

Supporting Information

Sensitivity of Molecular Packing and Photovoltaic Performance to Subtle Fluctuation of Steric Distortions within D-A Copolymer Backbones

Jianhong Gao[†], Wei Wang[†], Shubin Liu[‡], Chun Zhan[†], Shengqiang Xiao^{,†}, Xinhui*

Lu^{,§}, and Wei You^{*,†,||}*

[†] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing Wuhan University of Technology, Wuhan, 430070, P. R. China

[‡] Research Computing Center, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3420, United States

[§] Department of Physics, Chinese University of Hong Kong, Hong Kong, P. R. China

^{||} Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

Corresponding Author

Corresponding Author *E-mail addresses: shengqiang@whut.edu.cn (S.X.), xhlu@phy.cuhk.edu.hk (X.L.), wyou@unc.edu (W.Y.).

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6. References.

1. Materials and Synthesis

Reagents were used as purchased from *JK Chemical* and *Energy Chemical*. [6,6]-Phenyl C₇₁-butyricacid methyl ester (PC₇₁BM) was purchased from Solenne. 4,7-Bis(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]-thiadiazole and 4,7-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole were synthesized according to the literature.^{1,2} Anhydrous THF and toluene were obtained by distillation over sodium/benzophenone under nitrogen atmosphere.

2. Measurements and Instruments

¹H and ¹³C NMR spectra were recorded on a Bruker AV500 at 500 MHz using deuterated chloroform (CDCl₃) as the solvent. UV-vis spectra were recorded on a SHIMADZU UV-1750 spectrophotometer. The molecular weights of the polymers were determined by high temperature gel-permeation chromatography (GPC) with trichlorobenzene as the eluent at 150 °C relative to a polystyrene standard on an Agilent PL-GPC 220 system. Cyclic voltammetry (CV) experiments were performed with CHI 660D analyzer. All CV measurements were carried out in 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in anhydrous acetonitrile with a conventional three-electrode configuration employing a platinum wire as a counter electrode, platinum electrode coated with a thin polymer film as a working electrode, and Ag/Ag⁺ electrode as a reference electrode at a scan rate of 100 mV s⁻¹. Thermogravimetric analysis measurements were carried out on NETZSCH (STA449F3) at a heating rate of 10 °C min⁻¹ under nitrogen. The atomic force microscopy (AFM) images (5.0 μm × 5.0 μm) were obtained through tapping mode on Multimode 8 SPM at ambient conditions. RTESPA (0.01 - 0.025 ohm-cm Antimony (n) doped silicon) tips with a spring constant of 20 - 80 N m⁻¹ and a frequency of 305 - 356 kHz was used in imaging. The GIWAXS measurements of the pristine polymers and polymer:fullerene blend films were conducted at 23 Å SWAXS beamline of a superconductor wiggler at the National Synchrotron Radiation Research

Center, Hsinchu, Taiwan, using 10 keV beam incident at 0.15° and a C9728DK area detector.

3. Fabrication and Characterization of Polymer Solar Cells

The PSC devices were fabricated with the conventional configuration of ITO/PEDOT:PSS/donor (PTDTffBT(C6/EH) or PTDTffBT(EH/C6)): PC₇₁BM /Ca (~20 nm)/Al (80 nm). Prior to be used, indium tin oxide glass substrates were sequentially cleaned with distilled water, acetone, *iso*-propanol and were treated by UV-Ozone. For BHJ devices, poly(3,4-thylenedioxythiophene):polystyrenesulfonic acid (PEDOT:PSS) was spin-coated onto the ITO substrate and annealed at 150 °C for 20 min. To prepare the BHJ films, the polymer of PTDTffBT(C6/EH) or PTDTffBT(EH/C6) (10 mg mL⁻¹) was blended with PC₇₁BM in *o*-dichlorobenzene (*o*-DCB), respectively. BHJ films were spin-cast on the top of the PEDOT:PSS layers in a N₂ filled glove box. Subsequently, Ca (20 nm) and Al (80 nm) were sequentially deposited on the top of the active layers as the cathode at a pressure of 2×10^{-6} mbar through a shadow mask that defines 8 devices with each active area of 0.09 cm².

Current-voltage measurements were carried out in a glovebox under AM 1.5 G irradiation (100 mW cm⁻²) from a 450 W solar simulator (Newport 94023A-U) calibrated by a NREL certified standard silicon cell. Current versus potential (*J-V*) curves were recorded with a Keithley 2420 digital source meter. For external quantum efficiency (EQE) tests, the devices were transferred by a self-made testing box from the glovebox into the chamber of a 7-SCSpec spectral performance of solar cell test system consisting of a 500 watt SCS028-7ILX500 xenon light source, a 7ISW301 vertical grating spectrometer, a 71FW6 filter wheel, a SR810 lock-in amplifier. The calibration of the incident monochromatic light was carried out with a Hamamatsu S1337-1010 BQ Silicon photodetector.

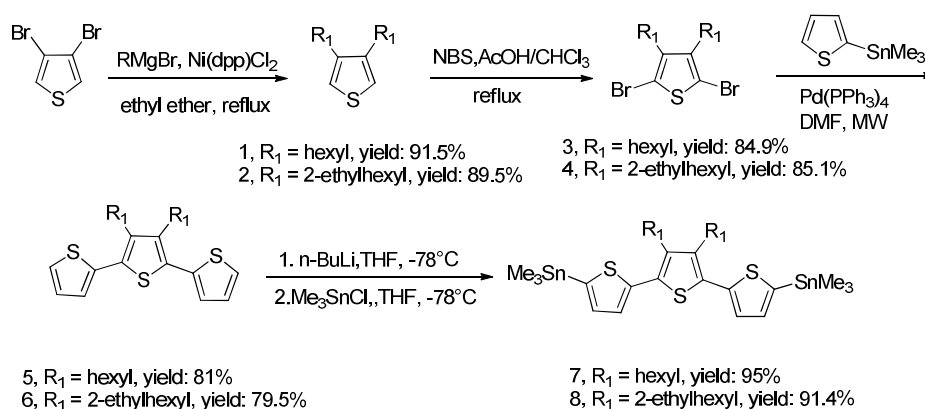
The SCLC *J-V* curves were obtained in the dark from the electron-only and hole-only device of ITO/ZnO/active-layer/Ca/Al and ITO/PEDOT:PSS/active-layer/MoO₃/Ag, respectively. The electron and hole mobility were calculated by the Mott-Gurney square law of $J = (9/8)\epsilon_0\epsilon_r\mu(V^2/L^3)$, where ϵ_0 is

vacuum permittivity, ϵ_r is the dielectric constant of the polymer used, μ is the charge carrier mobility, V is the effective applied voltage, and L is the thickness of the active film in the device.

All calculations were done at the level of B3LYP/6-311G(d) level of density functional theory with the Gaussian package, version E01.³⁻⁵

4. Synthesis of the Monomers.

Scheme S1. The synthetic route of the monomers of (3',4'-dialkyl-(2,2':5',2''-terthiophene)-5,5'-diyl)-bis(trimethylstannane)



3,4-dihexylthiophene (I). Hexylmagnesium bromide (1M in diethyl ether) (17.40 mL, 17.40 mmol) was gradually added to a mixture of 3,4-dibromothiophene (1.98 g, 8.27 mmol) and Ni(dppp)Cl₂ (92 mg, 0.17 mmol) in 30 mL of dry ethyl ether cooled in an ice bath. The reaction mixture was refluxed for 12 h and subsequently poured into 70 mL of ice water containing 1.5 mL of concentrated HCl. The product was extracted with ethyl ether and the combined organic layers were washed with water and brine sequentially. The organic extract was then dried over anhydrous MgSO₄, evaporated and purified with silica gel column chromatography eluted by petroleum ether to give 1.91 g of 3,4-dihexylthiophene (yield, 91.5%). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 6.90 (s, 2H), 2.52 (t, J = 7.8 Hz, 4H), 1.61-1.67 (m, 4H), 1.30-1.41

(m, 12H), 0.92 (t, J = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 142.09, 119.87, 31.74, 29.65, 29.29, 28.82, 22.64, 14.08. EI-MS for $\text{C}_{16}\text{H}_{28}\text{S}$: calcd. 252.19, found: 252.06 (M^+).

3,4-bis(2-ethylhexyl)thiophene (2). Self-made 15.0 mmol of 2-ethylhexylmagnesium bromide in 25.0 mL of anhydrous ethyl ether was added dropwisely into a mixture of 3,4-dibromo- thiophene (1.68 g, 7.0 mmol) and Ni(dppp)Cl_2 (78 mg, 0.14 mmol) in 30 mL of dry ethyl ether in an ice bath. The reaction mixture was then refluxed for 12 h under N_2 , subsequently cooled down to room temperature, and poured into 70 mL of ice water containing 1.5 mL of concentrated HCl. The mixture was extracted with ethyl ether (3×30 mL) and the combined organic layers were washed with water and brine subsequently. The organic extracts were dried over anhydrous MgSO_4 , evaporated and purified with column chromatography on silica gel with mineral ether as the eluent to give 1.93 g of the pure product (yield, 89.5%). ^1H NMR (500 MHz, CDCl_3), δ (ppm): 6.85 (s, 2H), 2.44 (d, J = 7.2 Hz, 4H), 1.53-1.60 (m, 2H), 1.23-1.35 (m, 16H), 0.89 (t, J = 3.6 Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 141.17, 120.73, 39.45, 33.30, 32.71, 28.93, 25.79, 23.09, 14.11, 10.83. EI-MS for $\text{C}_{20}\text{H}_{36}\text{S}$: calcd. 308.25, found: 308.32 (M^+).

2,5-dibromo-3,4-dihexylthiophene (3). To a solution of 3,4-dihexylthiophene (1.50 g, 5.95 mmol) in chloroform (15 mL) and acetic acid (15 mL) was added *N*-bromosuccinimide (2.54 g, 14.28 mmol) in the dark. The reaction mixture was refluxed for 2 h. After cooling to room temperature, the mixture was extracted with dichloromethane (3×30 mL) and washed with sodium carbonate solution and water. The organic extract was dried over anhydrous MgSO_4 , condensed at reduced pressure and purified with silica gel column chromatography using petroleum ether as the eluent to give 2.07 g of pure product (yield, 84.9%). ^1H NMR (500 MHz, CDCl_3), δ (ppm): 2.52 (t, J = 8.0 Hz, 4H), 1.45-1.49 (m, 4H), 1.30-1.38 (m, 12H), 0.91 (t, J = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 141.45, 107.81, 31.87, 29.52, 29.21, 28.96, 22.58, 14.06. EI-MS for $\text{C}_{16}\text{H}_{26}\text{Br}_2\text{S}$: calcd. 408.01, found: 410.22

$((M+2)^+)$.

