Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of 5-alkyl[3,4-c]thienopyrrole-4,6-dione-based polymers by a Pd-catalyzed oxidative C-H/C-H homopolymerization reaction

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Content

1. General experimental methods

Instrumentation

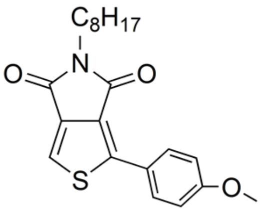
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 using residual solvent peak as a reference. High-resolution matrix-assisted laser desorption ionization (MALDI) mass spectra were collected with a Fourier transform-ion cyclotron resonance mass spectrometer instrument (Varian 7.0T FTICR-MS). Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) in tetrahydrofuran at 25 °C using Waters 1525 with Waters Styragel HT gel columns. For the calibration curve, a series of monodisperse polystyrene standards (Shodex) was used. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209 instrument under a purified nitrogen gas flow with a 10 °C min^{-1} heating rate. UV-vis-NIR absorption spectra were recorded using a Shimadzu UV-2550 and dropcast films on glass plates were used for the solid-state measurements. Optical bandgaps were determined from the onset of the absorption band. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer. All CV measurements were carried out at room temperature with a conventional three-electrode configuration using a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Acetonitrile was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 M) in acetonitrile was used as the support electrolyte, and the scan rate was 100 mV s $^{-1}$.

2. Synthesis of the monomers

Chemicals

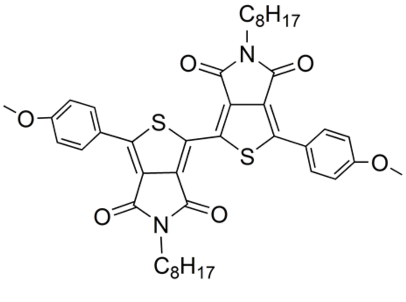
All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo-[1,2-b:4,5-b']dithiophene, ,4’-Bis(2-ethyl-hexyl)-5,5’-bis(trimethyltin)-dithieno[3,2-b:2,3-d]silole was bought from ZhongShen-huateng and all other starting organic compounds and organometallic compounds were purchased from Alfa Aesar, Aldrich, TCI and used without further purification. 1-iodo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 1-iodo-5-(2-octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione, 5-(2-octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione[1] were prepared according to procedures reported in the literature. All the monomers were carefully purified prior for use in the polymerization reaction.

1-(4-methoxyphenyl)-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione **(**Compound **1**, Scheme S1**)**



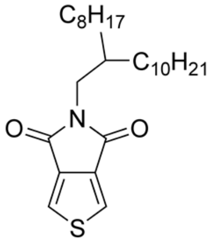
1-Iodo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione(0.1g, 0.255 mmol), 4-methoxyphenylboronic acid (0.043 g, 0.28 mmol), potassium carbonate (0.077 g, 0.56 mmol) in 3 ml of DMSO/toluene (1:1) was degassed twice with argon followed by the addition of Pd(dppf)Cl_2 (10 mg). After stirring at 80 °C for 4 h under argon, the reaction mixture was poured into water (30 mL) and extracted with dichloromethane. The organic layer was washed with water and then dried over Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluant to yield a white solid (0.08 g, 0.215 mmol, yield: 84.4%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 2H), 7.63 (s, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.87 (-OC$\underline{H}_3$, s, 3H), 3.68 (-NC$\underline{H}_2$, t, 2H), 1.65 (m, *J* = 6.9 Hz, 2H), 1.29 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39, 161.23, 137.98, 130.08, 129.58 (two peaks overlap), 128.02, 122.18, 114.83, 114.33 (two peaks overlap), 55.46, 38.56, 31.81, 29.20(two peaks overlap), 28.52, 26.96, 22.65, 14.09 ppm. MS (MALDI-TOF): $C_{21}H_{25}NO_3S$, calcd for $[M]^+$, 371.16; found, 371.13.

Bis(1-(4-methoxyphenyl)-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione) (Compound **2**, Scheme S1)



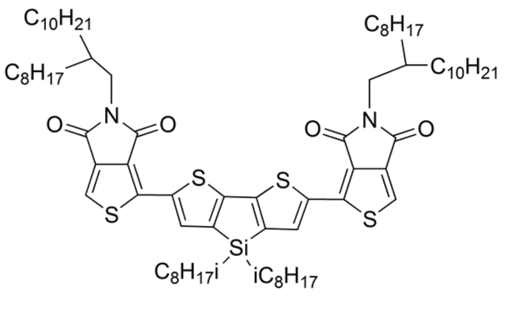
1-Methoxyphenyl-5-octyl-4H-thiophene [3,4-c] pyrrole-4, 6-(5H)-dione (0.06 g, 0.162 mmol), $Cu(OAc)_2$ (0.062 g, 0.340 mmol), potassium carbonate (0.048 g, 0.35 mmol) were put in a 25 mL round bottom flask then purged with N_2. DMAc (4 mL) was added and the mixture was stirred at 110 °C for 10 min, then palladium acetate (0.025 g, 0.111 mmol) dissolved in 1mL of DMAc was added to the reaction flask, and reacted for 5 hours. After the whole mixture was cooled to room temperature and poured in 20 mL of water, and extracted with chloroform, the organic phase was concentrated. The crude product was purified by column chromatography on silica gel using dichloromethane as eluent to yield a yellow solid (0.058 g, 0.079 mmol, yield: 98%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 4H), 6.97 (d, *J* = 8.7 Hz, 4H), 3.87 (-OC$\underline{H}_3$, s, 6H), 3.67 (-NC$\underline{H}_2$, t, 4H), 1.68 (m, 4H), 1.38–1.24 (m, 20H), 0.87 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.71, 162.49, 161.58, 148.17, 133.62, 130.20, 127.80, 122.91, 114.33, 55.47, 38.73, 31.80, 29.21 (two peaks overlap), 28.53, 27.02, 22.64, 14.11 ppm. MS (MALDI-TOF): $C_{42}H_{48}N_2O_6S_2$, calcd for $[M+H]^+$, 740.3; found, 741.33.

5-(2-Octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione (Compound **3**, Scheme S2)



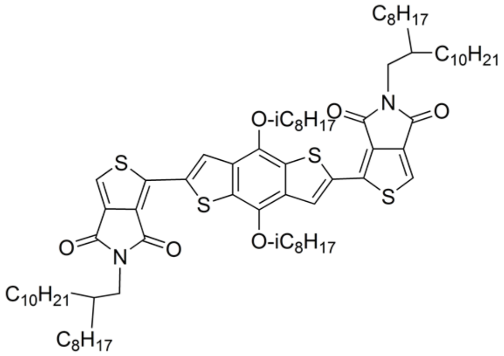
A solution of thieno[3,4-c]furan-1,3-dione (1.0 g, 6.49 mmol), DMAP (1.19 g, 9.7 mmol) and 2-octyldodecan-1-amine (2.90 g, 3.5 mL, 0.97 mmol) in dioxane (123 mL) was stirred at 55 °C for 20 hours. Acetic anhydride (36 mL) was added and the reaction mixture was stirred for 4 hours at 80 °C. Then the reaction was quenched with water (50 mL) and was extracted with dichloromethane (4×40 mL). The combined organic layers were dried with $MgSO_4$ and evaporated to dryness to obtain a dark powder. The crude product was purified by column chromatography using dichloromethane/petroleum ether (1:2) as eluent to yield the title product as a white solid (2.4 g, 5.53 mmol, yield: 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 2H), 3.50 (-NC$\underline{H}_2$, d, 2H), 2.04 (m, 1H), 1.26 (m, 32H), 0.88 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.97, 136.63, 125.45, 42.76, 36.88, 31.93 (two peaks overlap), 31.43, 31.22, 30.00, 29.77–29.47 (m), 29.35 (two peaks overlap), 26.70, 26.26, 22.71, 14.15 ppm. MS (MALDI-TOF): $C_{26}H_{43}NO_2S$, calcd for $[M+H]^+$, 433.3; found, 434.3.

