

Supporting Information

Side-Chain Engineering for Fine-Tuning of Molecular Packing and Nanoscale Blend Morphology in Polymer Photodetectors

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Characterizations. ^1H and ^{13}C NMR spectra were obtained from a Bruker Avance 400 NMR spectrometer. The absorption spectra were taken on a Shimadzu UV-3600 spectrophotometer. The molecular weight of the polymers was acquired by gel permeation chromatography (GPC) method, with polystyrene as standards and chloroform (CHCl_3) as eluent at room temperature. The element analysis was measured on Vario EL Elementar Analysis Instrument. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris Diamond TG from 50 to 800 °C at a heating rate of 10 °C/min with a continuous nitrogen flow. Differential scanning calorimetry (DSC) was measured on a TA-DSC Q100 from 20 °C to 350 °C with a heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

Cyclic voltammetry (CV) was studied to characterize electrochemical properties of the polymers. CV experiments were conducted on a CHI660b electrochemical workstation in acetonitrile solution containing $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) at a scan speed of 50 mV/s. Pt disk (2 mm diameter), Pt plate, and Ag/AgCl were used as working electrode, counter electrode, and reference electrode, respectively. The polymer thin

films for electrochemical measurements were obtained from a chloroform solution, ca. 5 mg/mL, onto a Pt disk electrode. Ferrocene was used as an internal standard of the redox potentials for calibration.

The out-of-plane grazing incidence X-ray diffraction (GIXD) were studied on a Bruker D8 Discover reflector, with a step-scan rate of 0.05° per 5 s and the scattering angle 2-theta ranging from 2° to 30° . The solid samples were obtained by spin-coating from concentrated polymer solutions (20 mg/mL) in chloroform on glass substrates.

Atomic force microscopy (AFM) was measured on a SPA300HV instrument equipped with a SPI3800N controller (Seikoin Instruments, Japan) in tapping mode under ambient conditions using silicon cantilevers (Applied Nanostructures, nominal spring constant of 2.0 N/m and nominal resonance frequency of ~ 75 kHz).

Photodetector Fabrication and Characterizations. The devices with the structure of ITO/PEDOT:PSS/Polymer:PC₇₁BM/ZnO/Al were fabricated with the following steps: ITO-coated glass substrates were cleaned sequentially in ultrasonic baths with acetone, deionized water, and isopropyl alcohol, and then dried at 120 °C for 1h. A thin layer of PEDOT:PSS (Baytron P VP Al 4083) was deposited on UV-ozone treated ITO at 3000 rpm for 60 s, and then baking for 30 min at 120 °C in the air. Each active blending solution (total of 24 mg mL⁻¹, polymer: PC₇₁BM, 1:2 w/w) for spin-coating contained 5% of 1, 8-diiodooctane (DIO) by volume as the additive in chlorobenzene. The blending solution was spin-coated at 1500 rpm for 40 s under nitrogen atmosphere. A butanol solution of ZnO was deposited on the active layer at

1500 rpm for 40 s, giving a ZnO layer of 20 nm. The Al (100 nm) layer was subsequently deposited on the surface of ZnO under high vacuum (3×10^{-4} Pa). Two pixels, each with an active area of 0.16 cm^2 , were fabricated per ITO. EQE measurements were measured under ambient conditions using the equipment from Beijing 7-Star Optical Instruments Co., Ltd. Incident light from a 250 W halogen lamp passing through two cascade monochromators was chopped at 25 Hz and concentrated on the active area of the device. The photocurrent signal was amplified by a low-noise current amplifier (DLPCA-200, Femto) and then detected with a lock-in amplifier (SR830, Stanford Research Systems). Keithley 236 Source Measure unit was used to measure the dark current density–voltage (J – V curve) properties of the devices. For the temporal response measurement, a green diode, modulated with a pulse generator, (8114A, Agilent) was used to trigger the samples. The photocurrent was amplified by a high speed transimpedance amplifier (DHPCA-100, Femto) and the output signal was showed on a 500 MHz bandwidth oscilloscope (54825A, Agilent).

Hole Mobility. Hole mobility of the polymers was measured with the space charge limited current model (SCLC), using the hole-only device structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/MoO₃/Al. The current-voltage measurements were done in the range of 0-10 V and the results were fitted to a space charge limited form, according to the SCLC equation: $J=(9/8)\epsilon_r\epsilon_0\mu(V^2/L^3)$, where J is the current density in the space-charge limited region, L is the thickness of the active layer as measured using step profiler, ϵ_0 is the permittivity of free space, ϵ_r is the dielectric

constant of the polymer (assumed to be 3 for conjugated polymers), V is the voltage drop ($V = V_{\text{appl}} - V_r - V_{\text{bi}}$, where V_{appl} is the applied voltage, V_r is the voltage drop, and V_{bi} is the built-in voltage) and μ is the hole mobility.

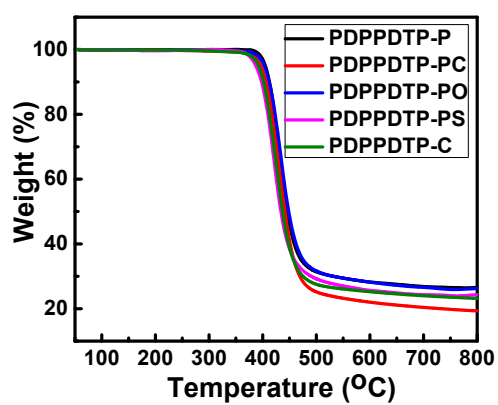


Figure S1. TGA thermograms of polymers under nitrogen flow.

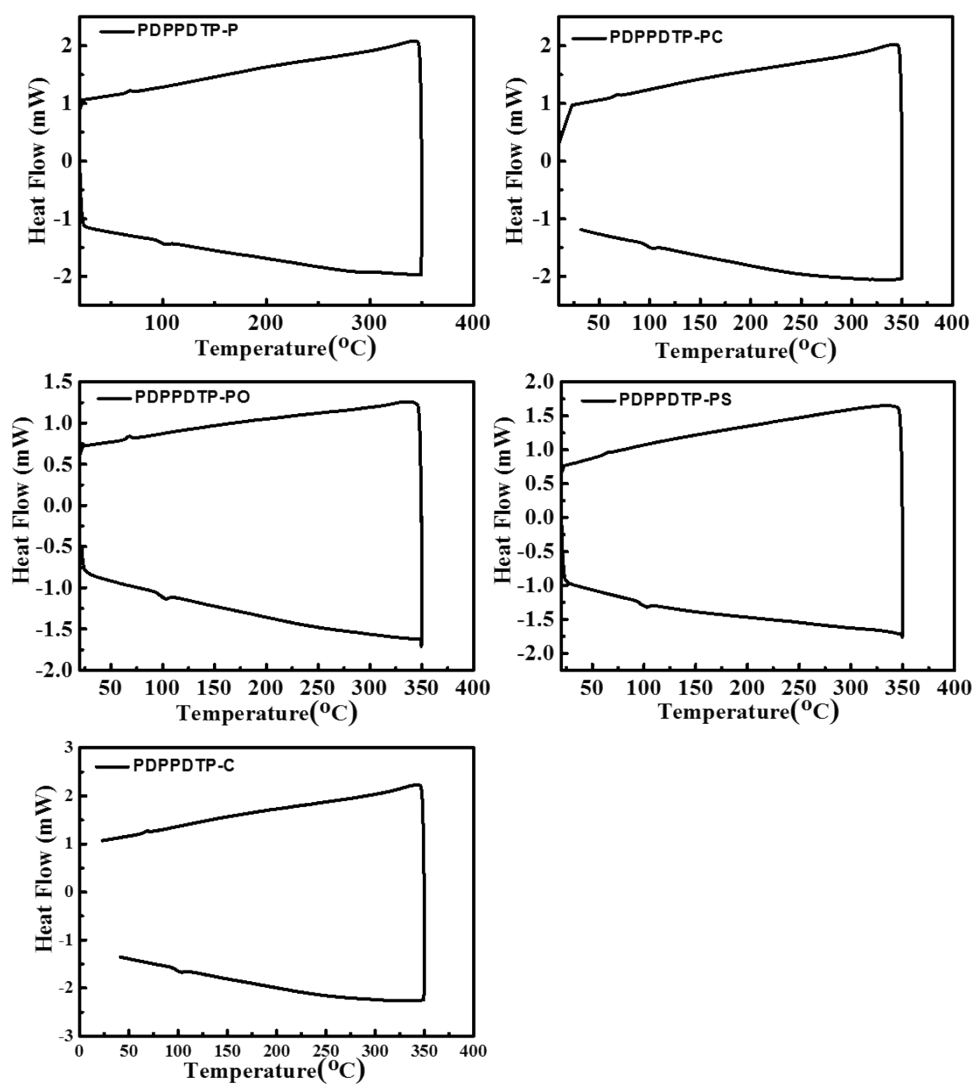


Figure S2. The second heating and cooling DSC scans of polymers under nitrogen flow.

