Supporting Information

Significant Enhancement of Photodetector Performance by Subtle Change at Side Chains of Dithienopyrrole-Based Polymers

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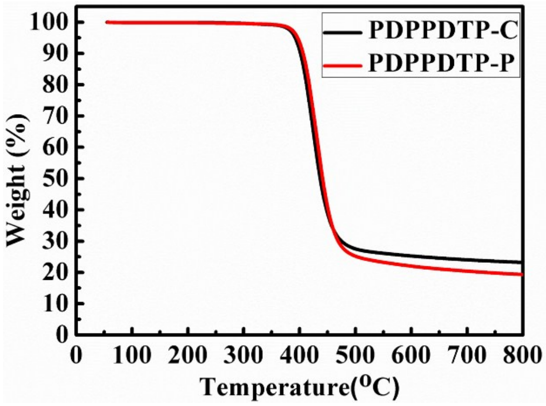


Figure S1. TGA traces of PDPPDTP-C and PDPPDTP-P under nitrogen flow.

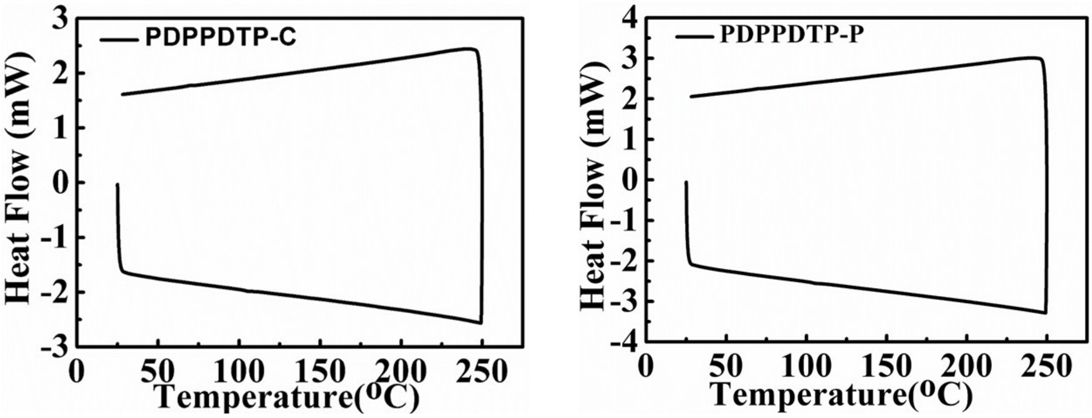


Figure S2. The second heating and cooling DSC scans of PDPPDTP-C and PDPPDTP-P under nitrogen flow.

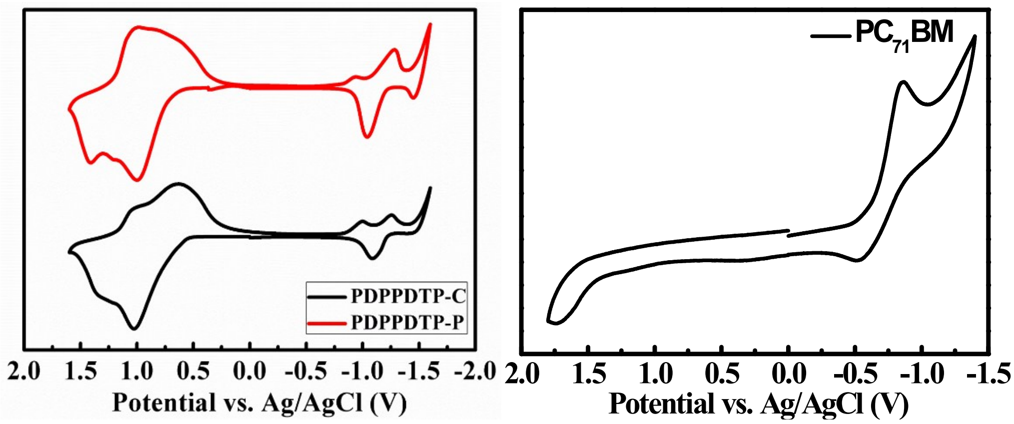


Figure S3. Cyclic voltammograms of PDPPDTP-C, PDPPDTP-P and $PC_{71}BM$ films on Pt electrode in 0.1 M n-Bu_4NPF_6 solution in dry acetonitrile with a scan rate of 50 mV/s.

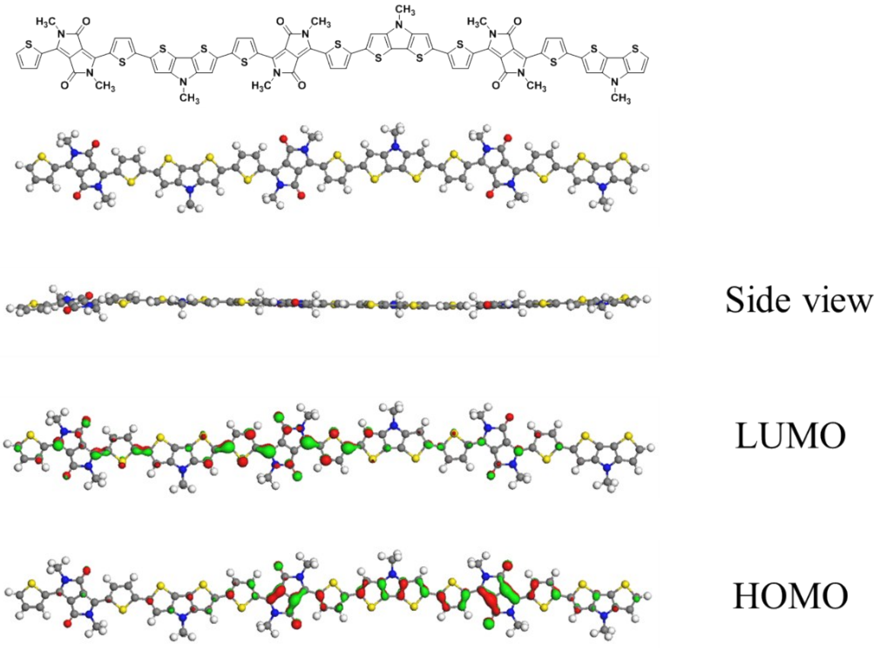


Figure S4. DFT-optimized geometries and frontier molecular orbitals of **DPP-DTP-C** trimer. The alkyl chains on **DPP** and **DTP** units were replaced by methyl groups.

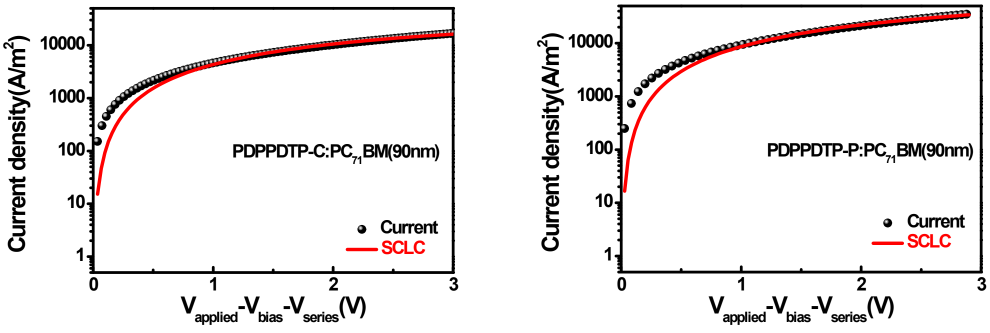


Figure S5. J–V characteristics of hole-only devices with structure of ITO/PEDOT:PSS/Polymers:$PC_{71}BM/MoO_3$/Ag for PDPPDTP-C and PDPPDTP-P, blended with $PC_{71}BM$ (1:2, w:w).