Synthesis of M2 (Compound **5**, Scheme S3)



1-Iodo-5-(2-octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione (1.58g, 2.82 mmol), 4,4'-Bis(2-ethyl-hexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2,3-d]silole (1.0 g, 1.34 mmol) in 30ml dry DMF was added $Pd(PPh_3)_4$ (180 mg, 0.15 mmol). The solution was heated at 80 °C under argon for 24 hours. The whole mixture was cooled to room temperature and poured into 50mL of water, and extracted with chloroform, the organic phase was concentrated. The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (2:1) as eluent to yield a red solid (1.26 g, 0.98 mmol, yield: 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.58 (s, 2H), 3.55 ($-NC\underline{H}_2$, d, 4H), 1.89 (m, 2H), 1.27 (m, 66H), 1.17 (m, 12H), 1.03 (dd, 4H), 0.88 (m, 12H), 0.80 (t, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.07, 162.59, 150.77 (three peaks overlap), 146.38 (three peaks overlap), 139.79, 137.45, 134.85, 132.86 (three peaks overlap), 127.24, 121.84, 42.86, 36.95, 35.87, 35.64, 31.94 (two peaks overlap), 31.49, 30.08, 30.07–29.52 (m), 29.37 (two peaks overlap), 28.89 (two peaks overlap), 26.32, 23.04 (two peaks overlap), 22.72, 17.50, 14.16 (two peaks overlap), 10.78 ppm. MS (MALDI-TOF): $C_{76}H_{120}N_2O_4S_4Si$, calcd for $[M]^+$, 1280.79; found, 1280.76.

Synthesis of M3 (Compound **7**, Scheme S4)



1-Iodo-5-(2-octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione (1.0 g, 2.55 mmol), 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (0.9867 g, 1.28 mmol) in 30ml dry DMF was added $Pd(PPh_3)_4$ (145 mg, 0.12 mmol). The solution was heated at 80 °C under argon for 24 hours. The whole mixture was cooled to room temperature and the precipitate was filtered. The compound was isolated as a red solid following drying under vacuum at 60 °C over a period of 12 hours(1.022 g, 1.05 mmol, yield: 82.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 7.70 (s, 2H), 4.31 ($-OC\underline{H}_2$, d, 4H), 3.56 ($-NC\underline{H}_2$, d, 4H), 1.88 (m, 4H), 1.78 – 1.57 (m, 8H), 1.34 (m, 70H), 1.06 (m, 6H), 0.97 (m, 6H), 0.86 (t, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.76, 145.20, 139.61, 137.86, 132.58, 132.32, 130.37, 129.58, 123.73, 123.31, 42.92, 40.69, 36.94, 31.95, 31.53, 30.50, 30.04, 29.52 (two peaks overlap), 29.27, 26.35, 23.88, 23.19, 22.72, 14.21 (two peaks overlap), 11.41 ppm. MS (MALDI-TOF): $C_{78}H_{12}0N_2O_6S_4$, calcd for $[M]^+$, 1308.8; found, 1308.5.

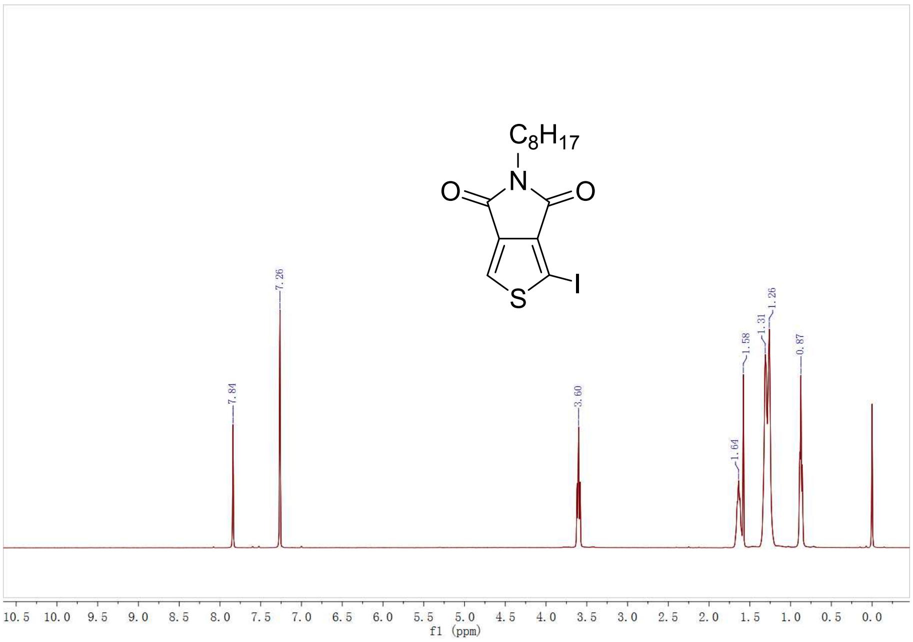


Fig. S1 ^{1}H NMR spectrum of 1-iodo-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione.

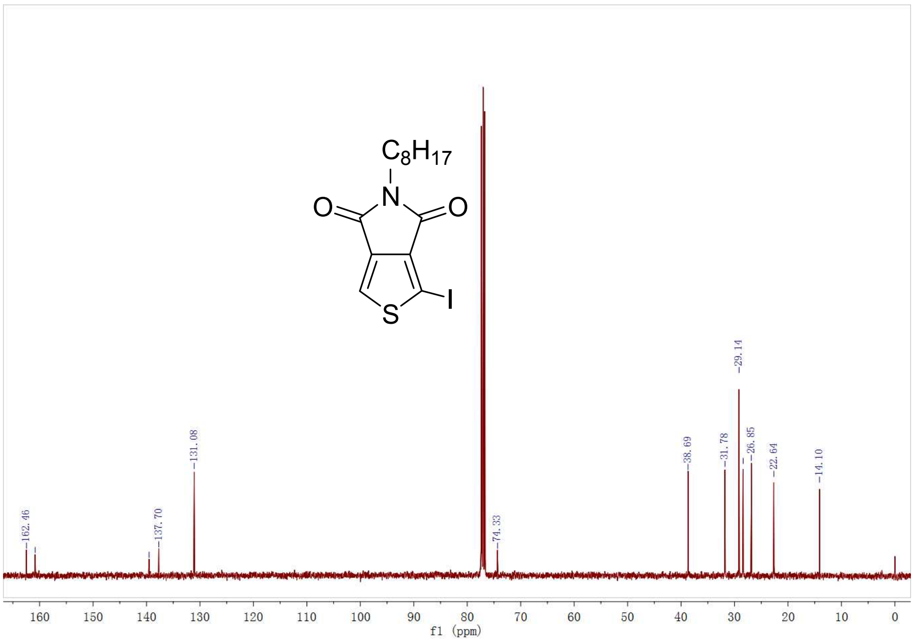


Fig. S2 ^{13}C NMR spectrum of 1-iodo-5-octyl-5H-thieno[3,4-c]pyrrole-4,6-dione.

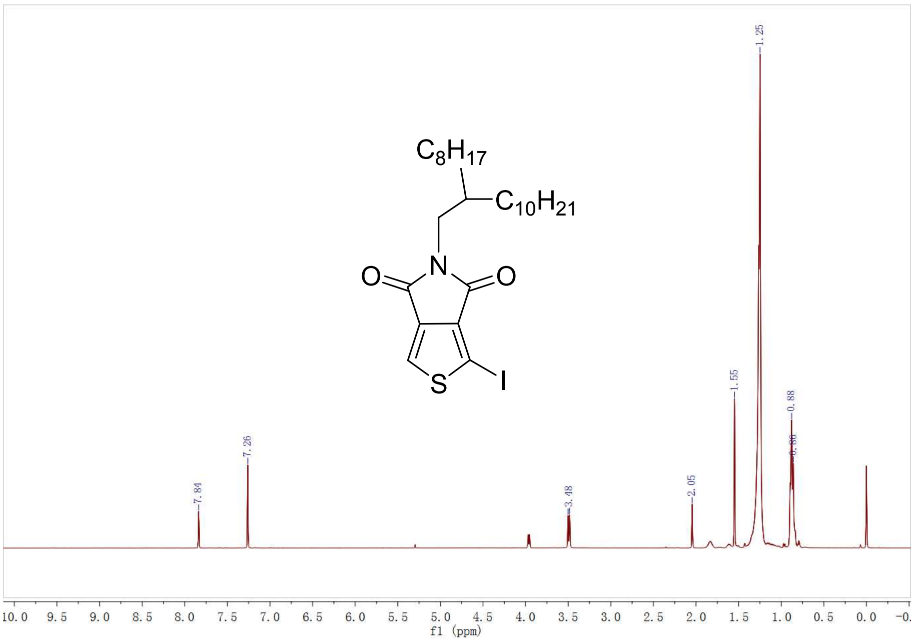


Fig. S3 ^{1}H NMR spectrum of 1-iodo-5-(2-octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione.

