Electronic Supplementary Information

Polymer Semiconductors Incorporating Head-to-Head Linked 4-Alkoxy-5-(3-alkylthiophen-2-yl)thiazole

Xin Zhou,[a,b,1] Peng Chen,[a,1] Chang Woo Koh,[c] Sheng Chen,[a] Jianwei Yu,[a] Xianhe Zhang,[a] Yumin Tang,[a] Luca Bianchi,[a] Han Guo,[a,]* Han Young Woo,[c,]* Xugang Guo[a,]*

[a] *Department of Materials Science and Engineering and The Shenzhen Key Laboratory for Printed Organic Electronics, Southern University of Science and Technology (SUSTech), No. 1088, Xueyuan Road, Shenzhen, Guangdong 518055, China*

[b] *Department of Chemistry, Southern University of Science and Technology (SUSTech), No. 1088, Xueyuan Road, Shenzhen, Guangdong 518055, China*

[c] *Research Institute for Natural Sciences, Department of Chemistry, Korea University, Seoul 02841, South Korea*

[1] *These authors contribute equally to this work.*

* To whom correspondence should be addressed.

Email: guoh3@sustc.edu.cn (H.G.); hywoo@korea.ac.kr (H.Y.W.);

guoxg@sustc.edu.cn (X.G.)

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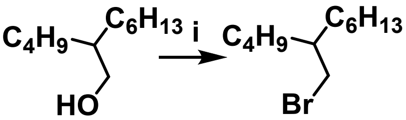
1 Materials and Instruments

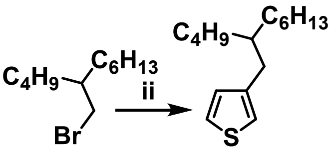
All commercially available reagents and chemicals were used as received without further purification unless otherwise specified. 4,7-Dibromobenzo[*c*][1,2,5]thiadiazole, 4,7-dibromo-5-fluorobenzo[*c*][1,2,5]thiadiazole, and 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole were purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd. (Shenzhen, Guangdong, China) and were further recrystallized before use. The synthesized distannylated monomer **8** was purified by Biotage SNAP Ultra C18 column via Biotage flash chromatography. Microwave-assisted polymerizations are carried out on an Initiator$^+$ Microwave Synthesizer (Biotage, Sweden).

^{1}H NMR and ^{13}C NMR spectra of the compounds were measured on Bruker Ascend 400 and 500 MHz spectrometers in $CDCl_3$, and the chemical shifts were referenced to residual protio-solvent signals. High-temperature NMR spectra were recorded on Bruker Ascend 400 MHz spectrometer in $C_2D_2Cl_4$ at 80 ºC. Mass spectrum data were collected from Agilent Technologies 5977A MSD or Q-Exactive. H, C, and N elemental analyses (EA) of the polymers were carried out at the Institute of Chemistry, Chinese Academy of Sciences. Polymer molecular weights were determined on Polymer Laboratories GPC-PL220 high temperature GPC/SEC system at 150 ºC vs polystyrene standards using trichlorobenzene as eluent. Cyclic voltammetry (CV) measurements were carried out under argon atmosphere using a CHI760 Evoltammetric analyzer with 0.1 M tetra-*n*-butylammonium hexafluorophosphate in acetonitrile as supporting electrolyte and Fc/Fc+ as internal reference. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed. UV-vis absorption spectra of solutions and films at room temperature were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer, while temperature dependent UV-vis spectra of the solutions were collected on Perkin Elmer Lambda 950 UV/VIS/NIR Spectrometer. Differential scanning calorimetry (DSC) curves were recorded using Mettler STAR^e at a heating rate of 10 ºC min^{-1} under nitrogen atmosphere, and thermogravimetric analysis (TGA) curves were collected by Mettler STAR^e TA Instrument at a heating rate of 10 ºC min^{-1}. Atomic Force Microscopy (AFM) measurements were conducted using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in the tapping mode. Transmission Electron Microscopy (TEM) images were obtained on Tecnai Spirit microscope (20 kV). For TEM samples, the films were first casted on PEDOT:PSS covered substrates, then they were floated off in deionized water before being transferred onto TEM copper grids. Two-dimensional grazing incidence wide angle x-ray scattering (2D GIWAXS) measurements were carried out at the PLS-II 9A U-SAXS beam line of Pohang Accelerator Laboratory, Korea.