2,5-dibromo-3,4-bis(2-ethylhexyl)thiophene (4). The compound was prepared according to the procedure for 2,5-dibromo-3,4-dihexylthiophene from 3,4-bis(2-ethylhexyl)thiophene (1.85 g, 6.0 mmol) with a yield of 85.1%. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 2.48 (dd, $J = 7.5, 2.5$ Hz, 4H), 1.56-1.64 (m, 2H), 1.23-1.35 (m, 16H), 0.88 (t, $J = 7.5$ Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 141.02, 108.56, 39.61, 33.44, 32.54, 28.89, 25.74, 23.07, 14.08, 11.08. EI-MS for $\text{C}_{20}\text{H}_{34}\text{Br}_2\text{S}$: calcd. 464.07, found: 465.95 $((M+2)^+)$,

3',4'-dihexyl-2,2':5',2''-terthiophene (5). To a 25 mL microwave glass vial in a glove box was charged with a stirring bar, 2,5-dibromo-3,4-dihexylthiophene (2.05 g, 5.0 mmol), 2-(tributylstannyl)thiophene (4.48 g, 12.0 mmol) and tetrakis(triphenylphosphine)palladium (115 mg, 0.1 mmol, 1% equiv.). Anhydrous DMF (15 mL) was added and the vial was then sealed. The vial was then heated at 150 °C for 40 min in a microwave reactor. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was redissolved in petroleum ether and washed with water and brine subsequently. The organic was dried over anhydrous MgSO_4 , condensed and purified with silica gel column chromatography eluted by petroleum ether to give the final pure product (1.67 g, yield 81%). ^1H NMR (500 MHz, CDCl_3), δ (ppm): 7.31 (d, $J = 5.1$ Hz, 2H), 7.14 (d, $J = 3.5$ Hz, 2H), 7.07 (t, $J = 4.4$ Hz, 2H), 2.70 (t, $J = 8.3$ Hz, 4H), 1.55-1.62 (m, 4H), 1.31-1.44 (m, 12H), 0.91 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 140.07, 136.21, 129.82, 127.29, 125.82, 125.24, 31.49, 30.73, 29.57, 28.13, 22.61, 14.05. MALDI-TOF MS for $\text{C}_{24}\text{H}_{32}\text{S}_3$: calcd. 416.17, found: 416.20 (M^+).

3',4'-bis(2-ethylhexyl)-2,2':5',2''-terthiophene (6). The compound was prepared according to the same procedure for 3',4'-dihexyl-2,2':5',2''-terthiophene (5) from 2,5-dibromo-3,4-bis(2-ethylhexyl)thiophene (2.33 g, 5.0 mmol) by a microwave assisted Stille cross-coupling condensation reaction. The pure product around 1.85 g was finally obtained with a yield of 79.5%. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 7.30 (d, $J = 5.0$ Hz, 2H), 7.12 (d, $J = 3.5$ Hz, 2H), 7.05 (t, $J = 4.3$ Hz, 2H), 2.70 (d, $J =$

7.4 Hz, 4H), 1.46-1.54 (m, 2H), 1.14-1.27 (m, 16H), 0.83 (t, $J = 6.7$ Hz, 6H), 0.78 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 139.83, 135.51, 130.25, 127.16, 126.52, 125.41, 39.80, 32.53, 32.36, 28.75, 25.80, 23.04, 14.06, 10.94. EI-MS for $\text{C}_{28}\text{H}_{40}\text{S}_3$: calcd. 472.23, found: 472.14 (M^+).

(3',4'-dihexyl-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane) (7). To a anhydrous flask containing compound 5 (0.42 g, 1.0 mmol) and 8 mL of anhydrous THF was added in dropwise 2.4 M of *n*-BuLi in hexane (1.0 mL, 2.4 mmol) at -78 °C under N_2 . After having been stirred for 30 min at -78 °C, the solution was allowed to warm to room temperature under stirring and reacted for another 30 min. The solution was then cooled to -78 °C again before 1 M of trimethyltin chloride in hexane (2.6 mL, 2.6 mmol) was added. The reaction was stirred overnight at room temperature and then quenched with water, extracted with diethyl ether, and dried over MgSO_4 . After removal of the solvent under reduced pressure, the product (0.70 g, yield 95%) was obtained as a pale-yellow liquid and used without further purification. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 7.24 (d, $J = 3.1$ Hz, 2H) 7.14 (d, $J = 3.2$ Hz, 2H), 2.71 (t, $J = 8.3$ Hz, 4H), 1.56-1.63 (m, 4H), 1.40-1.45 (m, 4H), 1.31-1.35 (m, 8H), 0.91 (t, $J = 6.7$ Hz, 6H), 0.40 (s, 18H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 142.10, 139.67, 137.81, 135.37, 129.89, 126.72, 31.46, 30.62, 29.54, 28.19, 22.61, 14.08, -8.22. MALDI-TOF MS for $\text{C}_{30}\text{H}_{48}\text{S}_3\text{Sn}_2$: calcd. 742.32, found: 742.10 (M^+).

(3',4'-bis(2-ethylhexyl)-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane) (8). The compound was prepared according to the same procedure for (3',4'-dihexyl-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane) (7) from compound 6 (0.47 g, 1.0 mmol) with a yield of 91.4% (0.73 g). ^1H NMR (500 MHz, CDCl_3), δ : 7.24 (d, $J = 3.3$ Hz, 2H) 7.12 (d, $J = 3.4$ Hz, 2H), 2.72 (m, 4H), 1.50-1.55 (m, 2H), 1.16-1.28 (m, 16H), 0.83 (t, $J = 6.1$ Hz, 6H), 0.79 (td, $J = 7.4, 2.0$ Hz, 6H), 0.39 (s, 18H). ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 142.40, 139.41, 137.83, 135.19, 130.28, 127.33, 39.89, 32.59, 32.49, 28.79, 25.88, 23.08, 14.12, 11.07, -8.25. MALDI-TOF MS for $\text{C}_{34}\text{H}_{56}\text{S}_3\text{Sn}_2$: calcd. 798.42, found: 798.20 (M^+).

4. ^1H and ^{13}C -NMR spectra and high resolution MALDI-TOF mass spectra of the compounds in this work.