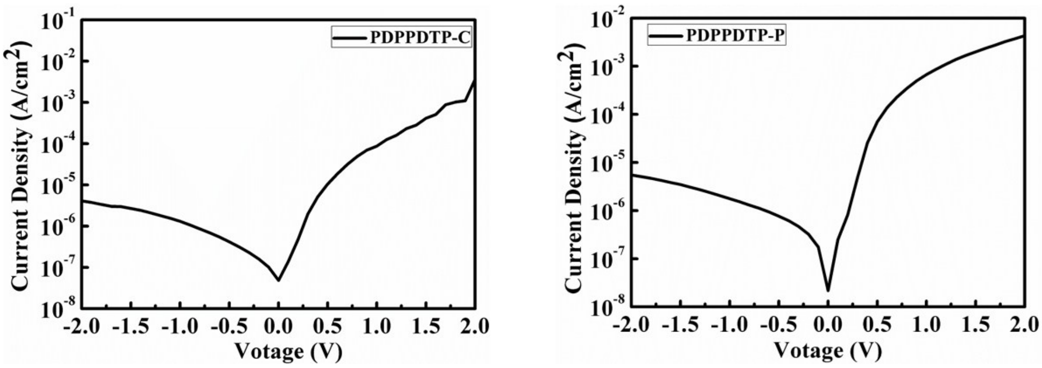


Figure S6. Current density-voltage (J-V) characteristics of the devices based on PDPPDTP-C and PDPPDTP-P in the dark.

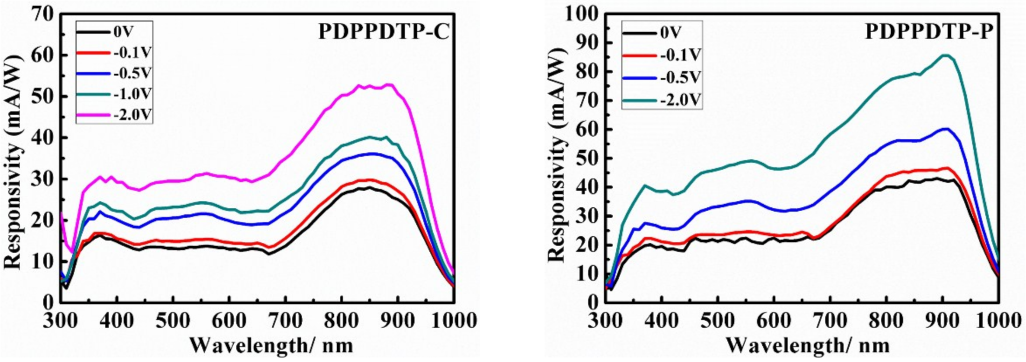


Figure S7. Spectral responsivity of the devices based on PDPPDTP-C and PDPPDTP-P at different biases.

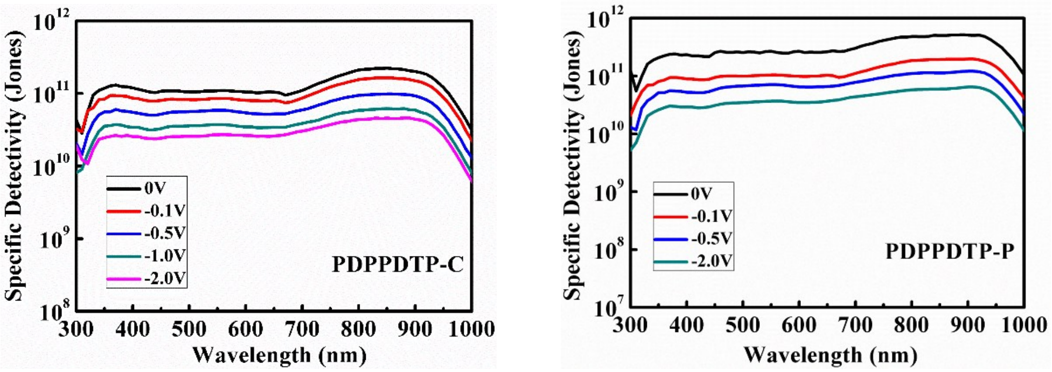


Figure S8. Spectral specific detectivity of the devices based on PDPPDTP-C and PDPPDTP-P at different biases.

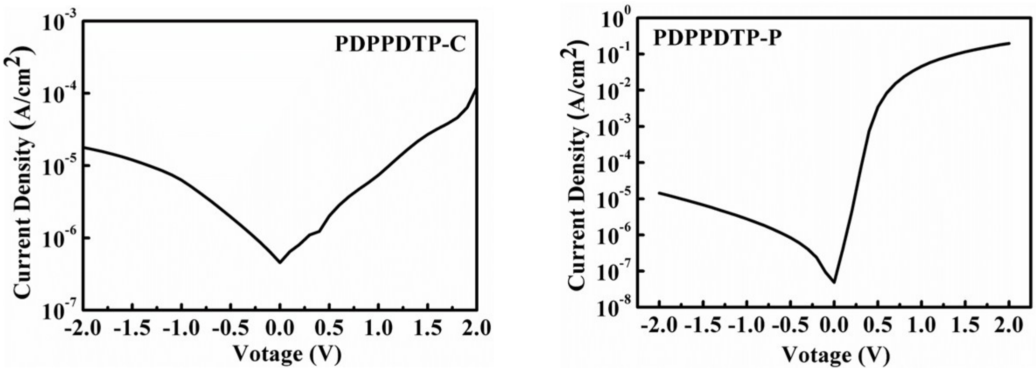


Figure S9. Current density-voltage (J-V) characteristics of the devices based on PDPPDTP-C and PDPPDTP-P with 5% DIO as additive in the dark.

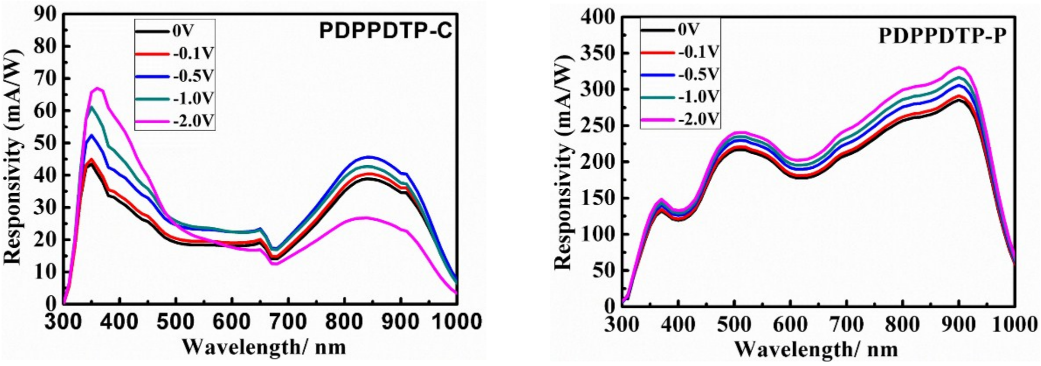


Figure S10. Spectral responsivity of the devices based on PDPPDTP-C and PDPPDTP-P with 5% DIO as additive at different biases.

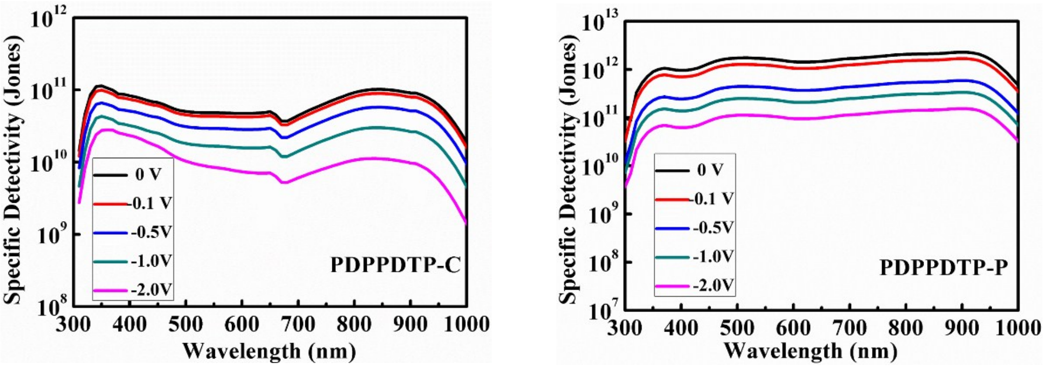


Figure S11. Spectral specific detectivity of the devices based on PDPPDTP-C and PDPPDTP-P with 5% DIO as additive at different biases.

