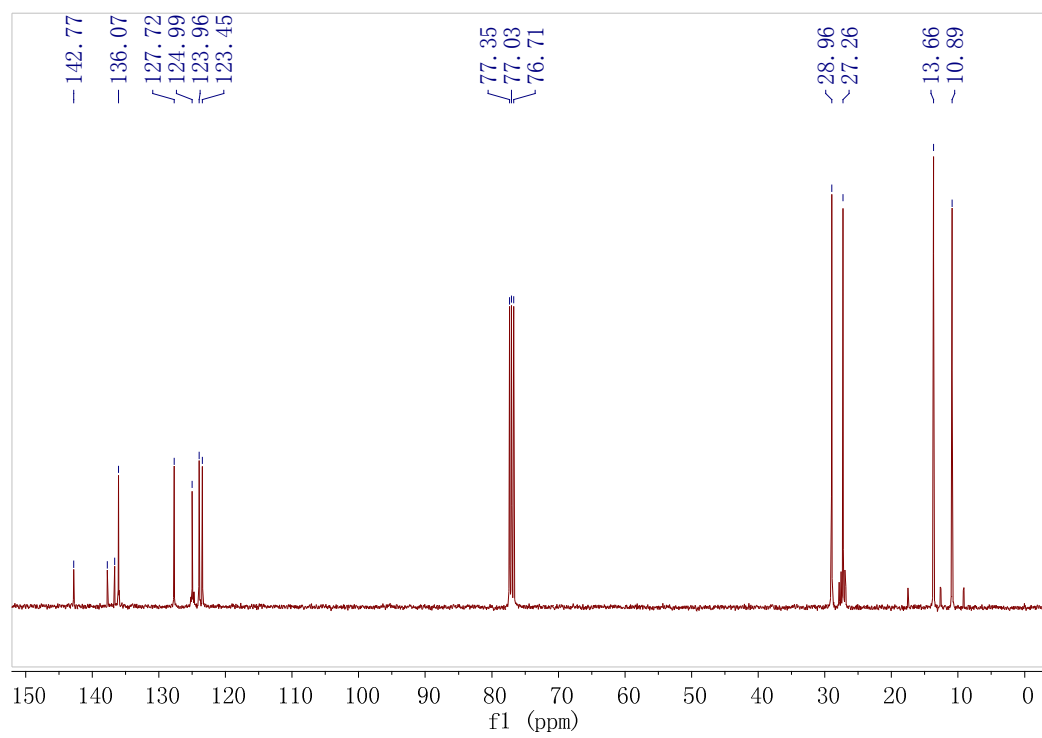
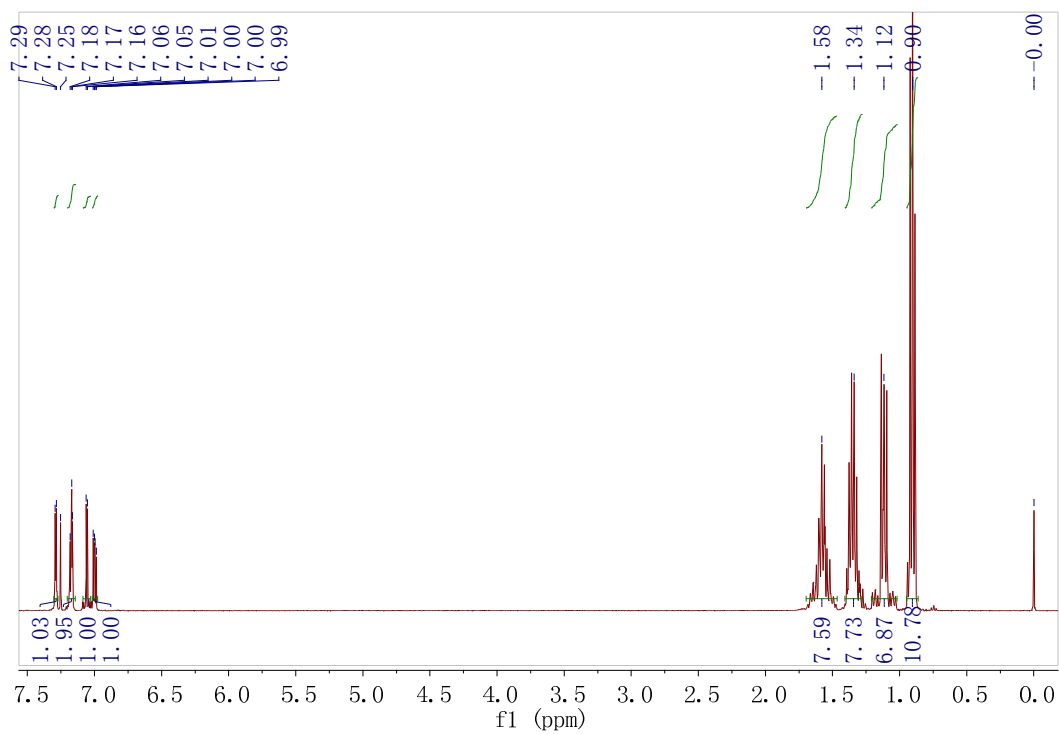
4H), 0.88 (t, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm): 140.45, 137.11, 134.17, 133.99, 127.83, 124.57, 123.79, 123.78, 38.99, 31.37, 29.42, 28.15, 22.56, 14.03.

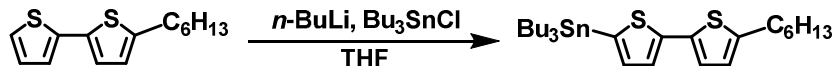




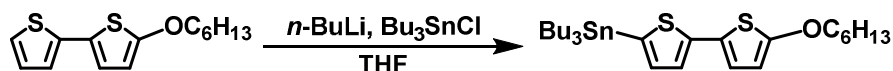
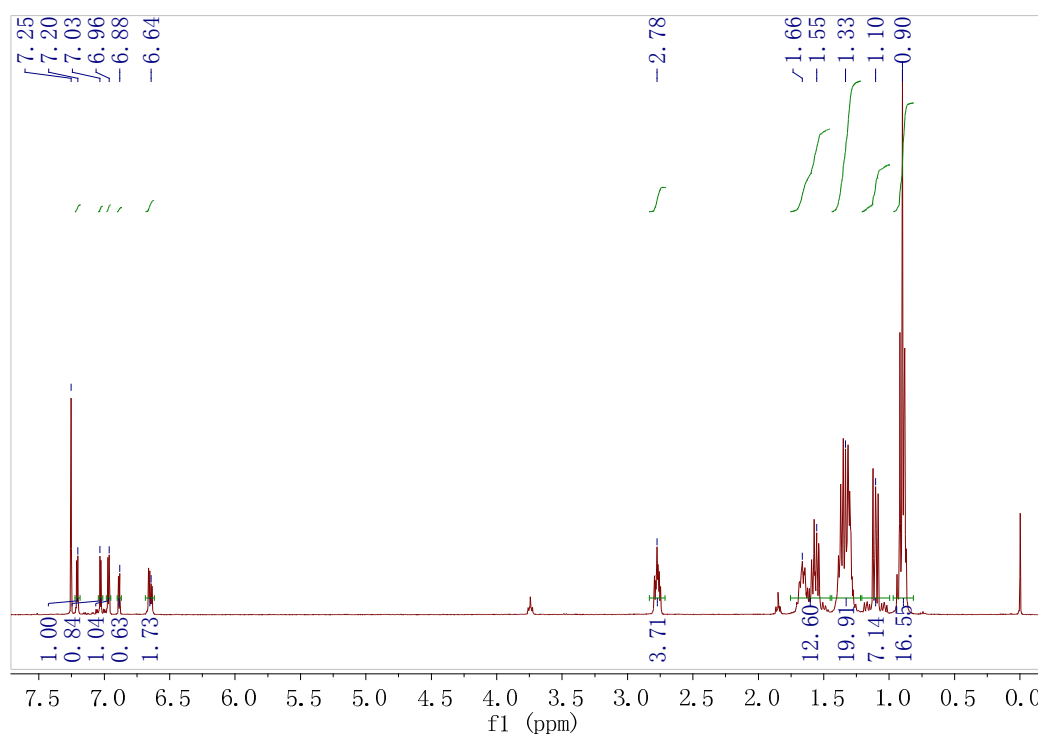
**Tributyl(2,2'-bithiophene-5-yl)stannane.** 2,2'-Bithiophene (1.66 g, 10 mmol) in dry THF (30 mL) was placed under argon and cooled to  $-78\text{ }^{\circ}\text{C}$  with dry ice-acetone, then a solution of  $n$ -butyllithium in hexane (2.5 M, 4 mL, 10 mmol) was added dropwise. The suspension was stirred at this temperature for 2 h. Tributyltinchloride (3.26 g, 10 mmol) was added and the reaction mixture was warmed to room temperature slowly and stirred overnight. The mixture was poured into water (30 mL) and extracted with diethyl ether, and the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure to afford a brownish oil. The product was used without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ )  $\delta$  (ppm): 7.29 (d, 1H), 7.14-7.20 (m, 2H), 7.06 (d, 1H), 7.00 (tetra, 1H), 1.46-1.69 (m, 6H), 1.28-1.40 (m, 6H), 1.02-1.21 (m, 6H), 0.90 (m, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ )  $\delta$  (ppm): 142.77,

137.72, 136.63, 136.07, 127.72, 124.99, 123.96, 123.45, 28.96, 27.26, 13.66, 10.89.