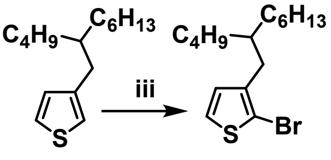
2 Synthesis of Monomers and Polymers


1

2-butyloctylbromide (1):[1] To a solution of 2-butyloctanol (40.13 g, 215.4 mmol) and triphenylphosphine (56.49 g, 215.4 mmol) in dichloromethane (600 mL), *N*-bromosuccinimide (45.99 g, 258.4 mmol) was added in small portions over 10 min at 0 °C. The mixture was stirred at 0 °C for 2 h and then at room temperature for 4 h. The solution was concentrated to ca. 2/3 of its original volume using rotary evaporator. After that, silica gel (40 g) was added and the solvent was completely removed under a reduced pressure to afford an orange powder, which was purified by column chromatography using petroleum ether as the eluent. After drying in vacuum, the product was obtained as a colorless liquid (45.10 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.45 (d, 2H), 1.59 (m, 1H), 1.40-1.21 (m, 16H), 0.90 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 39.75, 39.46, 32.56, 32.25, 31.80, 29.45, 28.77, 26.52, 22.84, 22.64, 14.10, 14.06. MS (EI, *m/z*): calcd for $C_{12}H_{25}Br$: 248.11; found, 248.1.

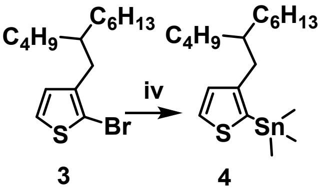

1 2

3-(2-butyloctyl)thiophene (2):[1] A round-bottom two-necked flask was charged with magnesium turnings (4.33 g, 178.15 mmol), iodine (193.1 mg, 0.76 mmol), and 150 mL THF solvent. The mixture was stirred for 0.5 h before 2-butyloctylbromide (45.01 g, 150.59 mmol) was added, which was further refluxed for 2 h to afford the Grignard reagent. Separately, 3-bromothiophene (23.55 g, 144.4 mmol) and Ni(dppp)Cl_2 (1.17 g, 2.16 mmol) were dissolved in 25 mL THF, and the Grignard reagent was added slowly at 0 °C. The reaction was warmed to room temperature and stirred overnight, followed by the addition of hydrochloric acid (40 mL, 2 M) to quench the reaction. The reaction was then washed with dichloromethane (DCM) three times (60 mL each), and the combined organic layer was washed with water 3 times (200 mL each) then dried over $MgSO_4$. After filtration and removal of solvent via rotary evaporator, the product was purified by column chromatography using petroleum ether as eluent to afford a colorless oil (20.33 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23 (dd, J = 4.9 Hz, 3.0 Hz, 1H), 6.90 (t, J = 4.2 Hz, 2H), 2.56 (d, J = 6.8 Hz, 2H), 1.66-1.58 (m, 1H), 1.24 (m, 16H), 0.86 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 142.07, 128.96, 124.91, 120.78, 39.08, 34.86, 33.53, 33.17, 32.10, 29.92, 29.10, 26.80, 23.27, 22.86, 14.30. MS (EI, *m/z*): calcd for $C_{16}H_{28}S$: 252.19; found, 252.2.

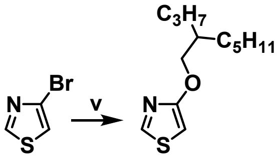


2 3

Synthesis of 2-bromo-3-(butyloctyl)thiophene (3):[1] To a 150 mL mixture of chloroform and acetic acid (1:1, volume ratio) was added 3-(2-butyloctyl)thiophene (20.0 g, 79.2 mmol). *N*-bromosuccinimide (14.1 g, 79.2 mmol) was then added in small portions over 10 min, after which the mixture was stirred at room temperature for 2 h. The reaction was washed with water and saturated sodium bicarbonate aqueous solution, sequentially. After the removal of solvent with a rotary evaporator, the residue was purified by column chromatography using petroleum ether as the eluent to afford a colorless oil (20.25 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.18 (d, *J* = 5.6 Hz, 1H), 6.76 (d, *J* = 5.6 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.68-1.59 (m, 1H), 1.37-1.15 (m, 16H), 0.88 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 141.18, 128.81, 124.91, 109.42, 38.54, 34.03, 33.37, 33.06, 31.89, 29.67, 28.78, 26.52, 23.04, 22.68, 14.11. MS (EI, *m/z*): calcd for $C_{16}H_{27}BrS$: 330.10; found, 330.1.