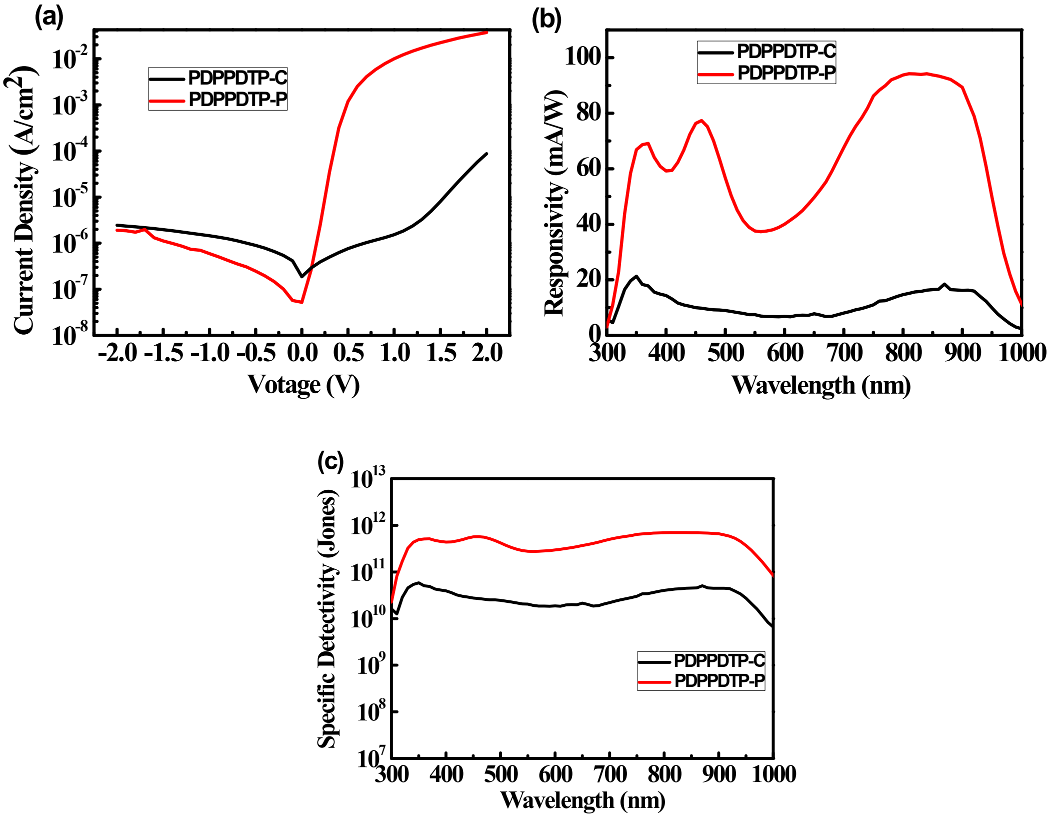


Figure S12. (a) Dark current density of the photodetectors. (b,c)Specific detectivity and spectral responsivity under -0.1V bias of the photodetectors based on PDDPDTP-C and PDDPDTP-P using 5% o-DCB in chlorobenzene for film processing.

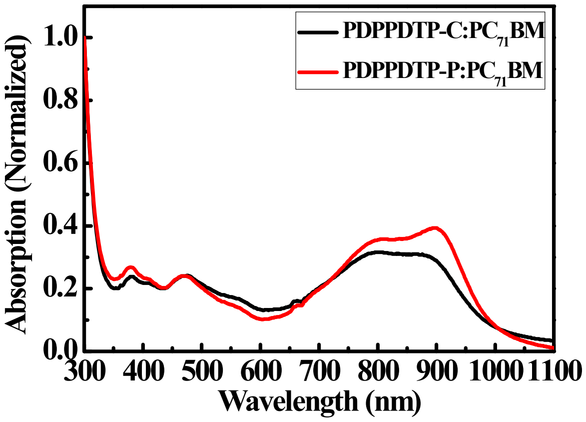


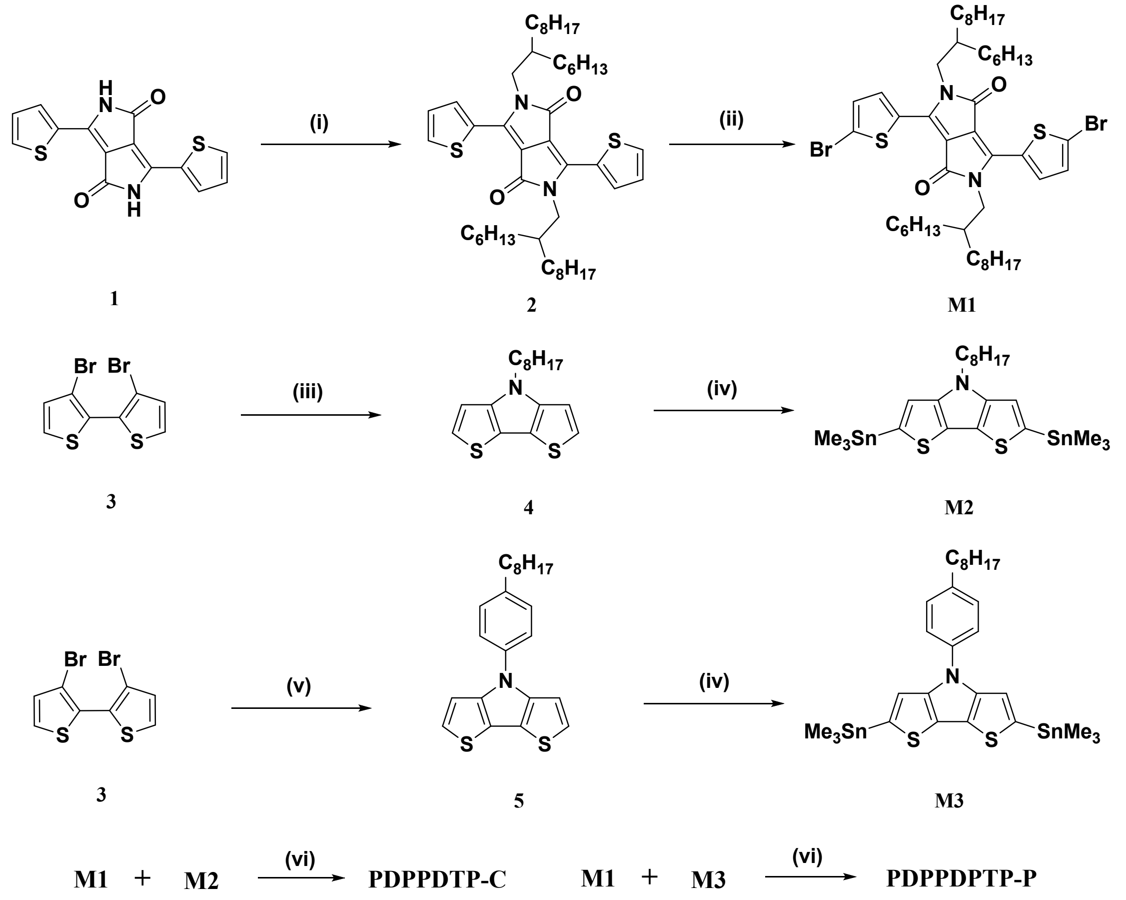
Figure S13. Absorption spectra of the mixed films of polymers and PCBM spin-coated on glass/ITO/PEDOT:PSS.