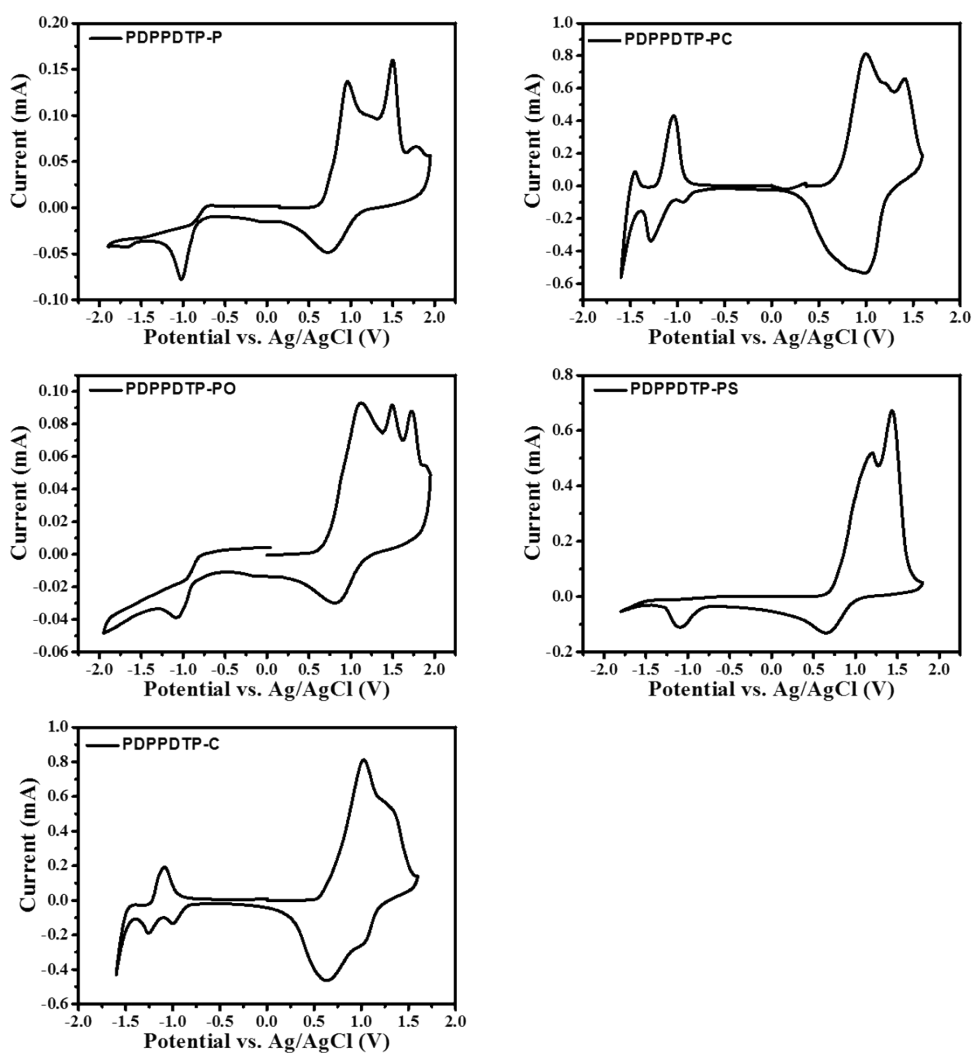


Figure S3. Cyclic voltammograms of polymer films on Pt electrode in 0.1 M *n*-Bu₄NPF₆ solution in dry acetonitrile with a scan rate of 50 mV/s.

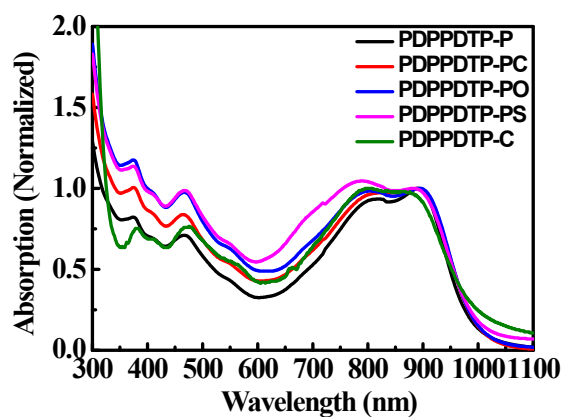


Figure S4. The absorption of the films of polymer:PC₇₁BM blends.

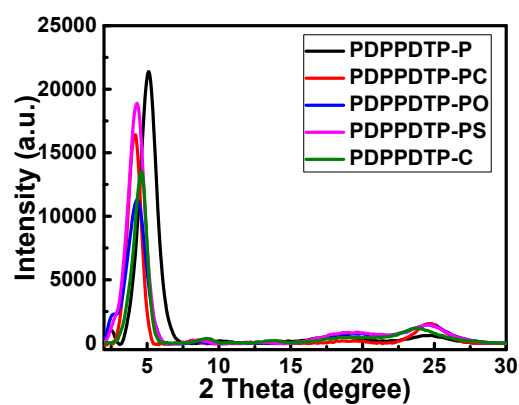


Figure S5. The out-of-plane GIXRD of the spin-coated films of polymers.

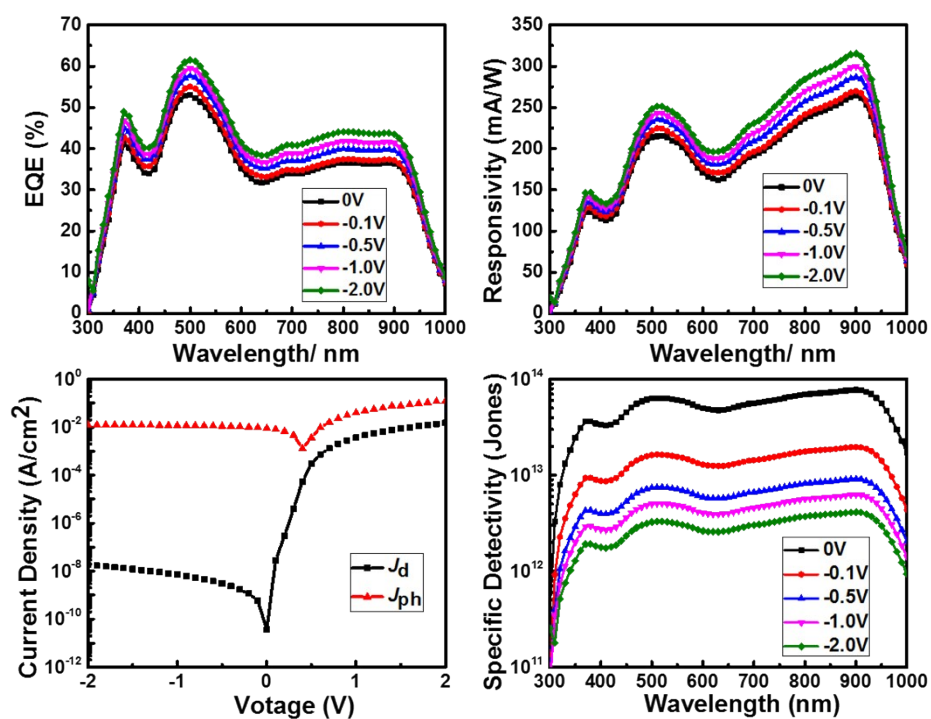


Figure S6. The device parameters of PDPPDTP-P based photodetector.

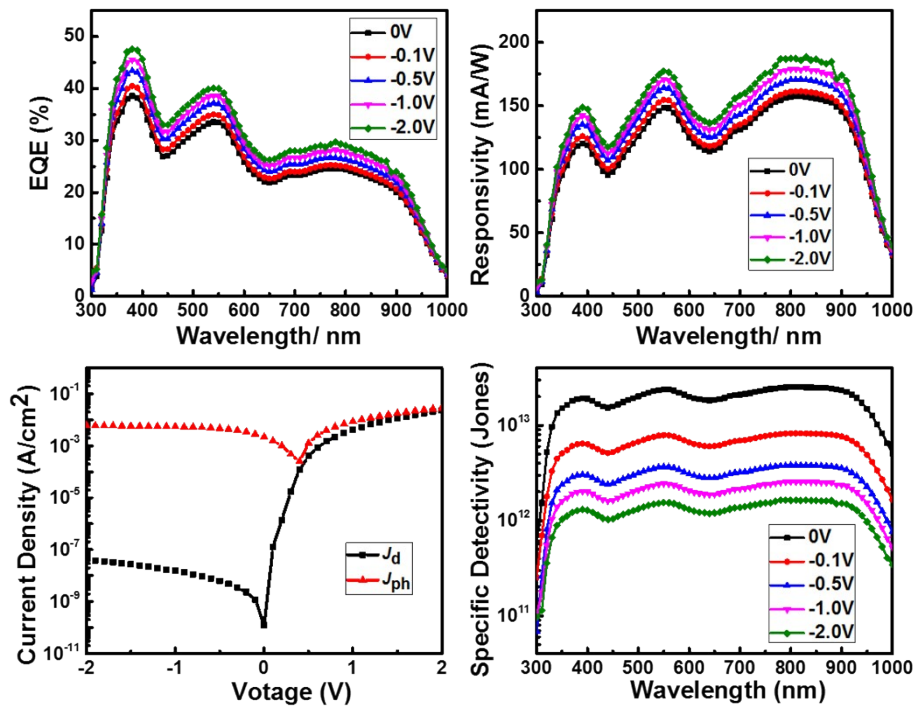


Figure S7. The device parameters of PDPPDTP-PC based photodetector.