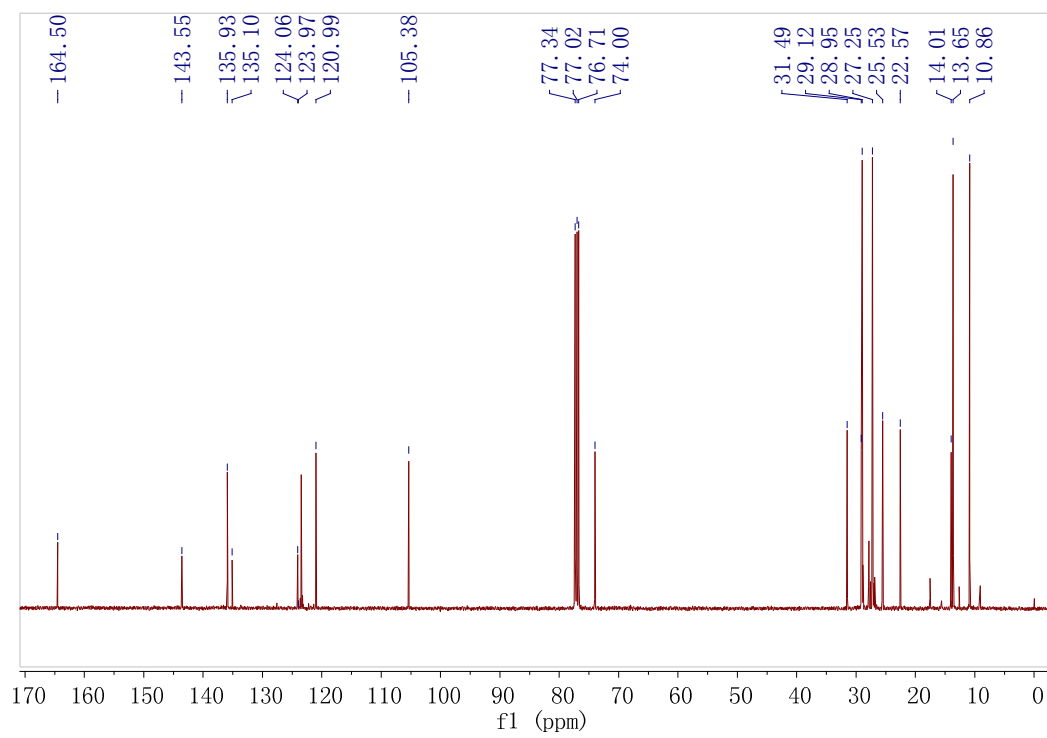
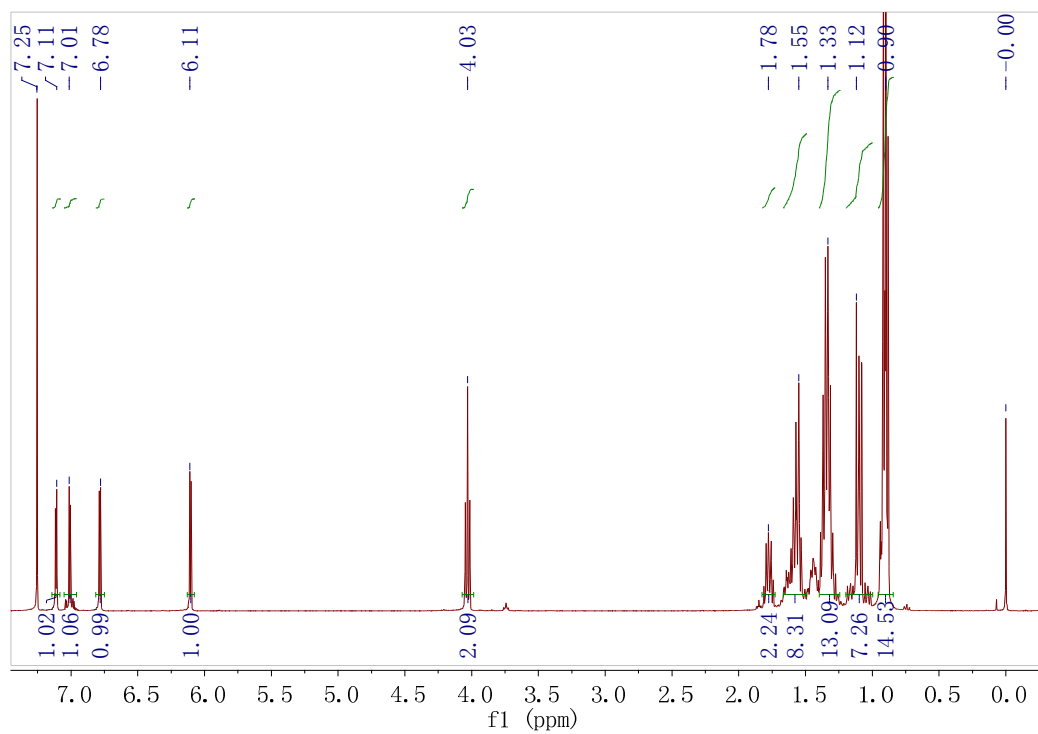


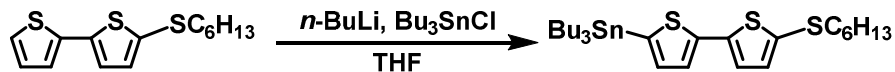
**Tributyl(5'-(hexyl)-2,2'-bithiophene-5-yl)stannane.** It was obtained as the procedure shown upon.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 7.20 (d, 1H), 7.03 (d, 1H), 6.96 (d, 1H), 6.64 (d, 1H), 3.71 (m, 2H), 1.50-1.72 (m, 10H), 1.25-1.42 (m, 14H), 1.10 (t, 8H), 0.90 (m, 15H).



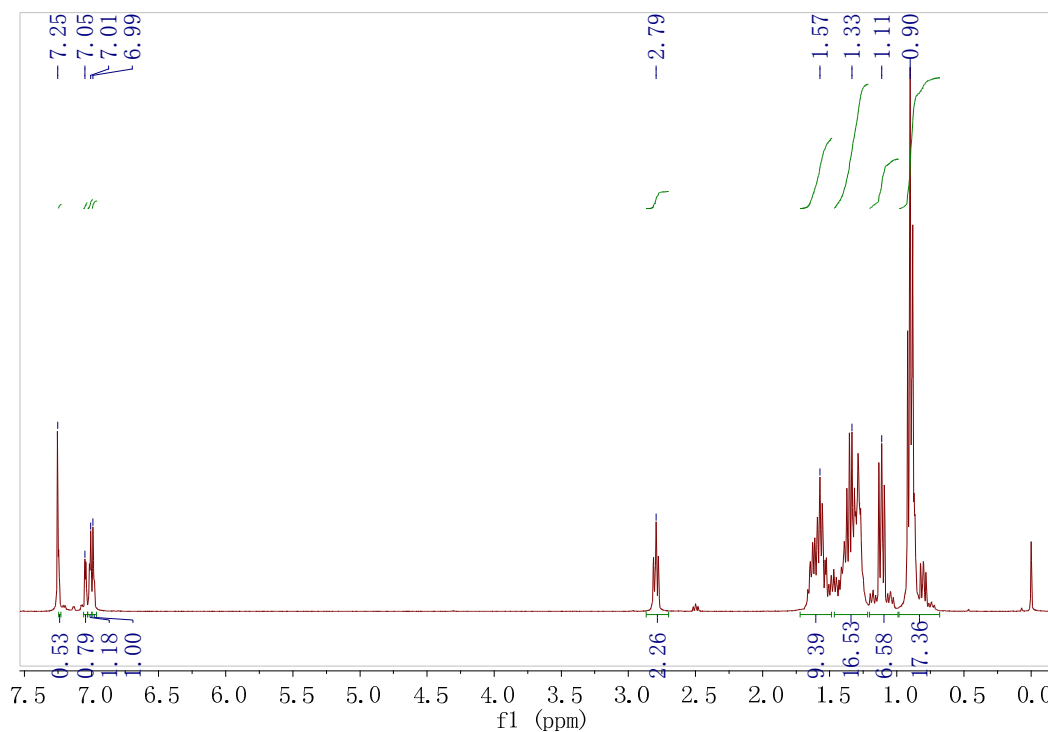
**Tributyl(5'-(hexyloxy)-2,2'-bithiophene-5-yl)stannane.** It was obtained as the procedure shown upon.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 7.11 (d, 1H), 7.01 (d, 1H), 6.78 (d, 1H), 6.11 (d, 1H), 4.03 (t, 2H), 1.78 (m, 2H), 1.55 (m, 8H), 1.33 (m, 14H), 1.12 (m, 8H), 0.90 (m, 15H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 164.50, 143.55, 135.93, 135.10, 124.06,