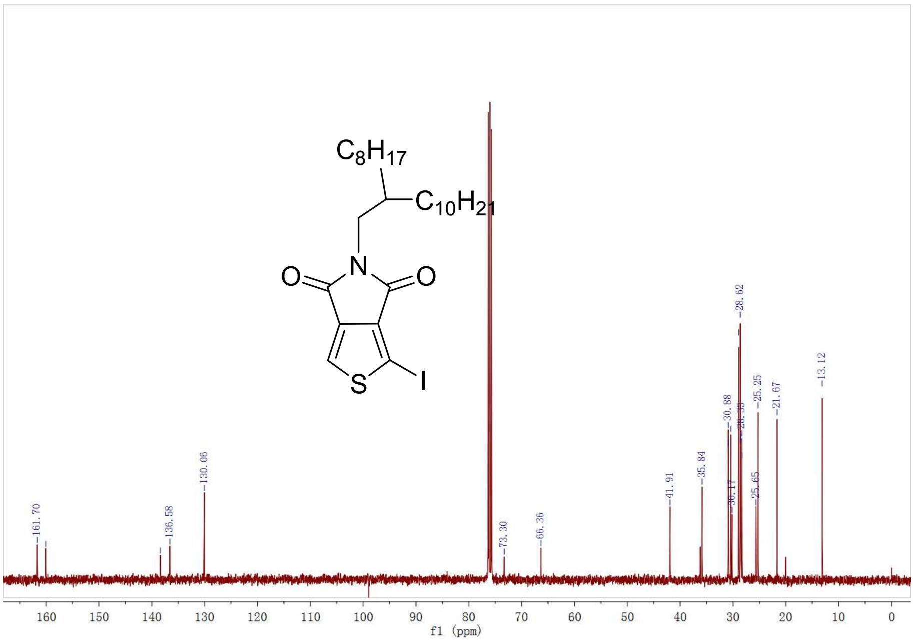


Fig. S4 ^{13}C NMR spectrum of 1-iodo-5-(2- octyldodecyl)-5H-thieno- [3,4-c]pyrrole-4,6-dione

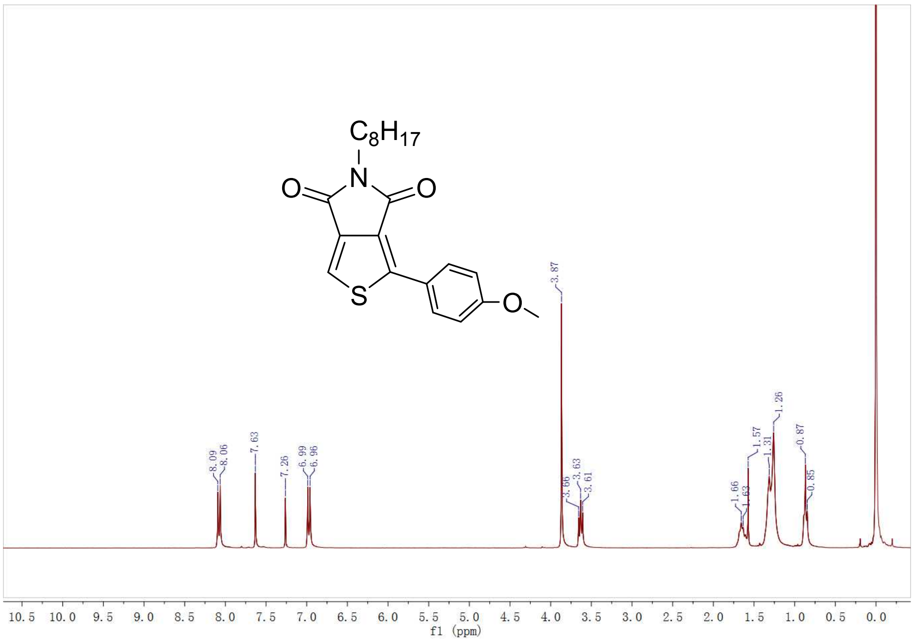


Fig. S5 ^{1}H NMR spectrum of 1-(4-methoxyphenyl)-5-octyl-5H-thieno-[3,4-c]-pyrrole-4,6-dione (Compound **1**).

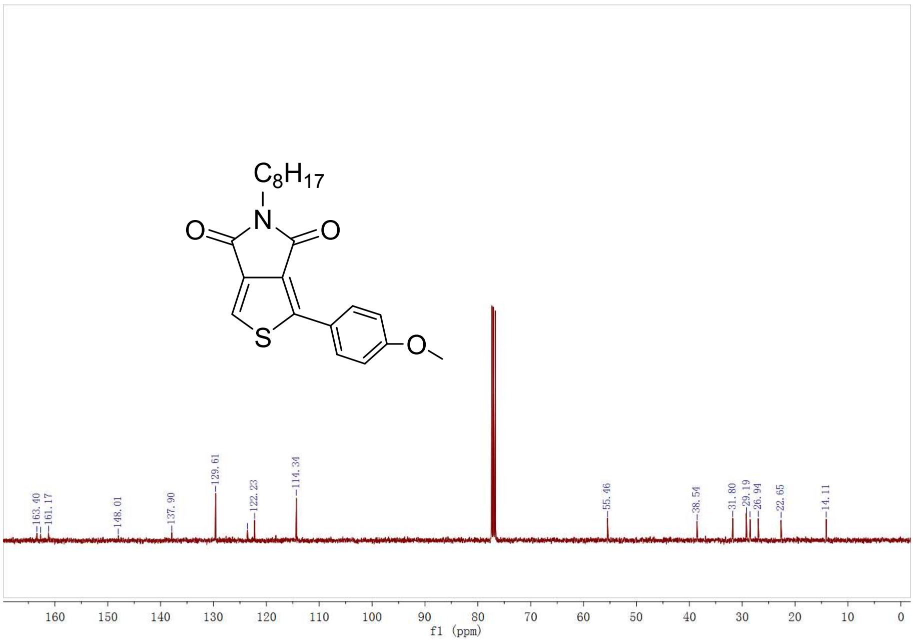


Fig. S6: ^{13}C NMR spectrum of 1-(4-methoxyphenyl)-5-octyl-5H-thieno- [3,4-c]pyrrole-4,6-dione (Compound **1**).

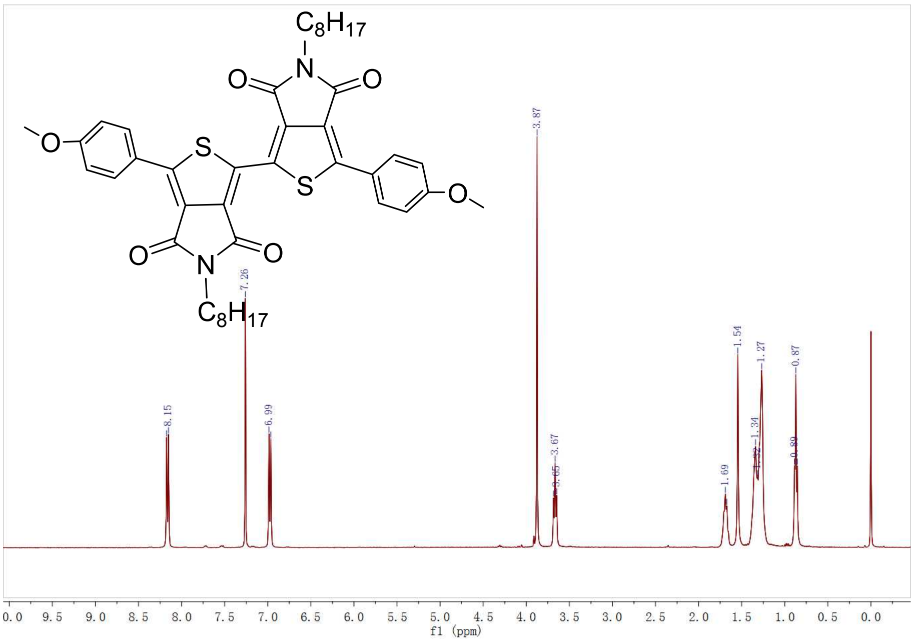


Fig. S7 ^{1}H NMR spectrum of Bis(1-(4-methoxyphenyl)-5-octyl-5H-thieno- [3,4-c]pyrrole-4,6-dione) (Compound **2**).

