

Electronic Supplementary Information

Interconnecting semiconducting molecules with non-conjugated soft linkers: a way to improve film formation quality without sacrifice in charge mobility

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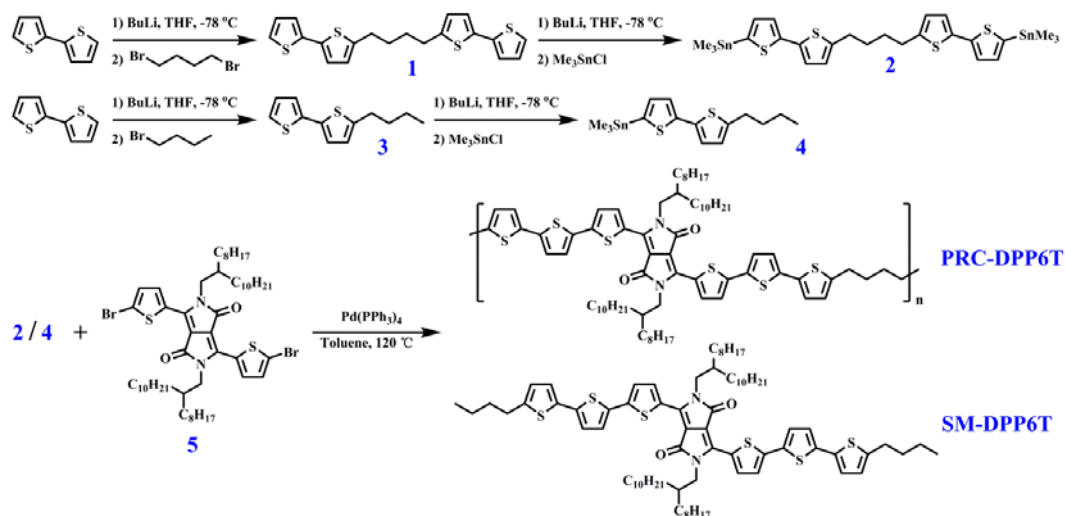
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1. Materials and Characterizations

All reagents were of commercial reagent grade (Energy Chemical, Aldrich, Tianlian and Suna Tech. Co.) and were used as received. Room temperature ^1H NMR spectra were recorded on a Varian 400 or an Agilent 400 MR spectrometer in CDCl_3 with tetramethylsilane (TMS) as an internal reference. High-temperature ^1H NMR and ^{13}C NMR were performed on a Varian or a Agilent 400-MR spectrometer at $110\text{ }^\circ\text{C}$ using $\text{C}_2\text{D}_2\text{Cl}_4$ as a solvent. Matrix-assisted laser deionization time-of-flight (MALDI-TOF) mass spectroscopy was performed on a Shimadzu Biotech Axima Performance Mass Spectrometer using dithranol or α -cyano-4-hydroxycinnamic acid (CHCA) as a matrix. Gel permeation chromatography (GPC) was carried out on PL-GPC 50, using 1,2,4-trichlorobenzene (TCB) as an eluent at $135\text{ }^\circ\text{C}$. The molecular weight and polydispersity index (Đ) were calculated based on polystyrene standards. UV-vis absorption spectroscopy was performed on a Hitachi U-3310 spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI 660C instrument using a three-electrode cell with a glassy carbon as working electrode, a platinum wire as counter electrode, and Ag/AgNO_3 as reference electrode. The samples were first casted on a glassy carbon electrode to form a film and then measured in CH_3CN in the presence of $0.1\text{ M Bu}_4\text{NPF}_6$ at a scan rate 50 mV s^{-1} . Thermogravimetric analysis (TGA) was carried out by a TGA Q500 instrument under N_2 with a temperature rate of $10\text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) was performed on a Q2000 modulated DSC instrument under N_2 with a temperature ramping rate of $10\text{ }^\circ\text{C min}^{-1}$. Optical microscopy was carried out by Olympus BX51 microscope. Raman Mapping was performed on a ThermoFisher DXR Raman microscope using 532 nm laser with an intensity of 2 mW . The diameter of aperture was $50\text{ }\mu\text{m}$ while the scan area was $600 \times 360\text{ }\mu\text{m}^2$. Atomic Force Microscopy (AFM) was performed on a JPK NanoWizard AFM system under a tapping mode with a silicon tip. X-ray diffraction (XRD) was carried out on a PANalytical X'Pert Pro diffractometer with $\text{Cu } K_\alpha$ beam (40 kV , 40 mA) in ϑ - 2ϑ scans.

2. Synthesis methods



Scheme S1 Syntheses of PRC-DPP6T and SM-DPP6T.

1,4-Di(2,2'-bithiophen-5-yl)butane (1): To a cooled solution of 2,2'-bithiophene (0.5 g, 3 mmol) in anhydrous THF (15 mL) at -78 °C, a solution of n-BuLi (3.15 mmol, 1.6 M) in n-hexane was added dropwise. After stirring for 30 min at -78 °C, the reaction mixture was slowly warmed up to room temperature by the removal of cooling bath. Afterward, the mixture was cooled to -78 °C again and added with 1,4-dibromobutane (0.291 g, 1.35 mmol) dropwise. After stirring at -78 °C for 30 min, the cooling bath was removed and the reaction mixture was allowed to naturally warm up to room temperature and then stir overnight. The reaction was quenched by adding 20 mL NH₄Cl-saturated water. After adding with 100 mL water, the resulted mixture was extracted with dichloromethane three times (3 × 50 mL). The combined organic layers were dried over Na₂SO₄ and concentrated by vacuum evaporation. The residue was subjected to silica gel chromatography using hexane as an eluent, affording the product (0.106 g) as a colorless solid in a yield of 21%. ¹H NMR (400 MHz, CDCl₃): δ 7.16 (dd, *J* = 5.2, 0.8 Hz, 2H), 7.10 (dd, *J* = 3.6, 1.2 Hz, 2H), 6.99 (t, *J* = 3.6 Hz, 4H), 6.69 (d, *J* = 3.6 Hz, 2H), 2.84 (t, *J* = 3.6 Hz, 4H), 1.79 (t, *J* = 7.2 Hz, 4H).