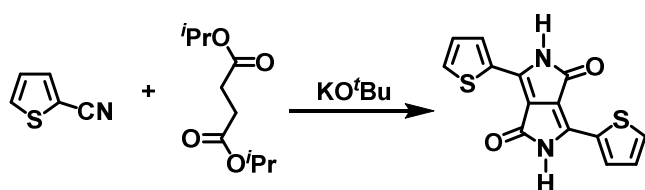
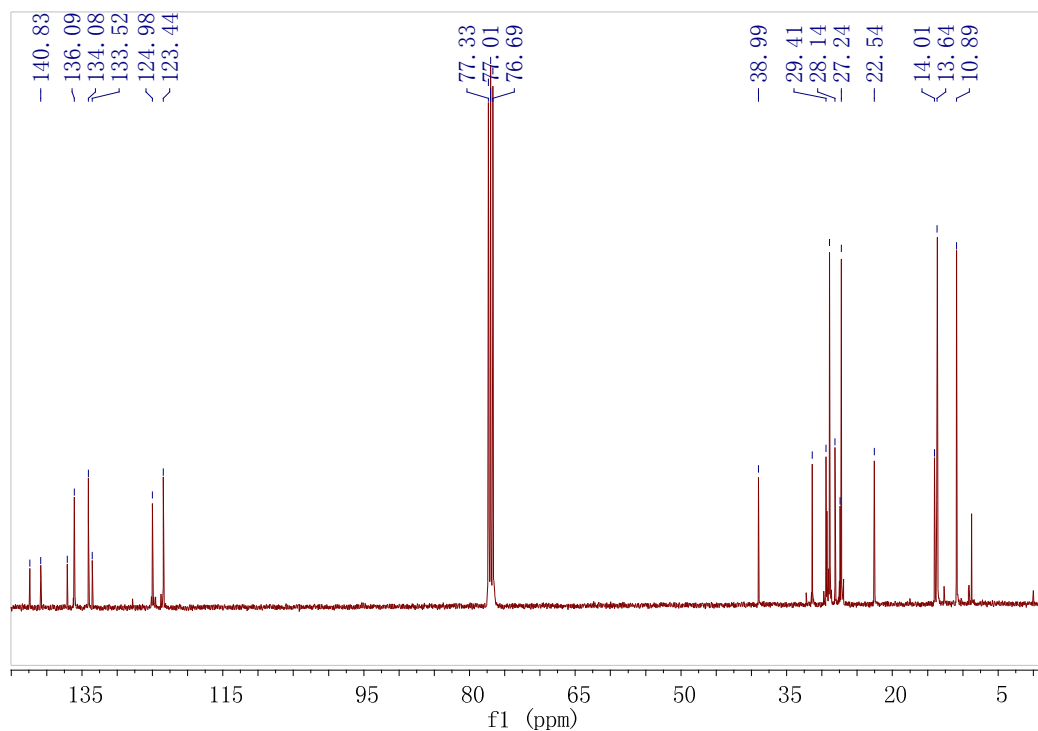
123.97, 120.99, 105.38, 74.00, 31.49, 29.12, 28.95, 27.25, 25.53, 22.57, 14.01, 13.65, 10.86.





**Tributyl(5'-(hexylthio)-2,2'-bithiophene-5-yl)stannane.** It was obtained as the procedure shown upon.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 7.24 (d, 1H), 7.05 (d, 1H), 7.01 (d, 1H), 6.99 (d, 1H), 2.79 (t, 2H), 1.57 (m, 10H), 1.33 (m, 14H), 1.11 (m, 8H), 0.90 (t, 15H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 142.40, 140.83, 137.06, 136.09, 134.08, 133.52, 124.98, 123.44, 38.99, 31.36, 29.41, 28.14, 27.24, 22.54, 14.01, 13.64, 10.89.

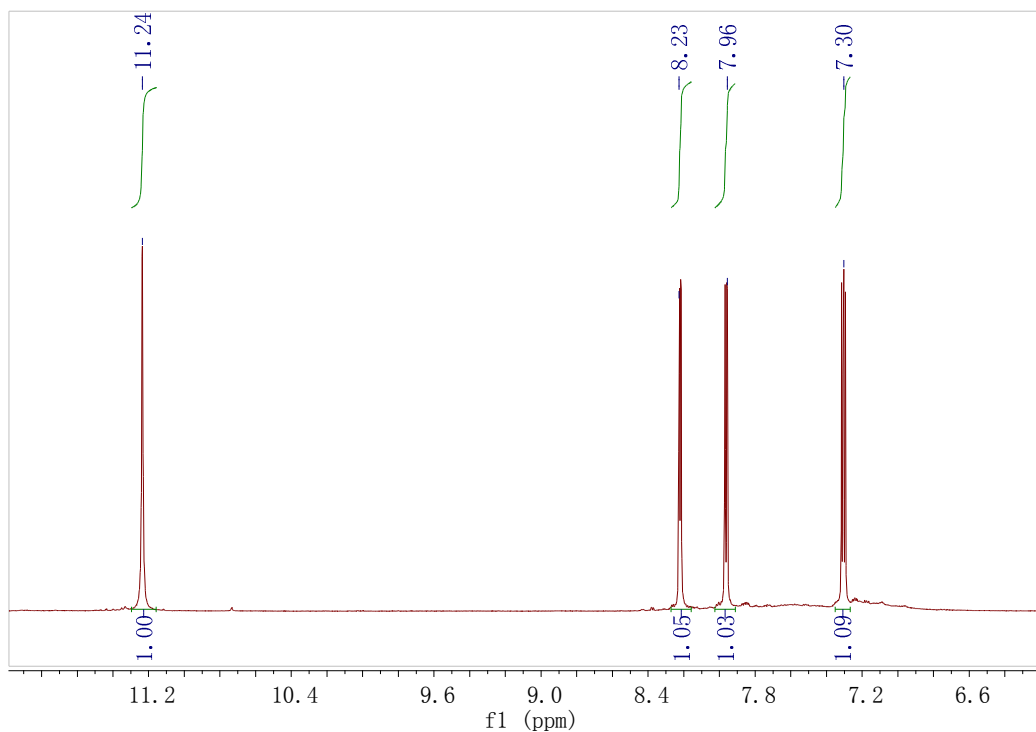


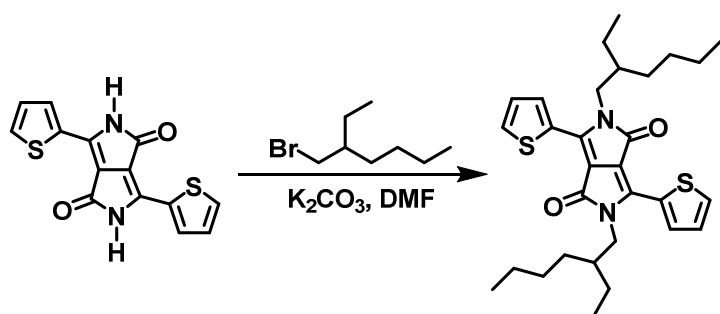
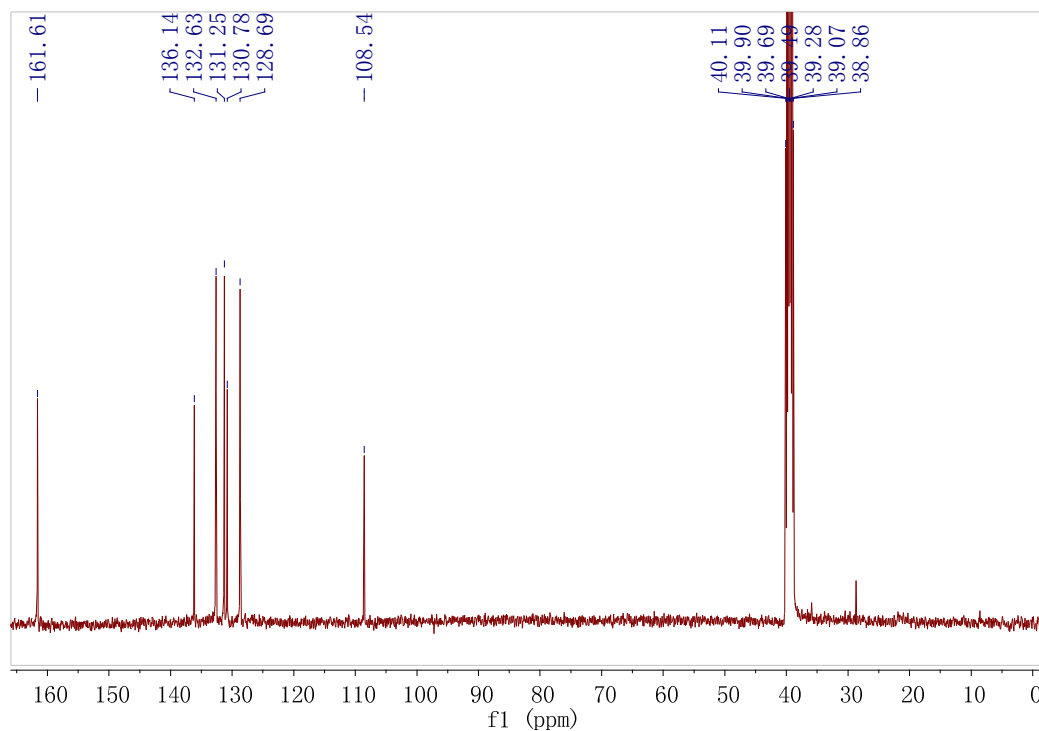


**3,6-Bis(thiophen-2-yl)-2H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione.** To an argon-protected three-neck round-bottom flask equipped with a mechanical stirrer, a thermometer and a reflux condenser, were added potassium *tert*-butoxide (67.4 g, 0.60 mol) and *tert*-amyl alcohol (400 mL). The mixture was heated to 105 °C for 1.5 h. 2-Thiophenenitrile was added to this mixture (55.2 g, 0.50 mol) and stirred at 105 °C for 30 min. A mixture of diisopropyl succinate (40.4 g, 0.20 mol) in *tert*-amyl alcohol (60 mL) was added dropwise with rapid stirring. The mixture was then stirred at 105 °C for further 2 h, then cooled to 50 °C, at which point a mixture of methanol (300 mL) and water (80 mL) were added. The reaction mixture was then heated refluxed for 45