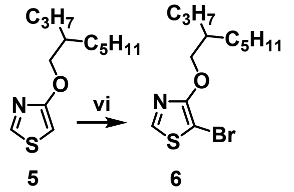


Synthesis of 3-(2-butyloctyl)-2-trimethylstannylthiophene (4): A solution of compound **3** (10.0 g, 30.2 mmol) in THF (20 mL) was cooled to −78 °C using dry ice/acetone bath. The resulting suspension was treated with *n*-BuLi (2.4 M in hexanes; 13.83 mL, 33.19 mmol) dropwise and stirred for 90 min. Trimethyltin chloride (1 M in hexane; 33.17 mL, 33.17 mmol) was added as one portion. The mixture was stirred at −78 °C for 1 h, then at ambient temperature for another 2 h. The reaction mixture was carefully quenched with saturated aqueous sodium chloride solution (40 mL). The reaction mixture was extracted with EtOAc (3 × 20 mL) and dried over $MgSO_4$. After the removal of solvent, compound **4** was obtained as a yellow liquid (11.36 g, yield 91%), which can be used for the following reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, *J* = 4.6 Hz, 1H), 7.06 (d, *J* = 4.6 Hz, 1H), 2.56 (d, *J* = 7.5 Hz, 2H), 1.62-1.55 (m, 1H), 1.37-1.05 (m, 16H), 0.95-0.79 (m, 6H), 0.45-0.25 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 149.82, 131.79, 130.21, 129.73, 39.71, 37.41, 33.55, 33.23, 31.90, 29.71, 28.90, 26.65, 23.04, 22.68, 14.11, −7.75. MS (EI, *m/z*): calcd for $C_{19}H_{36}SSn$: 416.16; found, 416.2.

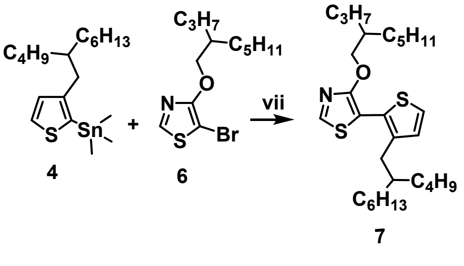


5

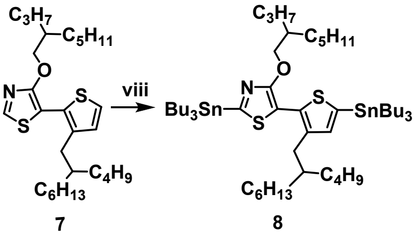
Synthesis of 4-(2-propylheptoxy)thiazole (5):[2] To a mixture of THF (80 mL) and NaH (60% in oil; 5.00 g, 125 mmol) was added 2-propylheptol (20.01 g, 126.4 mmol) dropwise, and then the mixture was stirred at room temperature for 2 h. After the sequential addition of copper(I) bromide (1.81 g, 12.6 mmol) and 3-bromothiazole (13.82 g, 84.3 mmol), the mixture was refluxed for 2 h. The reaction solvent was then removed by 1/2 with rotary evaporator. With the addition of silica gel powder (5 g), the solvent was removed under reduced pressure to afford a black powder. The resulting mixture was purified by column chromatography using petroleum ether:dichloromethane (1:2) as the eluent, and then dried under vacuum to afford a yellowish oil as the product (10.37 g, yield 51%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.54 (d, $J = 2.3$ Hz, 1H), 6.10 (d, $J = 2.4$ Hz, 1H), 3.99 (d, $J = 5.7$ Hz, 2H), 1.88-1.76 (m, 1H), 1.47-1.20 (m, 12H), 0.95-0.83 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 165.64, 150.05, 88.65, 73.03, 37.69, 33.44, 32.12, 31.08, 26.41, 22.57, 19.90, 14.35, 14.03. MS (EI, *m/z*): calcd for $C_{13}H_{23}NOS$: 241.15; found, 241.2.