1,4-Bis(5'-(trimethylstannyl)-2,2'-bithiophen-5-yl)butane (2): To a cooled solution of 1,4-di(2,2'-bithiophen-5-yl)butane (compound 1, 0.47 g, 1.22 mmol) in 20 mL of anhydrous THF at -78 °C, a solution of n-BuLi (1.6M, 2.5 mL, 4 mmol) in hexane was slowly added within 20 min. After stirred at -78 °C for 30 min, the reaction mixture was warmed up to room temperature by removal of

the cooling bath and stirred for additional 30 min. After the mixture was cooled to -78 °C again, trimethyltin chloride (1 M, 4 mL, 4 mmol) was added dropwise. Afterwards, the cooling bath was removed, and the reaction mixture was allowed to warm up to room temperature and stir overnight. After the reaction was quenched with 20 mL NH₄Cl-saturated water, 100 mL water was added and the resulted mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over Na₂SO₄ and evaporated to dryness under reduced pressure. The obtained crude product was recrystallized from acetone, affording pure product (0.66 g) as a white solid in a yield of 76%. ¹H NMR (400 MHz, CDCl₃): δ 7.20 (d, *J* = 3.2 Hz, 2H), 7.06 (d, *J* = 3.6 Hz, 2H), 6.96 (d, *J* = 3.6 Hz, 2H), 6.67 (d, *J* = 3.6 Hz, 2H), 2.83 (t, *J* = 8.8 Hz, 4H), 1.85–1.70 (m, 4H), 0.46–0.28 (m, 18 H).

1-(2,2'-Bithiophen-5-yl)butane (3): To a cooled solution of 2,2'-bithiophene (1 g, 6 mmol) in anhydrous THF (30 mL) at -78 °C, a solution of n-BuLi (4.8 mmol, 1.6 M) in hexane was added dropwise. After stirring at -78 °C for 30 min, the reaction mixture was slowly warmed up to room temperature by the removal of cooling bath. Afterwards, the reaction mixture was cooled to -78 °C again and then added with 1-bromobutane (0.641 g, 4.68 mmol) dropwise. Then, the reaction mixture was stirred at -78 °C for 30 min, warmed up to room temperature by the removal of cooling bath, and then stirred at room temperature overnight. After the reaction was quenched with 20 mL NH₄Cl-saturated water, 100 mL water was added and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over Na₂SO₄ and concentrated by vacuum evaporation. The residue was subjected to silica gel chromatography using hexane as an eluent. The obtained crude product was further purified by recycling preparative size-exclusion chromatography, affording pure product (0.483 g) as a colorless solid in a yield of 52 %. ¹H NMR (400 MHz, CDCl₃): δ 7.17 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.10 (d, *J* = 3.2 Hz, 1H), 7.02–6.97 (m, 2H), 6.68 (d, *J* = 3.2 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.75–1.6 (m, 2H), 1.5–1.35 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

1-(5'-(Trimethylstannyl)-2,2'-bithiophen-5-yl)butane (4): To a cooled solution of 1-(2,2'-bithiophen-5-yl)butane (compound **3**, 0.4832 g, 2.17 mmol) was dissolved in 20 mL of anhydrous THF at -78 °C, a solution of n-BuLi (1.6 M, 2.037 mL, 3.259 mmol) in hexane was slowly added within 20 min. After stirred at -78 °C for 30 min, the reaction mixture was warmed up to room temperature by removal of the cooling bath. After stirred at room temperature for 30 min, the reaction mixture was cooled to -78 °C again, and added with trimethyltin chloride (1 M, 3 mL, 3 mmol).

After the cooling bath was removed, the reaction mixture was naturally warmed up to room temperature and kept stirring overnight. The reaction was quenched with 20 mL NH₄Cl-saturated water, added with 100 mL water, and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over Na₂SO₄ and evaporated to dryness under reduced pressure. The obtained crude product was purified by recrystallization from acetone and gave pure form (0.77 g) as a white solid in a yield of 92%. ¹H NMR (400 MHz, CDCl₃): δ 7.21 (d, *J* = 3.2 Hz, 1H), 7.07 (d, *J* = 3.2 Hz, 1H), 6.98 (d, *J* = 3.6 Hz, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.73–1.62 (m, 2H), 1.45–1.34 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.45–0.28 (m, 9H).

PRC-DPP6T: The mixture of monomer **2** (0.146 g, 0.205 mmol) and monomer **5** (0.209 g, 0.205 mmol) and 15 mL anhydrous toluene was degassed via freeze-pump-thaw cycle for three times. After Pd(PPh₃)₄ (0.028 g, 0.0246 mmol) was added at the last freezing operation, the mixture was further degassed via freeze-pump-thaw cycle for three times. Then, the reaction mixture was stirred at 120 °C for 72 h under Ar. After cooled to room temperature, the reaction mixture was poured into 100 mL CH₃OH to precipitate the product. After filtration, the crude product was washed with CH₃OH, dried in vacuum, and subjected to Soxhlet extraction sequentially with methanol, hexane, acetone, and chloroform. The polymer was recovered from the chloroform fraction by precipitation with methanol. Finally, 0.17 g product was obtained as a dark greenish solid in a yield of 67%. ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂, 110 °C): δ 8.67 (br, 2H), 7.18 (br, 2H), 7.10 (br, 2H), 6.95 (d, *J* = 3.6 Hz, 4H), 6.64 (br, 2H), 3.93 (br, 4H), 2.78 (br, 4H), 1.74 (br, 4H), 1.17 (br, 66H), 0.77 (q, *J* = 4.8 Hz, 12H). Anal. calcd for (C₇₄H₁₀₂N₂O₂S₆)_n: C 71.45, H 8.26, N 2.25; found: C 71.89, H 8.56, N 2.36. GPC (1,2,4-trichlorobenzene, 135 °C): *M*_n = 14.4 kDa, *M*_w = 28.5 kDa, Đ = 1.98.