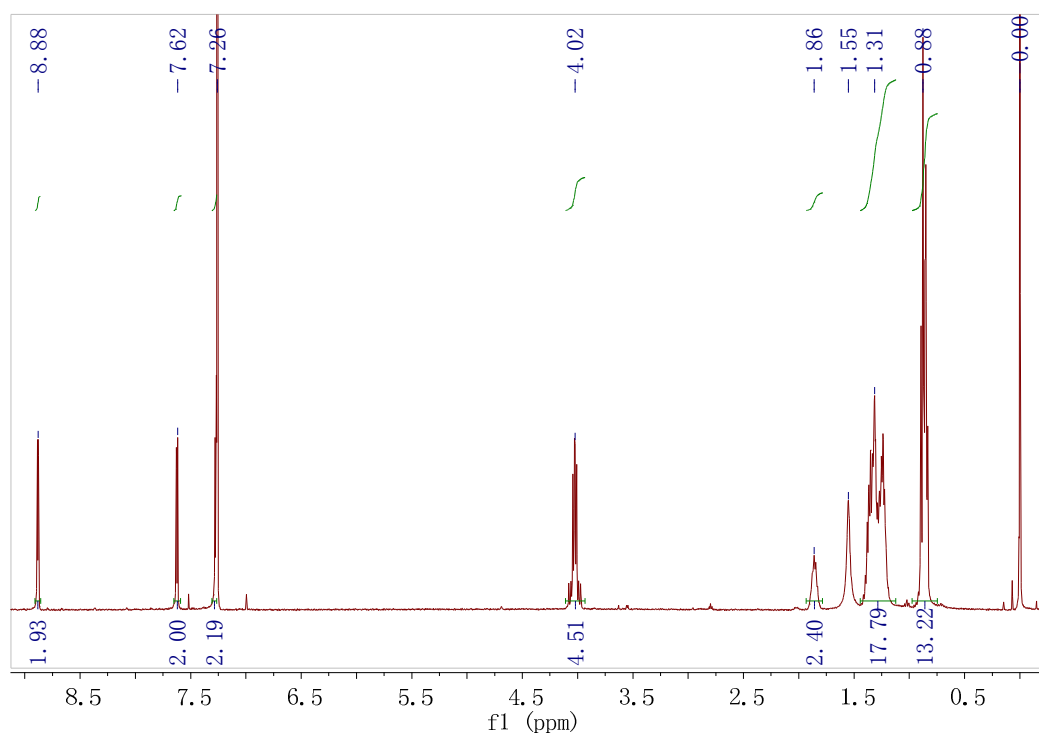
min before cooling to room temperature. The mixture was poured over 500 g of ice, then conc. hydrochloric acid (35% aq) (150 mL) and methanol (750 mL) were added and the mixture was stirred for 45 min. The mixture was filtered and the solid was washed with methanol (200 mL). The solid was then suspended in water (1 L) and stirred for 30 min before being filtered again. This suspension in water, stirring and filtration was repeated a further three times. After filtering for the last time, the solid was oven dried at 80 °C for 16 h, then dried under vacuum to give the compound (49.7 g, 82%) as a red solid. This compound was used without further purification.  $^1\text{H}$  NMR (400 MHz, DMSO, 25 °C)  $\delta$  (ppm): 11.24 (s, 1H), 8.23 (d, 1H), 7.96 (d, 1H), 7.30 (t, 1H).  $^{13}\text{C}$  NMR (100 MHz, DMSO, 25 °C)  $\delta$  (ppm): 161.61, 136.14, 132.63, 131.25, 130.78, 128.69, 108.54.

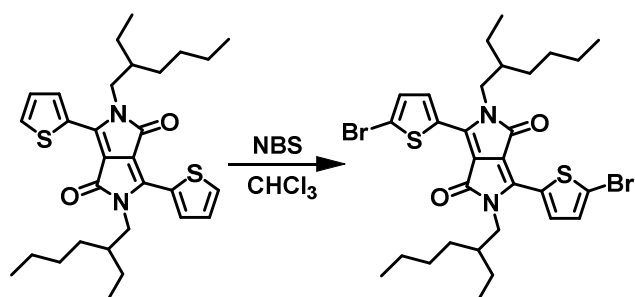
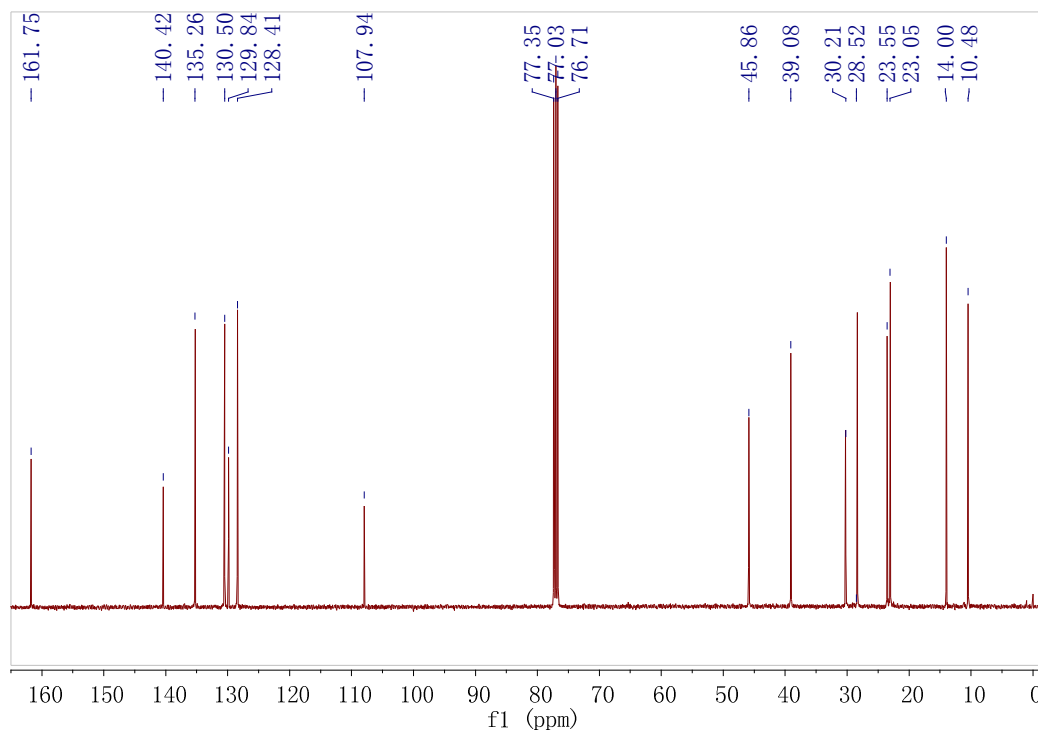




**2,5-Diethylhexyl-3,6-bis(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione.** 3,6-Bis(thiophen-2-yl)-2H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione (19.5 g, 64.9 mmol) and anhydrous potassium carbonate (36.8 g, 266 mmol) were stirred in anhydrous *N, N*-dimethylformamide (DMF) (300 mL) under argon at 130 °C for 1 h. 1-Bromoethylhexane (59.5 g, 195 mmol) was then added dropwise and the reaction mixture was stirred at 130 °C for 20 h. The reaction mixture was cooled to room temperature then poured into ice water (1 L) and the resulting suspension was stirred for 1 h. The mixture was filtered and the solid was suspended again in water (200 mL)

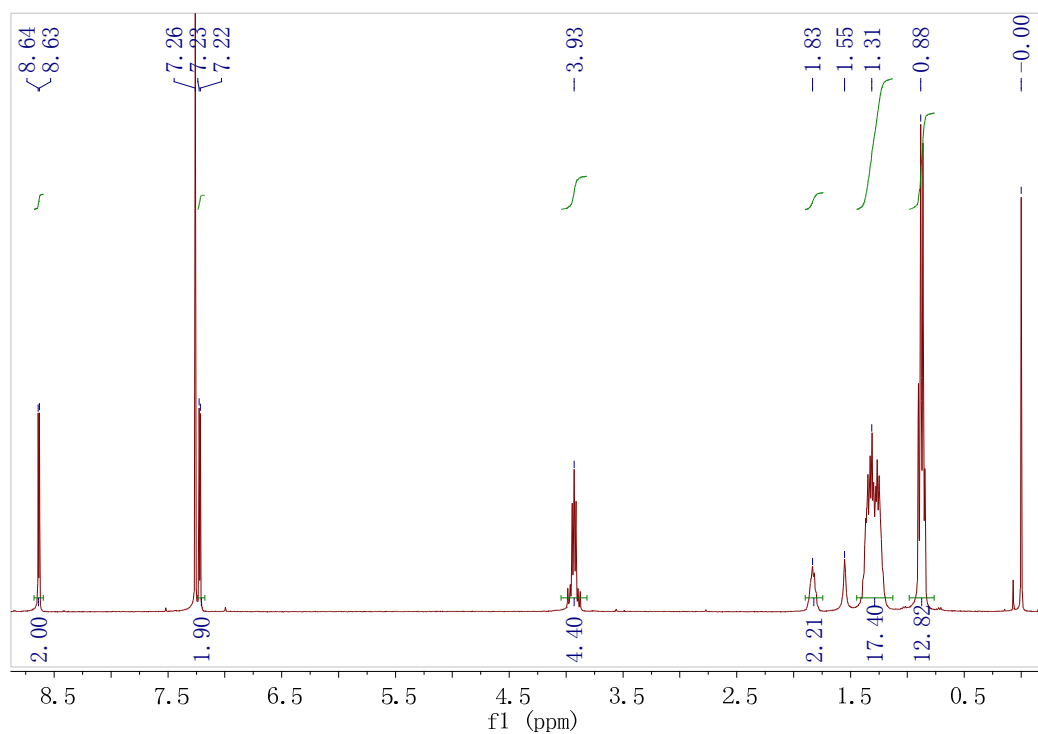
and stirred vigorously for 30 min before being filtered again. This suspension in water, stirring and filtration was repeated twice more, then the process was repeated three times to replace the water with methanol (200 mL). After filtering for the last time, the solid was dried under vacuum to give the product as a dark red solid (43.0 g, 88%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm): 8.88 (d, 2H), 7.62 (d, 2H), 7.27 (t, 2H), 4.02 (t, 4H), 1.86 (m, 2H), 1.18-1.40 (br, 16H), 0.88 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm): 161.75, 140.42, 135.26, 130.50, 129.84, 128.41, 107.94, 45.86, 39.08, 30.21, 28.52, 23.55, 23.05, 14.00, 10.48.