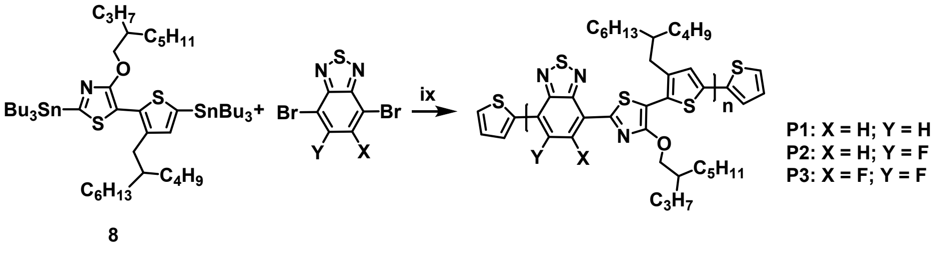
Synthesis of 5-bromo-4-(2- propylheptoxy)thiazole (6): To 200 mL chloroform was added 4-(2-propylheptoxy)thiazole (4.28 g, 17.7 mmol). *N*-bromosuccinimide (3.16 g, 17.7 mmol) was added in small portions over 10 min, and then the mixture was stirred at room temperature for 2 h. After the addition of water, the reaction was quenched and then extracted with dichloromethane. The combined organic layer was subjected to solvent removal with rotary evaporator, and the residue was purified by column chromatography using petroleum ether:dichloromethane (5:1) as the eluent to afford a yellowish oil (4.58 g, 81%) as the product. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.52 (s, 1H), 4.24 (d, J = 5.9 Hz, 2H), 1.82-1.72 (m, 1H), 1.47-1.22 (m, 12H), 0.94 -0.85 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 161.68, 149.08, 82.92, 74.15, 37.81, 33.49, 32.22, 31.13, 26.41, 22.62, 19.93, 14.43, 14.09. MS (EI, *m/z*): calcd for $C_{13}H_{22}BrNOS$: 319.06; found, 319.1.



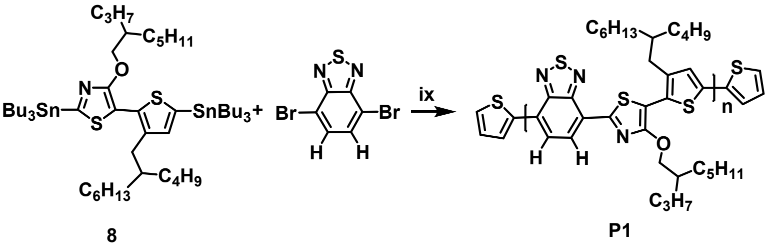
Synthesis of 5-(3-(2-butyloctyl)thiophen-2-yl)- 4-(2- propylheptoxy)thiazole (7): To a dry glass tube was charged with compound **4** (2.20 g, 5.3 mmol), compound **6** (0.95 g, 3.0 mmol), and bis (triphenylphosphine)palladium(II) dichloride (0.42 g, 0.60 mmol). Then, anhydrous toluene (20 mL) was added under argon. The tube was sealed under argon flow and then stirred at 140 °C for 3 h under microwave irradiation. After the removal of solvent, the crude product was purified over column chromatography using hexane as the eluent to afford a yellow liquid (0.60 g, 41%) as the product. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.48 (s, 1H), 7.25 (d, J = 5.4 Hz, 1H), 6.88 (d, J = 5.2 Hz, 1H), 4.27 (d, J = 5.8 Hz, 2H), 2.61 (d, J = 7.3 Hz, 2H), 1.82-1.72 (m, 1H), 1.68-1.52 (m,1H), 1.47-1.10 (m, 28H), 0.92-0.78(m, 12H). ^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm): 160.38, 147.47, 140.29, 129.56, 125.97, 124.54, 103.72, 73.56, 38.71, 37.88, 33.96, 33.48, 33.36, 33.04, 32.23, 31.89, 31.15, 29.68, 28.65, 26.41, 23.03, 22.68, 19.89, 14.44, 14.12. HRMS (ESI, m/z): calcd for $C_{29}H_{50}ONS_2$ [M+H]: 492.3328, Found: 492.3323.