SM-DPP6T: The mixture of compound **4** (0.2311 g, 0.6 mmol) and compound **5** (0.2038 g, 0.2 mmol) and 15 mL anhydrous toluene was degassed via freeze-pump-thaw cycle for three times. After Pd(PPh₃)₄ (0.028 g, 0.024 mmol) was added at the last freezing operation, the mixture was further degassed via freeze-pump-thaw cycle for three times. Then, the reaction mixture was stirred at 120 °C for 48 h under Ar. After cooled to room temperature, the reaction mixture was concentrated by vacuum evaporation and the residue was subjected to silica gel chromatography eluting with hexane and ethyl acetate. The obtained crude product was further purified by recycling preparative size-exclusion chromatography, and then recrystallized with chloroform and methanol. Finally, 0.23 g

pure product was obtained as a dark greenish solid in a yield of 89%. ^1H NMR (400 MHz, 1,1,2,2-tetrachloroethane- d_2 , 110 °C) δ 8.67 (d, J = 3.6Hz, 2H), 7.19 (d, J = 2.8Hz, 2H), 7.11 (d, J = 4Hz, 2H), 6.96 (d, J = 3.6Hz, 2H), 6.95 (d, J = 4Hz, 2H), 6.62 (d, J = 2.8Hz, 2H), 3.94 (d, J = 7.6Hz, 4H), 2.73 (t, J = 7.2Hz, 4H), 1.62 (t, J = 7.6Hz, 4H), 1.42–1.1 (m, 70H), 0.88 (t, J = 7.2Hz, 6H), 0.78 (q, J = 4.8Hz, 12H). ^{13}C NMR (100 MHz, 1,1,2,2-tetrachloroethane- d_2 , 110 °C): δ 144.40, 137.20, 131.84, 123.66, 122.77, 122.26, 122.03, 121.76, 44.51, 35.93, 31.26, 29.63, 27.77, 27.61, 26.97, 26.95, 24.37, 20.28, 19.85, 11.62, 11.31. MALDI-TOF MS m/z (%): 1301.5 (100) $[\text{M} + \text{H}]^+$, 1323.5 (20) $[\text{M} + \text{Na}]^+$. Anal. calcd for $\text{C}_{78}\text{H}_{112}\text{N}_2\text{O}_2\text{S}_6$: C 71.95, H 8.67, N 2.15; found: C 71.89, H 8.72, N 2.10.

3. Supporting figures

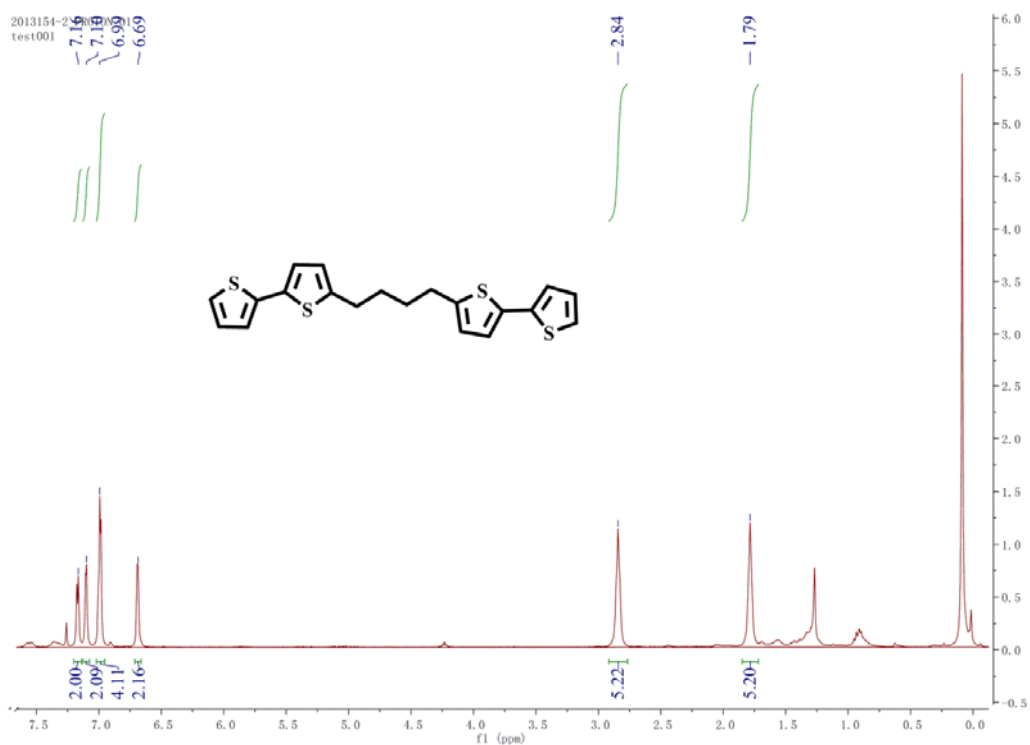


Fig. S1 ^1H NMR of compound **1** in CDCl_3 .