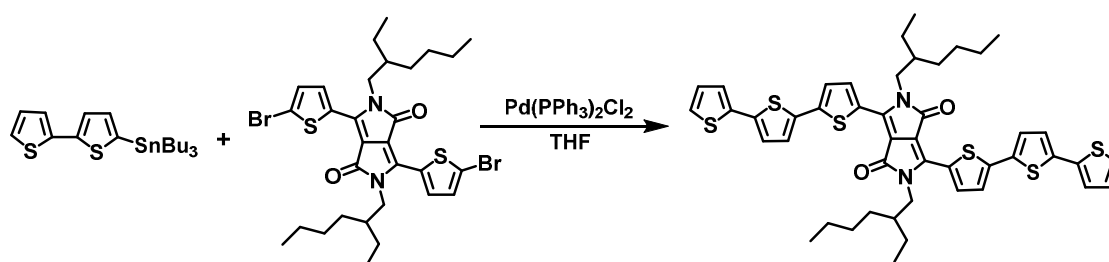
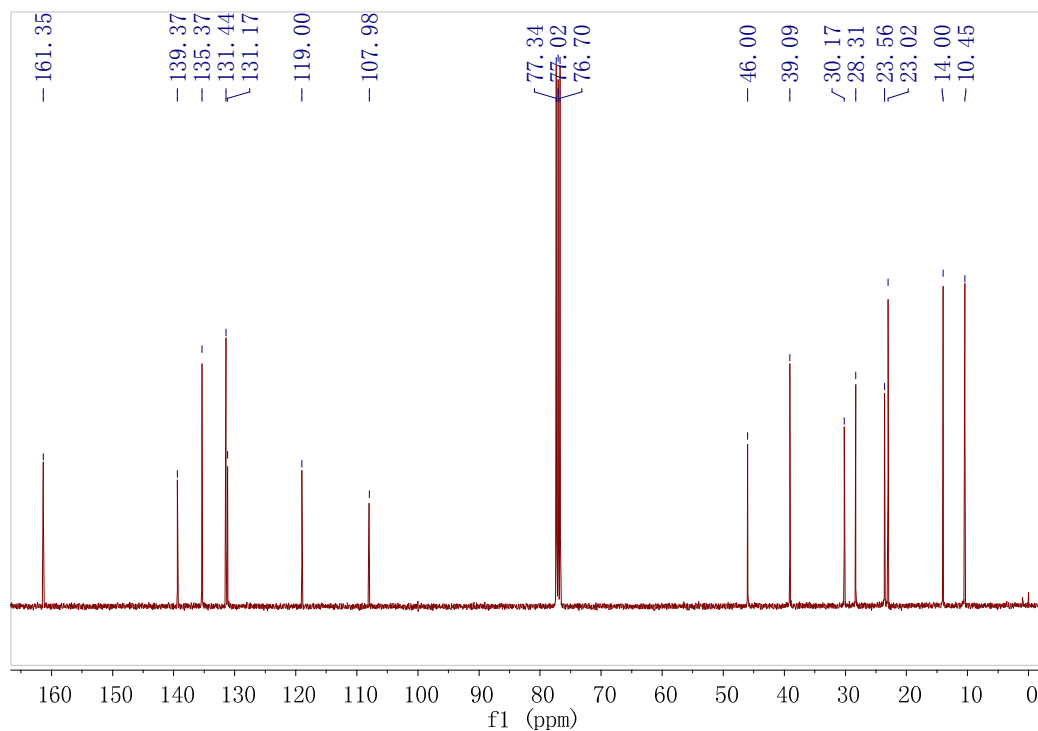




**3,6-Bis(5-bromothiophen-2-yl)-2,5-diethylhexylpyrrolo[3,4-c]pyrrole-1,4-dione.** *N*-Bromosuccinimide (6.33 g, 35.6 mmol) was added to a solution of 2,5-diethylhexyl-3,6-bis(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (13.0 g, 17.4 mmol) in chloroform (200mL) pre-heated to 60 °C in a 1 L flask, wrapped in aluminum foil to exclude light. The reaction was monitored by TLC and stopped as soon as no more mono-brominated species was observed by TLC (approximately 1 h), by pouring into methanol (600 mL) stirring in an ice bath. The mixture was filtered and the solid was washed with methanol (2 × 200 mL) then dried under vacuum. The

crude product was recrystallized from chloroform (200 mL) to give the product as a dark red solid (14.2 g, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm): 8.63 (d, 2H), 7.23 (d, 2H), 3.93 (t, 4H), 1.83 (m, 2H), 1.17-1.42 (m, 16H), 0.88 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm): 161.35, 139.37, 135.37, 131.44, 131.17, 119.00, 107.98, 46.00, 39.09, 30.17, 28.31, 23.56, 23.02, 14.00, 10.45.