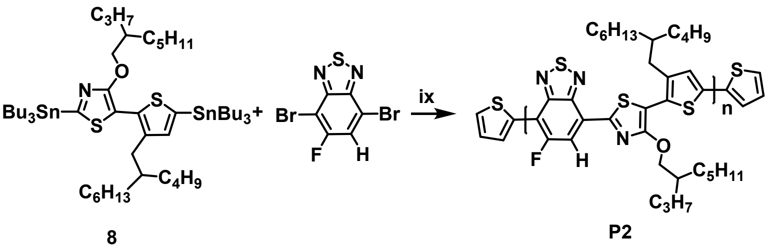
Synthesis of 5-(3-(2-butyloctyl)-5-tributylstannylthiophen-2-yl)-4-(2-propylheptoxy)-2-(tributylstannyl)thiazole (8): A solution of compound **7** (354 mg, 0.72 mmol) in THF (7 mL) was cooled to −78 °C by ice/acetone bath. The resulting suspension was treated with *n*-BuLi (2.4 M in hexane; 0.78 mL, 1.87 mmol) dropwise and stirred for 30 min at −78 °C, followed stirring at room temperature for 30 min. Then the mixture was cooled to −78 °C again and treated with tributyltin chloride (0.54 mL, 2.20 mmol) as one portion. After warmed to ambient temperature, the mixture was stirred at this temperature overnight. The reaction mixture was carefully quenched with saturated aqueous sodium chloride solution (10 mL) and extracted with EtOAc (3×20 mL). The combined organic layer was dried over $MgSO_4$. After the removal of solvent, the crude product was further purified by Biotage flash chromatography via Biotage SNAP Ultra C18 column using water and isopropanol with drops of EtN_3 as the eluent to afford monomer as a yellow oil (839 mg, yield 92.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.86 (s, 1H), 4.34 (d, J = 5.6 Hz, 2H), 2.67 (d, J = 7.1 Hz, 2H), 1.82-1.73 (m, 1H), 1.68-1.56 (m, 13H), 1.41-1.33 (m,20H), 1.28-1.09 (m, 32H), 0.96-0.86 (m, 30H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 167.57, 162.25, 139.98, 138.33, 134.40, 133.16, 106.93, 73.26, 38.58, 38.02, 33.96, 33.61, 33.41, 33.05, 32.32, 31.94, 31.28, 29.80, 28.96, 28.85, 28.63, 27.84, 27.25, 27.18, 27.13, 26.54, 26.41, 23.09, 22.72, 19.96, 15.58, 14.51, 14.14, 13.69, 13.66, 11.21, 10.70. HRMS (ESI, m/z): calcd for $C_{53}H_{102}ONS_2Sn_2$ [M+H]: 1072.5441, Found: 1072.5444.



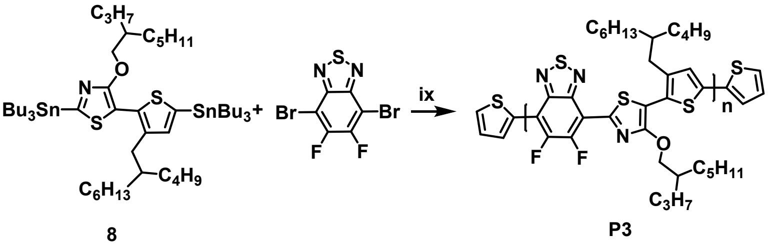
General synthetic procedures for TRTzOR-based polymers: Two monomers (0.15 mmol each), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 2.1 mg), and tris(*o*-tolyl)phosphine(P(*o*-tolyl)3, 5.5 mg) were added to an oven-dried glass tube. Anhydrous toluene (3 mL) was added under argon after the tube was subjected to 3 pump/purge cycles with argon. The tube was sealed under argon flow and then stirred at 80 °C for 10 min, followed 100 °C for 10 min and 140 °C for 3 h under microwave irradiation. After the addition of 2-(tributylstannyl)thiophene (0.2 mL) under argon flow, the mixture was stirred under microwave irradiation at 140 °C for 15 min. Then, 2-bromothiophene (0.2 mL) was added and stirred at 140 °C for another 15 min. After cooling to room temperature, the reaction mixture was precipitated in 100 mL methanol (containing 2 mL 12 N hydrochloric acid) under vigorous stirring. The polymer precipitate was collected and Soxhlet-extracted with different solvents. After the extraction with the final solvent, the polymer solution was concentrated and precipitated into methanol. The precipitates were filtrated and dried in vacuum to afford the polymer product.