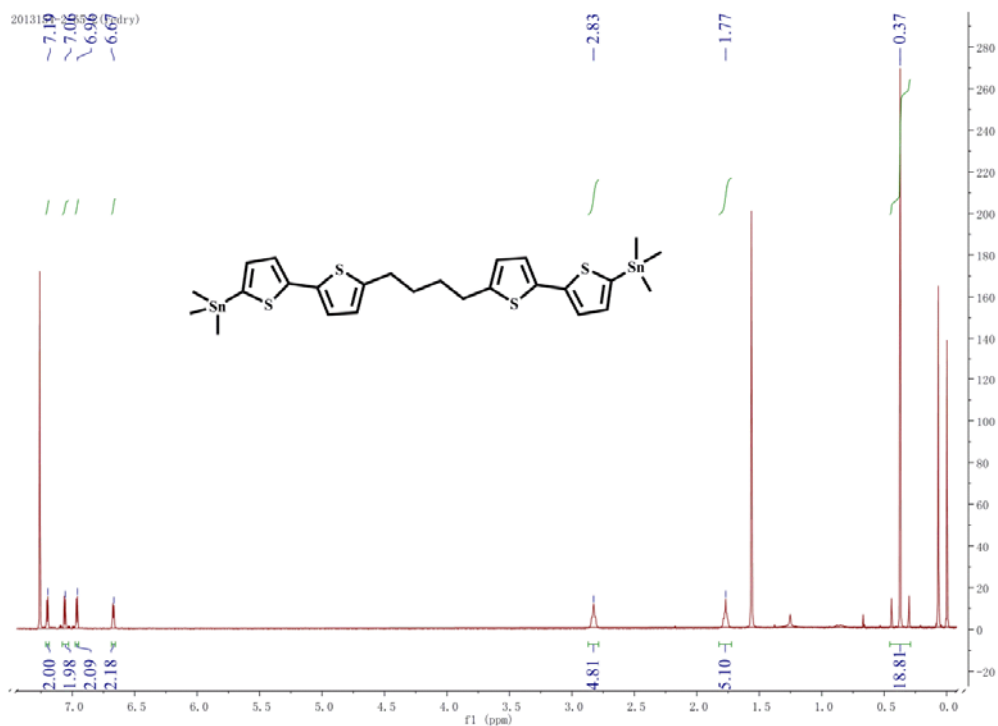


Fig. S2 ^1H NMR of compound **2** in CDCl_3 .

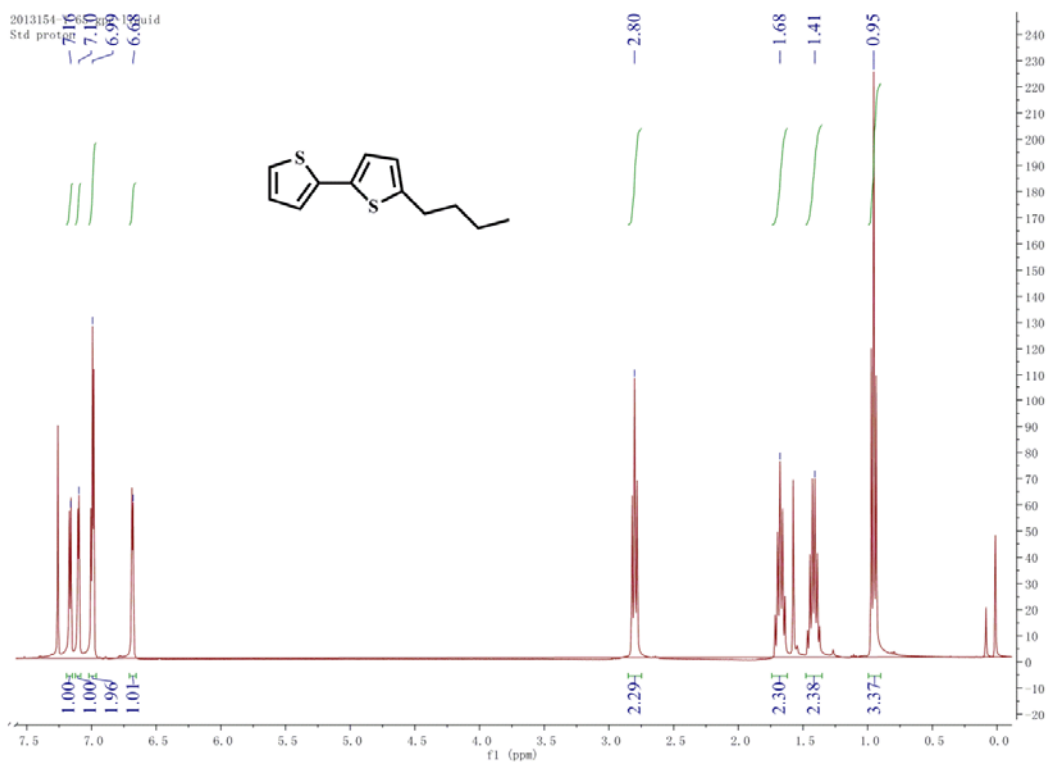


Fig. S3 ^1H NMR of compound 3 in CDCl_3 .