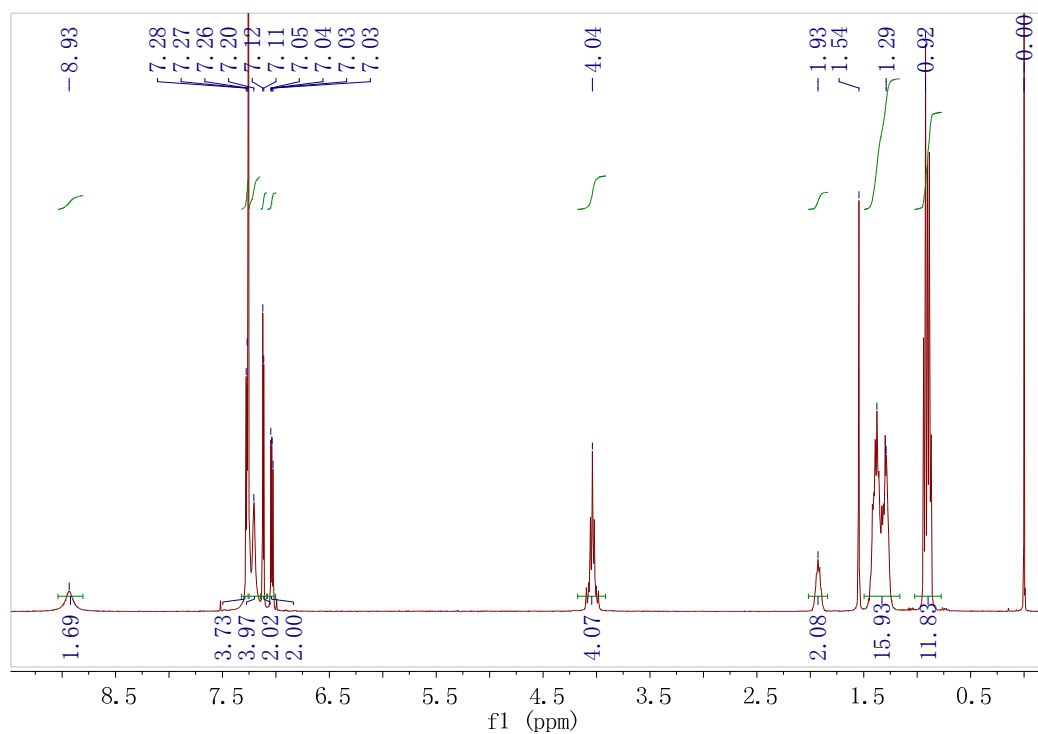


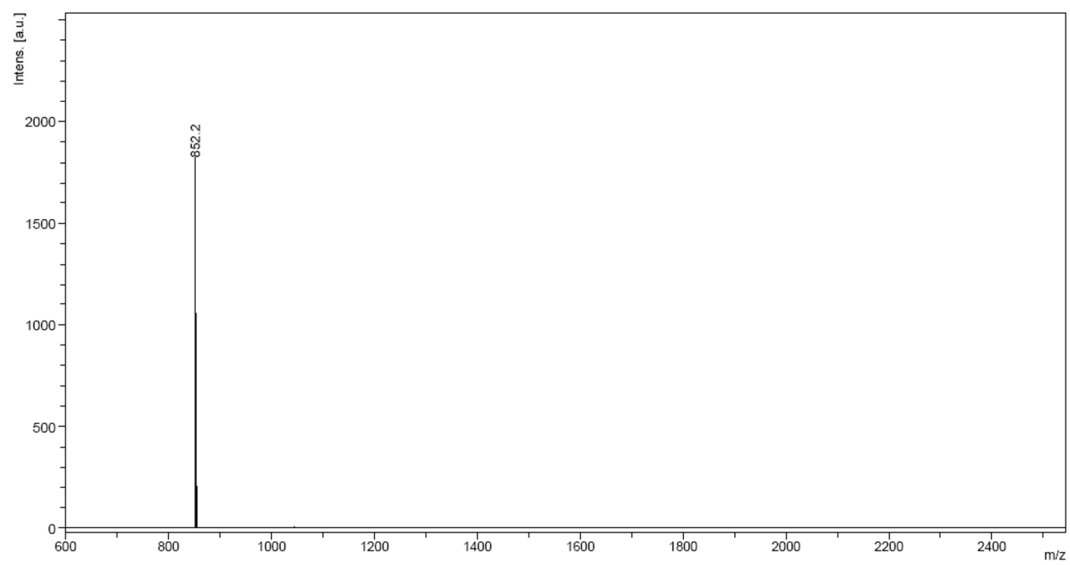
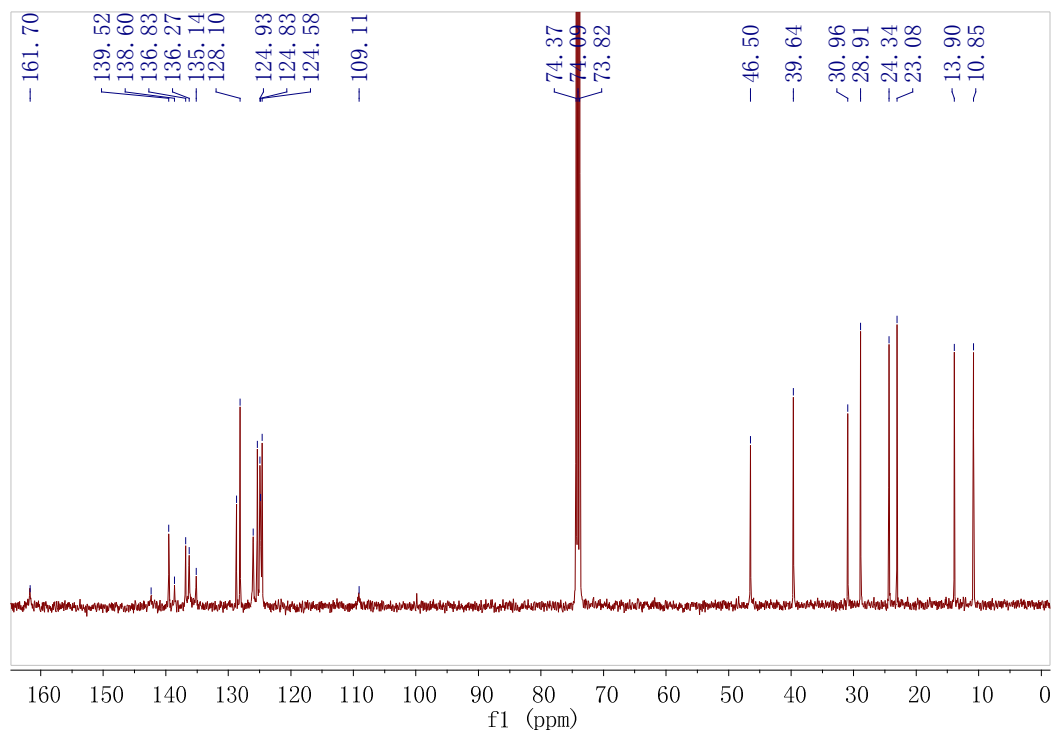
**2,5-Di-(2-ethylhexyl)-3,6-bis-([2,2',5',2'']terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione**

**(1).** Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.07 g, 0.1 mmol) was added to a solution of 5-bromo-2,2'-bithiophene (4.10 g, 9 mmol) and 3,6-bis(5-bromothiophen-2-yl)-2,5-diethylhexylpyrrolo[3,4-c]pyrrole-1,4-dione (2.73 g, 4 mmol) in THF (30 mL). The mixture was refluxed under argon atmosphere for 18 h in the absent of light, then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1:1), result in a dark solid. Then this solid was recrystallized from hexane several times to give a dark crystal (2.9 g, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 8.93 (br, 2H), 7.27 (m, 4H), 7.20 (br,

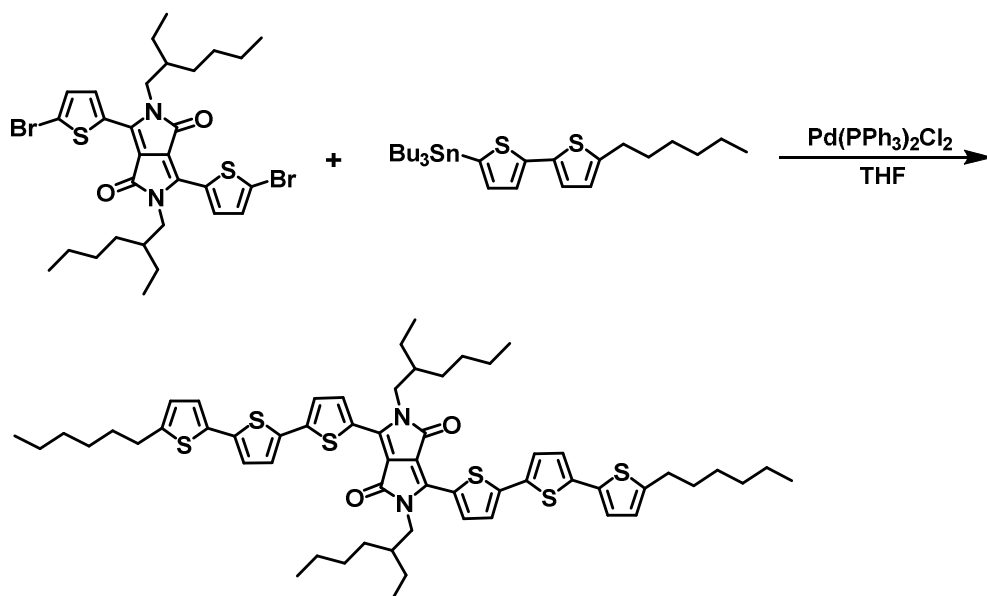
4H), 7.12 (d, 2H), 7.04 (m, 2H), 4.04 (t, 4H), 1.93 (m, 2H), 1.22-1.45 (m, 16H), 0.92 (m, 12H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 120  $^\circ\text{C}$ )  $\delta$  (ppm): 161.70, 142.35, 139.52, 138.60, 136.83, 136.27, 135.14, 128.69, 128.10, 126.04, 125.37, 124.93, 124.83, 124.58, 109.11, 46.50, 39.64, 30.96, 28.91, 24.34, 23.08, 13.90, 10.85. MALDI-TOF-MS:  $m/z$  852.2  $[\text{M}]^+$ . ( $\text{C}_{46}\text{H}_{48}\text{N}_2\text{O}_2\text{S}_6$ ) (852.2): Calcd. C, 64.75; H, 5.67; N, 3.28; S, 22.55. Found C, 64.76; H, 5.67; N, 3.24; S, 22.60.

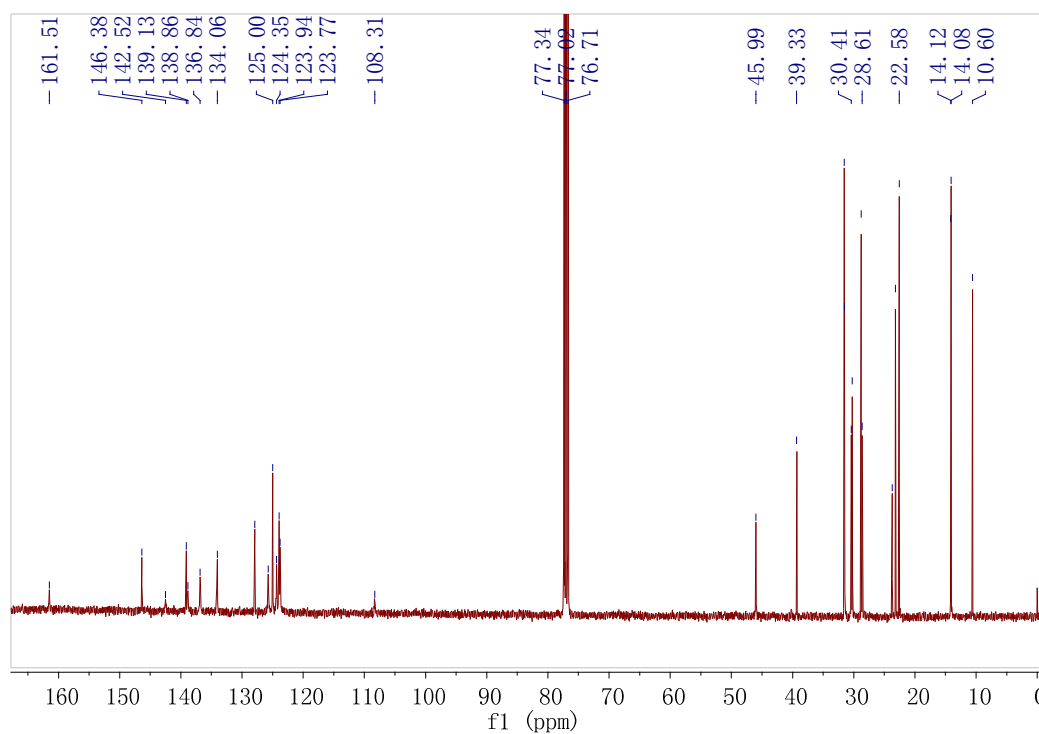
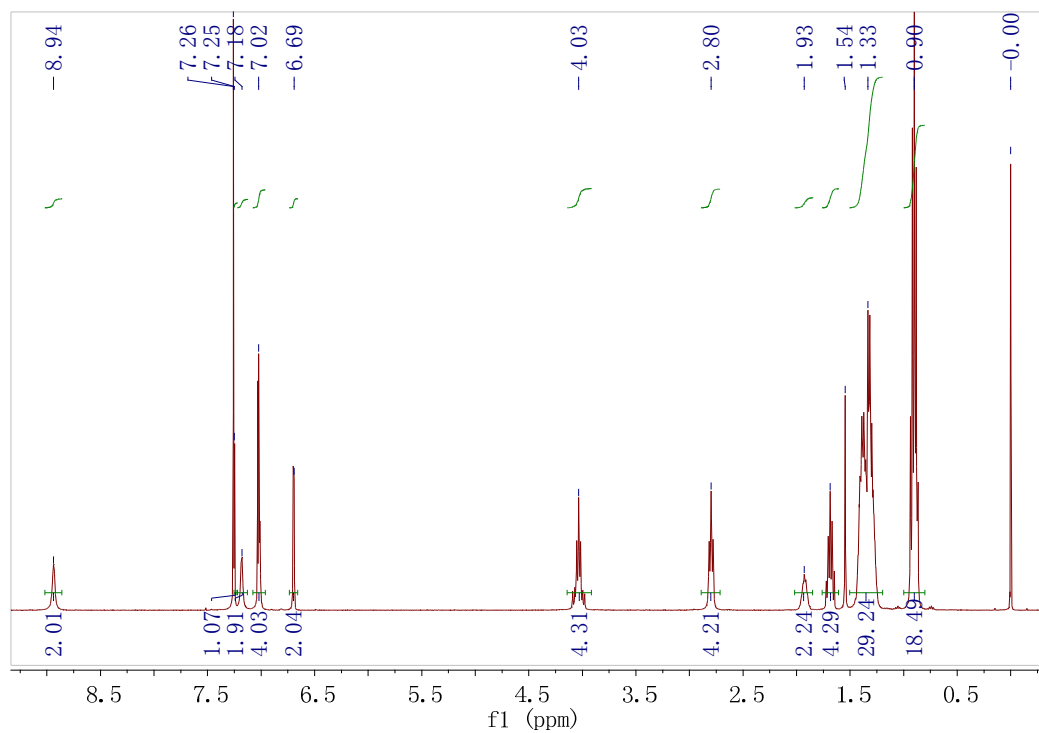