Polymer TRTzOR-BT (P1): The solvents used for Soxhlet extraction were methanol, acetone, hexane, and dichloromethane. After the final extraction using dichloromethane, the polymer was obtained as a black solid (59.8 mg, 64%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 ºC): δ (ppm) 8.35 (1H), 7.77 (2H), 4.50 (2H), 2.75 (2H), 2.14-0.56 (m, 42H). Elem. Anal.: Calcd. for $C_{35}H_{49}N_3OS_3$ (%): C, 67.37; H, 7.92; N, 6.73; O, 2.56; S, 15.41. Found (%): C, 67.23; H, 8.00; N, 6.50. Molecular weight: M_n = 21.9 kDa, M_w = 31.8 kDa, $Đ_M$ = 1.45.



Polymer TRTzOR-fBT (P2): The solvents used for Soxhlet extraction were methanol, acetone, hexane, and dichloromethane. After the final extraction using dichloromethane, the polymer was obtained as a black solid (59.8 mg, 62%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 ºC): δ (ppm) 8.02 (1H), 7.51 (1H), 4.50 (2H), 2.81 (2H), 2.19-0.68 (m, 42H). Elem. Anal.: Calcd. for $C_{35}H_{48}FN_3OS_3$ (%): C, 65.48; H, 7.54; F, 2.96; N, 6.55; O, 2.49; S, 14.98. Found (%): C, 65.37; H, 7.73; N, 6.20. Molecular weight: M_n = 23.8 kDa, M_w = 61.4 kDa, $Đ_M$ = 2.58.



Polymer TRTzOR-ffBT (P3): The solvents used for Soxhlet extraction were methanol, acetone, hexane, dichloromethane, and chloroform. After the final extraction using chloroform, the polymer was obtained as a black solid (51.0 mg by chloroform, 49%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 80 ºC): δ 8.09 (1H), 4.56 (2H), 2.75 (2H), 2.11-0.66 (m, 42H). Elem. Anal.: Calcd. for $C_{35}H_{47}F_2N_3OS_3$ (%): C, 63.70; H, 7.18; F, 5.76; N, 6.37; O, 2.42; S, 14.57. Found (%): C, 63.79; H, 7.06; N, 6.40. Molecular weight: M_n = 44.5 kDa, M_w = 98.3 kDa, $Đ_M$ = 2.21.

3 Thermal and Optical Properties of the Polymers.

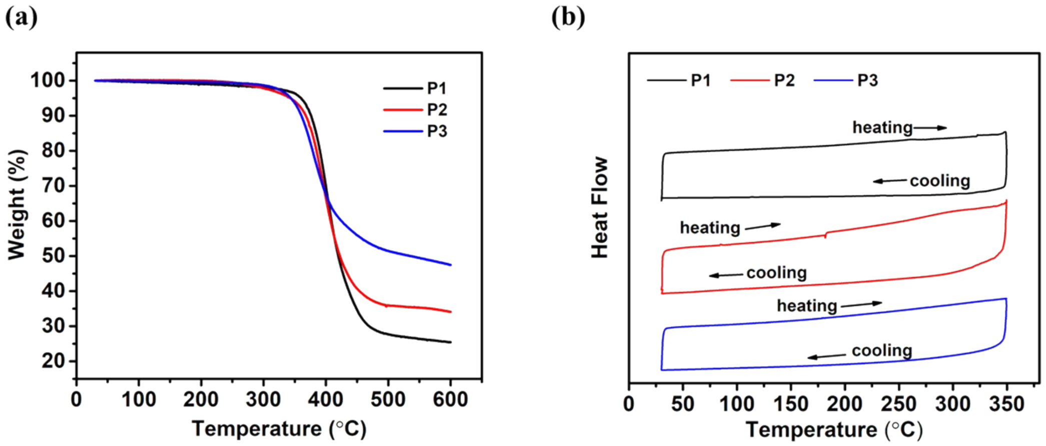


Figure S1. (a) TGA curves of polymers P1–P3 at a heating rate of 10 ºC min^{-1}, (b) DSC curves of polymers P1–P3 during the second heating and cooling cycle, the heating/cooling rate was 10 ºC min^{-1}.