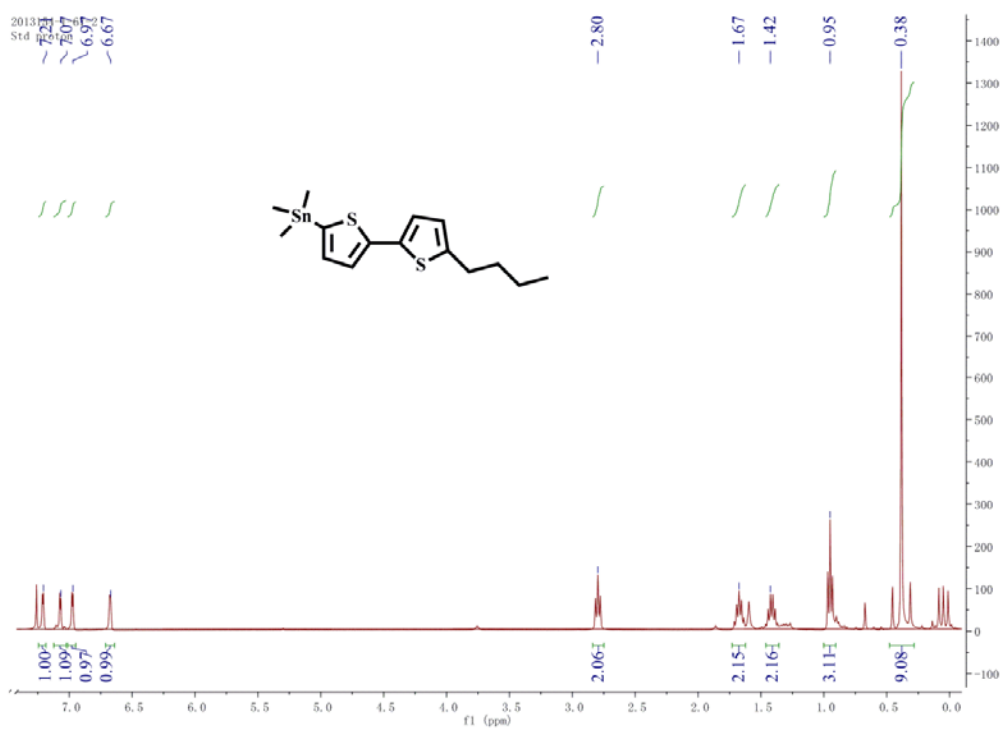


Fig. S4 ^1H NMR of compound 4 in CDCl_3 .

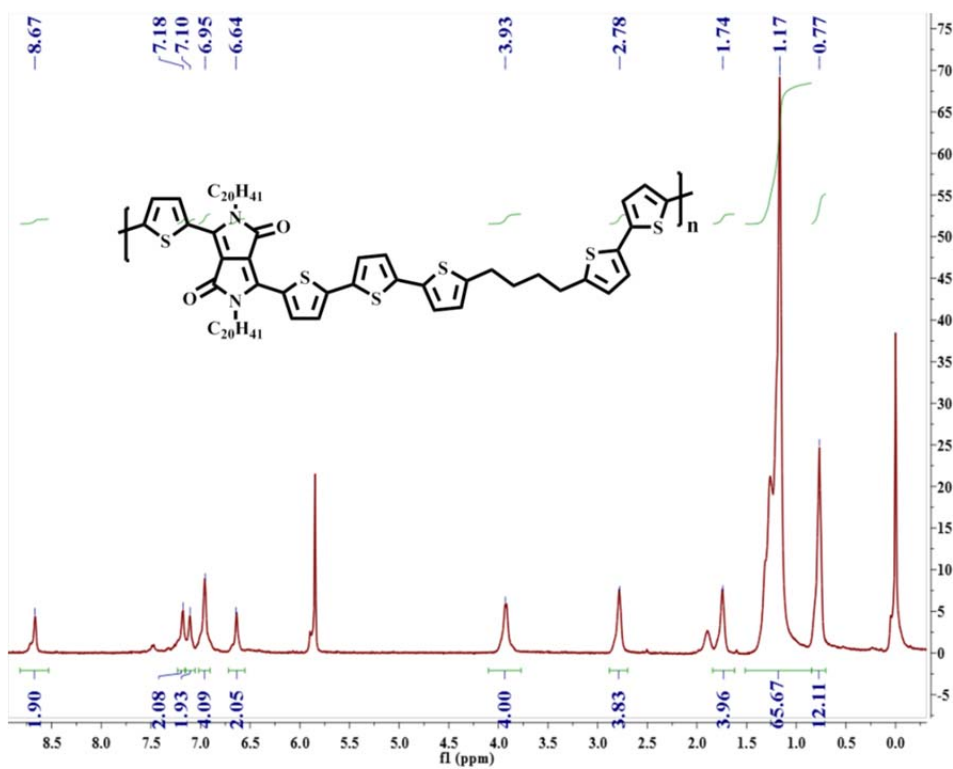


Fig. S5 ^1H NMR of PRC-DPP6T in $\text{C}_2\text{D}_2\text{Cl}_4$ at $110\text{ }^\circ\text{C}$.

MW Averages

Mp: 24295	Mn: 14399	Mv: 26046	Mw: 28538
Mz: 49196	Mz+1: 74707	PD: 1.9819	

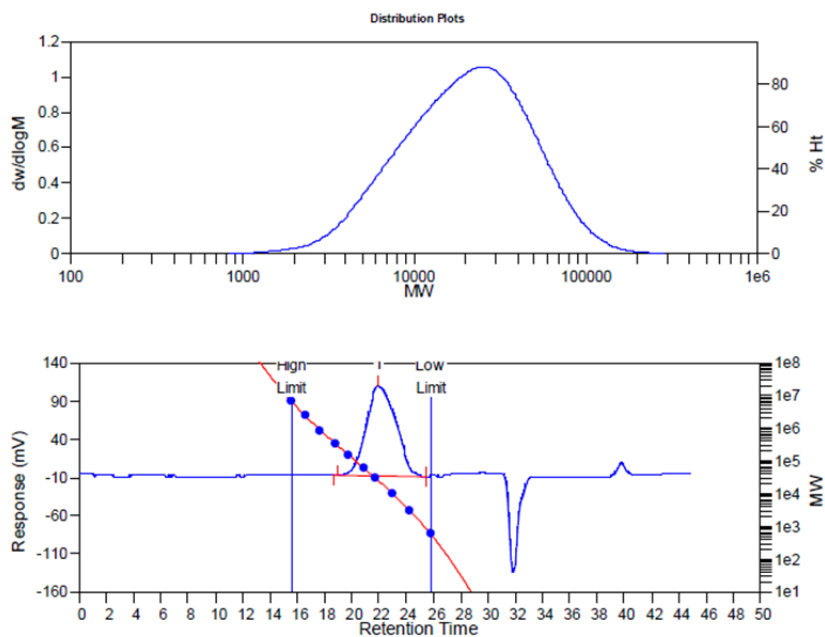


Fig. S6 GPC trace of PRC-DPP6T using 1,2,4-trichlorobenzene as an eluent at $135\text{ }^\circ\text{C}$.