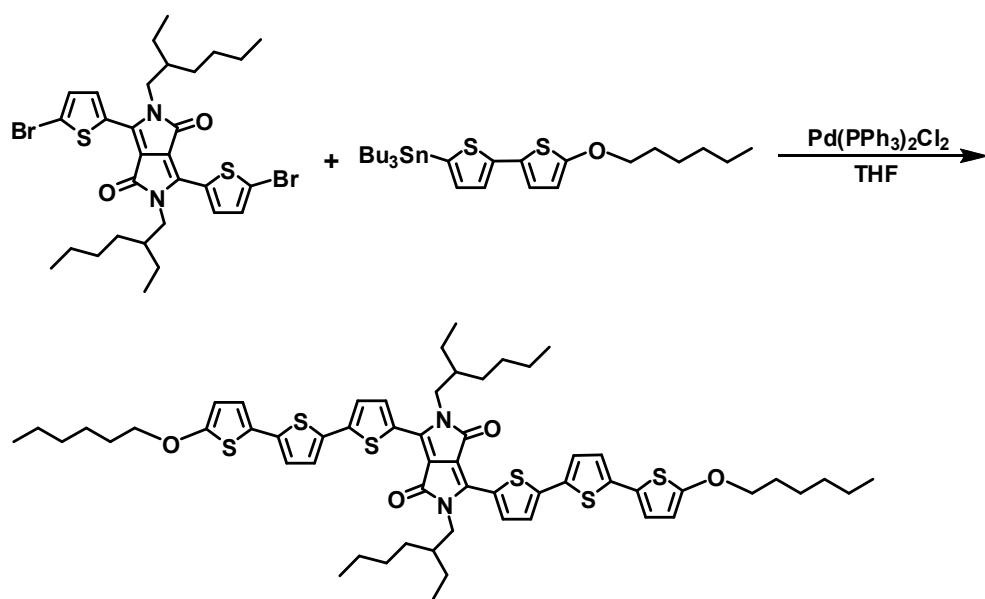
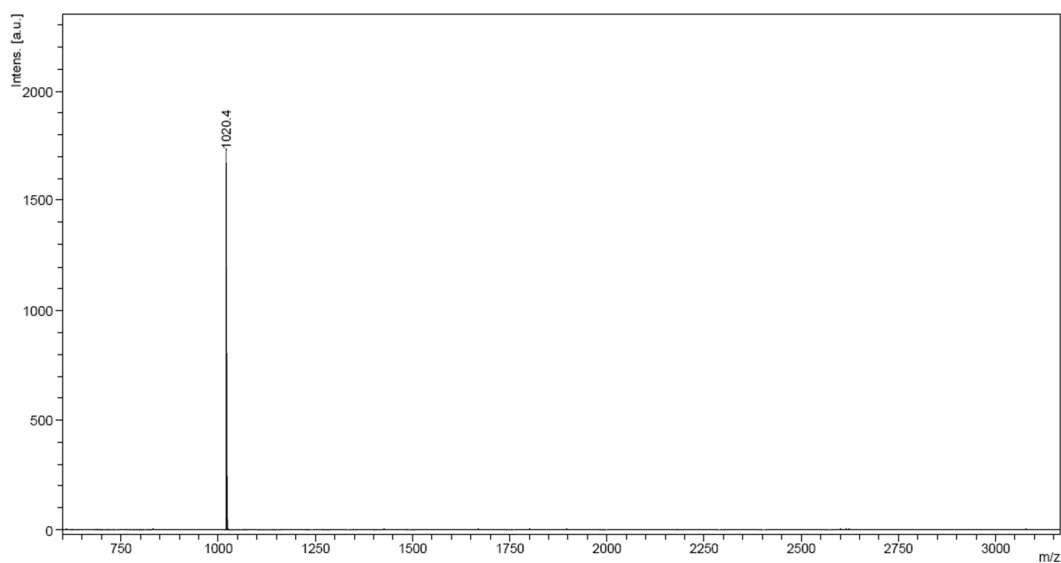






**2,5-Di-(2-ethylhexyl)-3,6-bis-(5''-*n*-hexyl-[2,2',5',2'']terthiophen-5-yl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (2).** It was obtained in the similar procedure as compound **1** (80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 8.94 (br, 2H), 7.25 (d, 2H), 7.18 (br, 2H), 7.02 (t, 4H), 6.69 (d, 2H), 4.03 (t, 4H), 2.80 (t, 4H), 1.93 (m, 2H), 1.69 (m, 4H), 1.23-1.45 (m, 28H), 0.90 (m, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm): 161.51, 146.38, 142.52, 139.13, 138.86, 136.84, 134.06, 127.93, 125.72, 125.00, 124.35, 123.94, 123.77, 108.31, 45.99, 39.33, 31.57, 31.52, 30.41, 30.23, 28.79, 28.61, 23.71, 23.16, 22.58, 14.12, 14.08, 10.60. MALDI-TOF-MS: *m/z* 1020.4 [M]<sup>+</sup>. (C<sub>58</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>) (1020.4): Calcd. C, 68.19; H, 7.10; N, 2.74; S, 18.83. Found C, 68.22; H, 7.12; N, 2.73; S, 18.86.