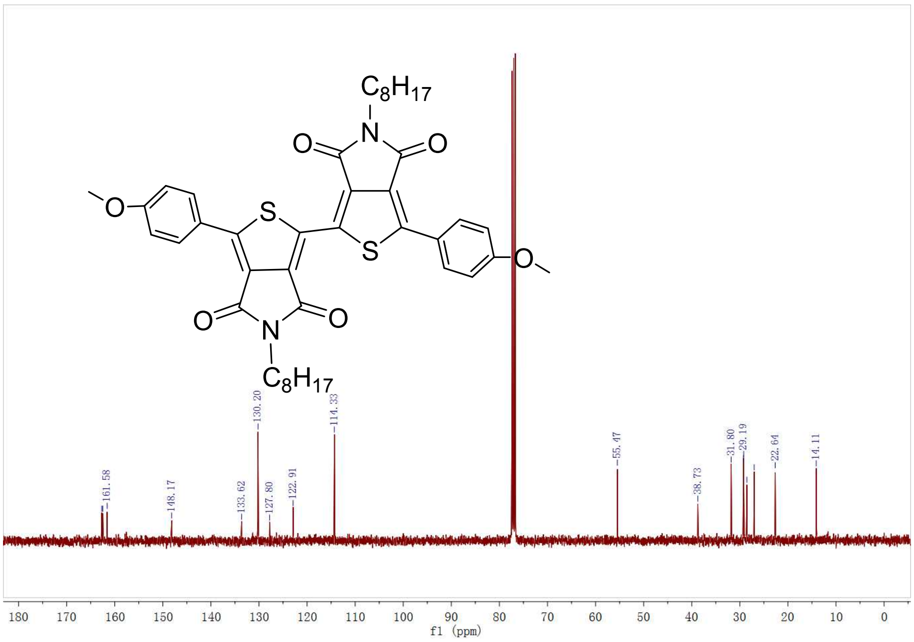


Fig. S8 ^{13}C NMR spectrum of Bis(1-(4-methoxyphenyl)-5-octyl-5H-thieno- [3,4-c]pyrrole-4,6-dione) (Compound **2**).

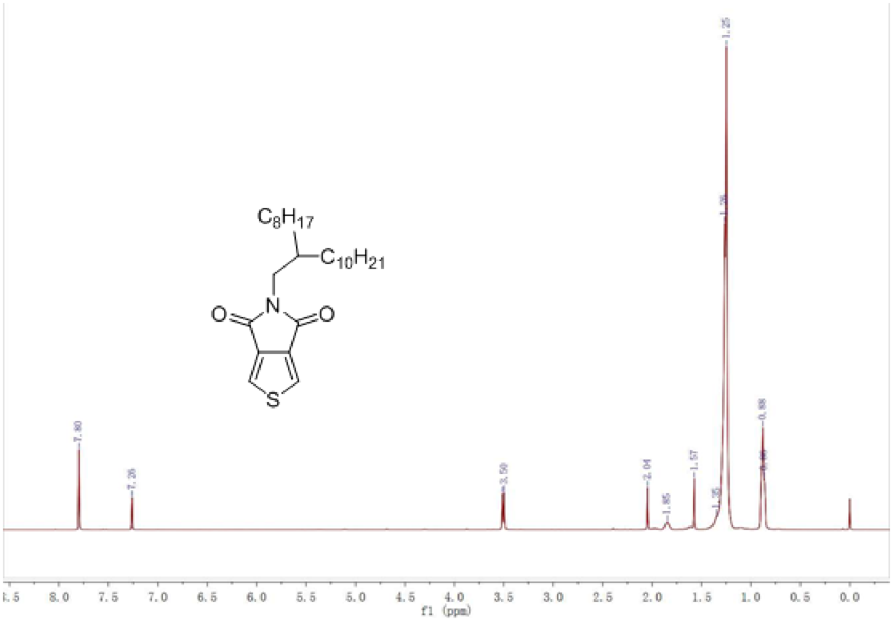


Fig. S9 ^1H NMR spectrum of 5-(2-octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione (Compound **3**).

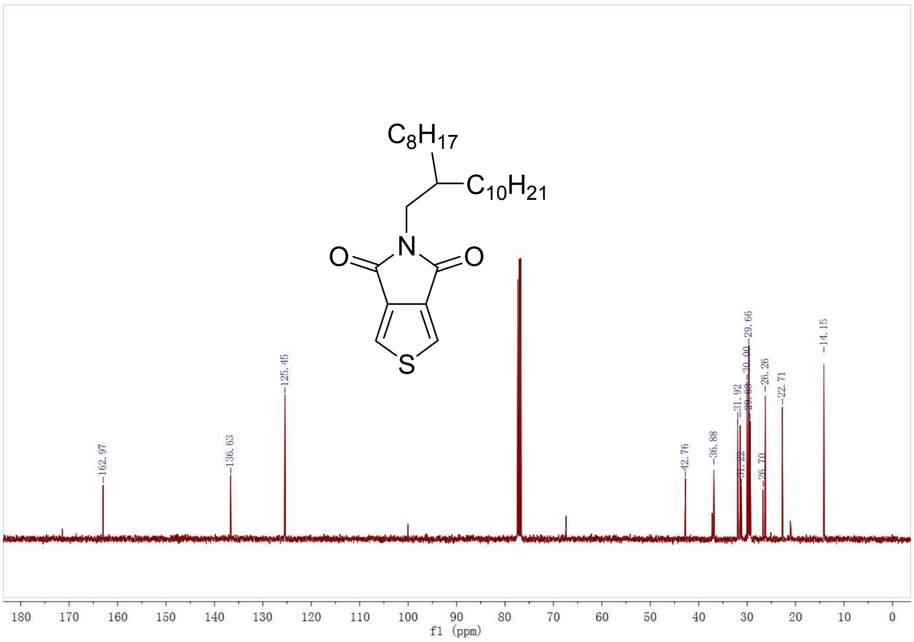


Fig. S10 ^{13}C NMR spectrum of 5-(2-octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione (Compound **3**).

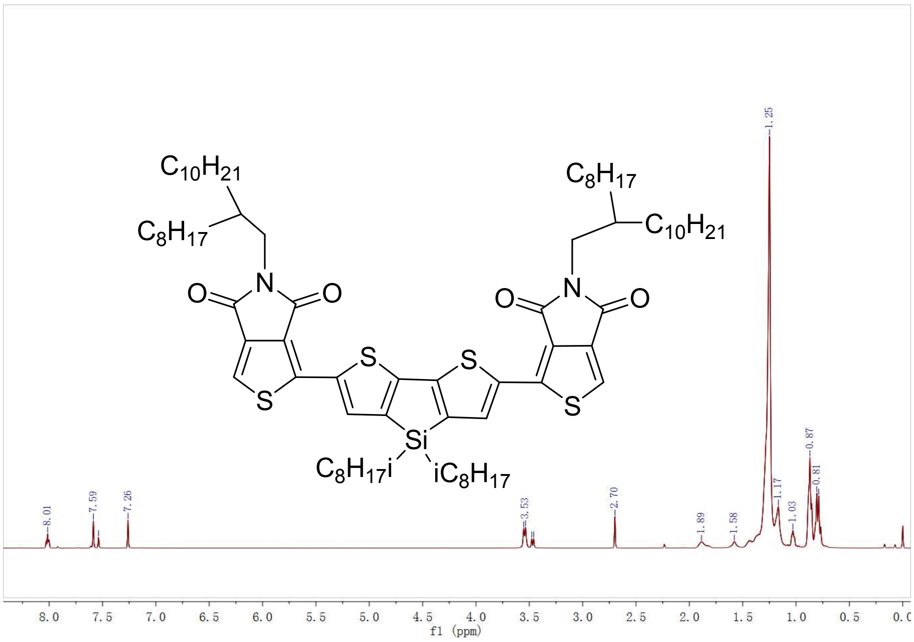


Fig. S11 ^{1}H NMR spectrum of **M2** (Compound **5**).