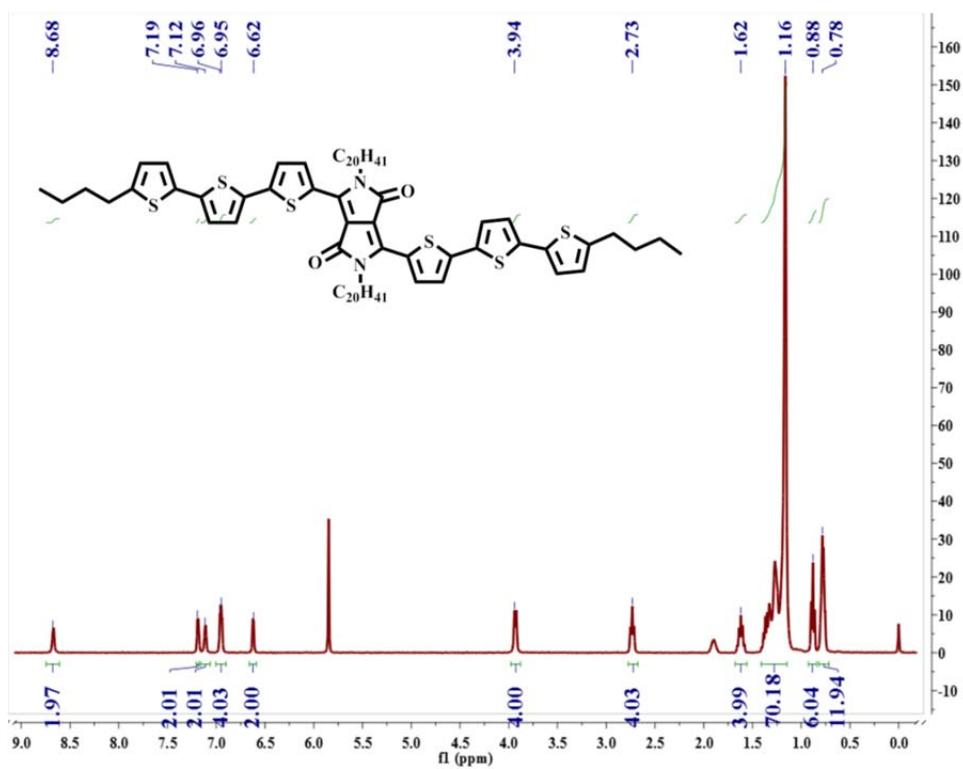


Fig. S7 ^1H NMR of SM-DPP6T in $\text{C}_2\text{D}_2\text{Cl}_4$ at $110\text{ }^\circ\text{C}$.

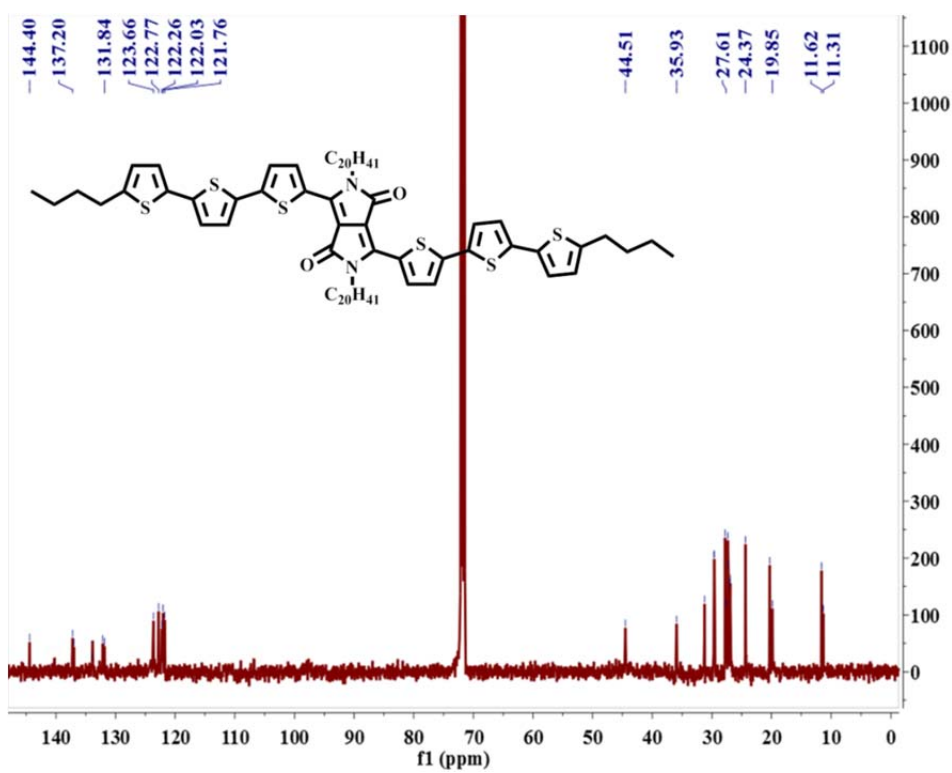


Fig. S8 ^{13}C NMR of SM-DPP6T in $\text{C}_2\text{D}_2\text{Cl}_4$ at $110\text{ }^\circ\text{C}$.