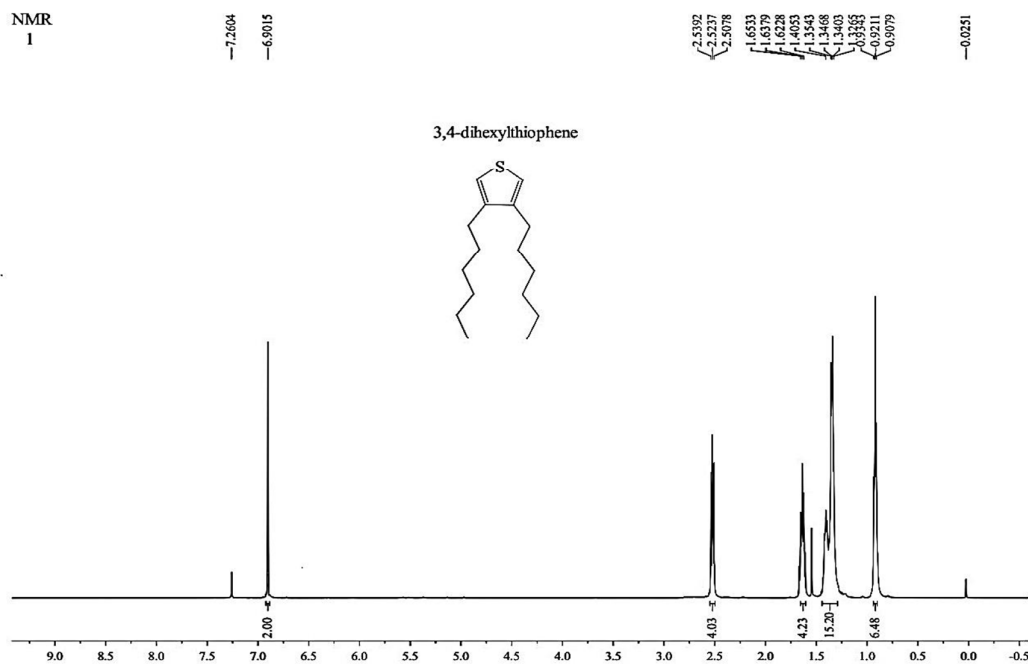


Figure S1. ^1H NMR spectra of 3,4-dihexylthiophene

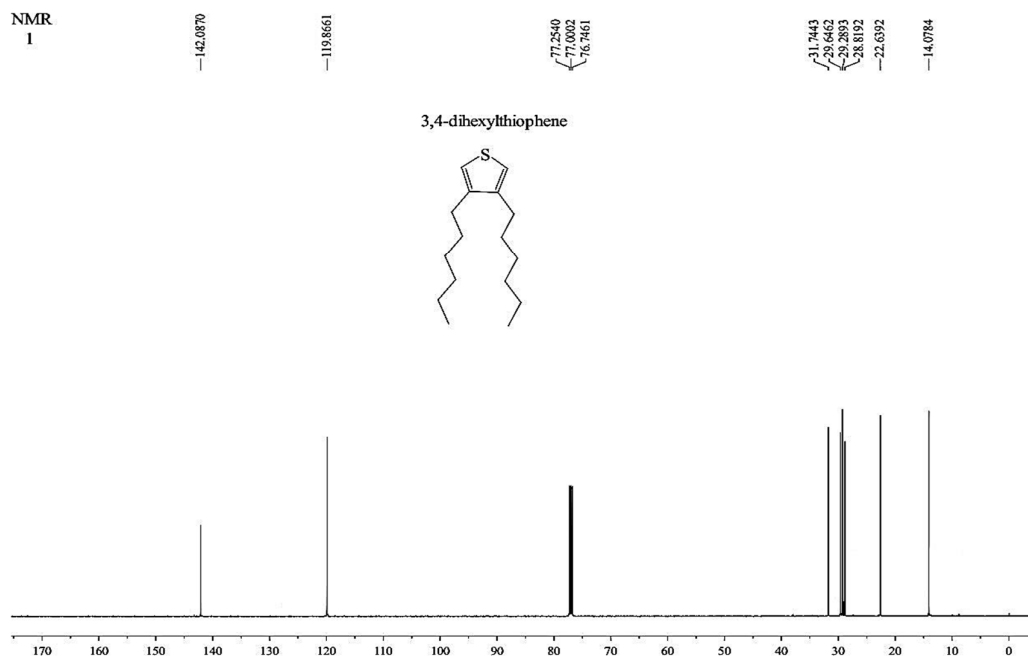


Figure S2. ^{13}C NMR spectra of 3,4-dihexylthiophene

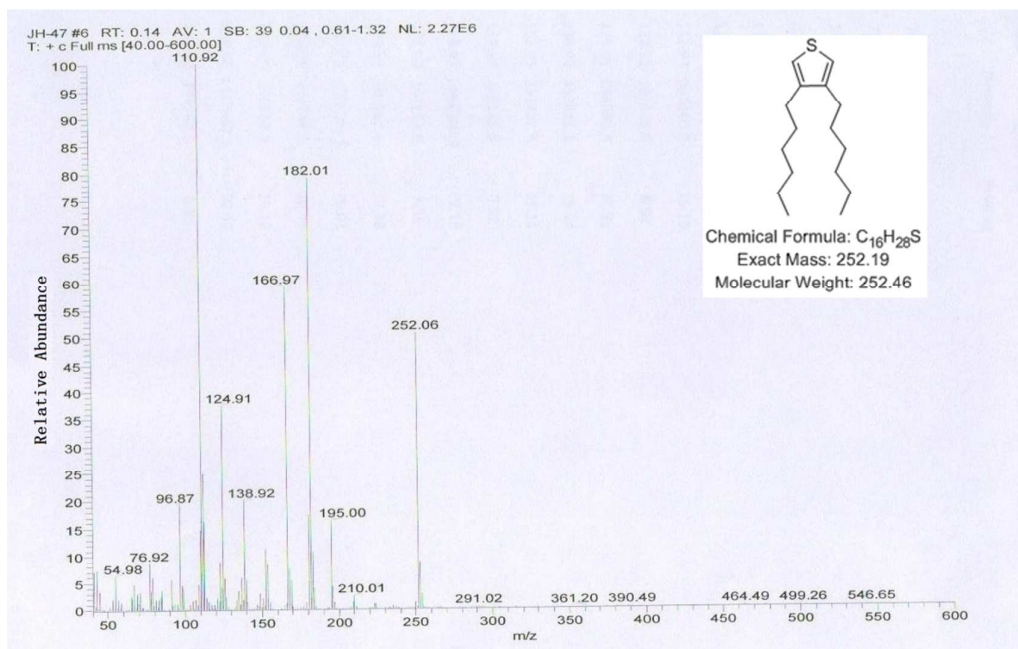


Figure S3. Mass spectra of 3,4-dihexylthiophene

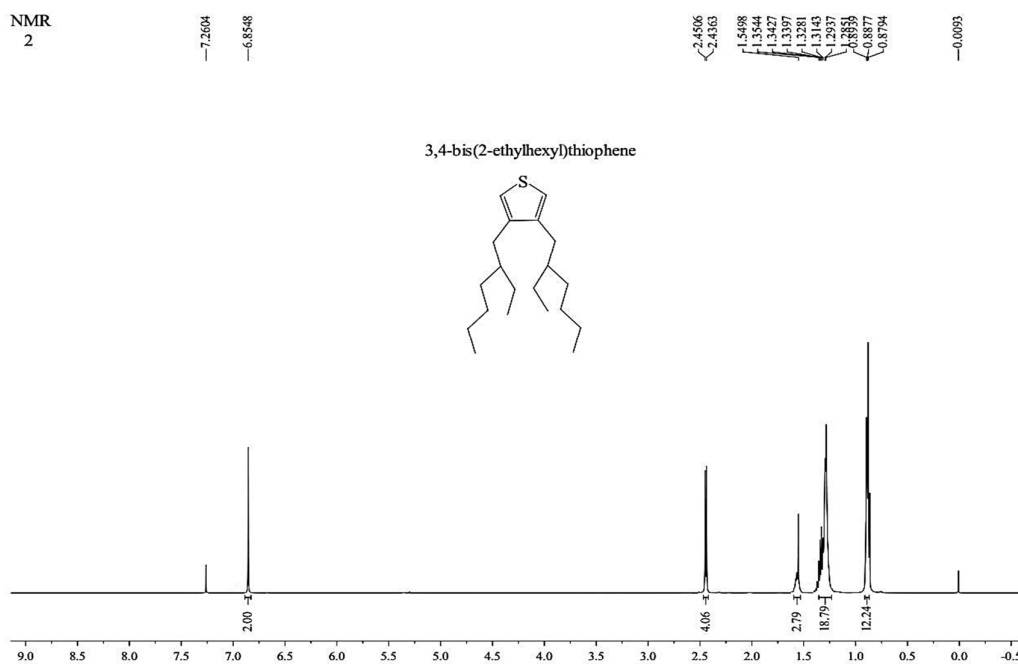


Figure S4. 1H NMR spectra of 3,4-bis(2-ethylhexyl)thiophene

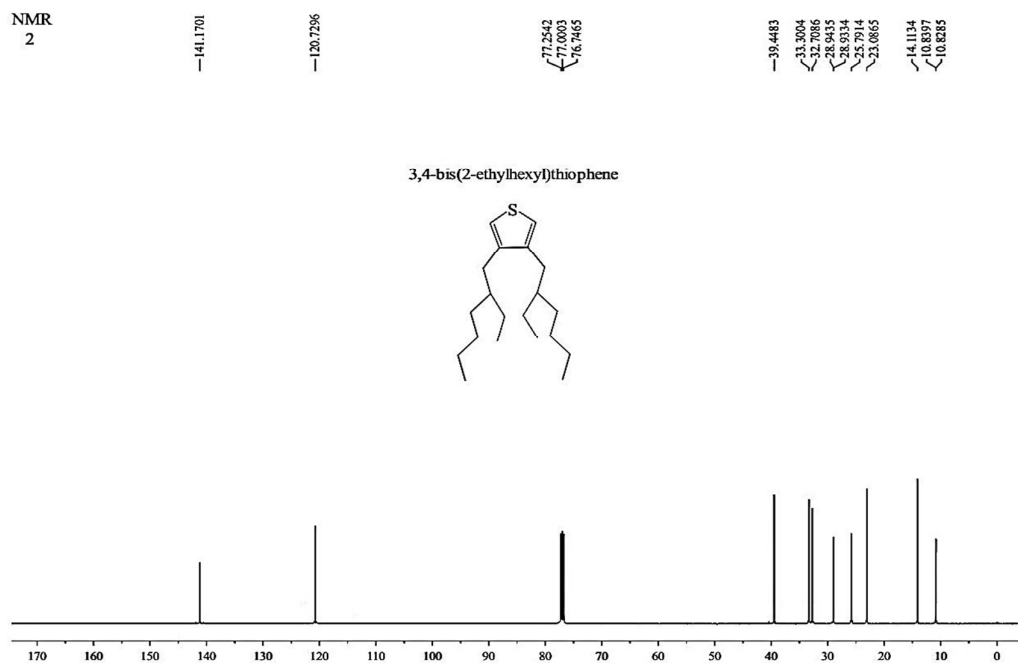


Figure S5. ^{13}C NMR spectra of 3,4-bis(2-ethylhexyl)thiophene

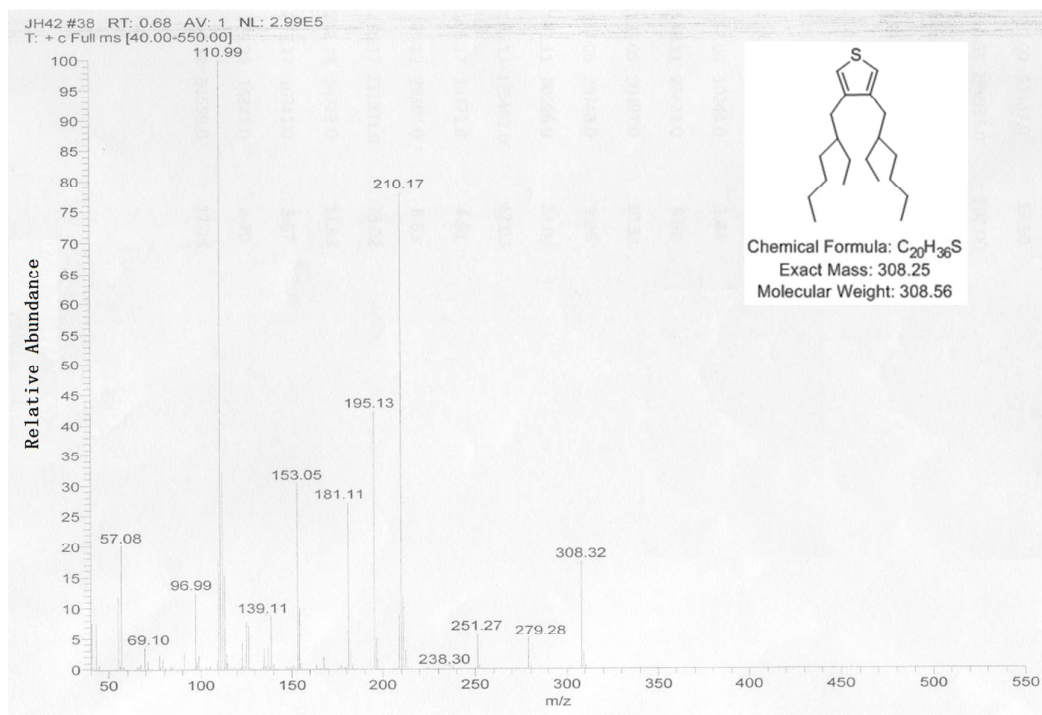


Figure S6. Mass spectra of 3,4-bis(2-ethylhexyl)thiophene

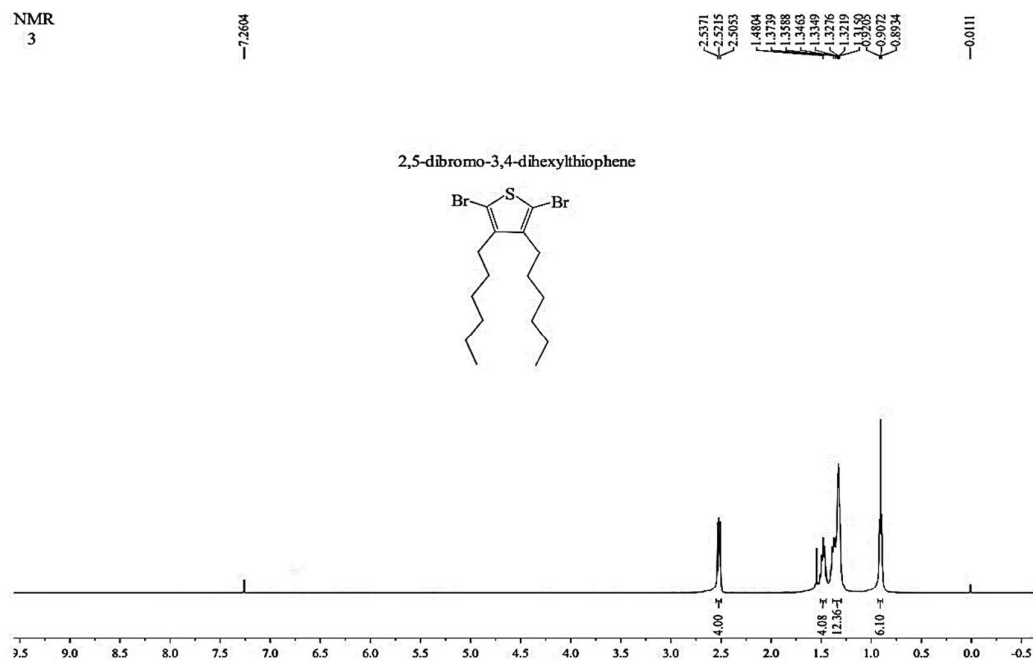