Table S1. Responsivity and Detectivity of the Optimized Photodetectors at Various Wavelength.

polymer	processing solvent	R_{400} (mA/W)[a]	R_{900} (mA/W)[a]	D^*_{400} (Jones)[a]	D^*_{900} (Jones)[a]
PDPPDTP-C	CB	15.6	27.1	8.6×10^{10}	1.5×10^{11}
	CB+DIO	33.6	36.1	7.4×10^{10}	8.0×10^{10}
PDPPDTP-P	CB	21.1	46.5	8.9×10^{10}	1.9×10^{11}
	CB+DIO	121.2	291.3	7.0×10^{11}	1.7×10^{12}

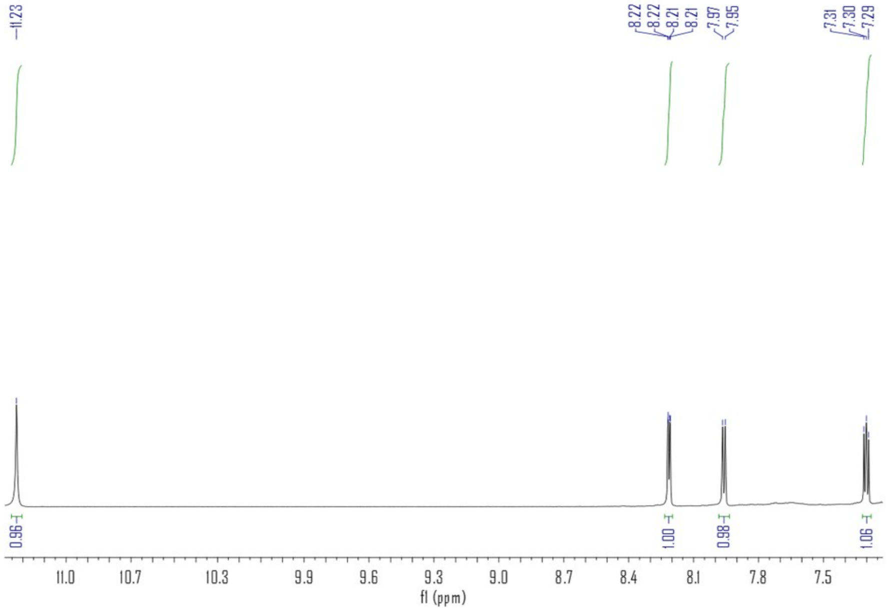
[a] Responsivity and specific detectivity under -0.1V bias.

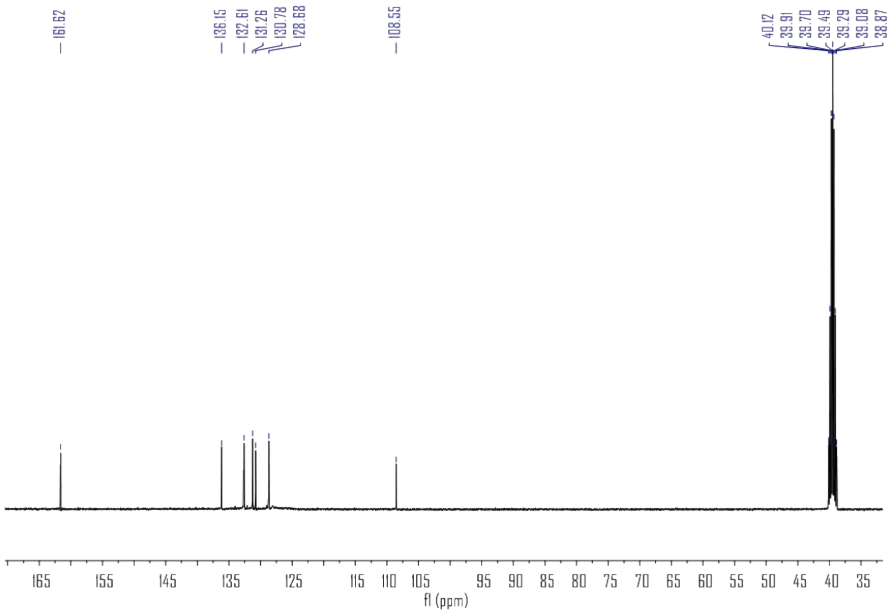
Scheme S1. Synthesis of the Monomers and Polymers.



[a] (i) 2-Hexyldecyl bromide, K_2CO_3, DMF, 140 °C. (ii) NBS, $CHCl_3$, room temperature. (iii) $Pd_2(dba)_3$, BINAP, NaO^tBu, $C_8H_{17}NH_2$, Tol,110 °C. (iv) n-Butyl lithium, then $SnMe_3Cl$, in THF, room temperature. (v) $Pd_2(dba)_3$, DPPF, NaO^tBu, 4-octylaniline, Tol,110 °C. (vi) $Pd_2(dba)_3$, P(o-tol)$_3$, Tol/DMF, 110 °C.

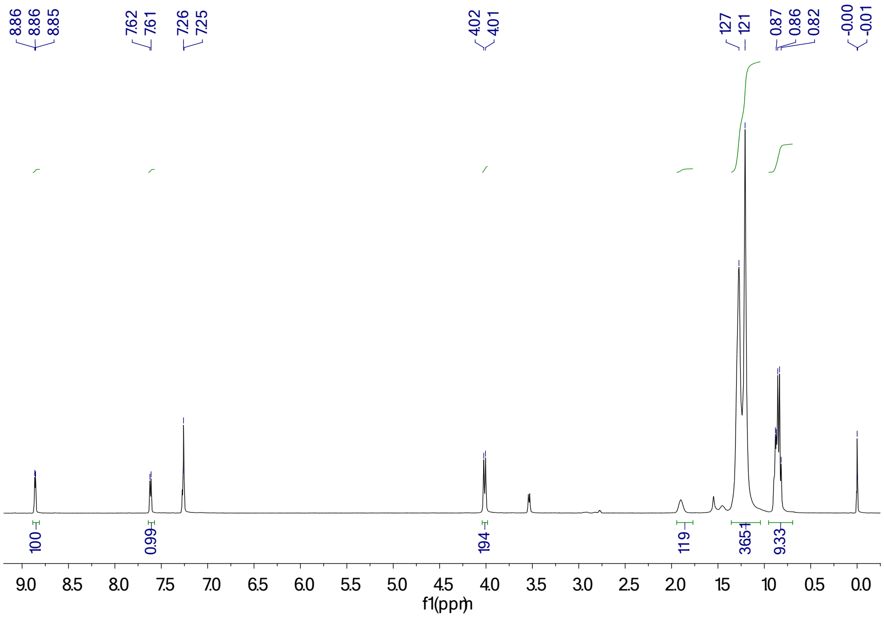
3,6-Dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1). To an argon-protected three-neck round-bottom flask, were added potassium tert-butoxide (33.6 g, 0.30 mol) and tert-amyl alcohol (180 mL). The solution was heated to 105 °C for 90 min. Then 2-thiophenenitrile (23.3 ml, 0.25 mol) was added and the stirring keeped at 105 °C for 30 min. A solution of diisopropyl succinate (20.4 ml, 0.10 mol) in tert-amyl alcohol (30 mL) was added dropwise over a period of 1 h. Then, the mixture was stirred at 105 °C for another 2 h. When the reaction was cooled to 50 °C, a mixture of methanol (150 mL) and water (40 mL) were added. The reaction mixture was refluxed for 45 min before cooling to room temperature. The mixture was added into a mixture of 250 g of ice, conc. hydrochloric acid (35% aq) (80 mL) and methanol (300 mL) and stirred for 50 min. The mixture was filtered and the residue was washed with methanol. The solid was then dispersed in water (500 ml) and filtered again after stirring for 30 min. This behavior was repeated twice to remove the impurity. The obtained solid was oven dried under vacuum at 80 °C to give the product as a red solid (21 g, 70% yield). ^{1}H NMR (400 MHz, DMSO-d$_6$, 25 ºC) δ (ppm): 11.23 (s, 2H), 8.22 (d, 2H), 7.97 (d, 2H), 7.31 (t, 2H). ^{13}C NMR (100 MHz, DMSO-d$_6$, 25 ºC) δ (ppm): 161.62, 136.15, 132.61, 131.26, 130.78, 128.68, 108.55.