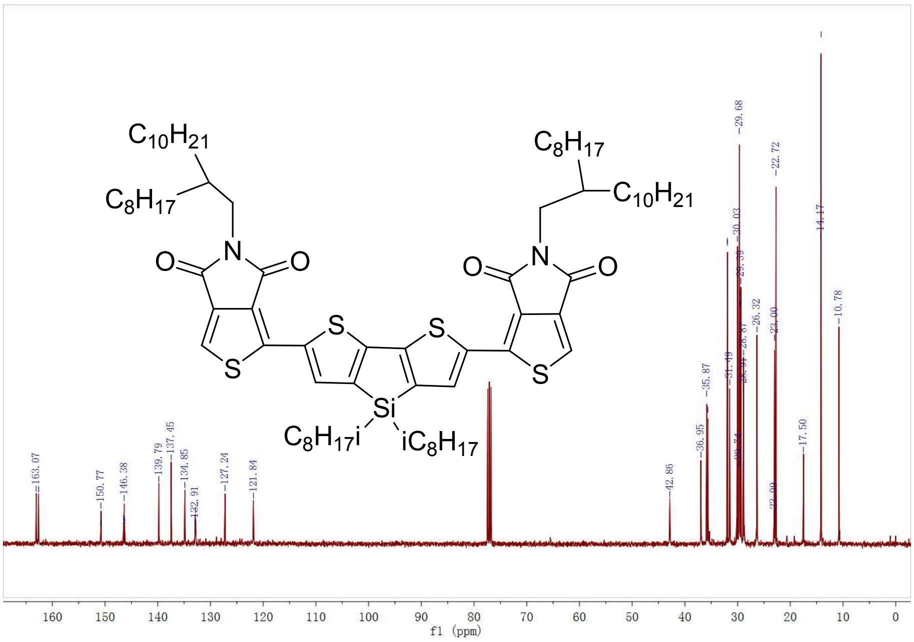


Fig. S12 ^{13}C NMR spectrum of **M2** (Compound **5**).

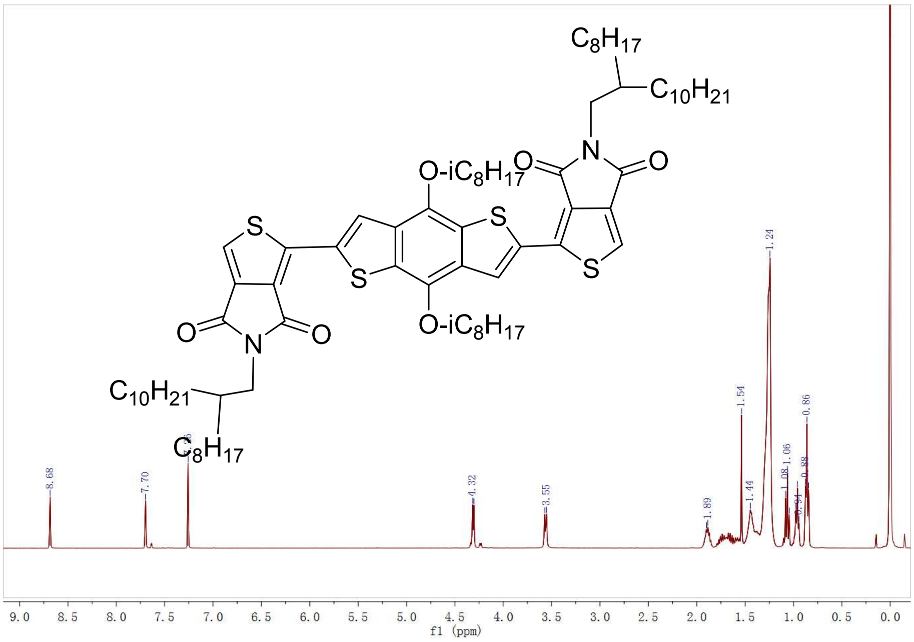


Fig. S13 ^{1}H NMR spectrum of **M3** (Compound **7**).

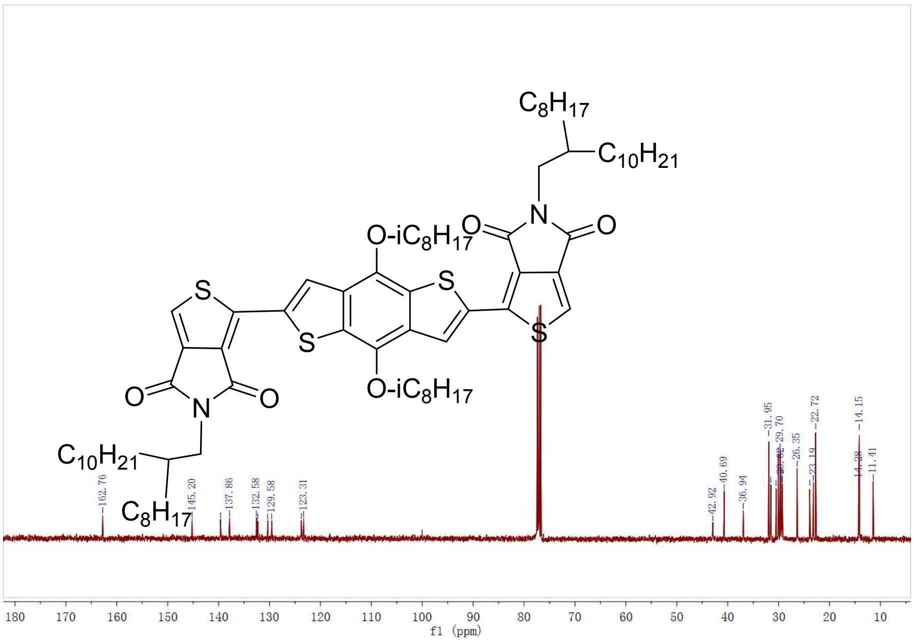


Fig. S14: ^{13}C NMR spectrum of **M3** (Compound **7**).