Figure S7. ¹H NMR spectra of 2,5-dibromo-3,4-dihexylthiophene

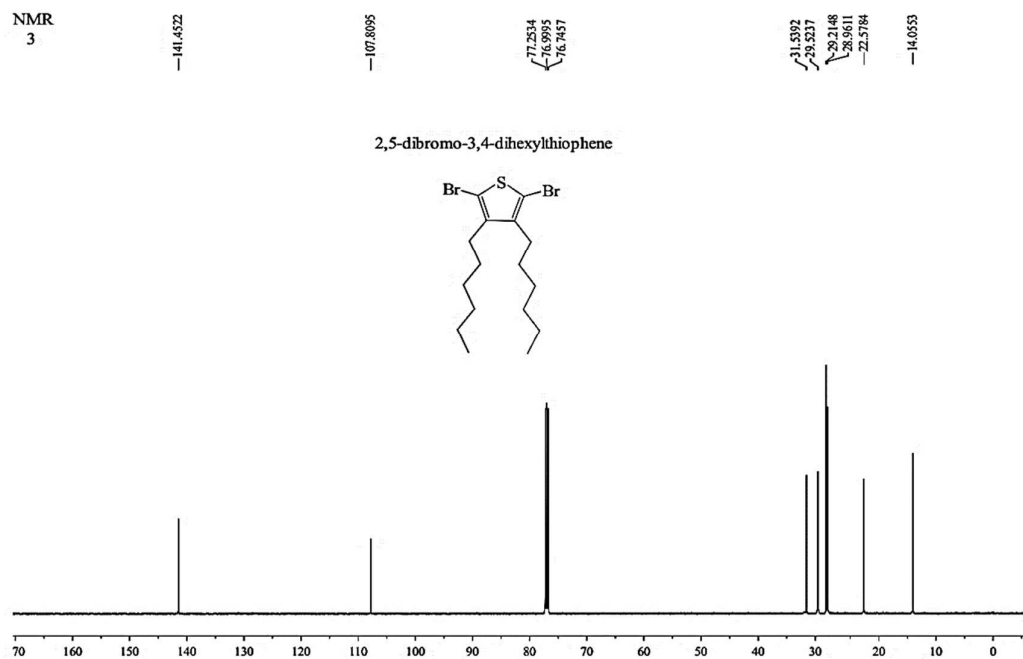


Figure S8. ¹³C NMR spectra of 2,5-dibromo-3,4-dihexylthiophene

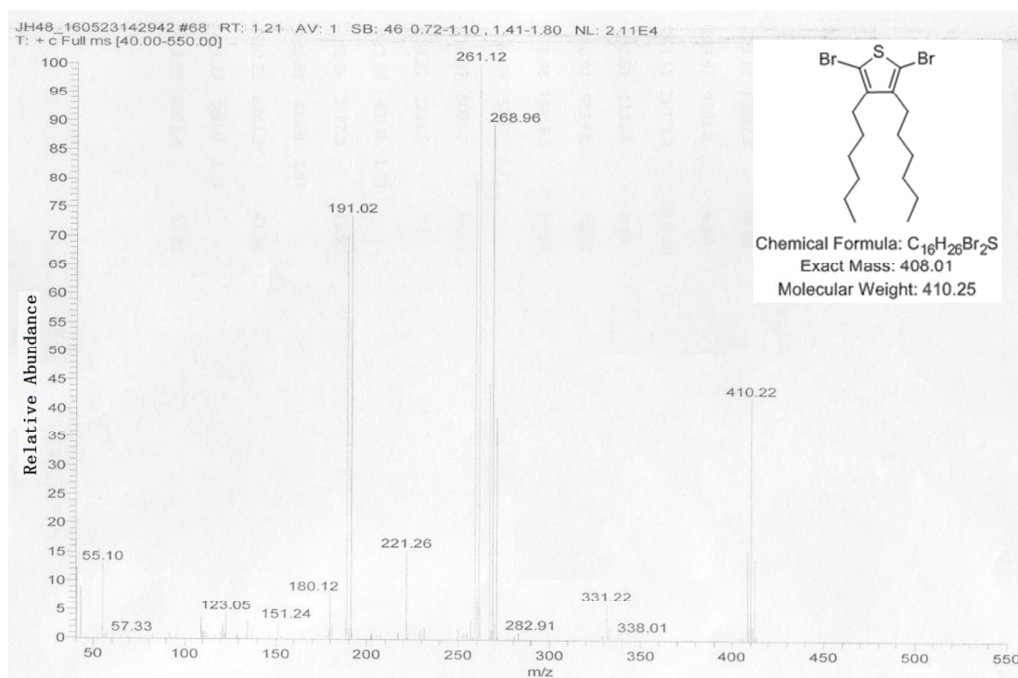


Figure S9. EI Mass spectra of 2,5-dibromo-3,4-dihexylthiophene

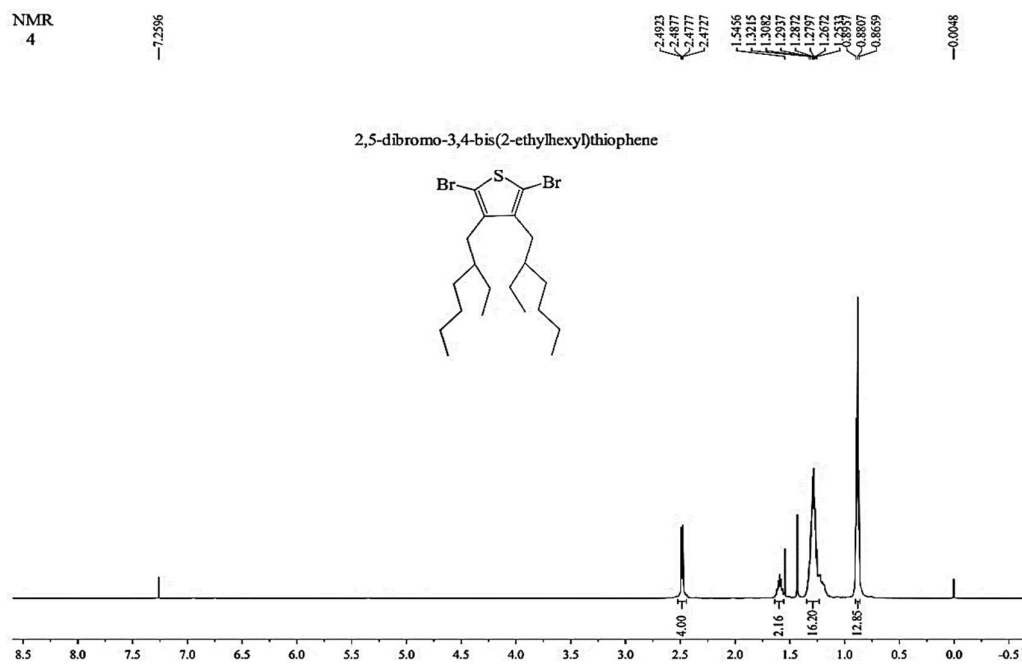


Figure S10. 1H NMR spectra of 2,5-dibromo-3,4-bis(2-ethylhexyl)thiophene

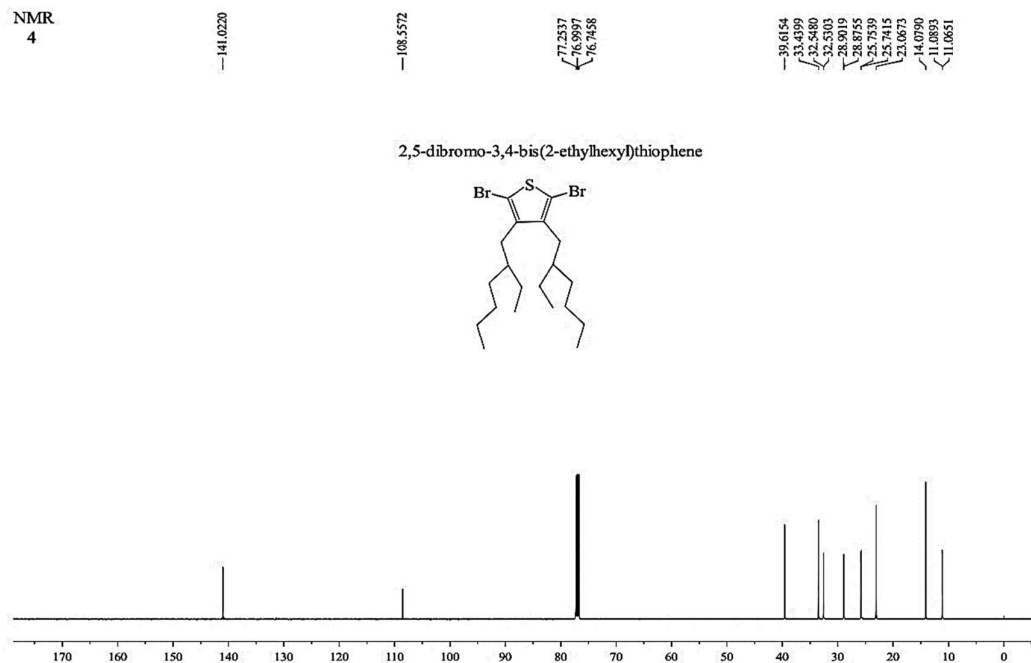


Figure S11. ^{13}C NMR spectra of 2,5-dibromo-3,4-bis(2-ethylhexyl)thiophene

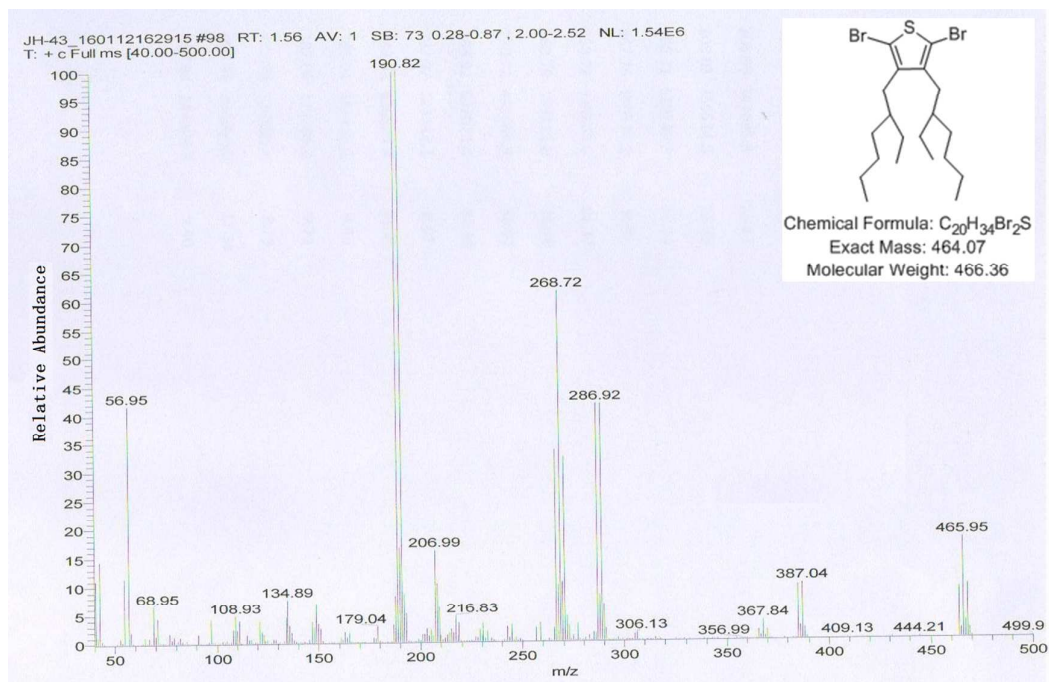


Figure S12. Mass spectra of 2,5-dibromo-3,4-bis(2-ethylhexyl)thiophene