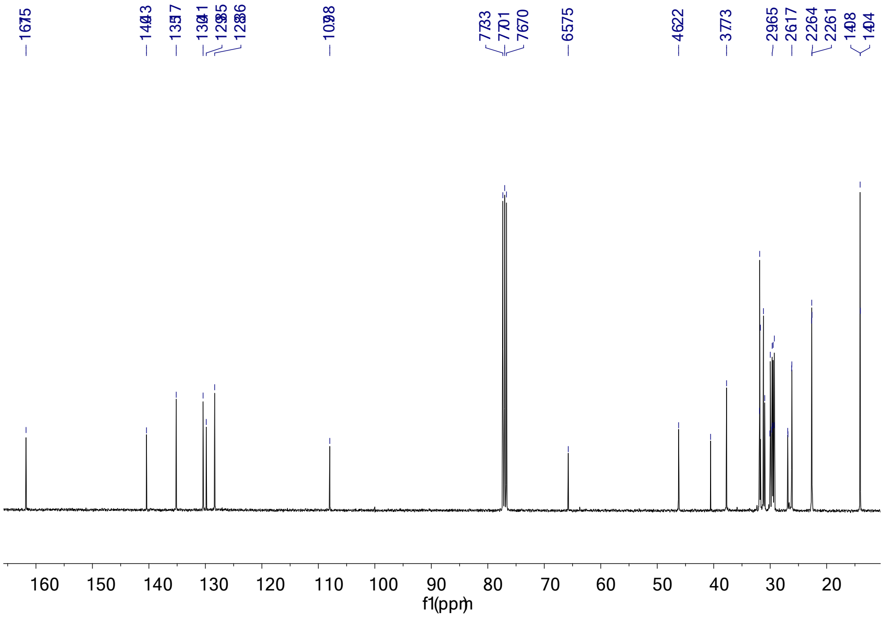




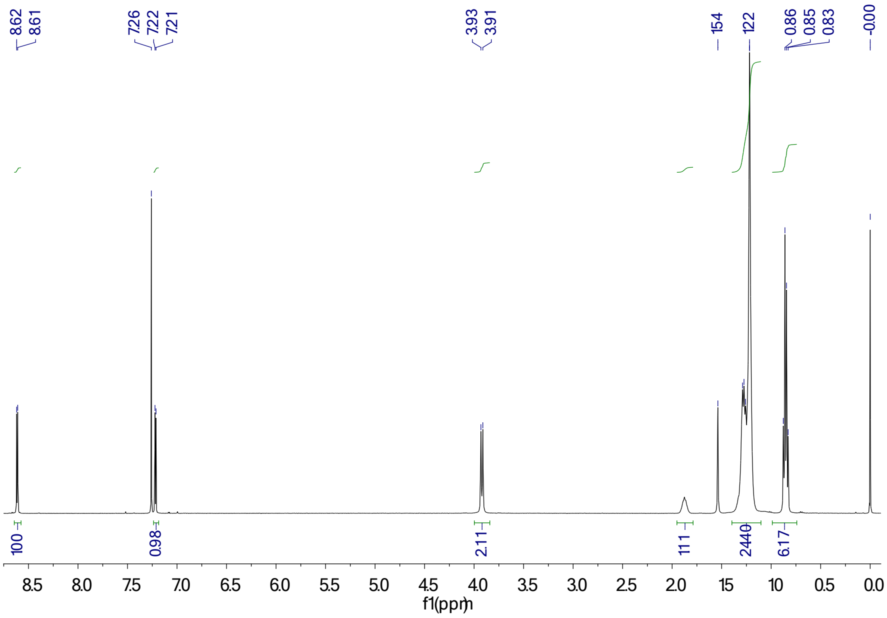
2,5-Dihexadecyl-3,6-bis(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (2). Compound **1** (9.0 g, 30 mmol) and dried potassium carbonate (16.65 g, 120 mmol) were added into N,N-dimethylformamide (120 mL) in a two-neck round flask. The mixture was heated to 140 °C for 60 min under argon protection. 1-bromohexadecane (30.6 g, 100 mmol) was added in one portion by syringe. After the reaction was performed for 24 h at 140 °C, the reaction was cooled to room temperature. The solvent was removed under reduced pressure. The residue was dissolved into $CHCl_3$, washed with water, dried over the anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography using dichloromethane: hexane (1:2) as eluent to obtain a dark-red solid powder (5.2 g, yield 23%). ^1H NMR (400 MHz, $CDCl_3$, 25 ºC) δ (ppm): 8.85 (d, 2H), 7.61 (d, 2H), 7.27 (t, 2H), 4.01 (d, 4H), 1.90 (br, 2H), 1.10-1.39 (m, 48H), 0.86 (t, 12H),. ^{13}C NMR

(100 MHz, $CDCl_3$, 25 ºC) δ (ppm): 161.75, 140.43 135.17 130.41 129.85, 128.36, 107.98, 46.22, 37.73, 31.89, 31.74, 31.21, 29.99, 29.65, 29.47, 29.27, 26.20, 26.17, 22.66, 22.61, 14.08, 14.04.