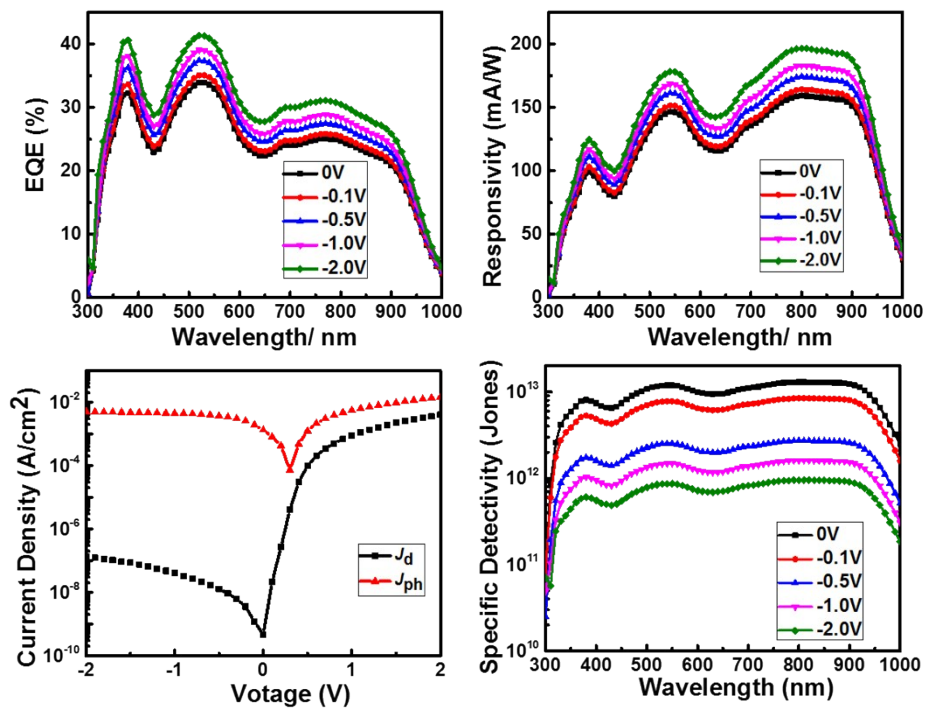


Figure S8. The device parameters of PDPPDTP-PO based photodetector.

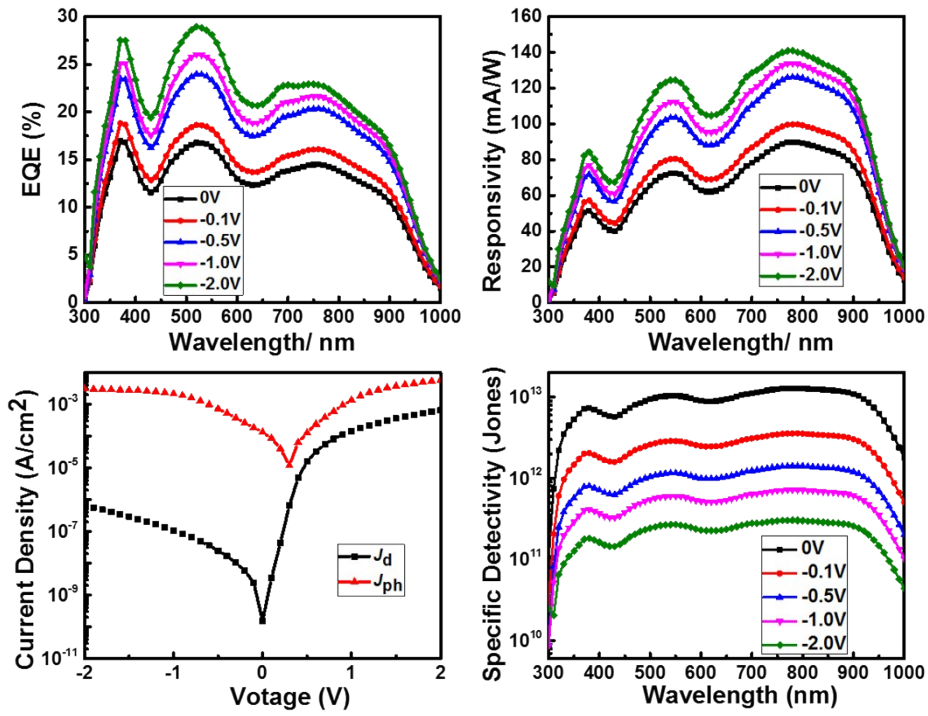


Figure S9. The device parameters of PDPPDTP-PS based photodetector.

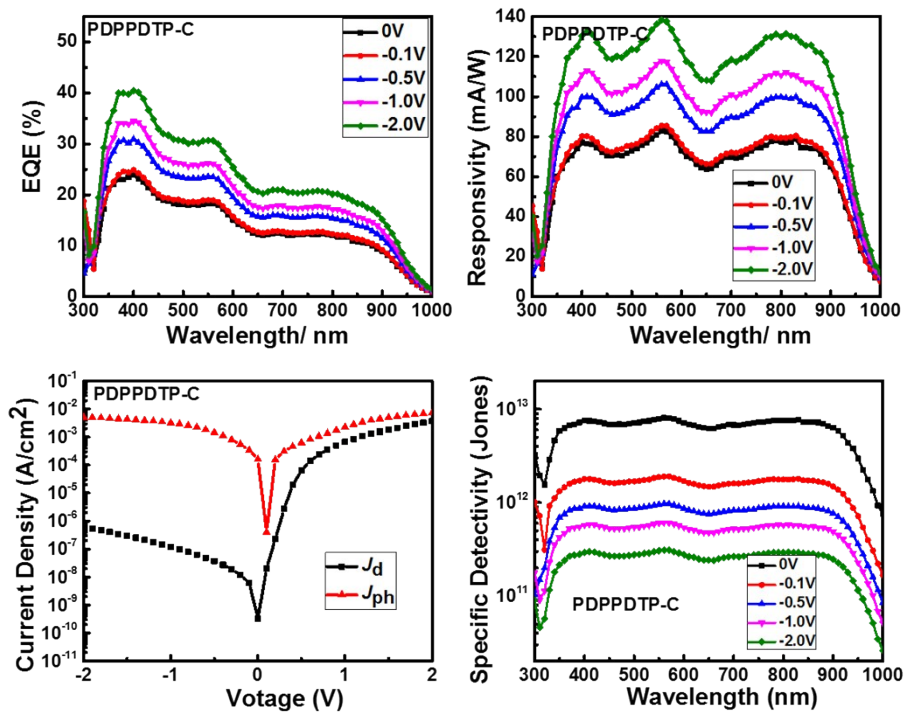


Figure S10. The device parameters of PDPPDTP-C based photodetector.

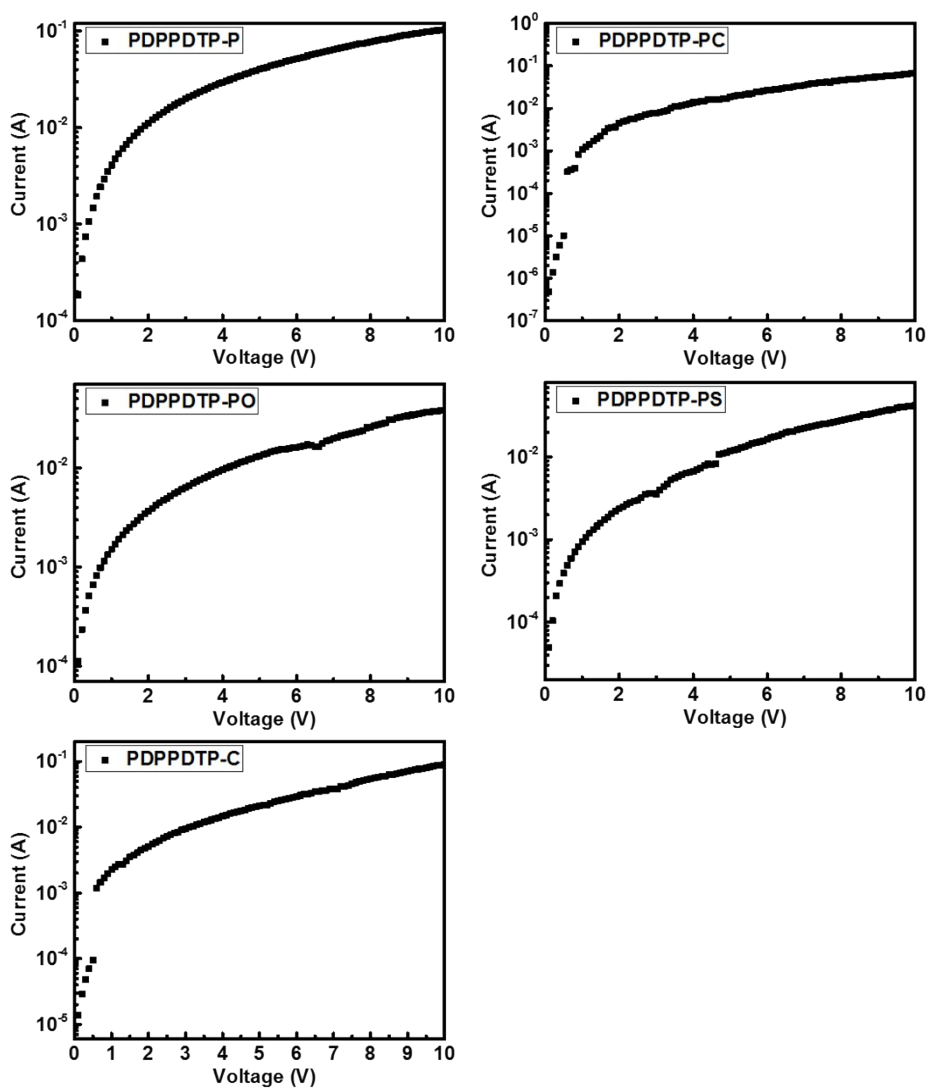


Figure S11. The current-voltage curves of the polymer:PC₇₁BM blend films in hole-only SCLC devices: ITO/PEDOT:PSS/blend/MoO₃/Al.