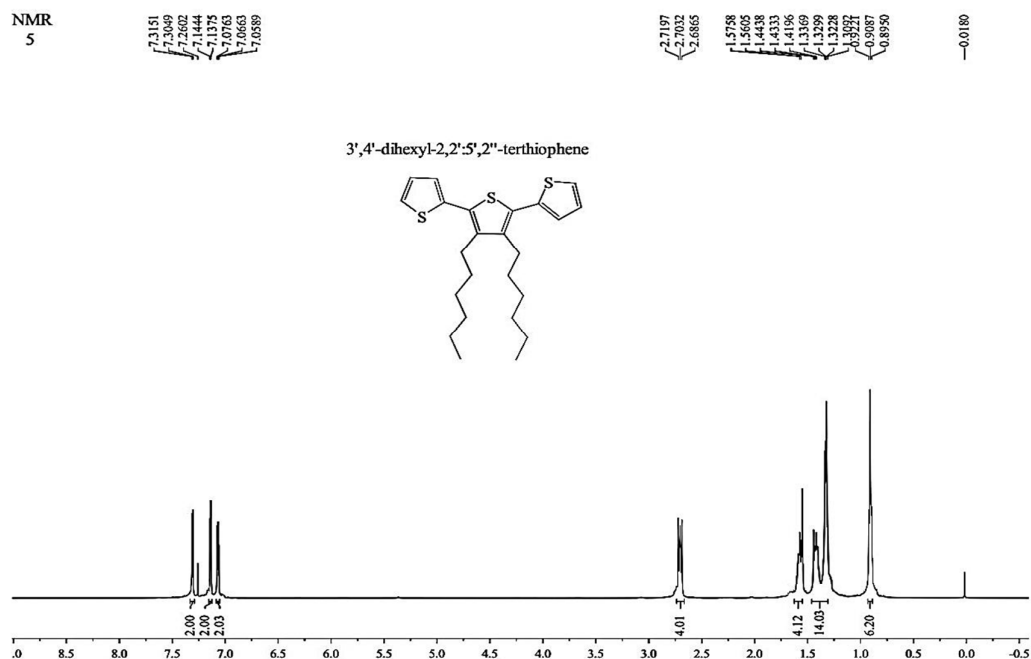


Figure S13. ^1H NMR spectra of 3',4'-dihexyl-2,2':5',2''-terthiophene

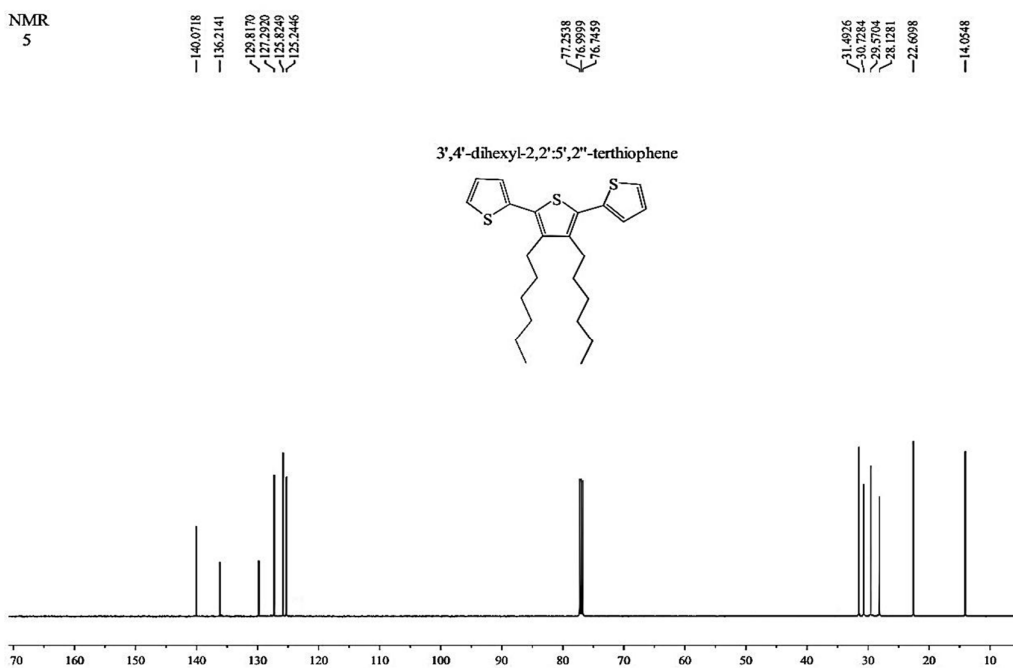


Figure S14. ^{13}C NMR spectra of 3',4'-dihexyl-2,2':5',2''-terthiophene

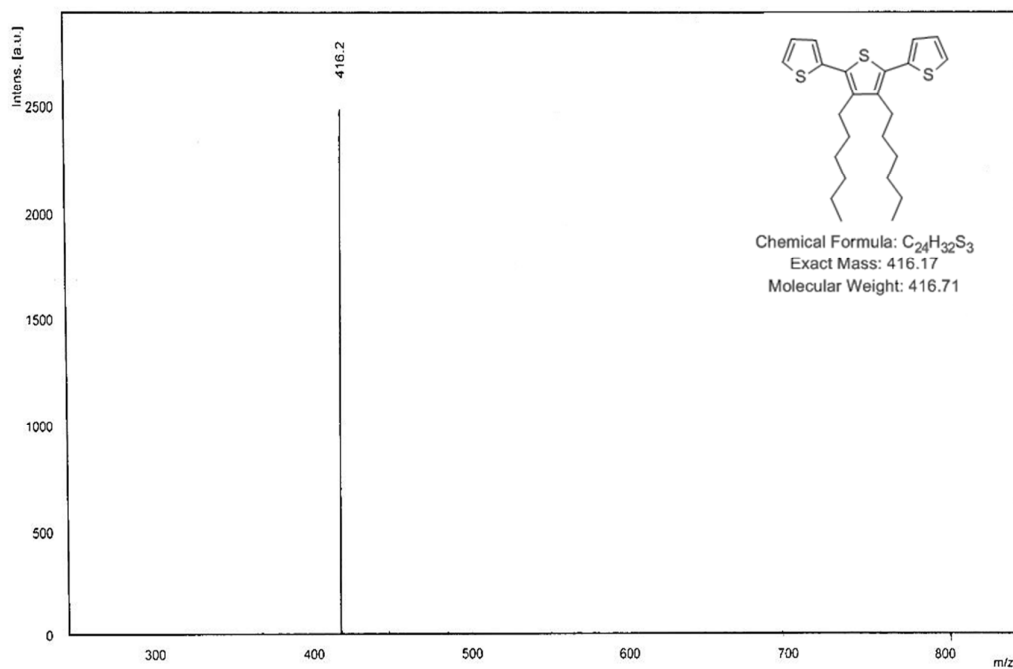


Figure S15. MALDI-TOF mass spectra of 3',4'-dihexyl-2,2':5',2''-terthiophene

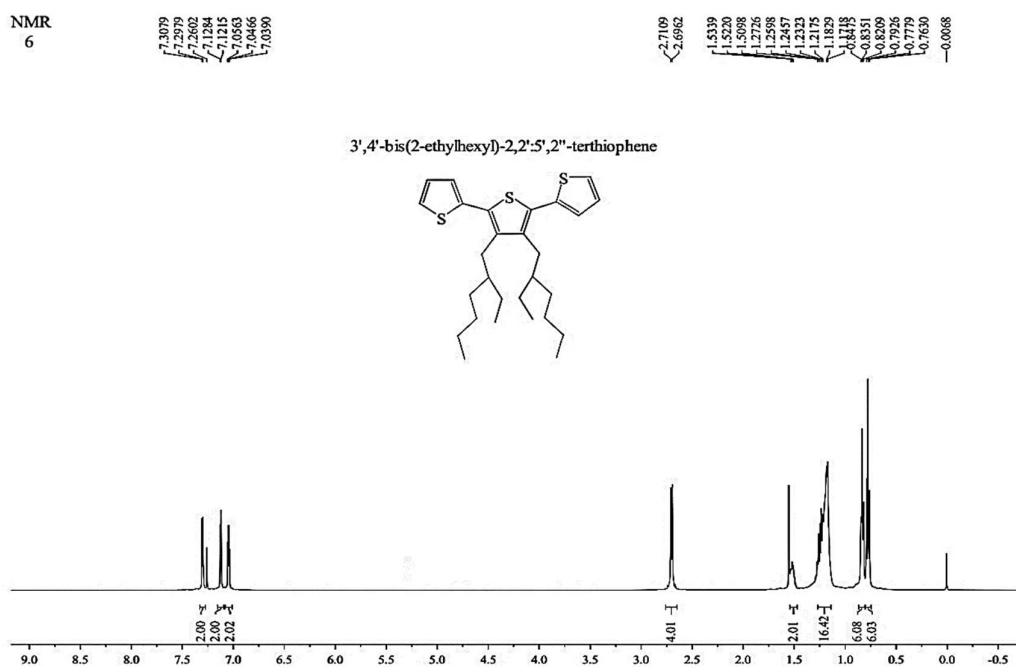


Figure S16. 1H NMR spectra of 3',4'-bis(2-ethylhexyl)-2,2':5',2''-terthiophene

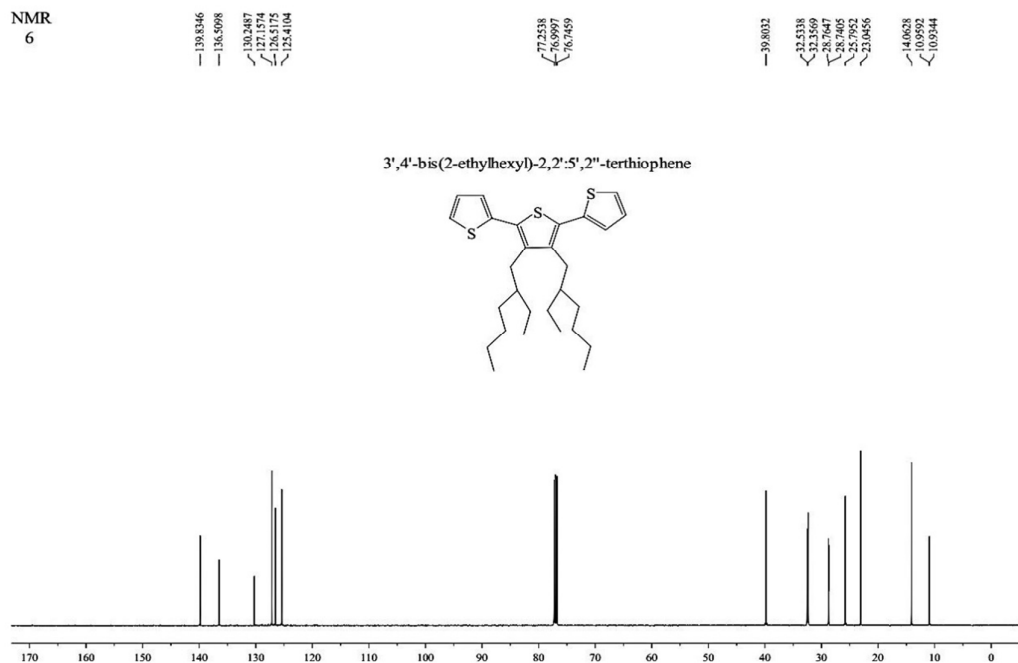


Figure S17. ^{13}C NMR spectra of 3',4'-bis(2-ethylhexyl)-2,2':5',2''-terthiophene