3,6-Bis(5-bromothiophen-2-yl)-2,5-dihexadecylpyrrolo[3,4-c]pyrrole-1,4-dione (M1). Compound **2** (3.75 g, 5 mmol) and N-bromosuccinimide (1.96 g, 11 mmol) were added into chloroform (100 mL) in a round-bottom flask under argon protection, and then the solution was stirred at room temperature in the dark overnight. The solution was diluted with $CHCl_3$, washed with brine, dried over the anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane: dichloromethane (1:1) as the eluent, and recrystallized from isopropanol to give **M1** as purple solid (2.54 g, yield 56%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ (ppm): 8.61 (d, 2H), 7.21 (d, 2H), 3.91 (d, 4H), 1.88 (br, 2H), 1.12-1.39 (m, 48H), 0.86 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ (ppm): 161.37, 139.38, 135.29, 131.40, 131.17, 118.95, 108.01, 46.33, 37.74, 31.88, 31.75, 31.17, 29.97, 29.64, 29.49, 29.28, 26.17, 26.14, 22.67, 22.62, 14.11, 14.07. MALDI-TOF-MS: m/z 904.3 $[M]^+$. Elemental analysis. Calculated for $C_{46}H_{70}Br_2N_2O_2S_2$: C, 60.91%; H, 7.78%; N, 3.09%; S, 7.07%. Found: C, 60.86%; H, 7.80%; N, 3.11%; S, 7.14%.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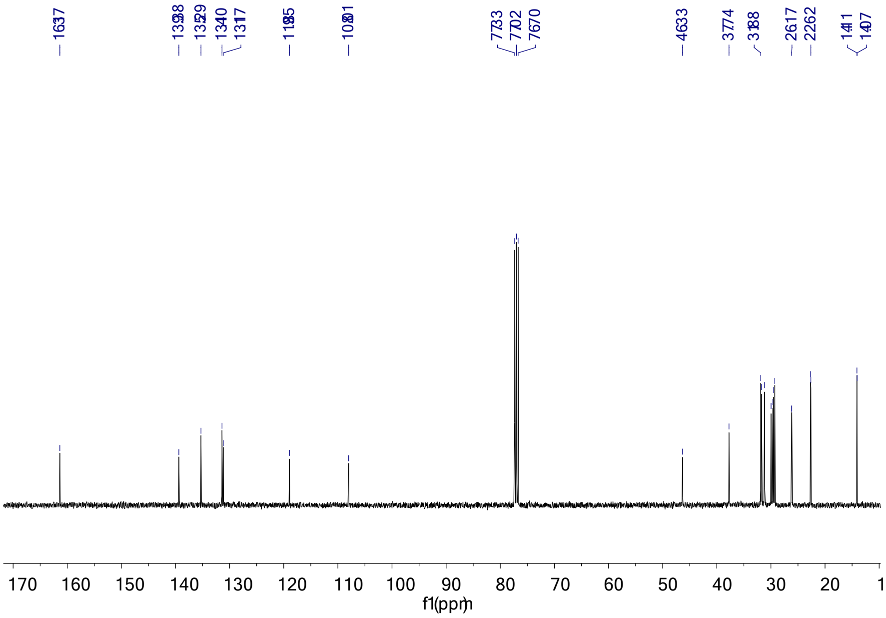
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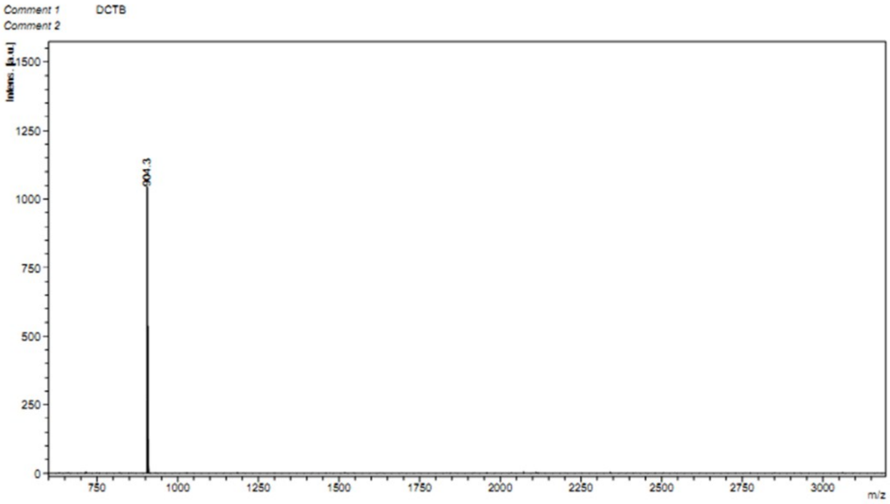
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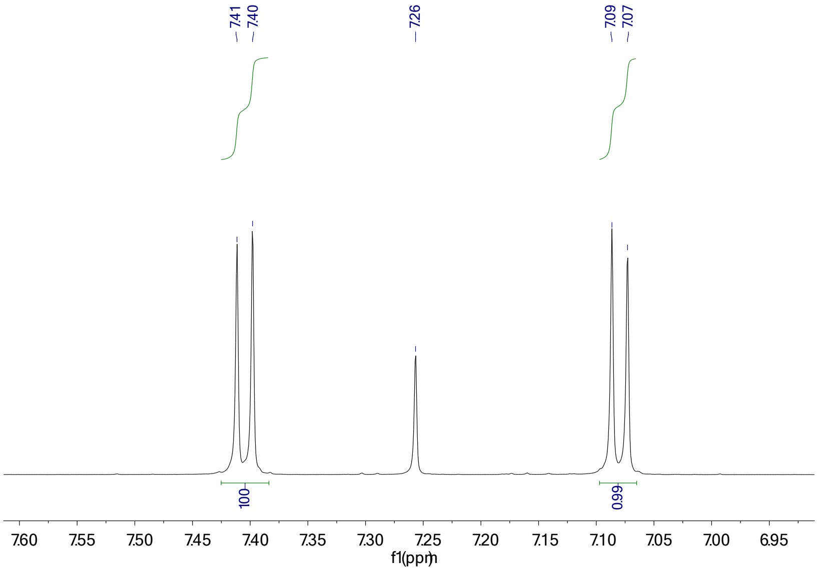
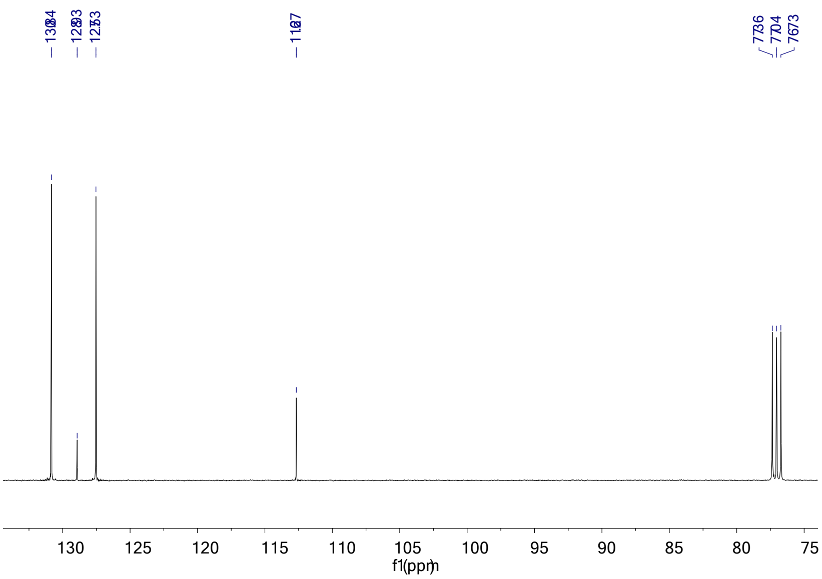
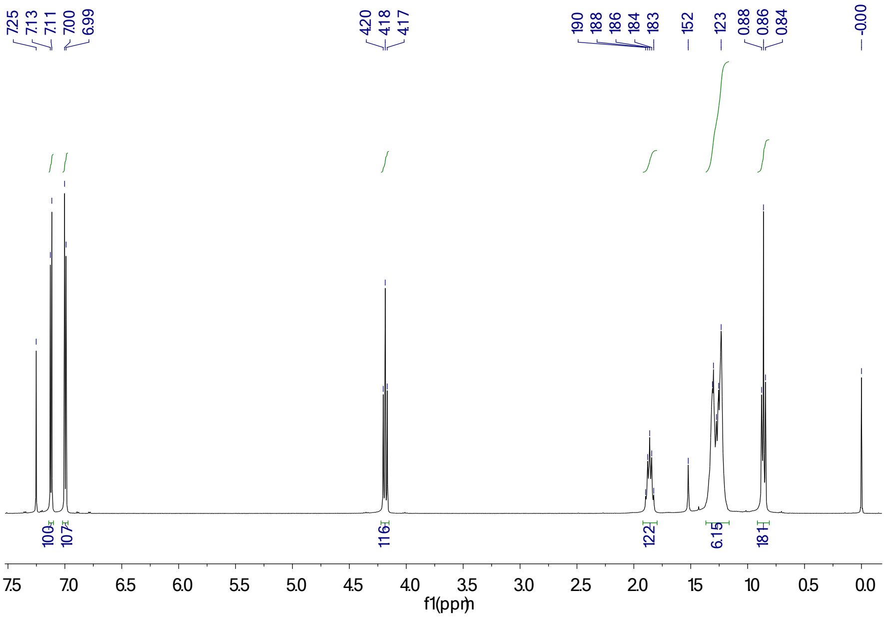
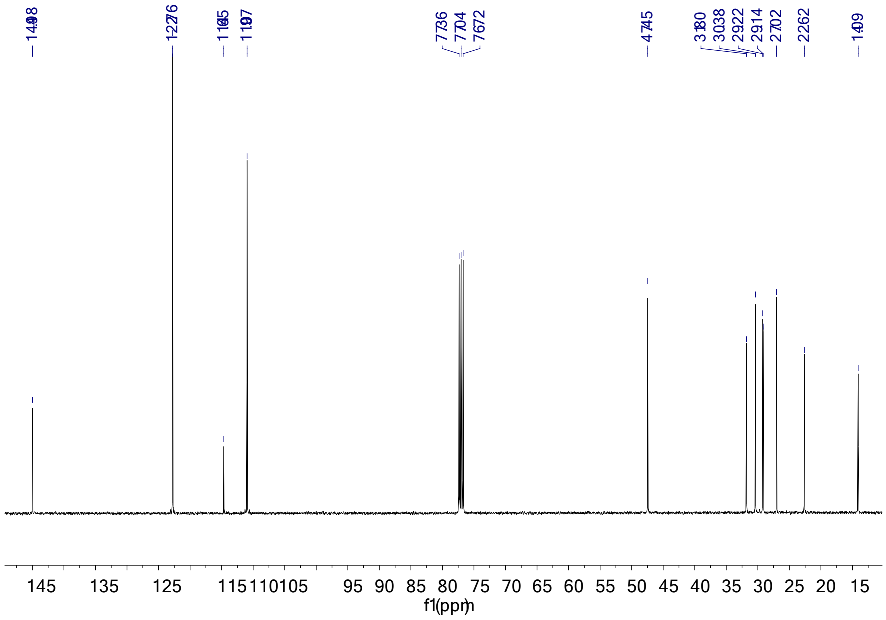
3,3′-Dibromo-2, 2′-Bithiophene (3). Diisopropylamine (21.2 mL, 0.15 mol) was added in dry THF (110 mL) and cooled to 0 ºC under argon. n-BuLi (60.0 mL, 0.15 mol) was then added slowly. After the mixture was stirred at 0 ºC for 30 min, and 3-bromothiophene (24.5 g, 0.15 mol) was added slowly via syringe. The resulting mixture was kept stirring at 0 ºC for 2 h. After the reaction was cooled to -78 ºC in a dry ice bath, $CuCl_2$ (40.5 g, 0.30 mol) was added. After this addition, the mixture was performed at -78 ºC for 2 h and then naturally warmed to room temperature and stirred overnight. The reaction was quenched with H_2O and extracted with diethyl ether. The organics were washed with brine, dried over anhydrous $NaSO_4$, and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane: dichloromethane (10:1) as the eluent, and recrystallized from the hexane to afford 10.8 g of pure product as light yellow solid in 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ (ppm): 7.41 (d, 2H), 7.09 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ (ppm): 130.84, 128.93, 127.53, 112.67.