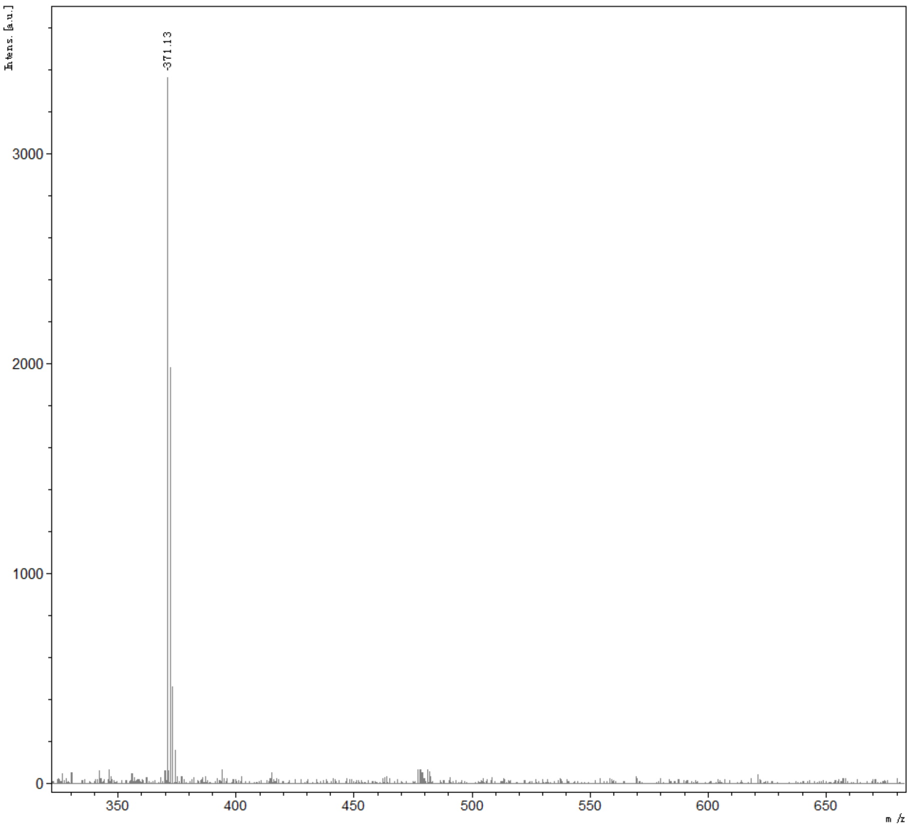


Fig. S15 MS(MALDI-TOF) spectrum of of 1-(4-methoxyphenyl)-5-octyl-5H-thieno-[3,4-c]pyrrole-4,6-dione (Compound **1**).

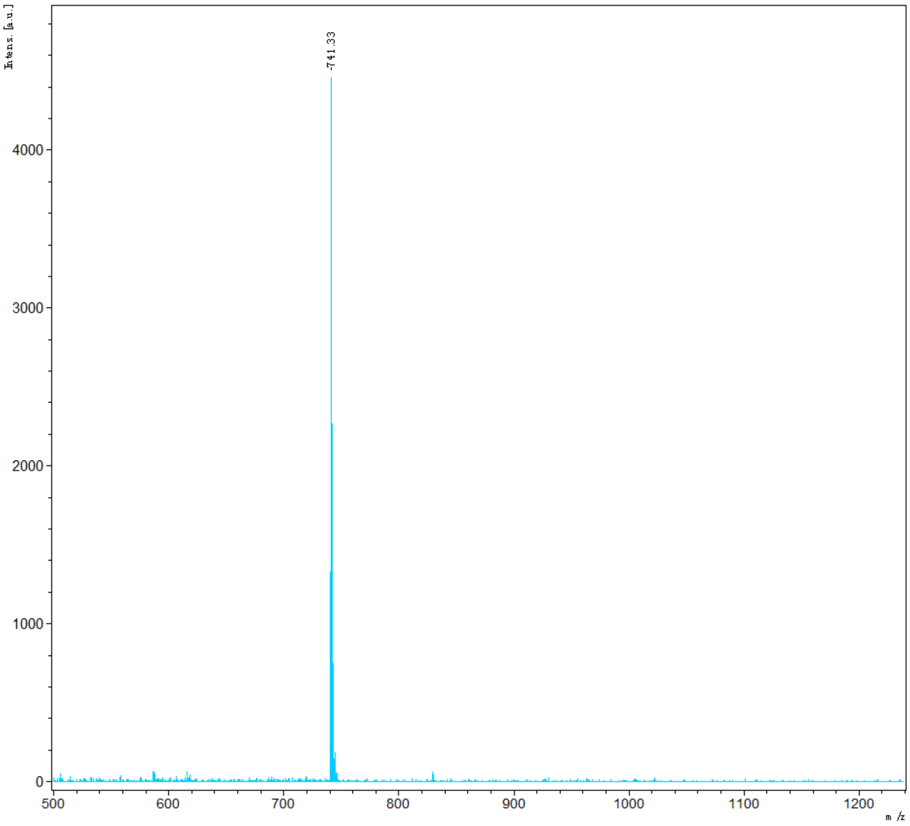
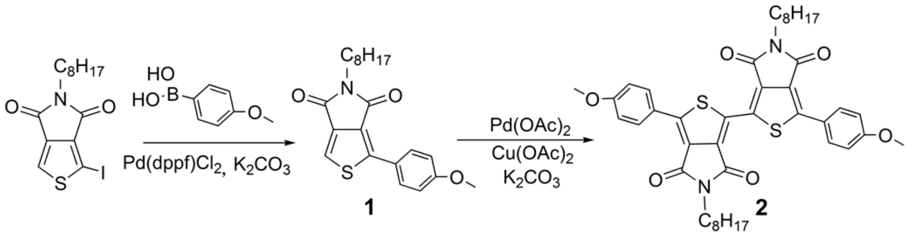
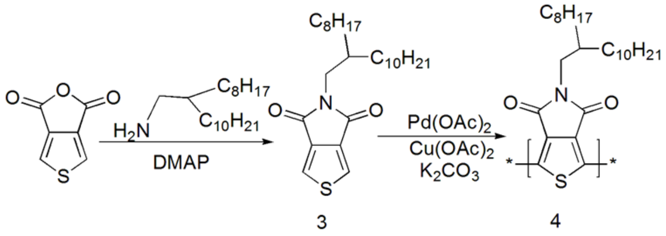


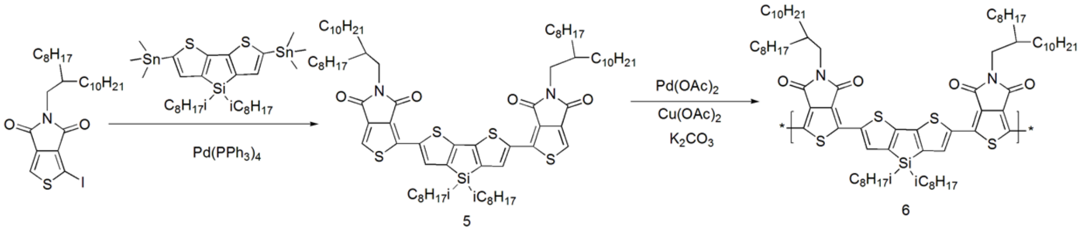
Fig. S16 MS(MALDI-TOF) spectrum of Bis(1-(4-methoxyphenyl)-5-octyl-5H-thieno-[3,4-c]pyrrole-4,6-dione) (Compound **2**).



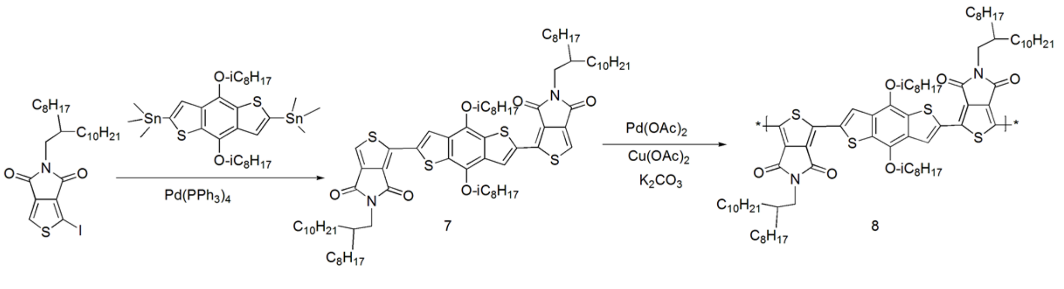
Scheme S1 Synthesis route of Compound **2**.



Scheme S2 Synthesis route of **P1** (Compound **4**).



Scheme S3 Synthesis route of **P2** (Compound **6**).



Scheme S4 Synthesis route of **P3** (Compound **8**).

3. Synthesis of polymers by Pd-catalytic oxidative C-H/C-H coupling reaction

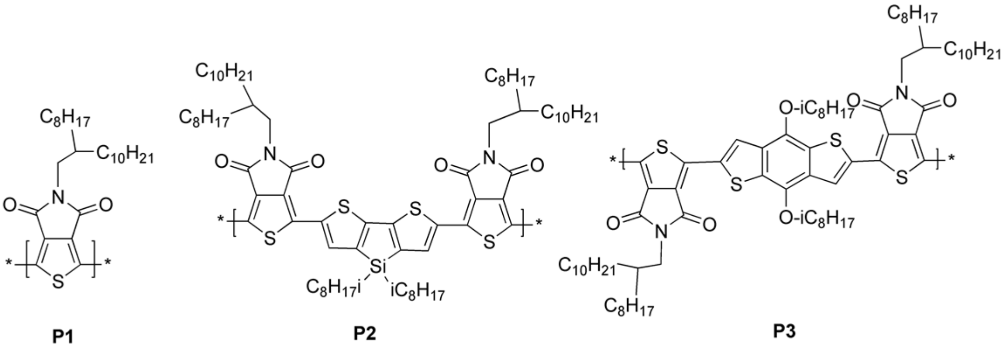


Fig. S17 Chemical structures of **P1, P2, P3**.