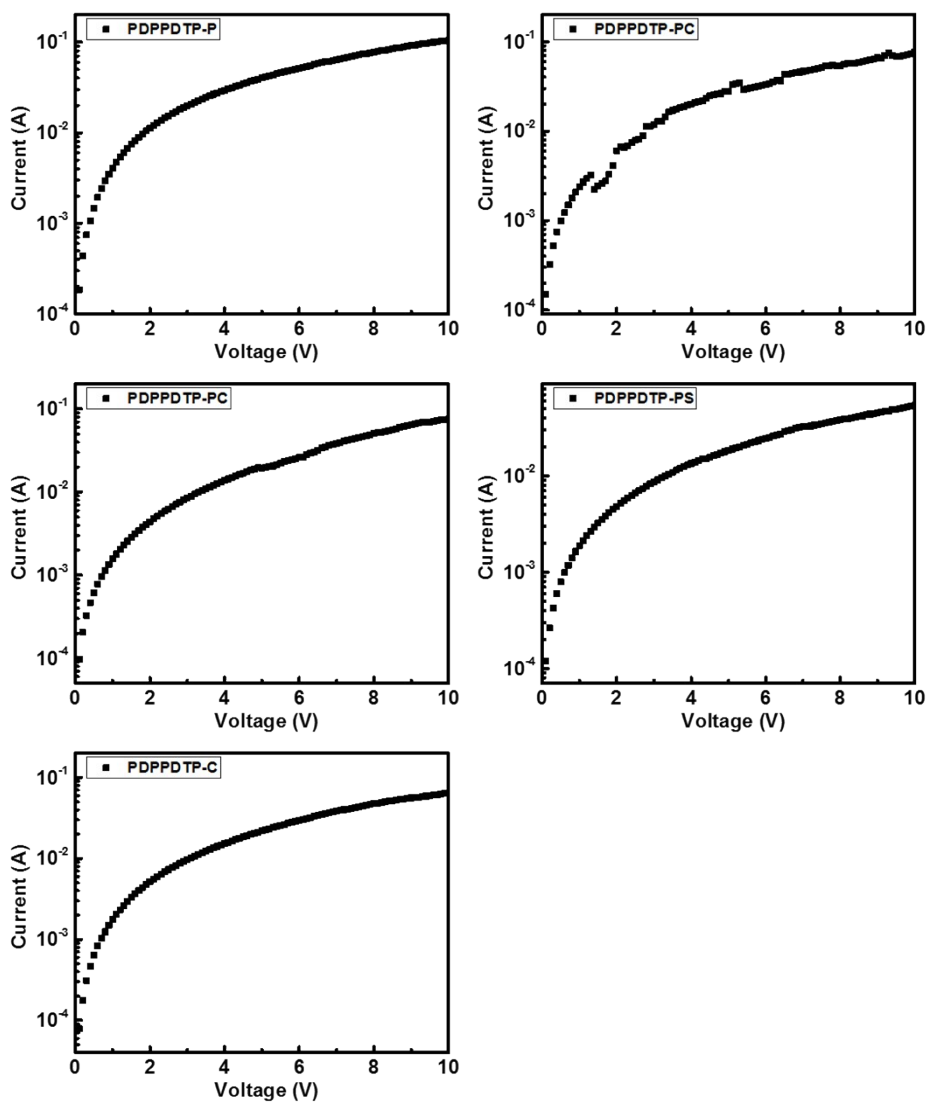


Figure S12. The current-voltage curves of the polymer:PC₇₁BM blend films in electron-only SCLC devices: ITO/ZnO/blend/LiF/Al.

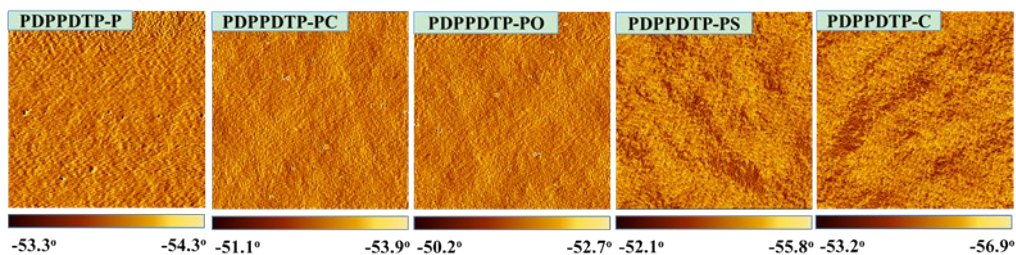
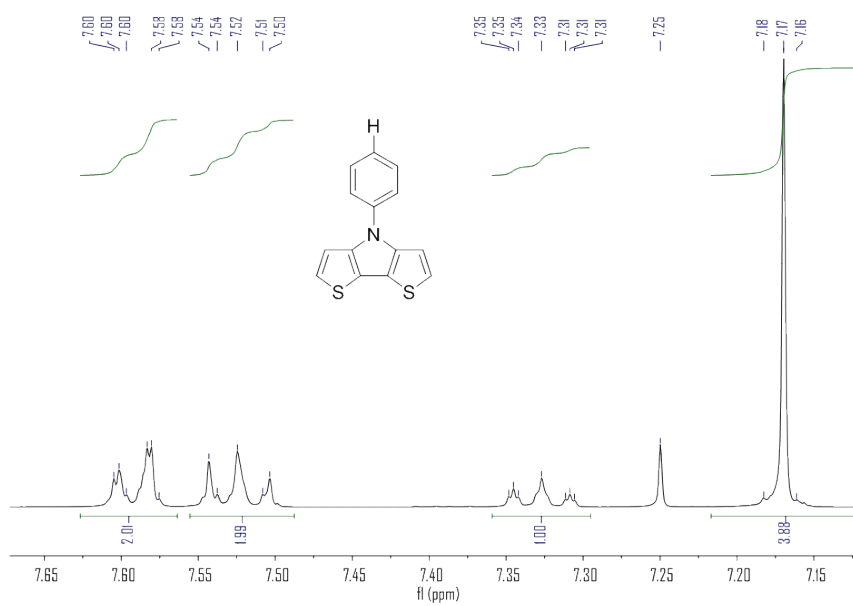
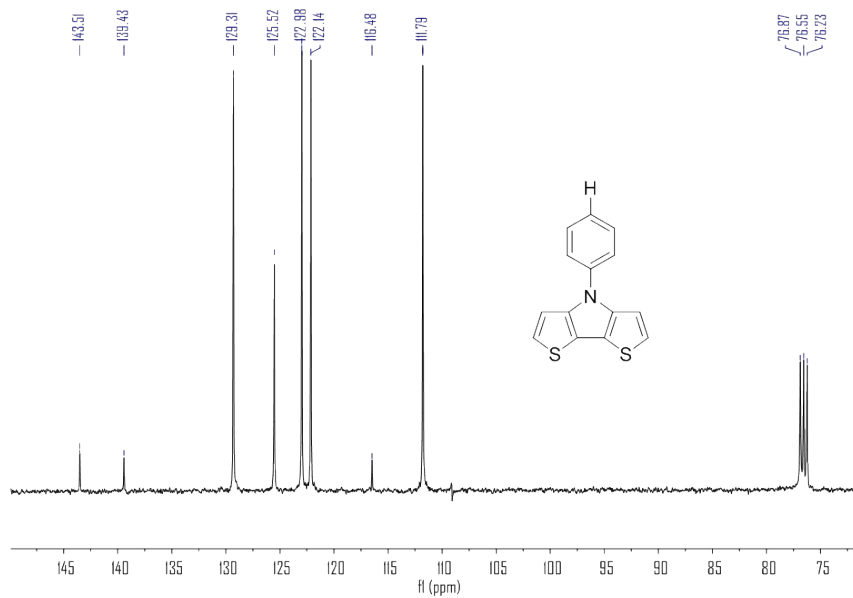


Figure S13. AFM phase images of polymer:PC₇₁BM blend films (2×2 μm).

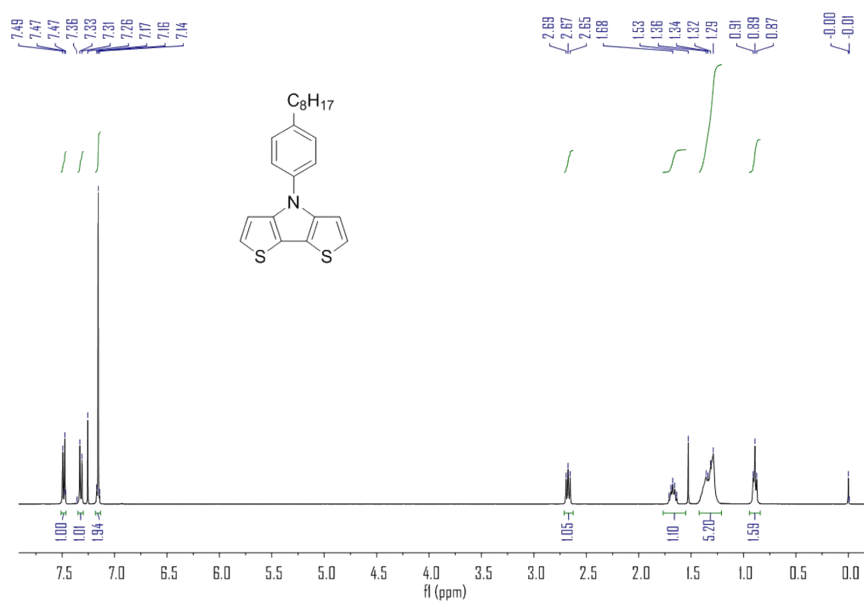
^1H NMR spectrum of compound **2a**.