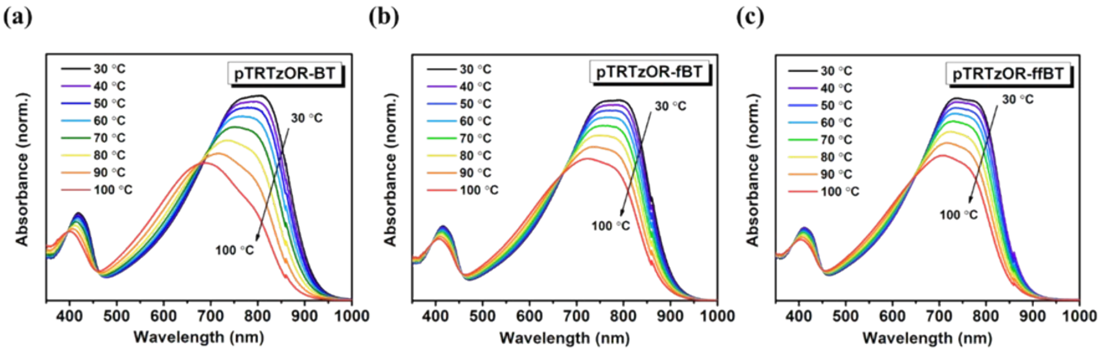


Figure S2. Temperature-dependent UV-vis absorption spectra of TRTzOR-based polymers P1–P3 in diluted solutions (10^{-5} M in chloroform).

4 DFT Calculations

The density functional theory (DFT) calculations were carried out by Gaussian 16 (Revision A.03) program[3] supported by High Performance Computer of Southern University of Science and Technology (SUSTech HPC). Natural transition orbitals (NTOs) for the S_0 to S_1 transition of the polymers were calculated on non-empirically TD-DFT//tuned ωB97X-D/6-31G(d,p) level of theory.[4]