Polymerization procedure of P1 (compound 4, Scheme S2)

5-(2-Octyldodecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione(compound **3**) (0.50 g, 0.40 mmol), $Cu(OAc)_2$ (0.17 g, 0.85 mmol), potassium carbonate (0.185 g, 1.2 mmol) were put in a 25 mL round bottom flask then purged with N_2. DMAc (4 mL) was added and the mixture was stirred at 110 °C for 10 min, then palladium acetate (9.0 mg) dissolved in 1mL of DMAc was added to the reaction flask, reacted for 48 hours. After the whole mixture was cooled to room temperature and poured into 50 mL of water, and extracted with chloroform, the organic phase was concentrated. Then it was dissolved in a little chloroform, and poured into 100mL of cold methanol, the precipitate was filtered. Soxhlet extractions with methanol followed by hexanes removed catalytic residues and low-molecular-weight materials. Polymers were then extracted with chloroform. The solvent was reduced to about 2 mL and the mixture was poured into cold methanol. The precipitate was filtered, and the polymer was isolated as a dark solid following drying under vacuum at 60 °C for 12 hours. P1 was achieved in 96% yield of soluble fraction on $CHCl_3$. M_n of 4kDa.

Polymerization procedure of P2 (compound 6, Scheme S3)

See **P3** (Compound **8**, Scheme S4). **P2** was achieved in 81% yield of soluble fraction on $CHCl_3$. M_n of 16 kDa.

Polymerization procedure of P3 (compound 8, Scheme S4)

Compound **7** (0.5 g, 0.38 mmol), $Cu(OAc)_2$ (0.16 g, 0.76 mmol), potassium carbonate (0.11 g, 0.80 mmol) were put in a 25 mL round bottom flask then purged with N_2. DMAc (4 mL) was added and the mixture was stirred at 110 °C for 10 min, then palladium acetate (8.5 mg) dissolved in 1 mL of DMAc was added to the reaction flask and reacted for 72 hours. The mixture was cooled to room temperature and poured into 100 mL of cold methanol. The precipitate was filtered out as the crude product. Soxhlet extraction with methanol was used to remove the catalyst. The polymer products were then obtained by extraction using chloroform. The extract was condensed to about 2 mL and the mixture was poured into cold methanol and this was followed by hexane extraction to remove the low-molecular-weight materials. The precipitate was filtered, and the final polymer was isolated as a dark solid following drying under vacuum at 60 ºC for 12 hours. **P3** was achieved in 88% yield of soluble fraction on $CHCl_3$. M_n of 18 kDa.

Polymerization procedure of P3´´

P3´ (0.4 g, M_n ~7 kDa, which was prepared under the similar reaction conditions to **P3** except the polymerization time of 24 hours), $Cu(OAc)_2$ (0.12 g, 0.60 mmol), potassium carbonate(0.87g, 0.63mmol)were put in a 25 mL round bottom flask then purged with N_2. DMAc (4 mL) was added and the mixture was stirred at 110 ºC for 10 min, then palladium acetate (7.0 mg) dissolved in 1mL of DMAc was added to the reaction flask and reacted for 48 hours. The mixture was cooled to room temperature and poured into 100 mL of cold methanol. The precipitate was filtered out as the crude product. Soxhlet extraction with methanol was used to remove the catalyst. The polymer products were then obtained by extraction using chloroform. The extract was condensed to about 2 mL and the mixture was poured into cold methanol. The precipitate was filtered, and the final polymer was isolated as a dark solid following drying under vacuum at 60 ºC for 12 hours. **P3´´** was achieved in 80% yield of soluble fraction on $CHCl_3$. M_n of 23 kDa.

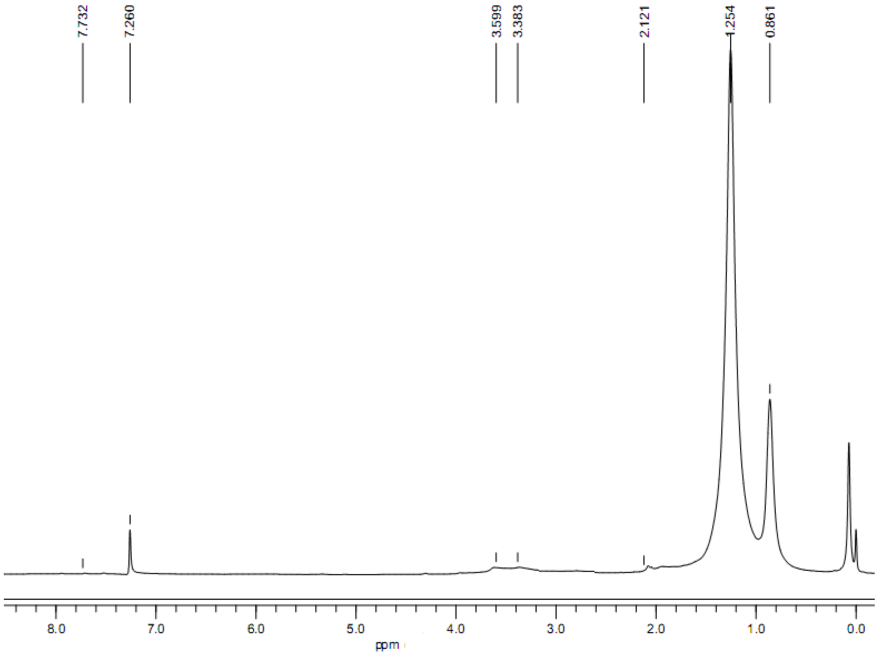


Fig. S18 ^{1}H NMR spectrum of **P1**.

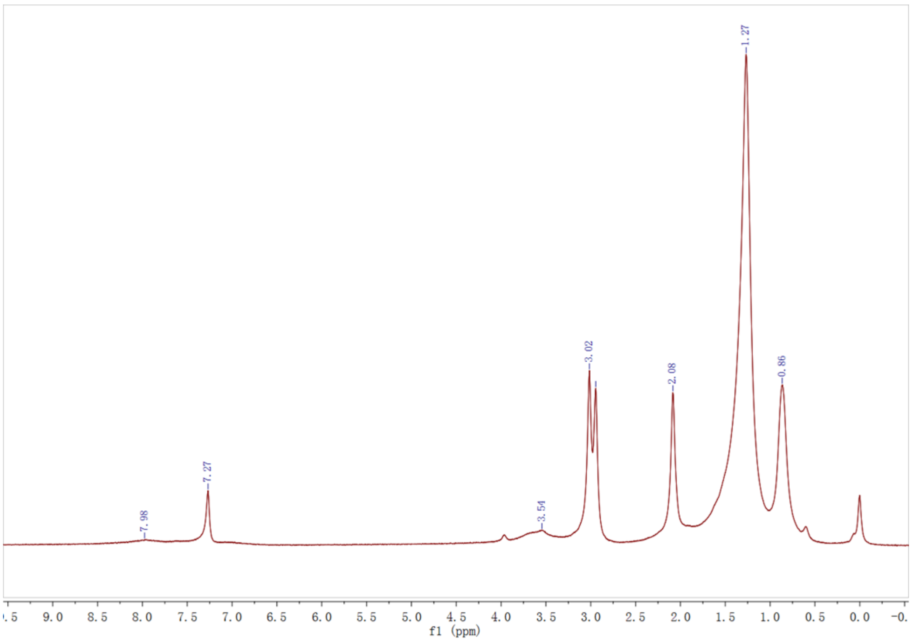


Fig. S19 ^{1}H NMR spectrum of **P2**.