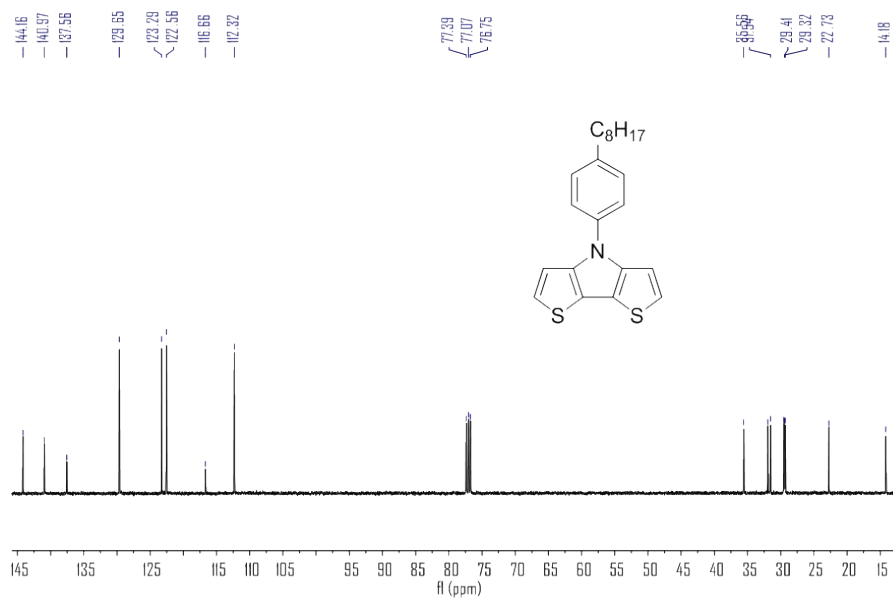
^{13}C NMR spectrum of compound **2a**.



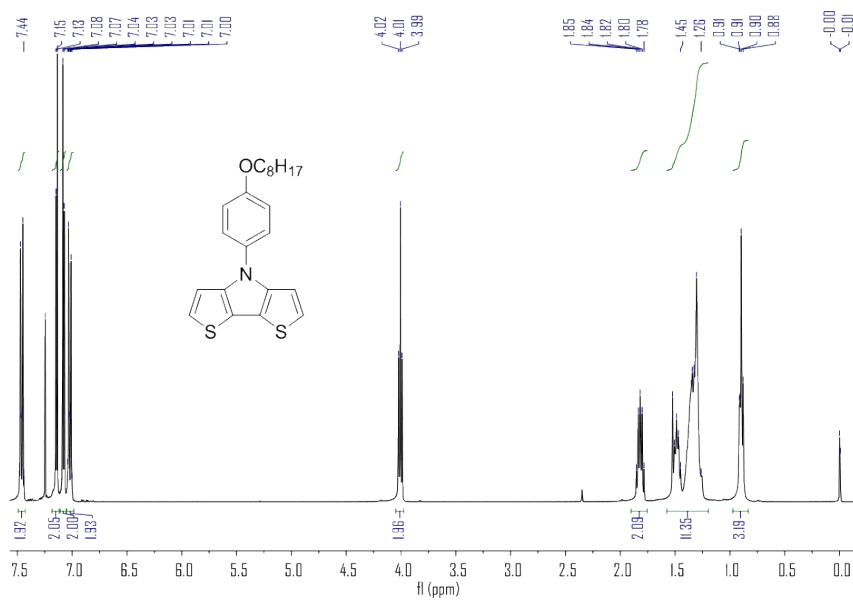
^1H NMR spectrum of compound **2b**.



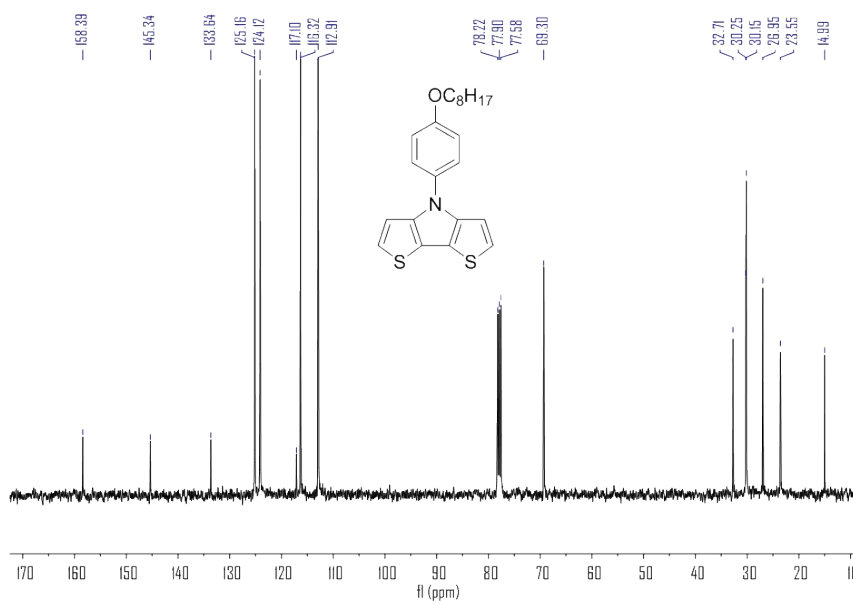
^{13}C NMR spectrum of compound **2b**.



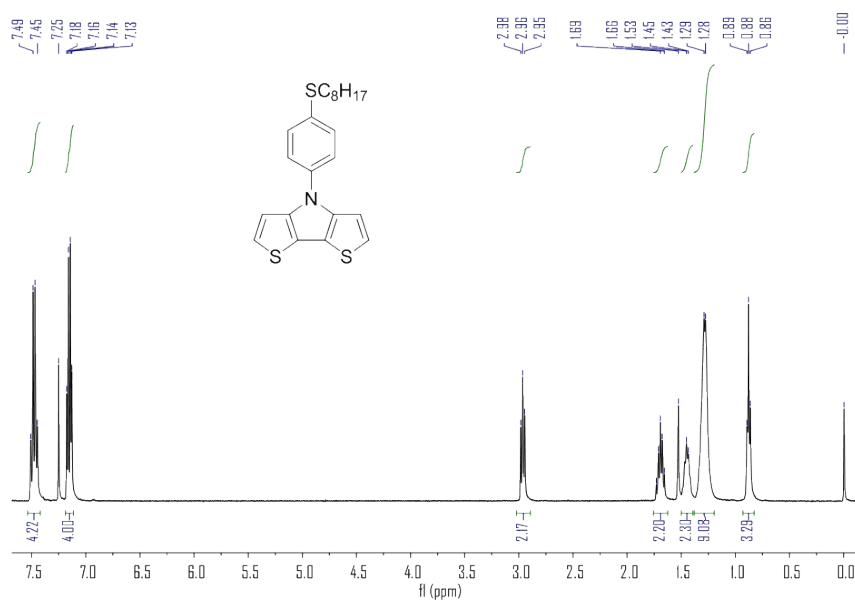
^1H NMR spectrum of compound **2c**.



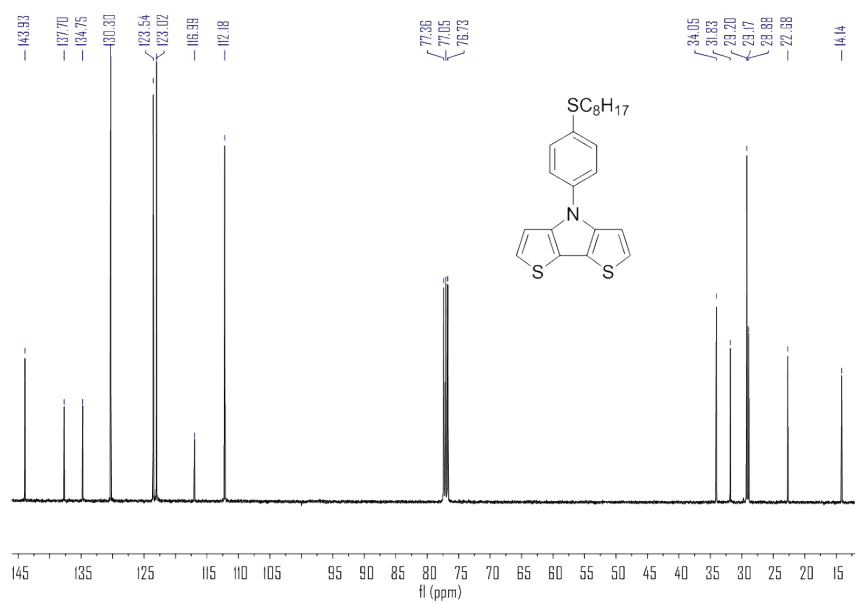
^{13}C NMR spectrum of compound **2c**.