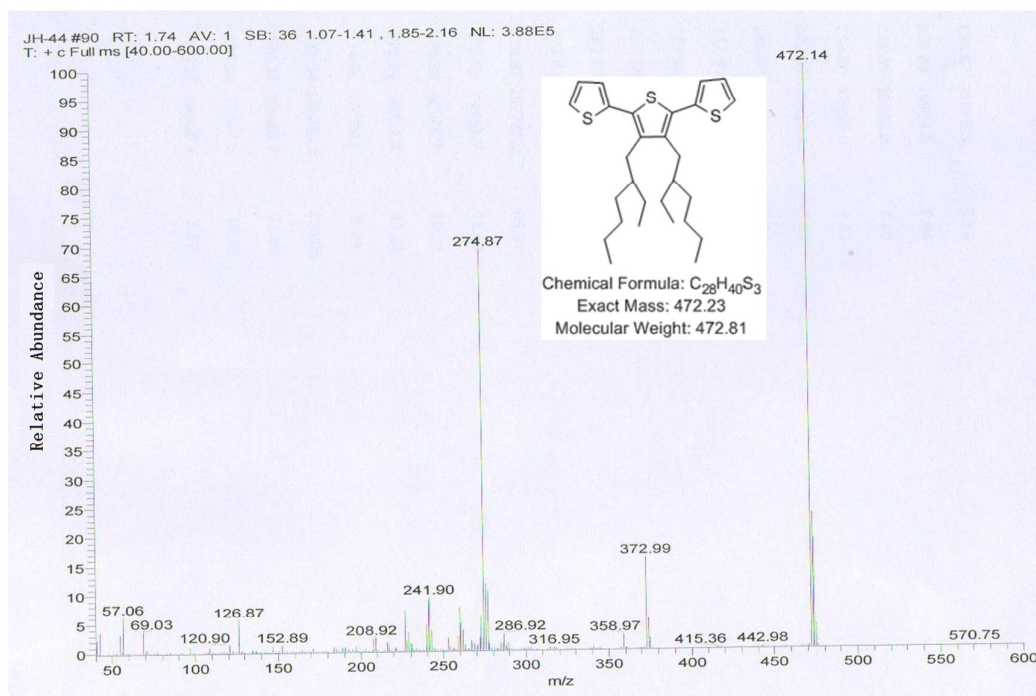


Figure S18. EI mass spectra of 3',4'-bis(2-ethylhexyl)-2,2':5',2''-terthiophene

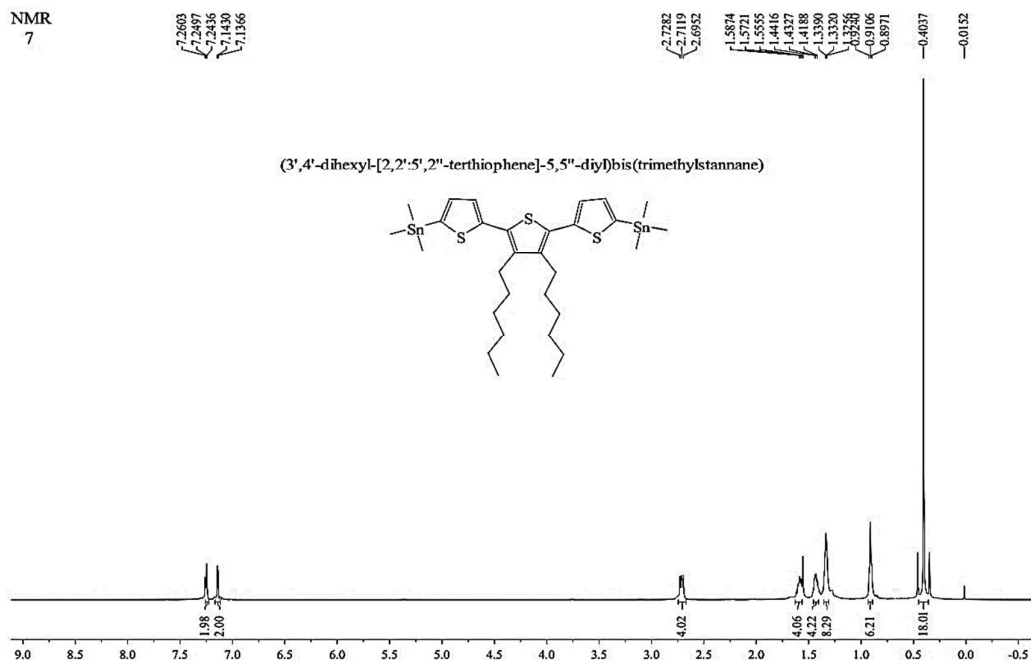


Figure S19. ^1H NMR spectra of (3',4'-dihexyl-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane)

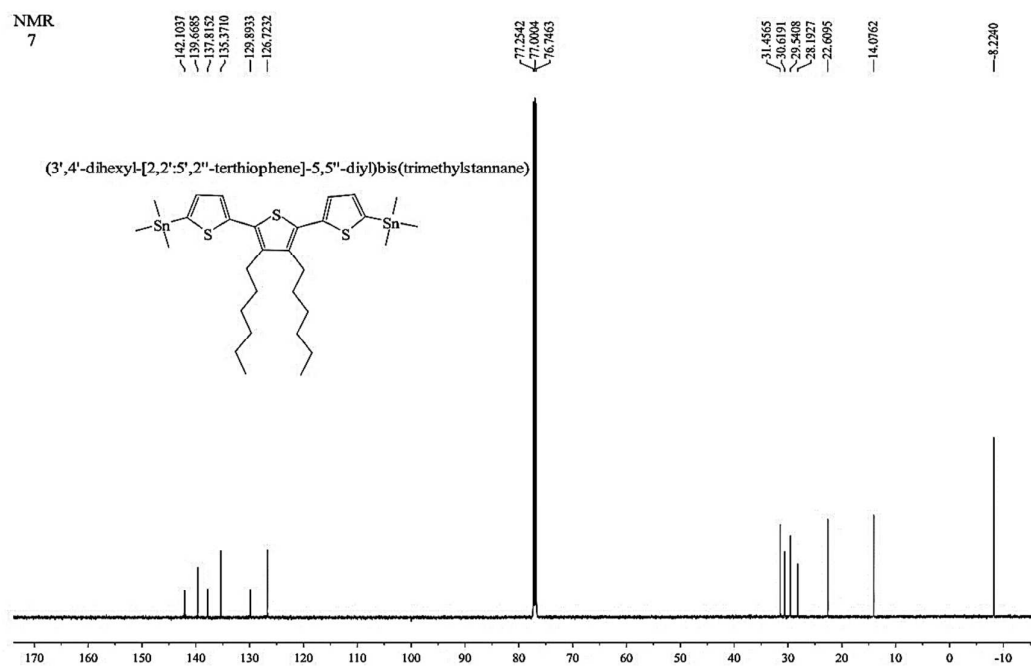


Figure S20. ^{13}C NMR spectra of (3',4'-dihexyl-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane)

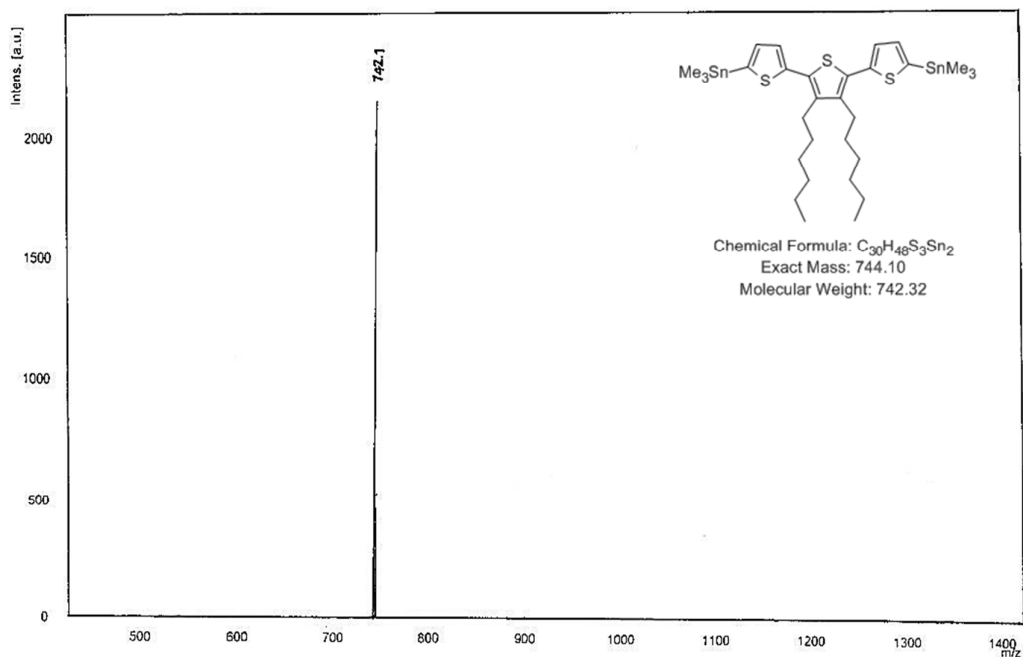


Figure S21. MALDI-TOF mass spectra of
 (3',4'-dihexyl-[2,2':5',2''-terthiophene]-5,5''-diyl)bis- (trimethylstannane)