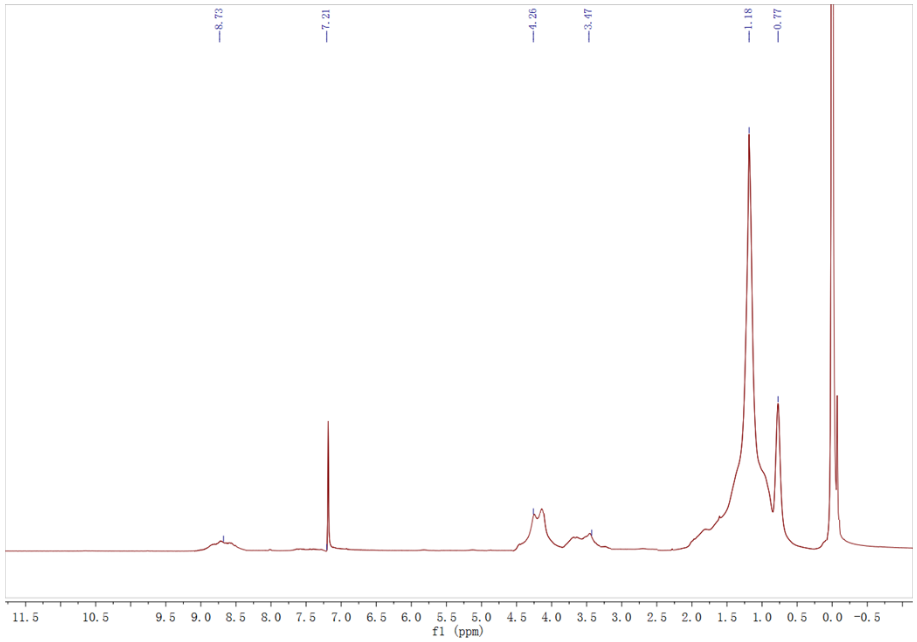


Fig. S20 ^{1}H NMR spectrum of **P3**.

4. Solution-, solid-state UV-visible absorption spectra, TGA and SEC Trace of P1, P2, P3

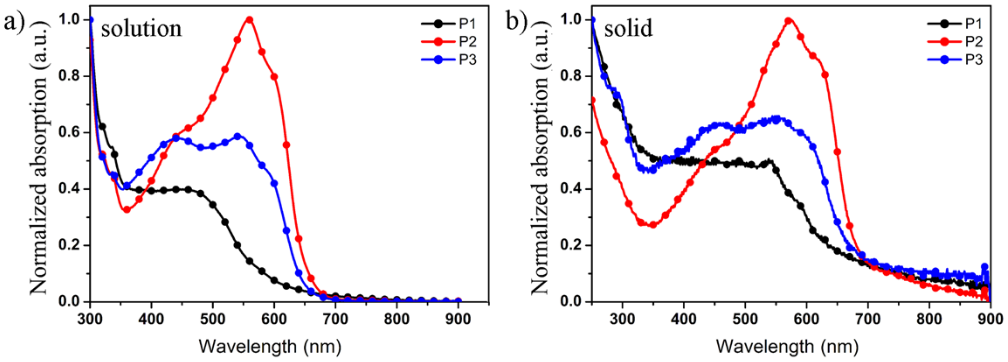


Fig. S21 solution-, solid-state UV-visible absorption spectra of **P1, P2, P3**.

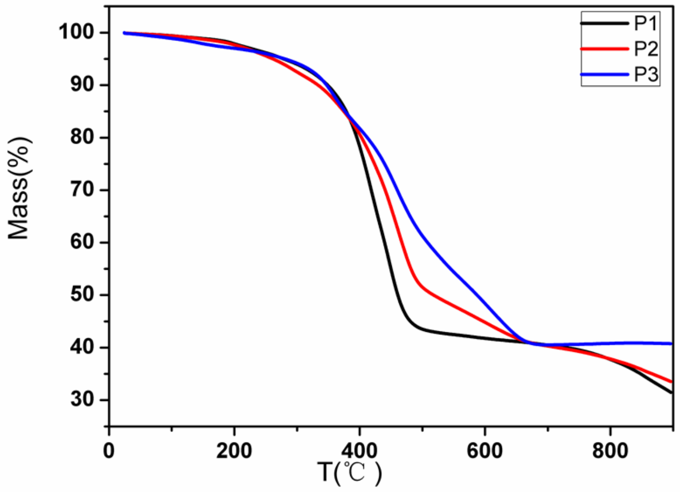


Fig. S22 TGA of **P1, P2, P3**.

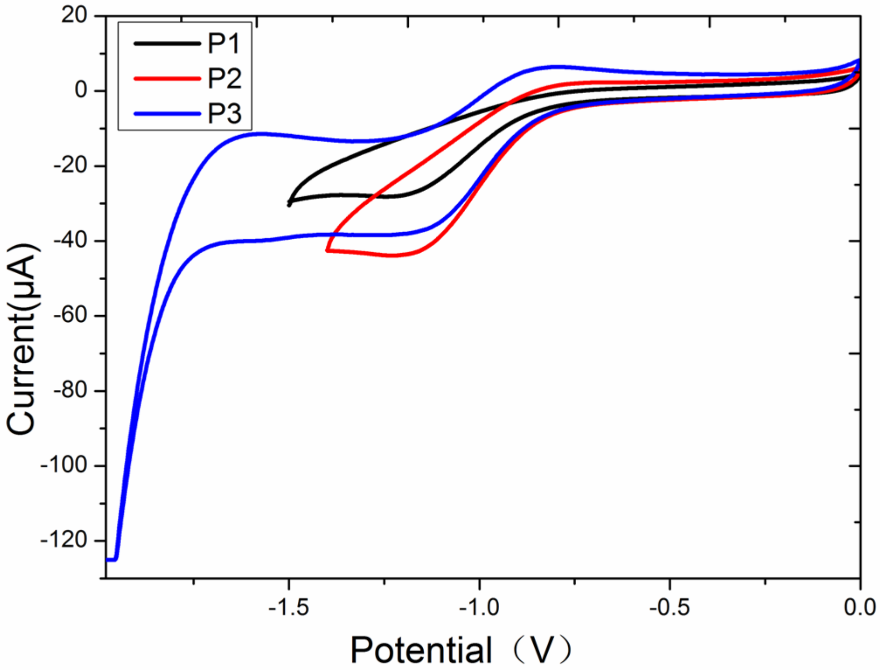


Fig. S23 Reduction analysis of **P1, P2** and **P3** in the solid state.

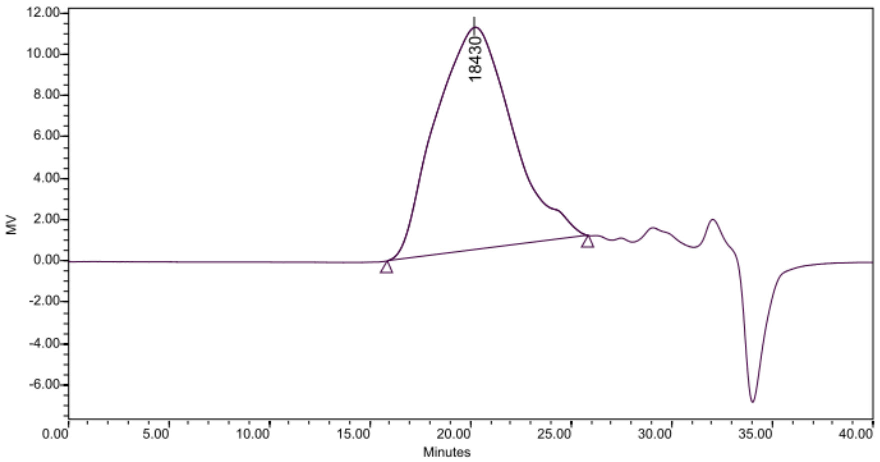


Fig. S24 SEC trace of **P3**. M_n = 18 kDa, PDI = 1.28.

5. References

1 P. Berrouard, F. Grenier, J.-R. Pouliot, E. Gagnon, C. Tessier and M. Leclerc, *Org. Lett.*, 2011, **13**, 38.