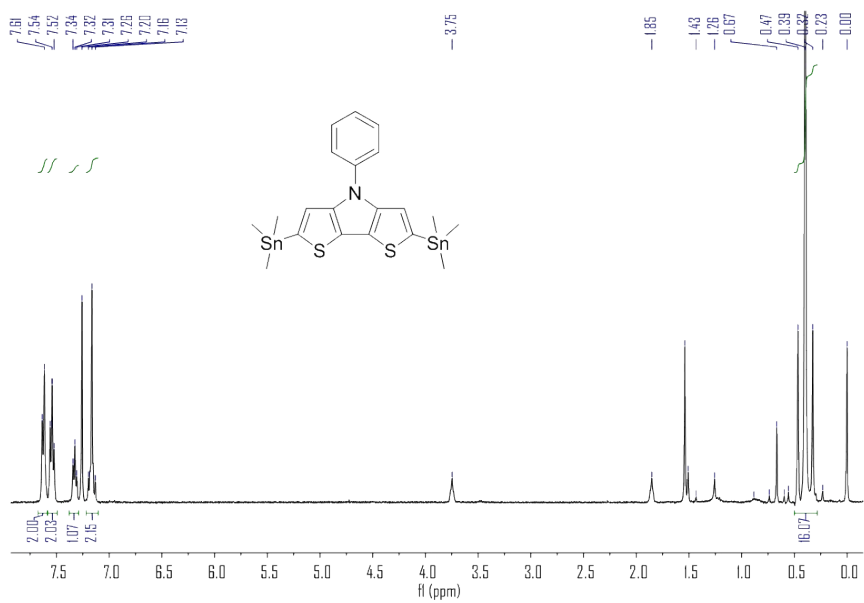
^1H NMR spectrum of compound **2d**.



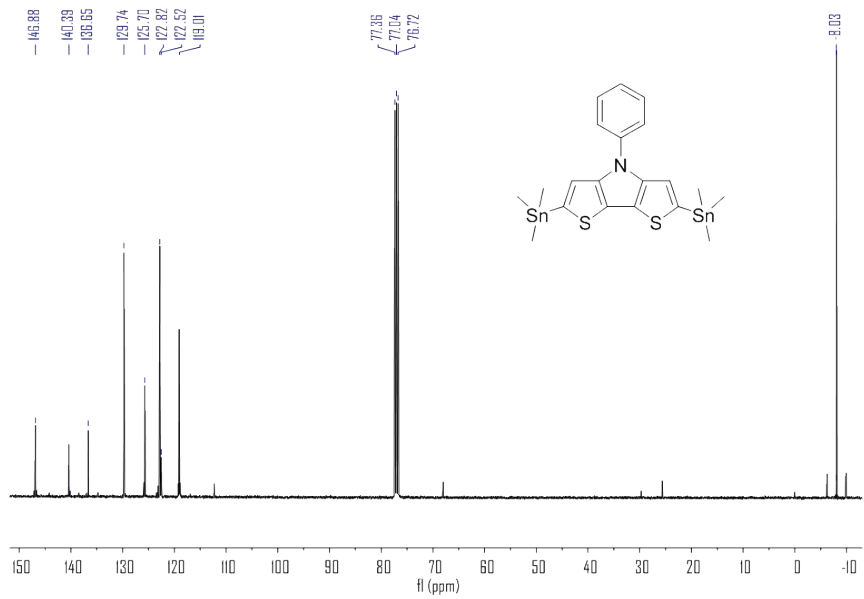
^{13}C NMR spectrum of compound **2d**.



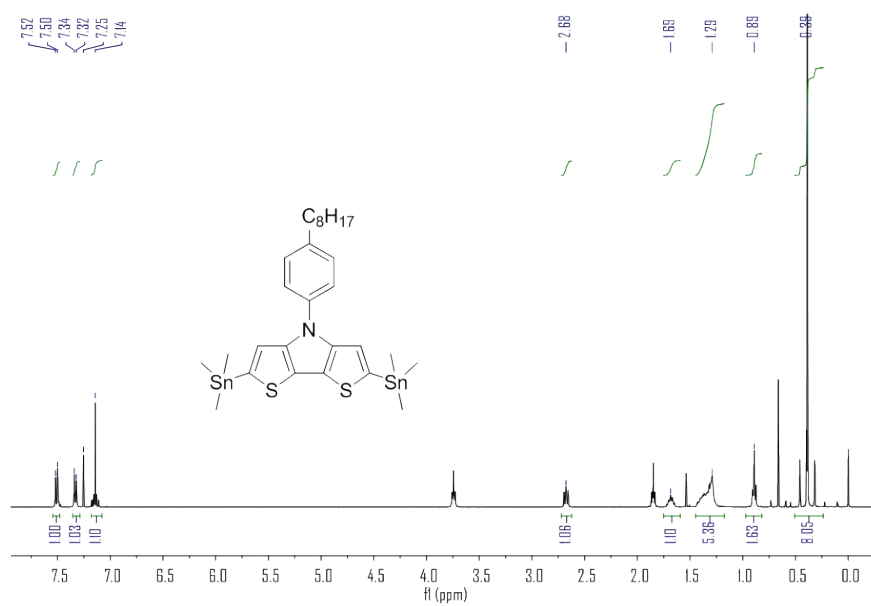
^1H NMR spectrum of compound **3a**.



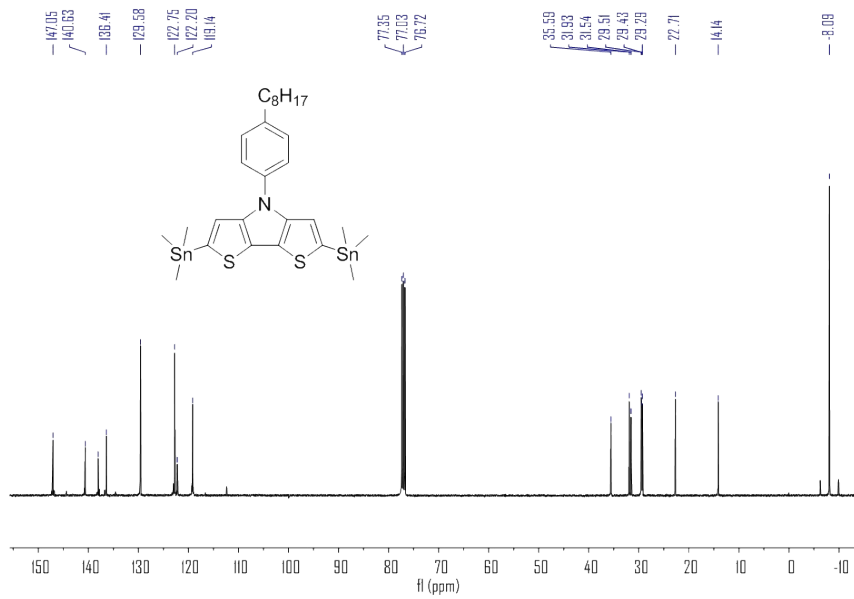
^{13}C NMR spectrum of compound **3a**.



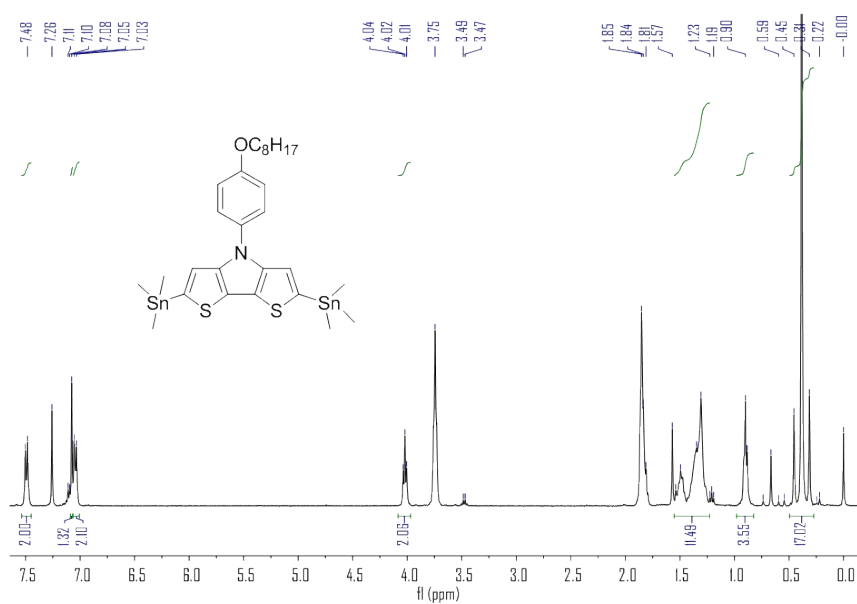
^1H NMR spectrum of compound **3b**.



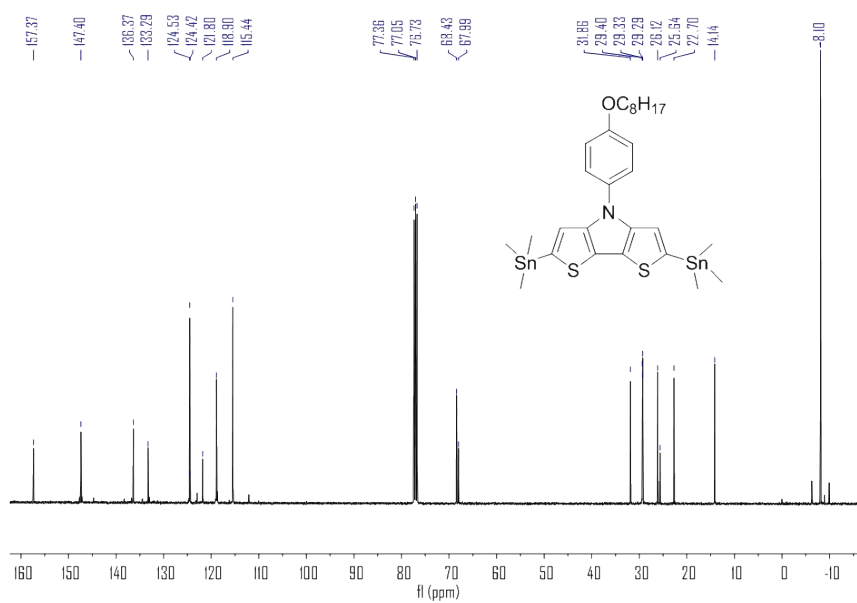
^{13}C NMR spectrum of compound **3b**.