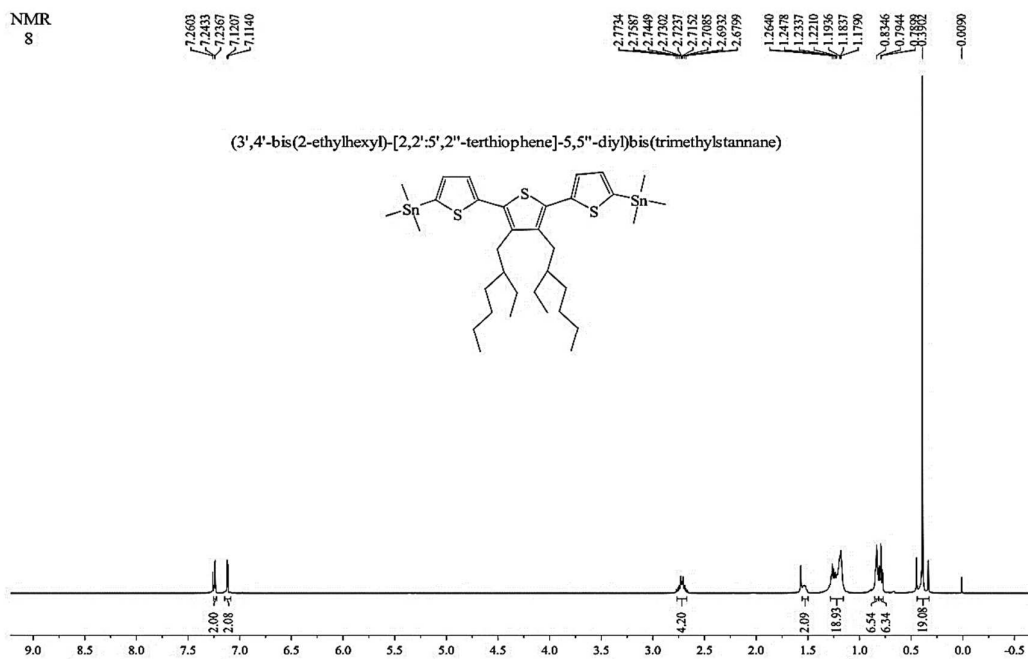


Figure S22. 1H NMR spectra of
 (3',4'-bis(2-ethylhexyl)-[2,2':5',2''-terthiophene]-5,5''-diyl)bis- (trimethylstannane)

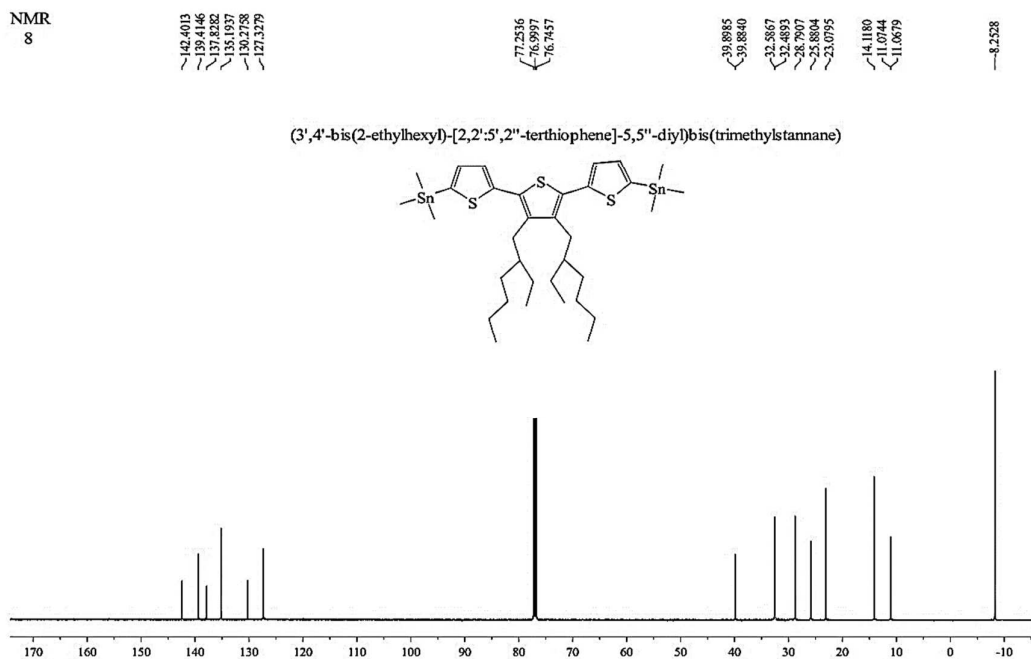


Figure S23. ^{13}C NMR spectra of
(3',4'-bis(2-ethylhexyl)-[2,2':5',2''-terthiophene]-5,5''-diyl)bis- (trimethylstannane)

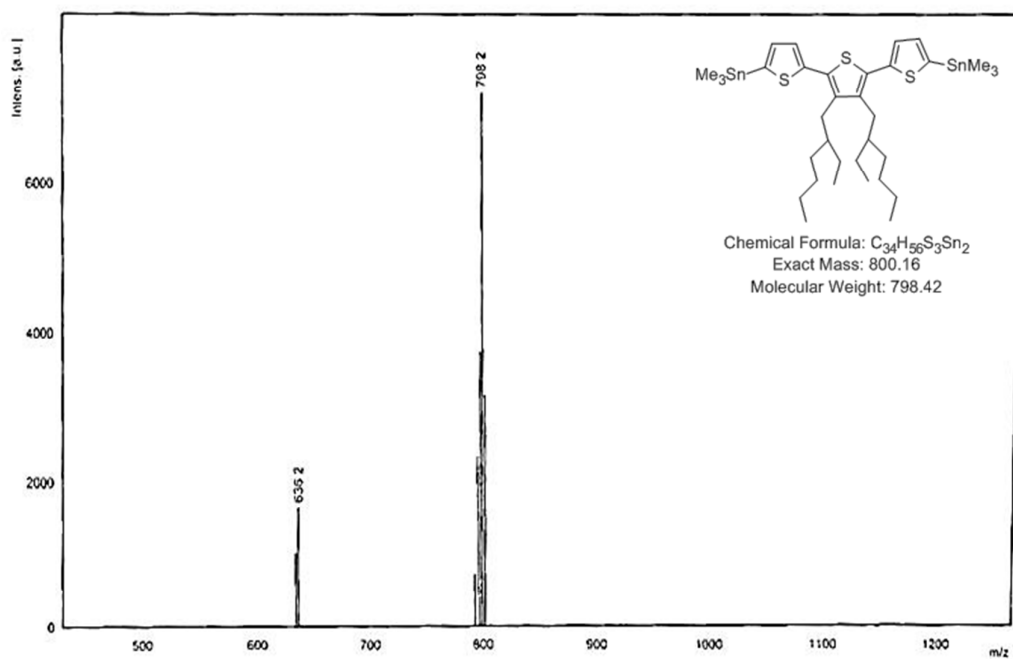


Figure S24. MALDI-TOF mass spectra of
(3',4'-bis(2-ethylhexyl)-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane)

5. Supplementary Figures and Tables.

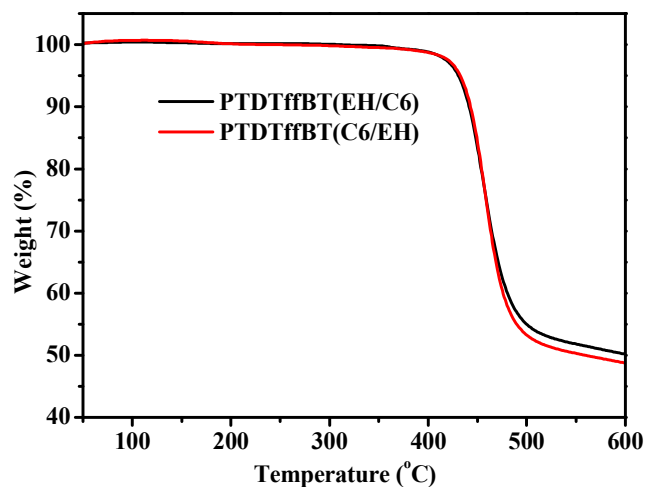


Figure S25. TGA curves of PTDTffBT(EH/C6) and PTDTffBT(C6/EH) at a heating rate of 10 °C min⁻¹ under N₂.

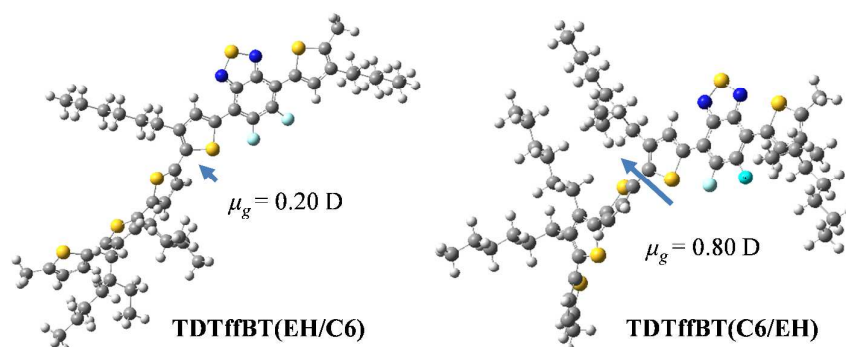


Figure S26. Ground state dipole moments of TDTffBT(EH/C6) and TDTffBT(C6/EH) calculated using DFT with a basis set of B3LYP/6-31G(d).

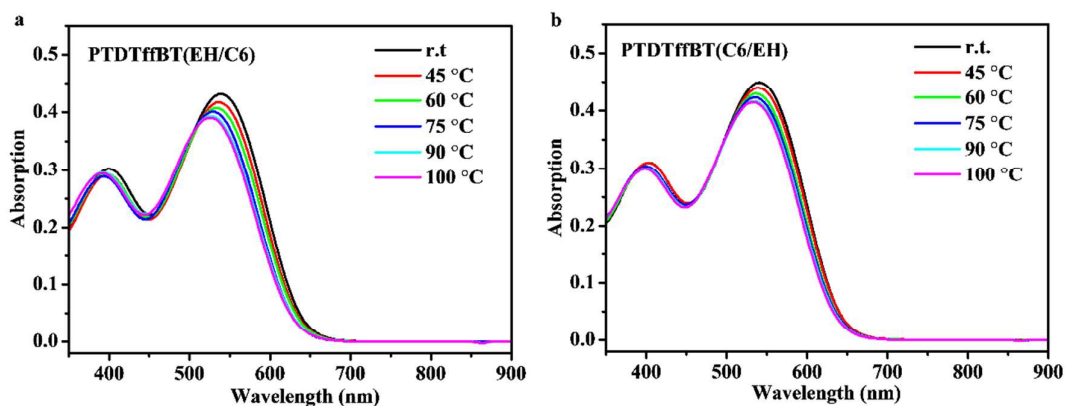


Figure S27. Temperature dependent UV-vis absorption spectra of a) PTDTffBT(EH/C6) and b) PTDTffBT(C6/EH) in diluted dichlorobenzene solution (1.0×10^{-5} mg mL⁻¹).