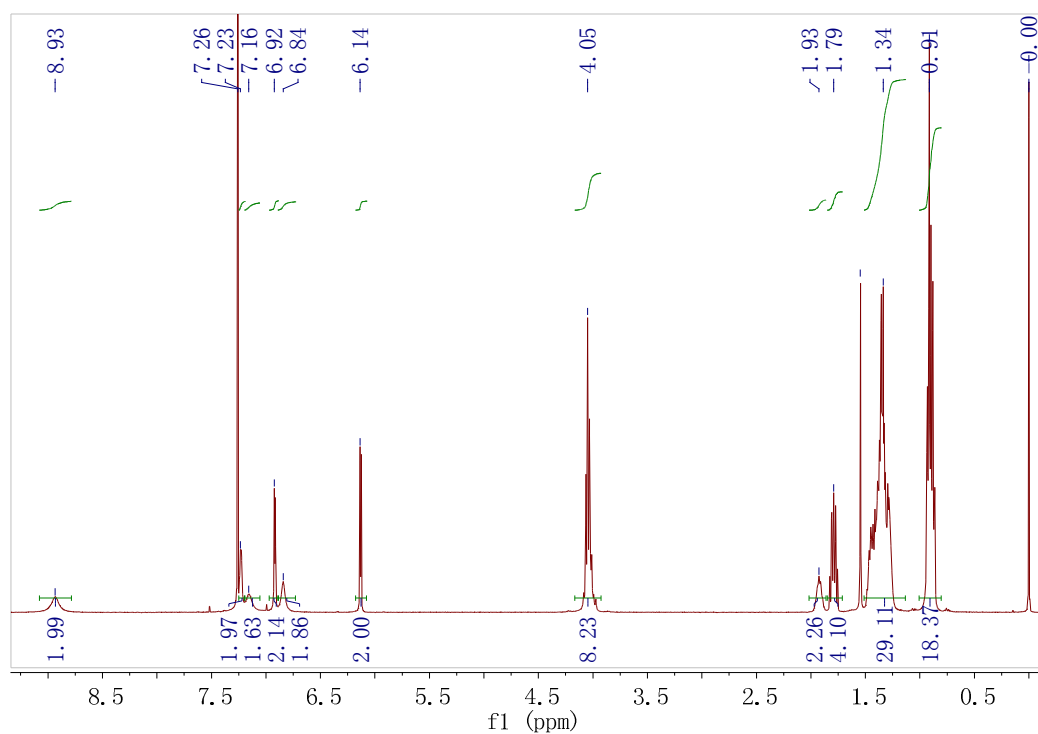


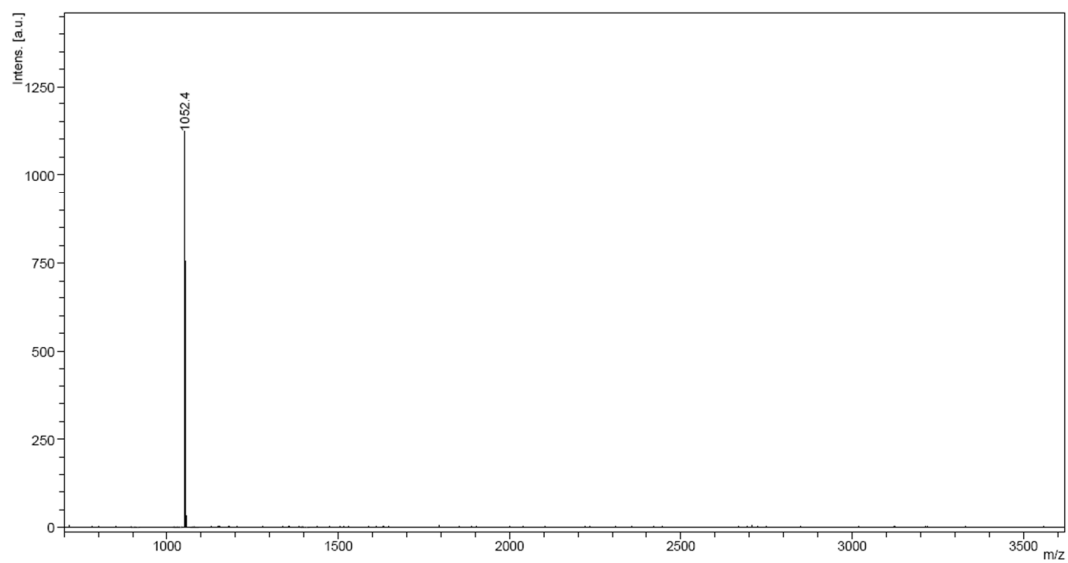
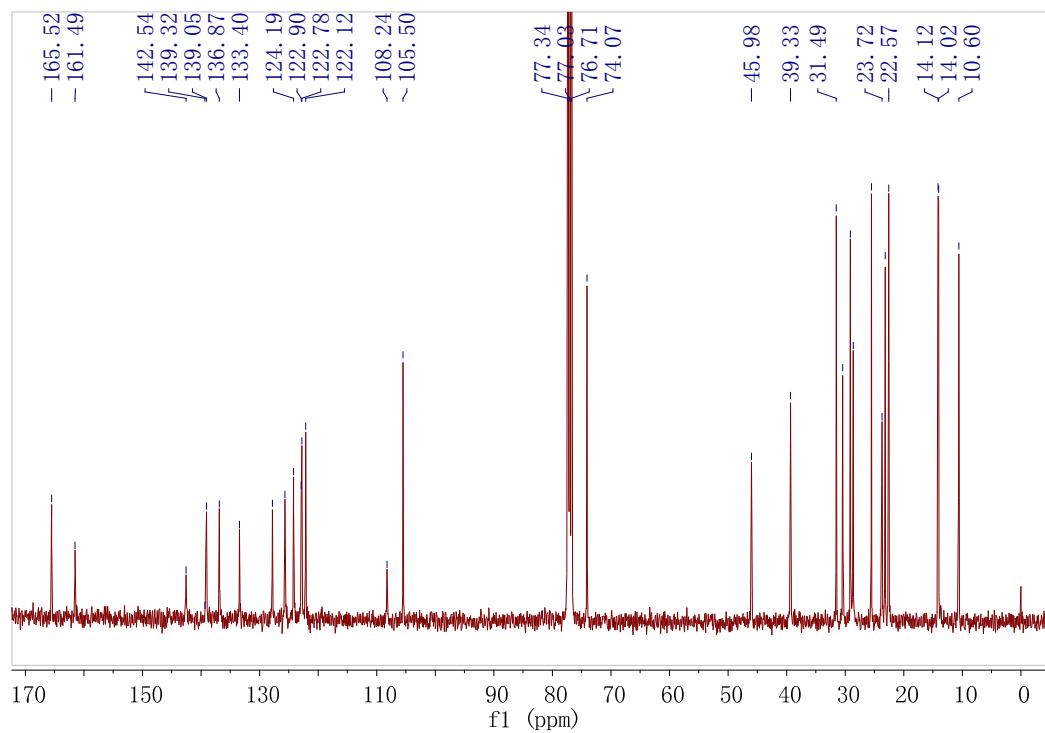
**2,5-Di-(2-ethylhexyl)-3,6-bis-(5''-*n*-(hexyloxy)-[2,2',5',2'']terthiophen-5-yl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (3).** It was obtained in the similar procedure as compound **1** (83% yield).

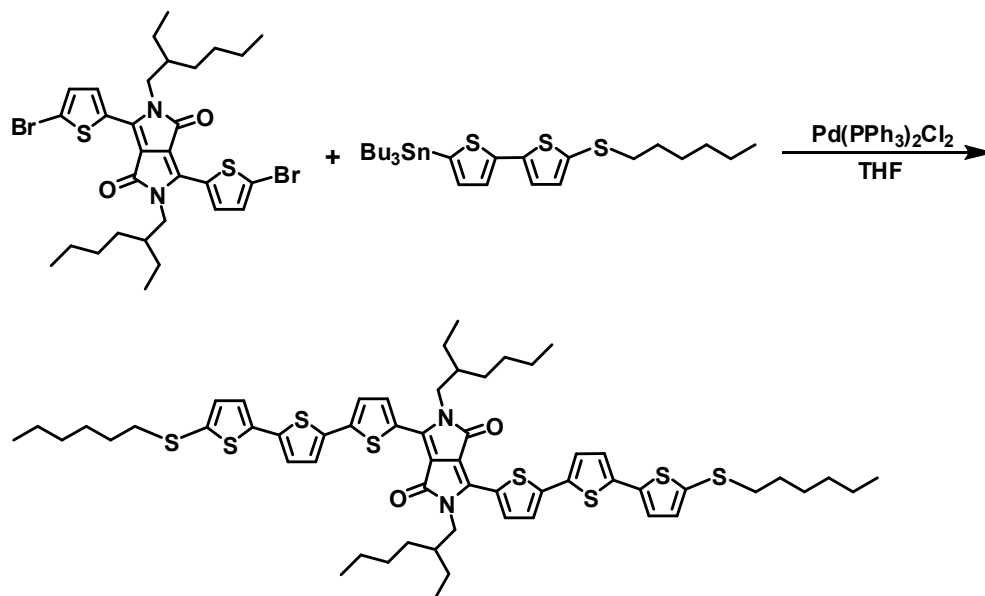
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 8.93 (br, 2H), 7.23 (d, 2H), 7.16 (br, 2H), 6.92 (d, 2H), 6.84 (br, 2H), 6.14 (d, 2H), 4.05 (m, 8H), 1.93 (m, 2H), 1.79 (m, 4H), 1.22-1.49 (m, 28H), 0.91 (m, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 165.52, 161.49, 142.54, 139.32, 139.05, 136.87, 133.40, 127.79, 125.65, 124.19, 122.90, 122.78, 122.12, 108.24, 105.50, 74.07,

45.98, 39.33, 31.49, 30.41, 29.10, 28.61, 25.52, 23.72, 23.17, 22.57, 14.12, 14.02, 10.60.

MALDI-TOF-MS:  $m/z$  1052.4  $[M]^+$ . ( $C_{58}H_{72}N_2O_4S_6$ ) (1052.4): Calcd. C, 66.12; H, 6.89; N, 2.66; S, 18.26. Found C, 66.18; H, 6.91; N, 2.65; S, 18.20.







**2,5-Di-(2-ethylhexyl)-3,6-bis-(5''-*n*-(hexylthio)-[2,2',5',2'']terthiophen-5-yl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (4).** It was synthesized in the similar procedure as compound **1** (82% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 8.92 (br, 2H), 7.27 (d, 2H), 7.19 (br, 2H), 7.07 (d, 2H), 7.04 (br, 2H), 7.01 (d, 2H), 4.03 (m, 4H), 2.84 (m, 4H), 1.92 (m, 2H), 1.65 (m, 4H), 1.22-1.48 (m, 28H), 0.89 (m, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  (ppm): 161.44, 142.19, 139.33, 139.08, 136.83, 135.49, 134.96, 133.69, 128.21, 125.75, 124.56, 124.20, 108.35, 45.83, 39.33, 38.90, 31.35, 30.42, 29.42, 28.61, 28.16, 23.73, 23.16, 22.55, 14.12, 14.02, 10.60.

MALDI-TOF-MS:  $m/z$  1084.3  $[\text{M}]^+$ . ( $\text{C}_{58}\text{H}_{72}\text{N}_2\text{O}_2\text{S}_8$ ) (1084.3): Calcd. C, 64.16; H, 6.68; N, 2.58; S, 23.63. Found C, 64.19; H, 6.70; N, 2.57; S, 23.60.