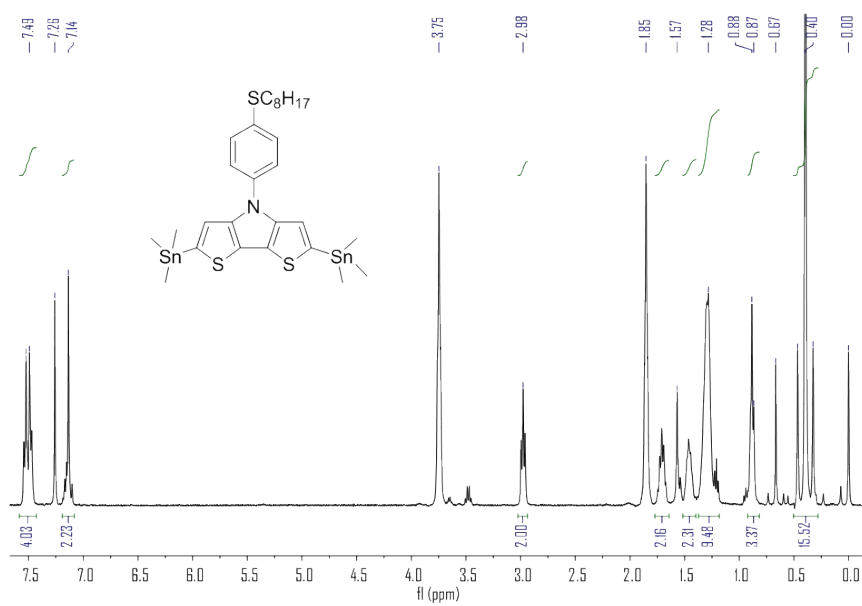
^1H NMR spectrum of compound **3c**.



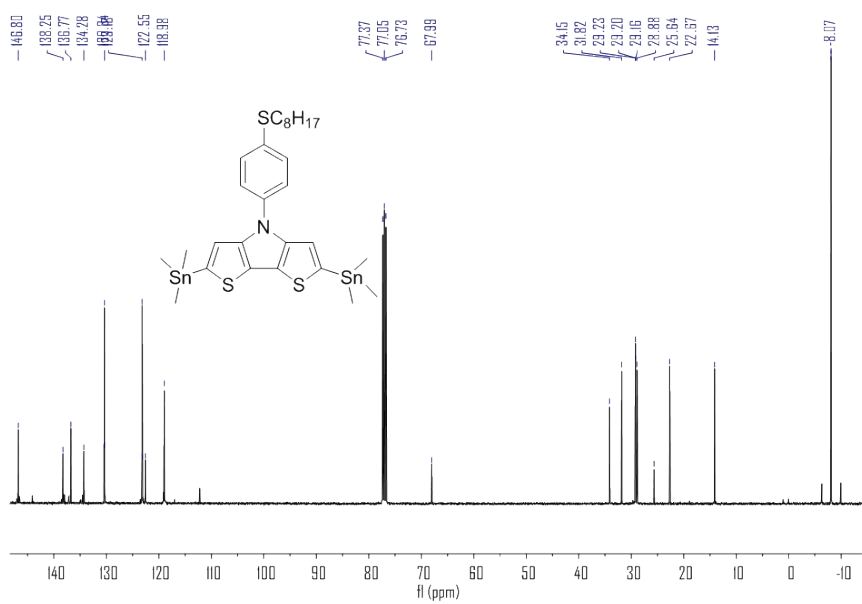
^{13}C NMR spectrum of compound **3c**.



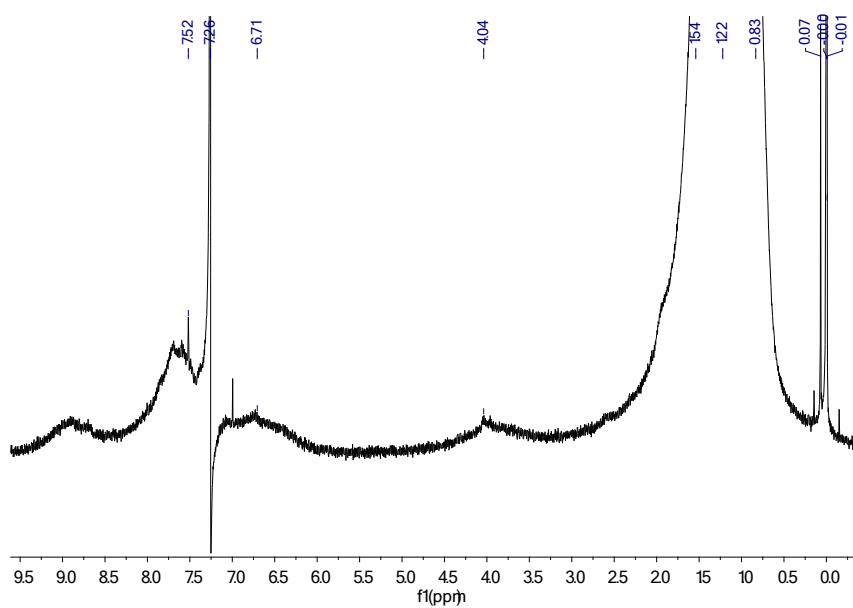
^1H NMR spectrum of compound **3d**.



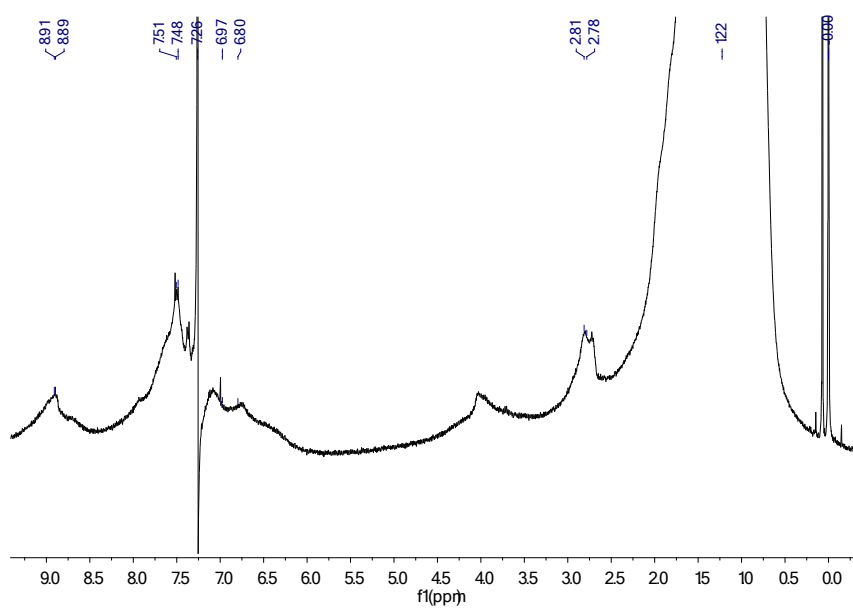
^{13}C NMR spectrum of compound **3d**.



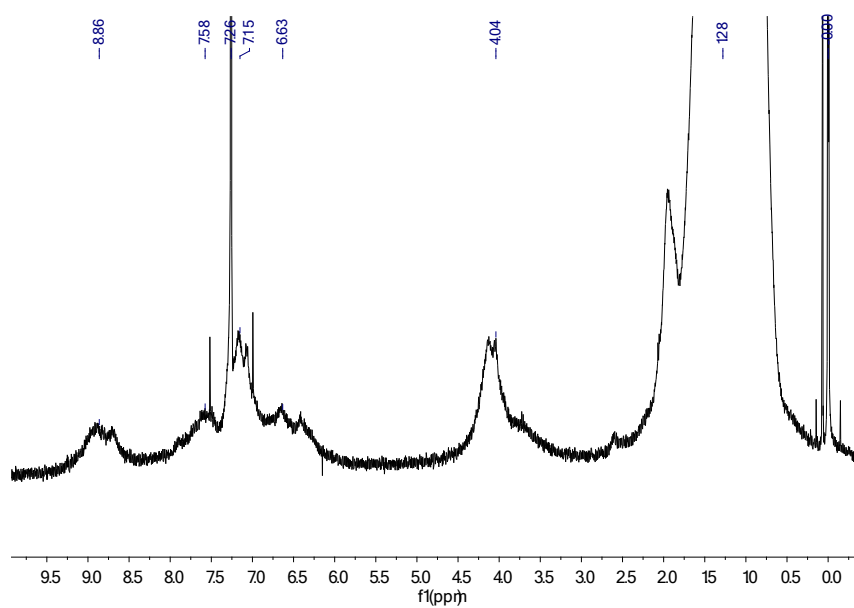
^1H NMR spectrum of compound PDPPDTP-P.