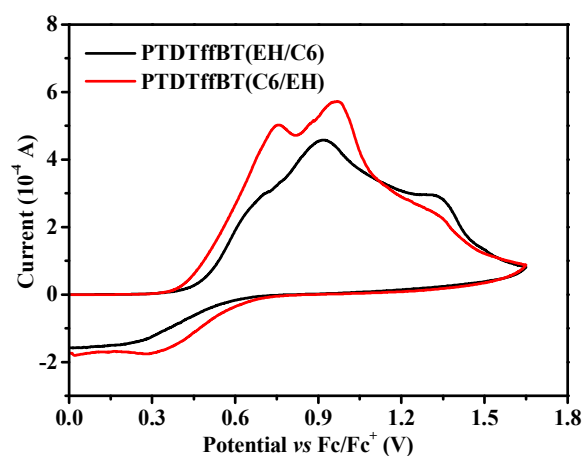


Figure S28. Cyclic voltammograms curves of the two copolymers in thin film (drop cast from 3 mg mL⁻¹ chloroform solution) were measured in 0.1 M Bu₄NPF₆ in acetonitrile at a scan rate of 100 mV S⁻¹.

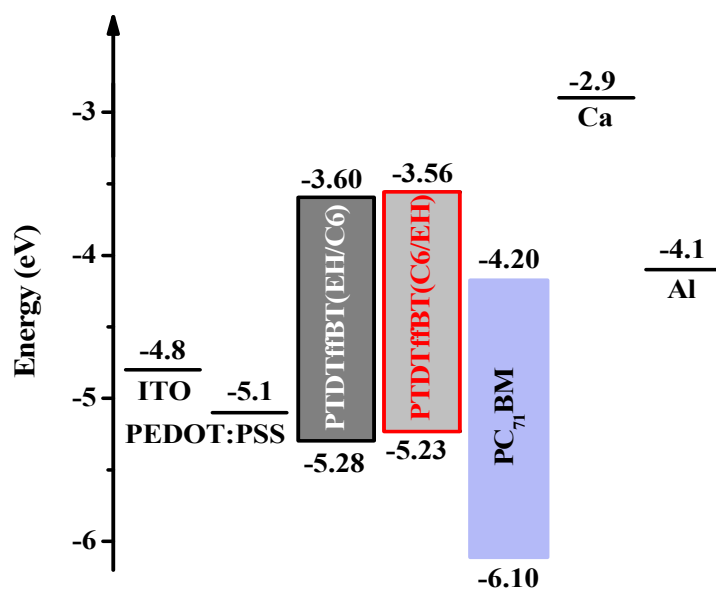


Figure S29. Energy level diagrams of electronic materials within the BHJ PSCs.

Table S1. Photovoltaic properties of Polymers:PC₇₁BM PSCs in conventional architecture at different D/A weight ratio without the additives.

Polymer	Polymer: PC ₇₁ BM	Thickness (nm)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE ^a (%)
PTDTffBT (EH/C6)	3:2	115	0.786	12.12	0.50	4.81 (4.62)
	1:1	102	0.793	14.63	0.53	6.13 (6.04)
	2:3	110	0.750	13.83	0.48	5.02 (4.84)
PTDTffBT (C6/EH)	3:2	113	0.751	15.94	0.51	6.14 (5.97)
	1:1	106	0.789	17.36	0.60	8.24 (8.10)
	2:3	108	0.795	15.73	0.57	7.08 (6.87)

^a Data represent the best performing device, and average PCEs from more than 15 devices are shown in parentheses.

Table S2. The optimized photovoltaic properties of PTDTffBT (EH/C6):PC₇₁BM and PTDTffBT(C6/EH):PC₇₁BM PSCs in conventional architecture with D/A ratio of 1:1 with variable processing additives (v/v, *o*-DCB).

BHJ blend	Additive	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE ^a (%)
PTDTffBT (EH/C6):PC ₇₁ BM=1:1	W/O	0.793	14.63	0.53	6.13 (6.04)
	2% DIO	0.641	15.82	0.49	4.96 (4.83)
	2% DPE	0.689	15.89	0.48	5.26 (5.11)
	1% CN	0.712	13.17	0.53	4.99 (4.79)
PTDTffBT (C6/EH):PC ₇₁ BM=1:1	W/O	0.789	17.36	0.60	8.24 (8.10)
	2% DIO	0.691	15.12	0.61	6.35 (6.21)
	3% DPE	0.703	15.84	0.61	6.79 (6.58)
	3% CN	0.783	14.80	0.58	6.70 (6.52)

^a Data represent the best performing device, and average PCEs from more than 15 devices are shown in parentheses.

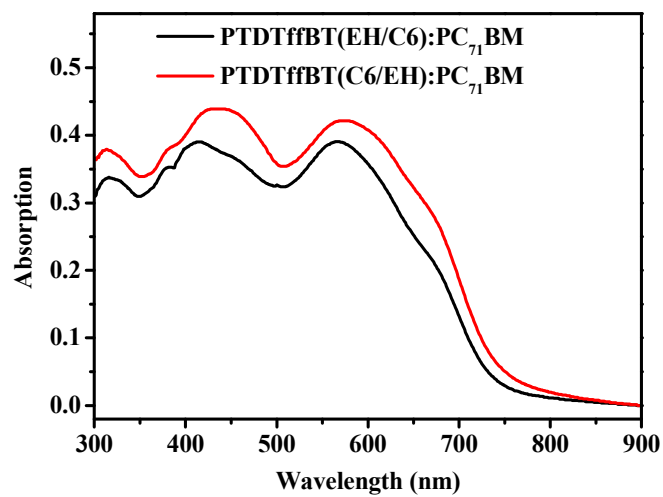


Figure S30. The absorption of the BHJ blends of the two copolymers with PC₇₁BM.

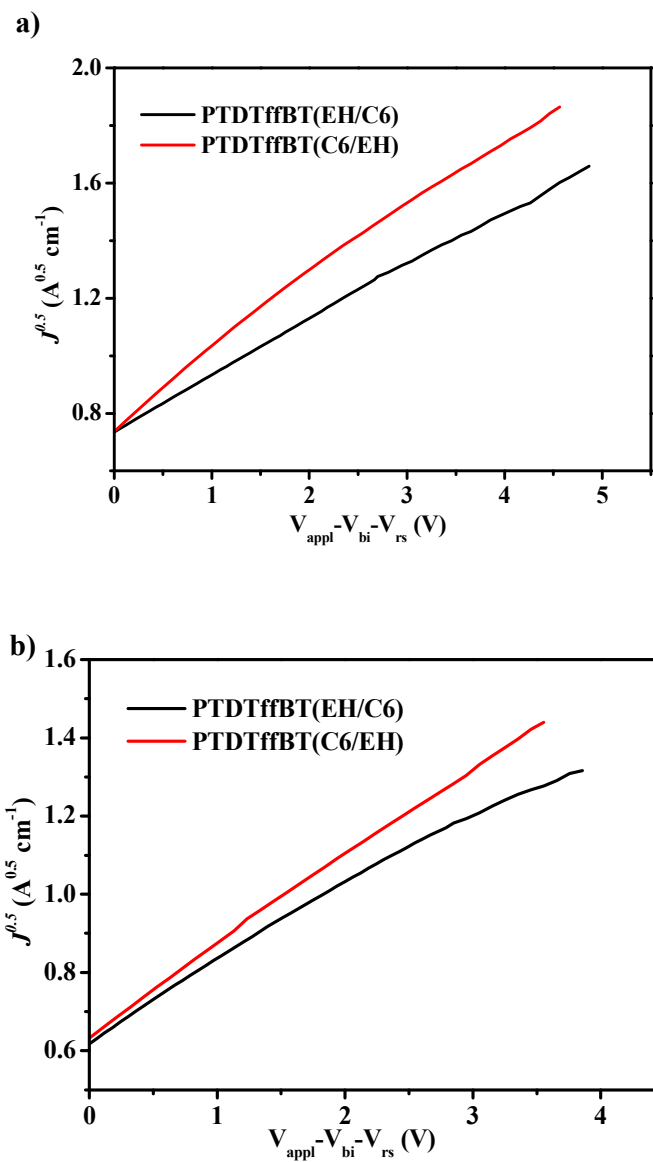


Figure S31. $J^{0.5}$ vs $V_{\text{appl}} - V_{\text{bi}} - V_{\text{rs}}$ plots for a) hole-only and b) electric-only devices of PTDTffBT(EH/C6) and PTDTffBT(C6/EH).

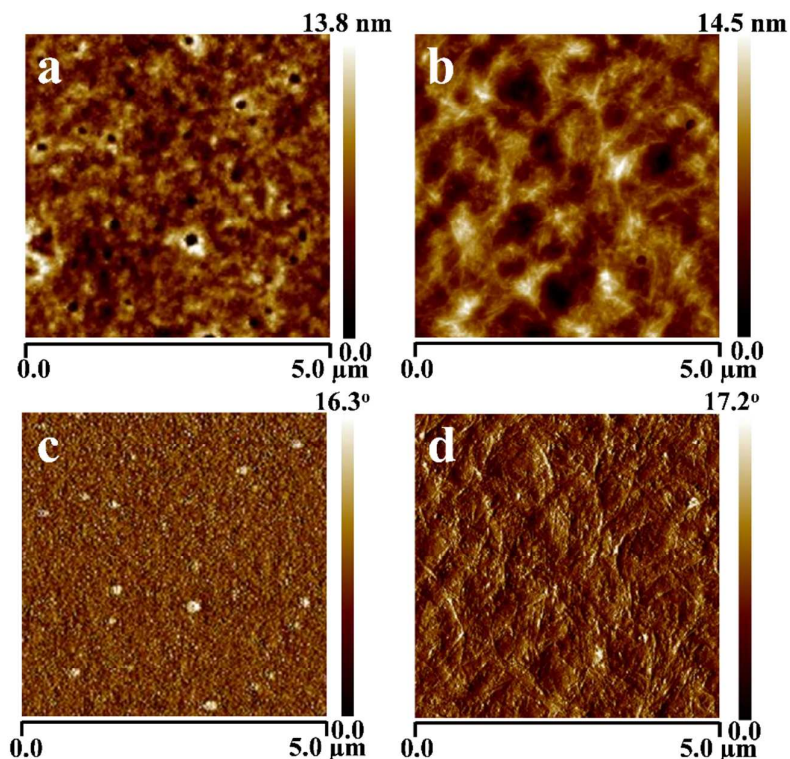


Figure S32. Tapping-mode AFM height (a and b) and phase (c and d) images of optimized PTDTffBT(EH/C6):PC₇₁BM (a and c) and PTDTffBT(C6/EH):PC₇₁BM (b and d) blends respectively.

6. Reference

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