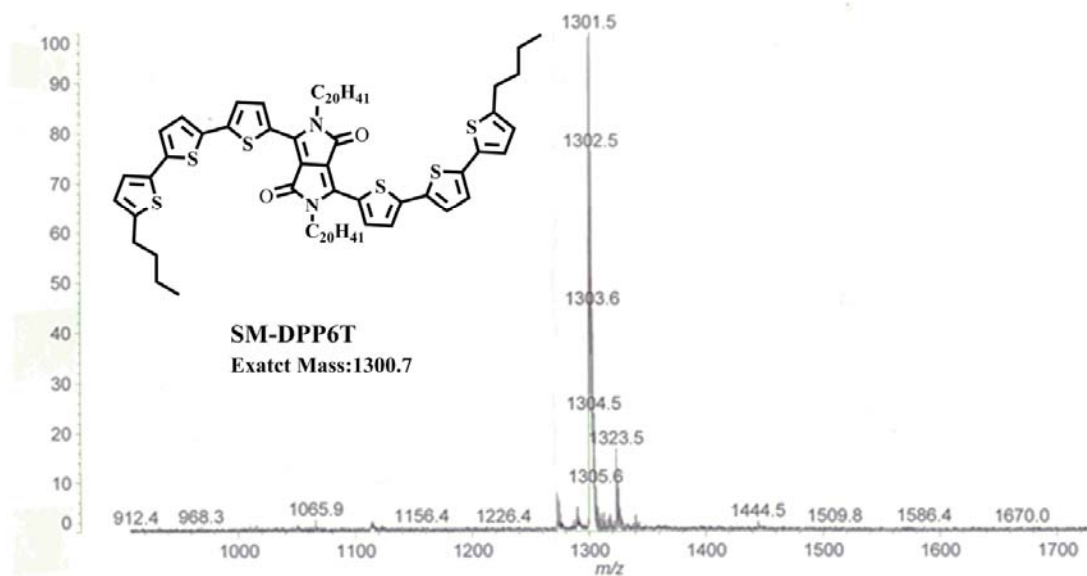


Fig. S9 MALDI-TOF Mass spectrum of SM-DPP6T.

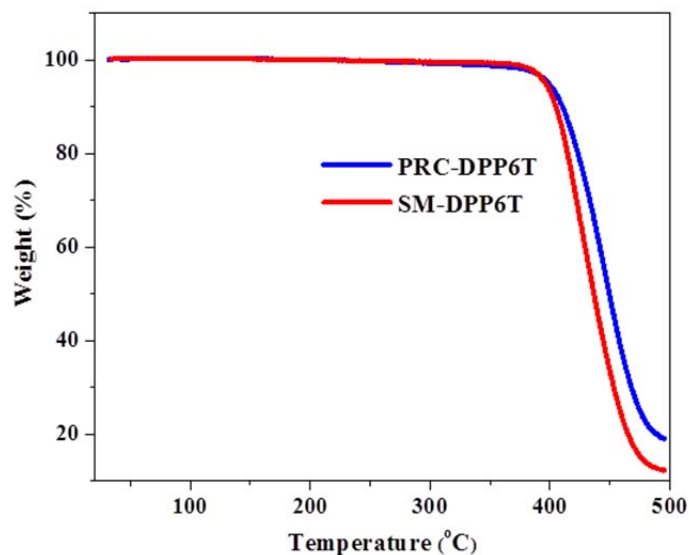


Fig. S10 Thermogravimetric analysis of PRC-DPP6T (red) and SM-DPP6T (blue) at a temperature ramping rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 atmosphere.

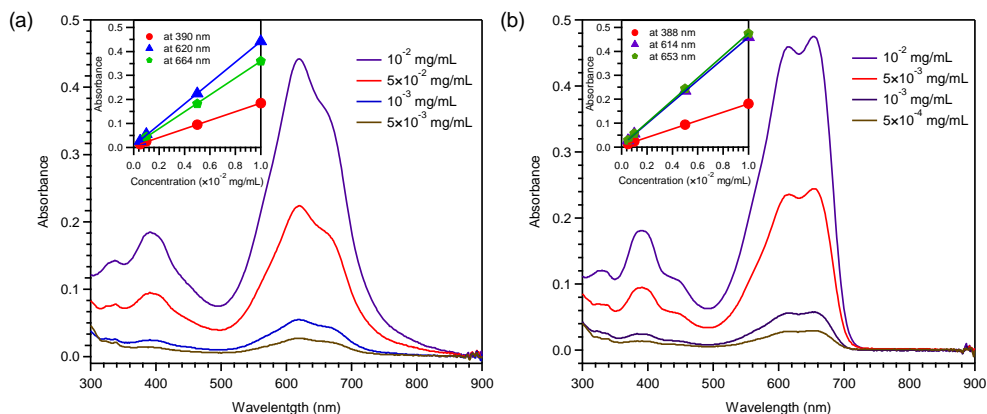


Fig. S11 Concentration-dependent UV-vis absorption spectra of (a) PRC-DPP6T and (b) SM-DPP6T in chlorobenzene solutions. Insets show the plots of absorbance of various peaks versus their concentrations.

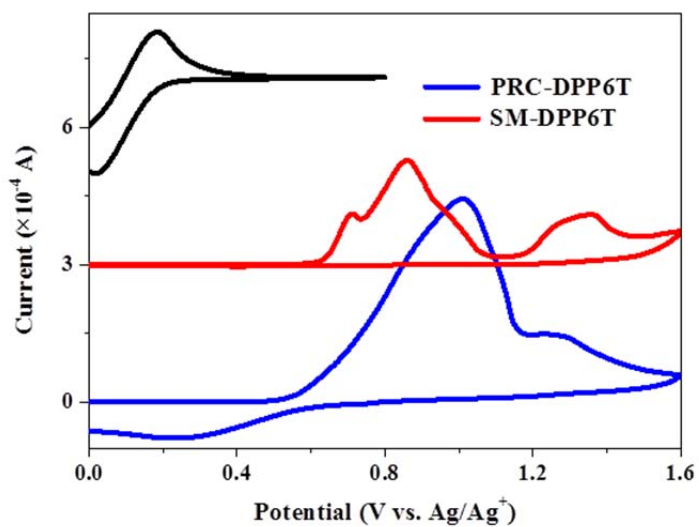


Fig. S12 Cyclic voltammograms of PRC-DPP6T and SM-DPP6T thin films drop-casted on a glassy carbon electrode and tested in CH_3CN solution containing 0.1 M Bu_4NPF_4 at a scan rate of 50 mV s^{-1} .