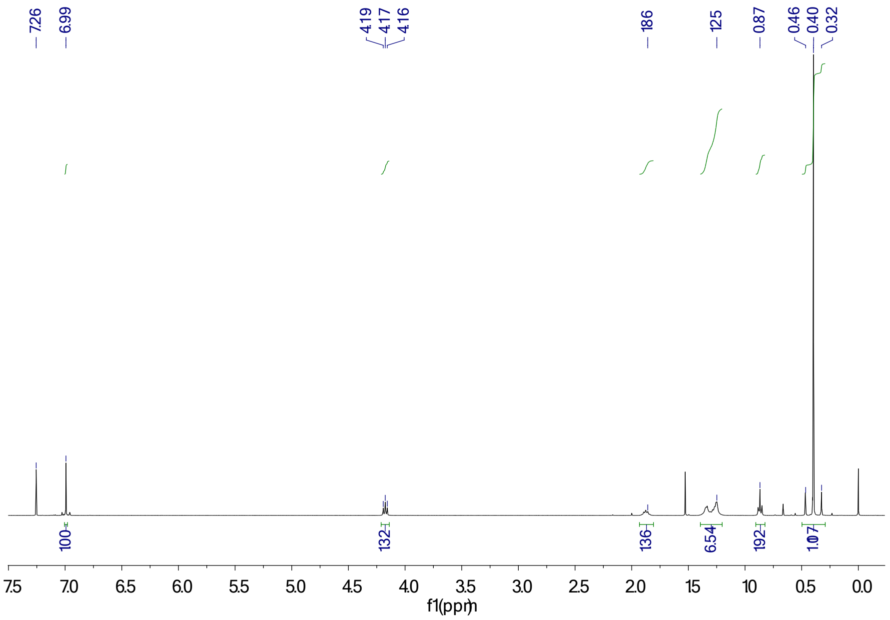


N-Octyl dithieno[3,2-b:2′,3′-d]pyrrole (4). Compound **3** (1.62 g, 5.0 mol) was added in 10 mL of dry toluene. NaO^{t}Bu (1.20 g, 12.5 mmol), $Pd_2(dba)_3$(0.14 g, 0.15 mmol), BINAP (0.37 g, 0.6 mmol) were added to the mixture and heated to 35 ºC. At this point n-octylamine (1 mL, 6 mmol) was added via syringe. The resulting solution was heated to 110 ºC for 6 h in the dark. After the reaction cooled to room temperature, water was added and the aqueous layer extracted with diethyl ether. The organics were washed with brine, dried over anhydrous $NaSO_4$, and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane as the eluent afforded 1.16 g of pure product as white solid in 80% yields. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ (ppm):7.13 (d, 2H), 7.00 (d, 2H), 4.18 (t, 2H), 1.90 (m, 2H); 1.30 (m, 10H); 0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC) δ (ppm):144.98, 122.76, 114.65, 110.97, 47.45, 31.80, 30.38, 29.22, 29.14, 27.02, 22.62, 14.09. Elemental analysis. Calculated for $C_{16}H_{21}NS_2$: C, 65.93%; H, 7.26%; N, 4.81%; S, 22.00%. Found: C, 65.85%; H, 7.28%; N, 4.79%; S, 21.95%.

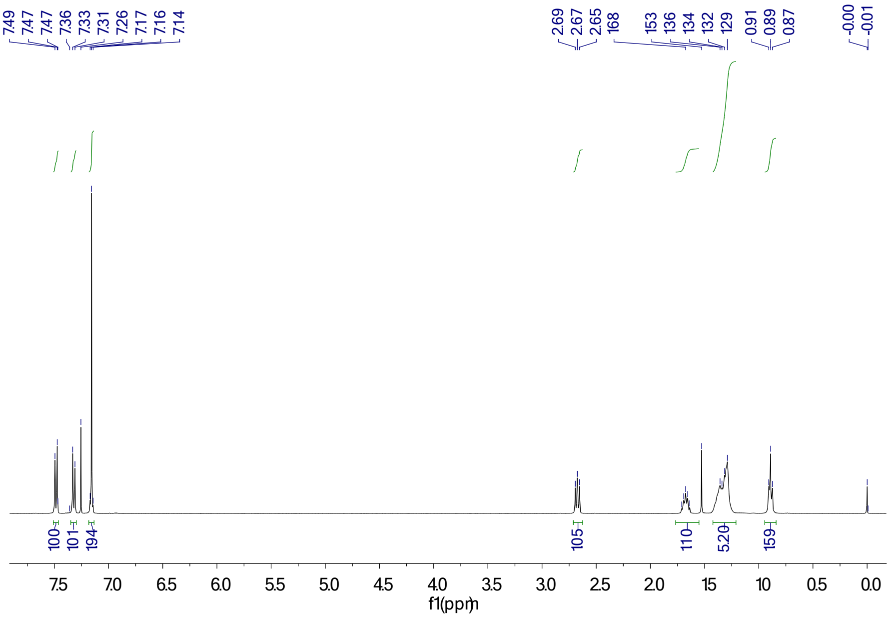


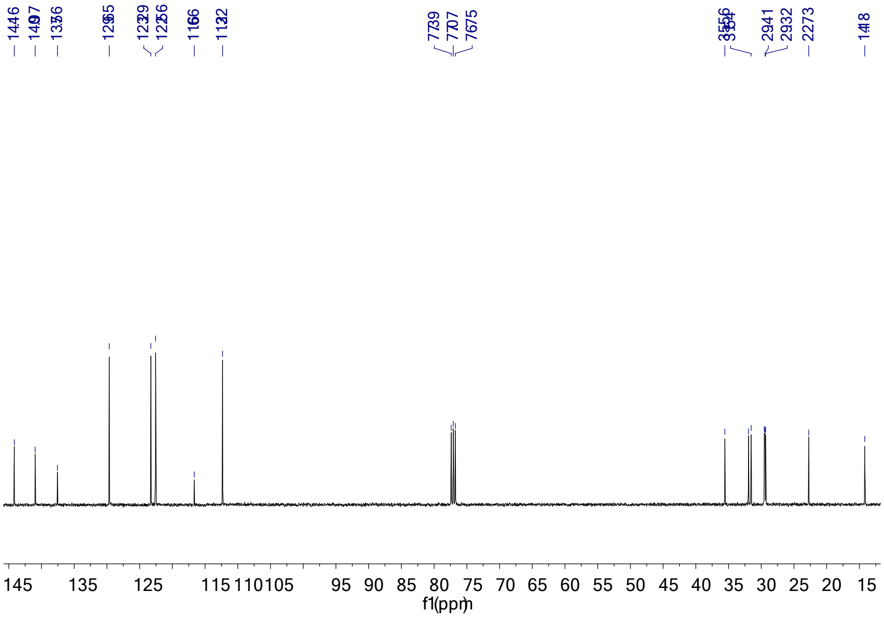


N-Octyl-2,6-bis(trimethylstannyl)dithieno[3,2-b:2’3′-d]-pyrrole (M2). Compound **4** (2.0 mmol, 583 mg) was dissolved in dry THF (50 mL) and cooled to -78 °C under argon. n-Butyllithium (5.0 mmol, 2.0 mL) was then added dropwise via syringe. Then the resulting solution was slowly warmed to room temperature and stirred for 2h, followed by cooling to -78 °C for 30 min. Trimethyltin chloride (5.0 mmol, 5.0 mL) was added in one portion. After addition, the mixture was warmed to room temperature and stirred overnight. The reaction was quenched with H_2O, and the aqueous layer was extracted with diethyl ether. The organics were washed with brine, dried over anhydrous $NaSO_4$, and then concentrated under reduced pressure to afford the product as brown oil in 91% yield. ^1H NMR (400MHz, $CDCl_3$, 25 ºC) δ (ppm): 6.99 (s, 2H), 4.17 (t, 2H), 1.86 (m, 2H), 1.28 (m, 10H), 0.87 (t, 3H), 0.40 (s, 18H).