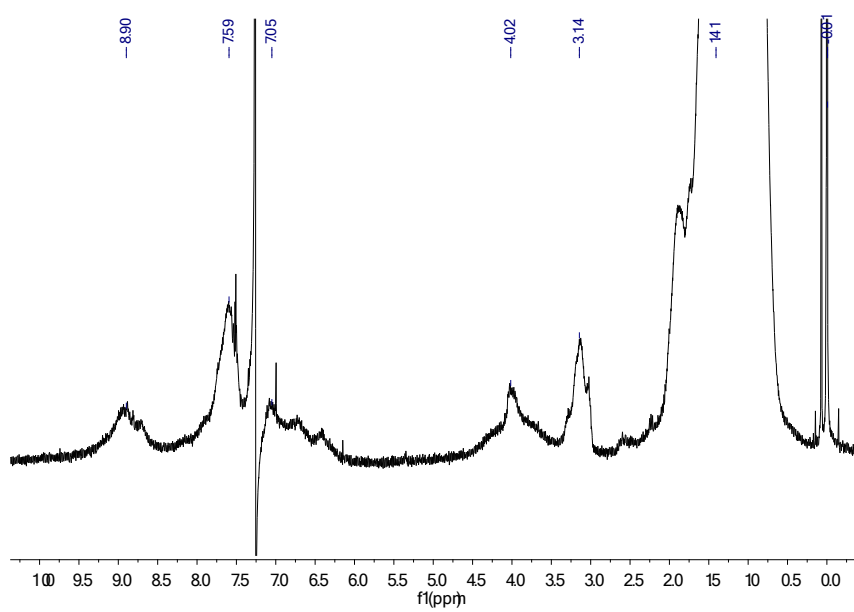
^1H NMR spectrum of compound PDPPDTP-PC.



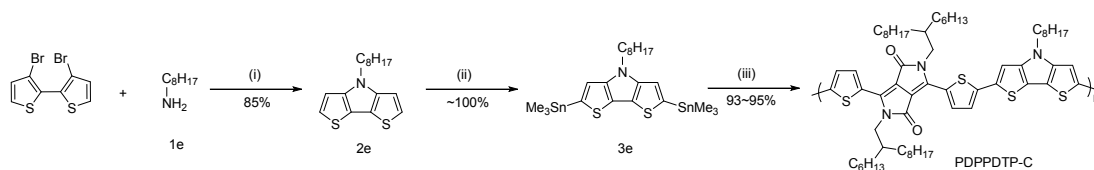
^1H NMR spectrum of compound PDPPDTP-PO.



^1H NMR spectrum of compound PDPPDTP-PS.



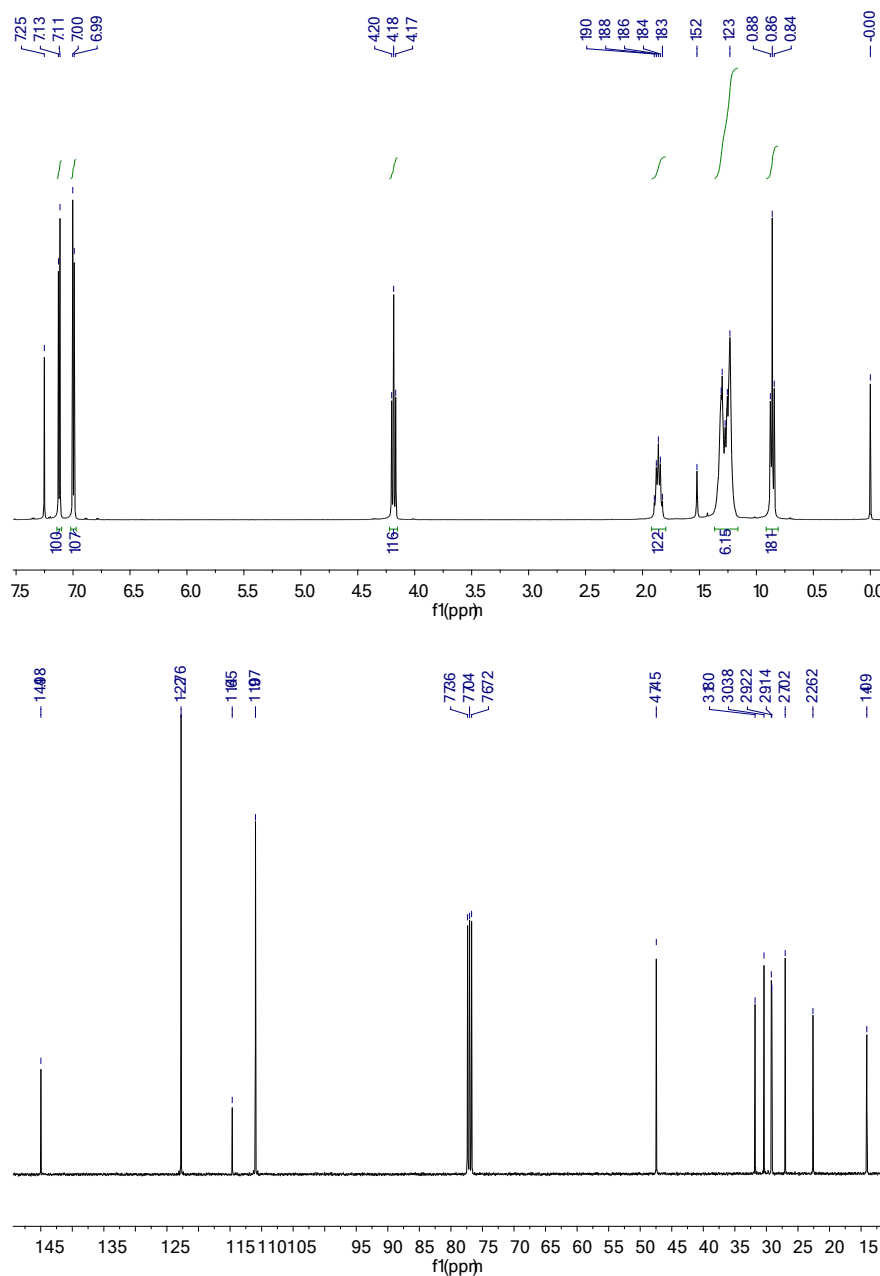
Synthesis of PDPPDTP-C



Reagents and conditions: (i) Pd₂(dba)₃, BINAP, NaO^tBu, Toluene, 110 °C. (ii) a) n-Butyl lithium, in THF, -78°C, b) SnMe₃Cl, 0°C–room temperature.

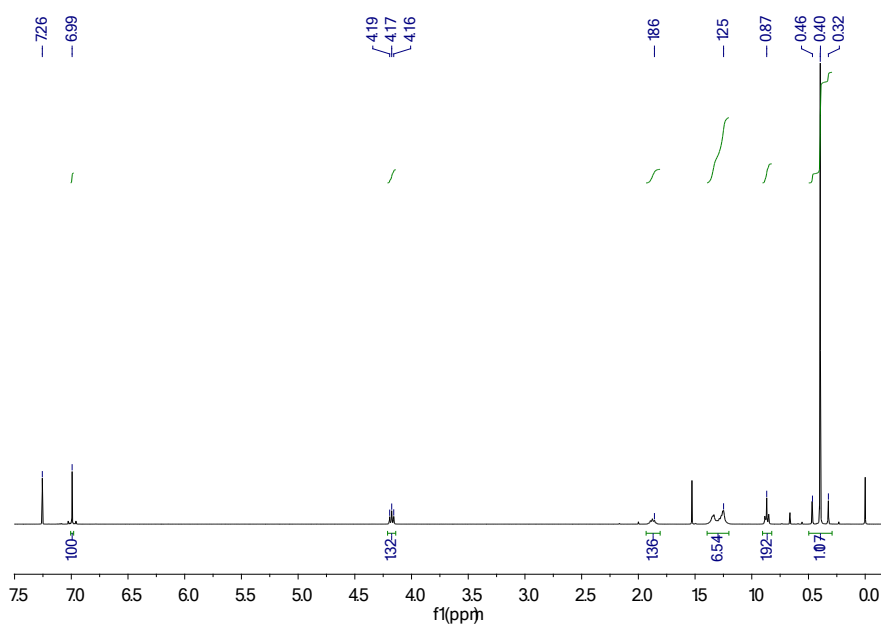
(iii) 3,6-bis(5-bromothiophen-2-yl)-2,5-dihexadecylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, Pd₂(dba)₃, P(o-tol)₃, Toluene/DMF, 110°C.

N-Octyl dithieno[3,2-b:2',3'-d]pyrrole (**2e**). 3,3'-Dibromo-2,2'-bithiophene (1.62 g, 5.0 mol) was added in 10 mL of dry toluene. Then NaO^tBu (1.20 g, 12.5 mmol), Pd₂(dba)₃ (0.14 g, 0.15 mmol), BINAP (0.37 g, 0.6 mmol) were added to the mixture and heated to 35 °C. At this point, n-octylamine (1 mL, 6 mmol) was added via syringe. The resulting solution was heated to 110 °C 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 organic phase was washed with brine, dried over anhydrous NaSO₄, 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 pure product as white solid in 80% yield. ¹H NMR (400 MHz, CDCl₃, 25 °C) 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); ¹³CNMR (100 MHz, CDCl₃, 25 °C) 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.



N-Octyl-2,6-bis(trimethylstannyl)dithieno[3,2-b:2'3'-d]-pyrrole (**3e**). Compound **2e** (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 H₂O, and the aqueous layer was extracted with diethyl ether. The organics were washed with brine, dried over anhydrous NaSO₄, and then concentrated under reduced pressure to afford the product as brown oil in 91% yield. ¹H NMR (400 MHz, CDCl₃, 25 °C) 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).



PDPPDTP-C. **DPP** (0.22675 g, 0.25 mmol) and compound **3e** (0.15427 g, 0.25 mmol) were dissolved into 5 mL of toluene and 0.5 mL of DMF in a flask protected by argon, and then 10 mg of Pd₂(dba)₃ and 25 mg of P(o-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 CHCl₃ (24 h). The CHCl₃ 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 C₆₄H₉₅N₃O₂S₄: 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 %.