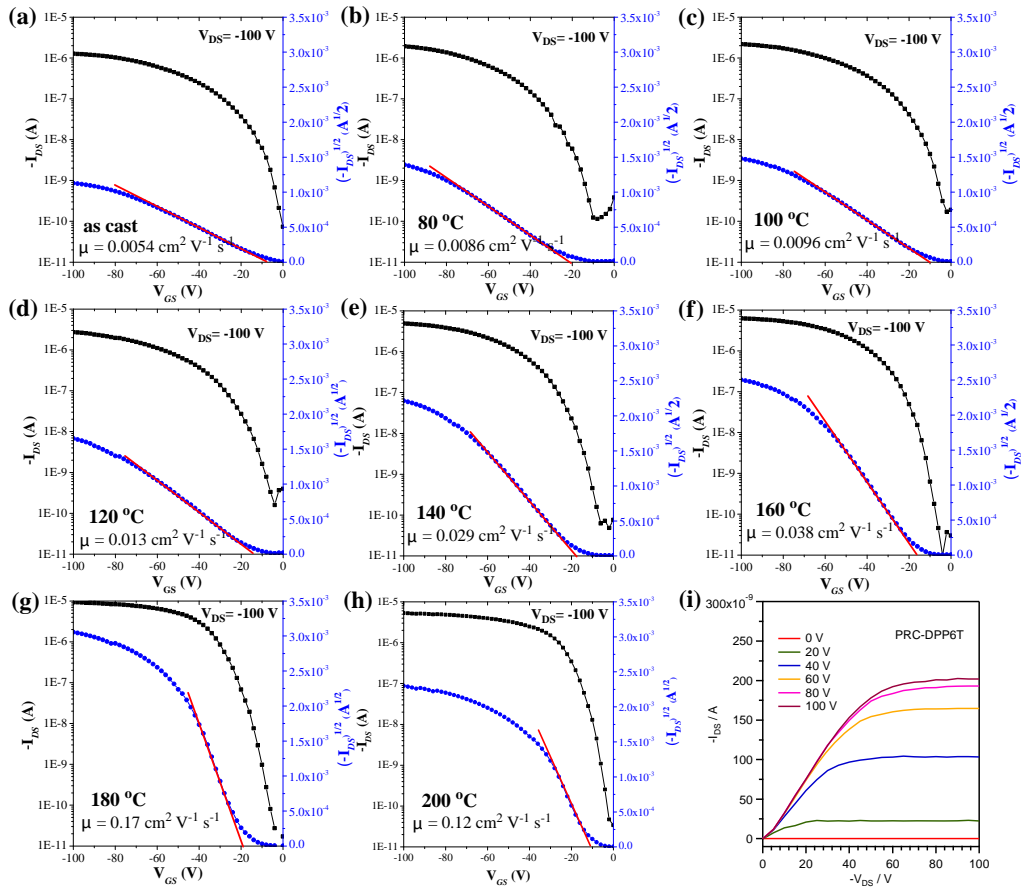


Fig. S13 (a)-(h) Typical transfer curves of the best performance of PRC-DPP6T OFET devices under different annealing temperatures. (i) Typical output curves of an as-cast PRC-DPP6T OFET device.

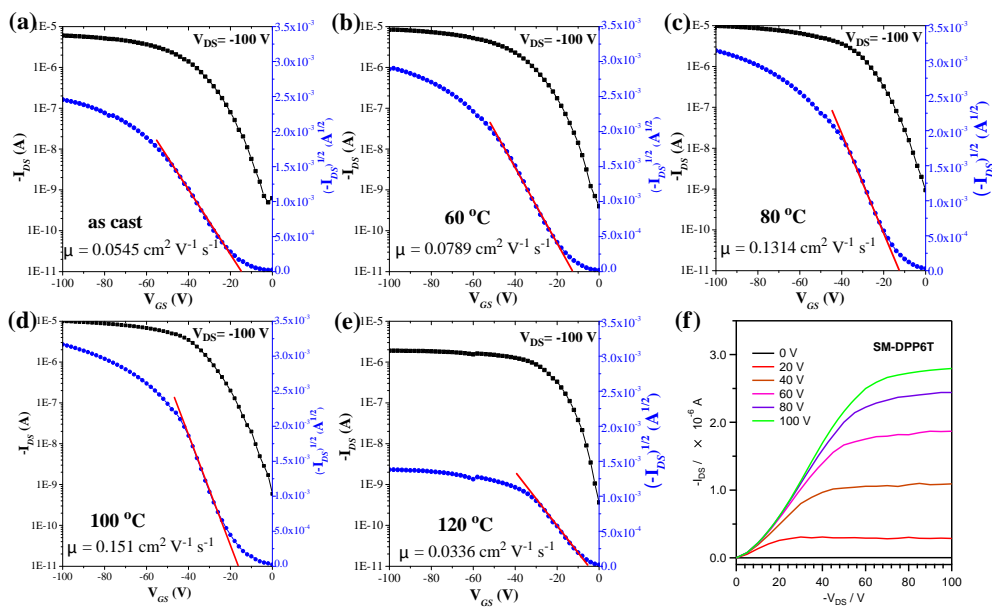


Fig. S14 (a)-(e) Typical transfer curves of the best performance of SM-DPP6T OFET devices under different annealing temperatures. (f) Typical output curves of an as-cast SM-DPP6T OFET device.