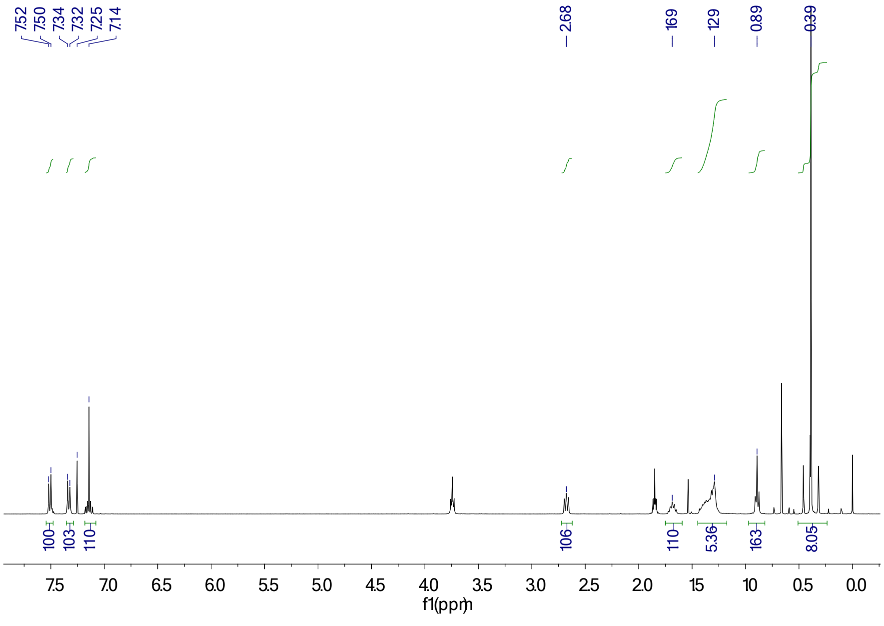


N-[4-Octylphenyl]dithieno[3,2-b:20,30-d]pyrrole (5). Compound **3** (3.24 g, 10.0 mol) was added in 30 mL of dry toluene. NaO^{t}Bu (2.9 g, 30 mmol), $Pd_2(dba)_3$(0.28 g, 0.30 mmol), 1,1'-bis(diphenylphosphine)ferrocene (0.3 g, 0.6 mmol) were added to the mixture and heated to 35 ºC. Then 4-octylaniline (2.8 mL, 12 mmol) was added via syringe. The resulting solution was heated to 110 ºC for 12 h in the dark. After cooling to room temperature, water was added and the aqueous layer extracted with diethyl ether. The organic layer was washed with brine, dried over anhydrous $NaSO_4$, and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane as the eluent afforded 3.45 g of pure product as white solid in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC) δ (ppm): 7.49 (d, 2H), 7.33 (d, 2 H), 7.17 (s, 4 H), 2.67 (t, 2H), 1.60–1.71 (m, 2 H), 1.22–1.44 (m, 10 H), 0.89 (t, 3H). ^{13}C NMR (100MHz, $CDCl_3$, 25 ºC) δ (ppm): 144.16, 140.97, 137.56, 129.65, 123.29, 122.56, 116.66, 112.32, 35.56, 31.95, 31.54, 29.54, 29.41, 29.32, 22.73, 14.18. Elemental analysis. Calculated for $C_{22}H_{25}NS_2$: C, 71.89%; H, 6.86%; N, 3.81%; S, 17.45%. Found: C, 71.99%; H, 6.88%; N, 3.67%; S, 17.20%.

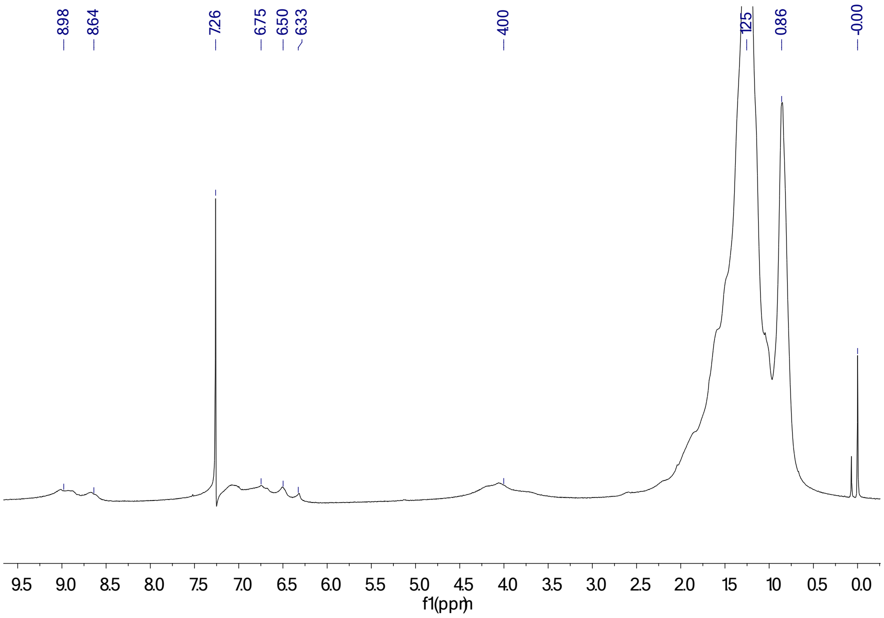




2,6-Di(trimethyltin)-N-[4-octylphenyl]dithieno[3,2-b:20,30-d]pyrrole (M3). **M3** was prepared using the same procedure as **M2**. ^{1}H NMR (400MHz, $CDCl_3$, 25 ºC) δ (ppm): 7.52 (d, 2H), 7.34 (d, 2 H), 7.14 (s, 2 H), 2.68 (t, 2H), 1.60–1.74 (m, 2 H), 1.22–1.44 (m, 10 H), 0.90 (t, 3H), 0.39 (s, 18 H).



Polymerization for PDPPDTP-C. **M1** (0.22675 g, 0.25 mmol) and **M2** (0.15427 g, 0.25 mmol) were dissolved into 5mL of toluene and 0.5 mL of DMF in a flask protected by argon, and then 10 mg of $Pd_2(dba)_3$ and 25 mg of $P(o\text{-}tol)_3$ was added into the flask. The oil bath was heated to 110 °C gradually, and the reaction mixture was stirred for 72 h at 110 °C under argon atmosphere. Next, the reaction was cooled to room temperature, and the polymer was precipitated into 200 mL of methanol. The precipitated solid was collected by filtration and purified by Soxhlet extraction sequentially using acetone (24 h), hexane (24 h), and $CHCl_3$ (24 h). The $CHCl_3$ solution was concentrated under reduced pressure. The concentrated solution was added dropwise into methanol (150 mL). The precipitate was collected by filtration and dried under vacuum at room temperature for 8 h to afford PDPPDTP-C as a dark green solid (227 mg, yield: 87.6%).The polymer was thermally stable up to 392 °C (5% weight loss by TGA). Mn = 39.9 kDa; polydispersity = 2.75. Elemental analysis. Calculated for $C_{64}H_{95}N_3O_2S_4$: C, 72.06 %; H, 8.98 %; N, 3.94 %; S, 12.02 %. Found: C, 71.36%; H, 8.70 %; N, 3.88 %; S, 12.27 %.



Polymerization for PDPPDTP-P. PDPPDTP-P was prepared using the same procedure as PDPPDPT-C. The polymer was thermally stable up to 396 °C (5% weight loss by TGA). Mn = 48.4 kDa; polydispersity = 2.65. Elemental analysis. Calculated for $C_{70}H_{99}N_3O_2S_4$: C, 73.57 %; H, 8.73%; N, 3.68 %; S, 11.22 %. Found: C, 73.00%; H, 8.55 %; N, 3.59 %; S, 11.41 %.