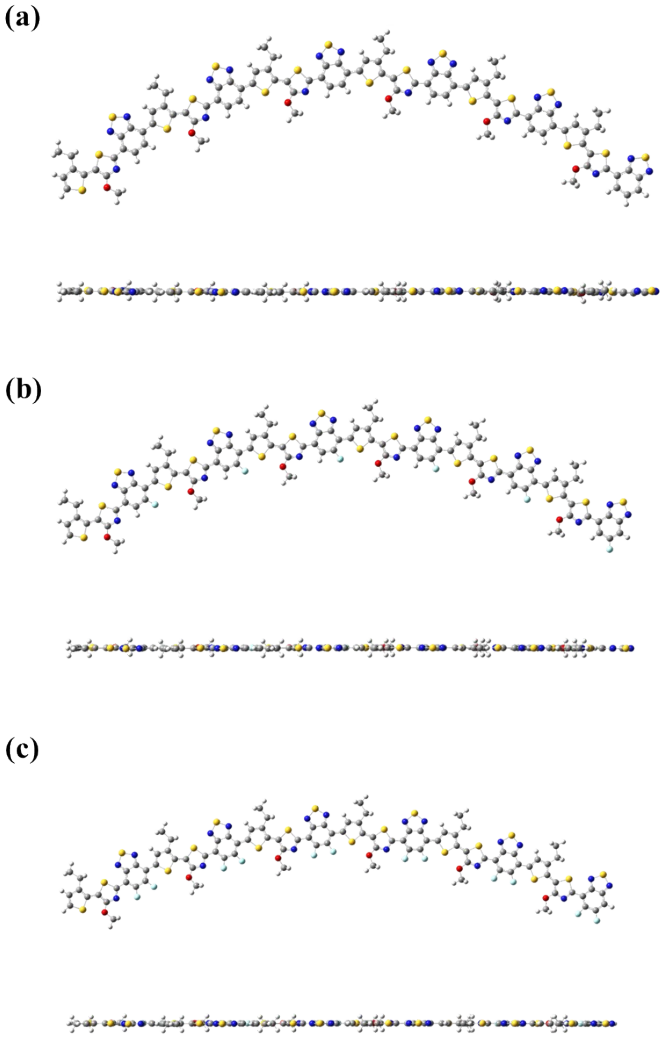
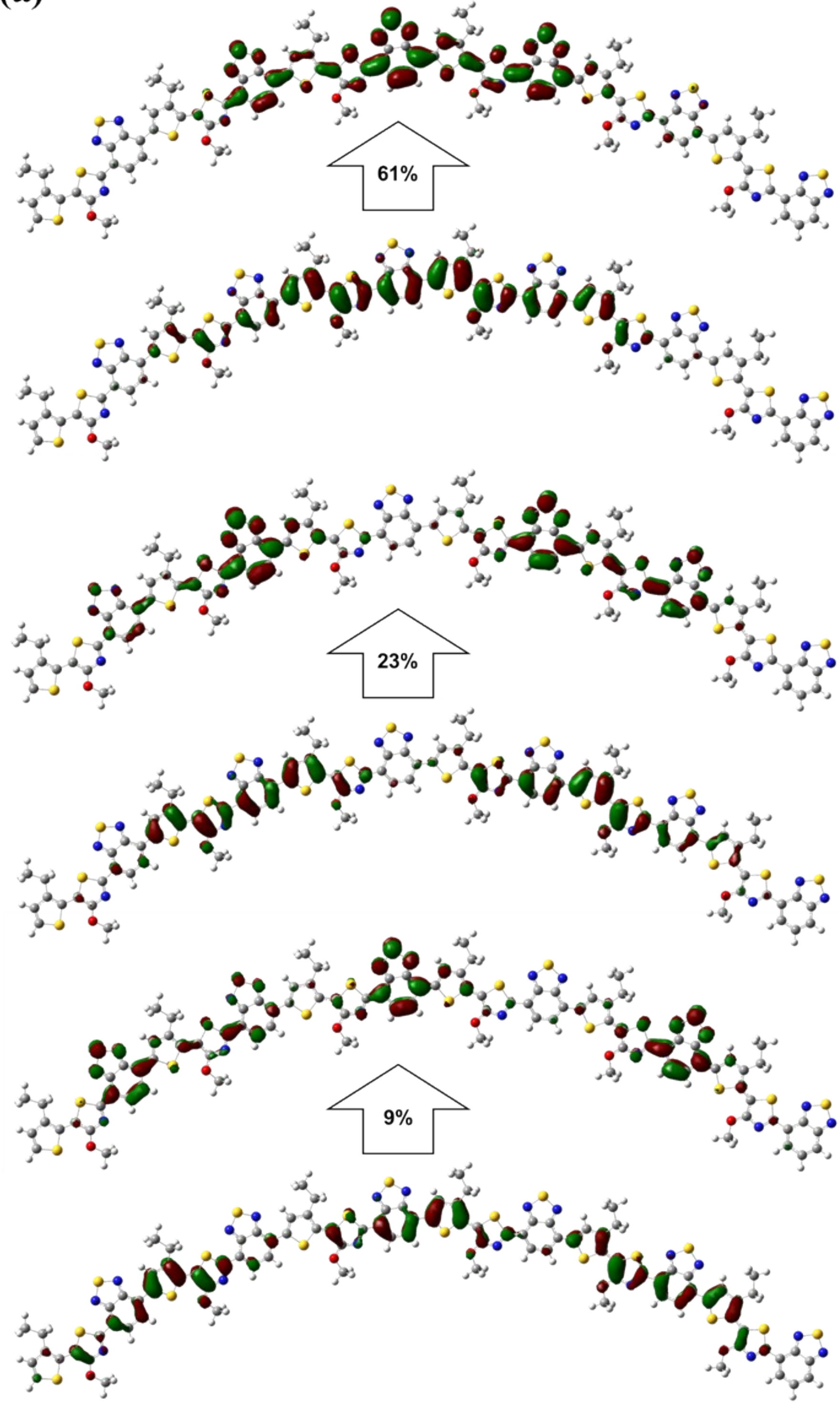
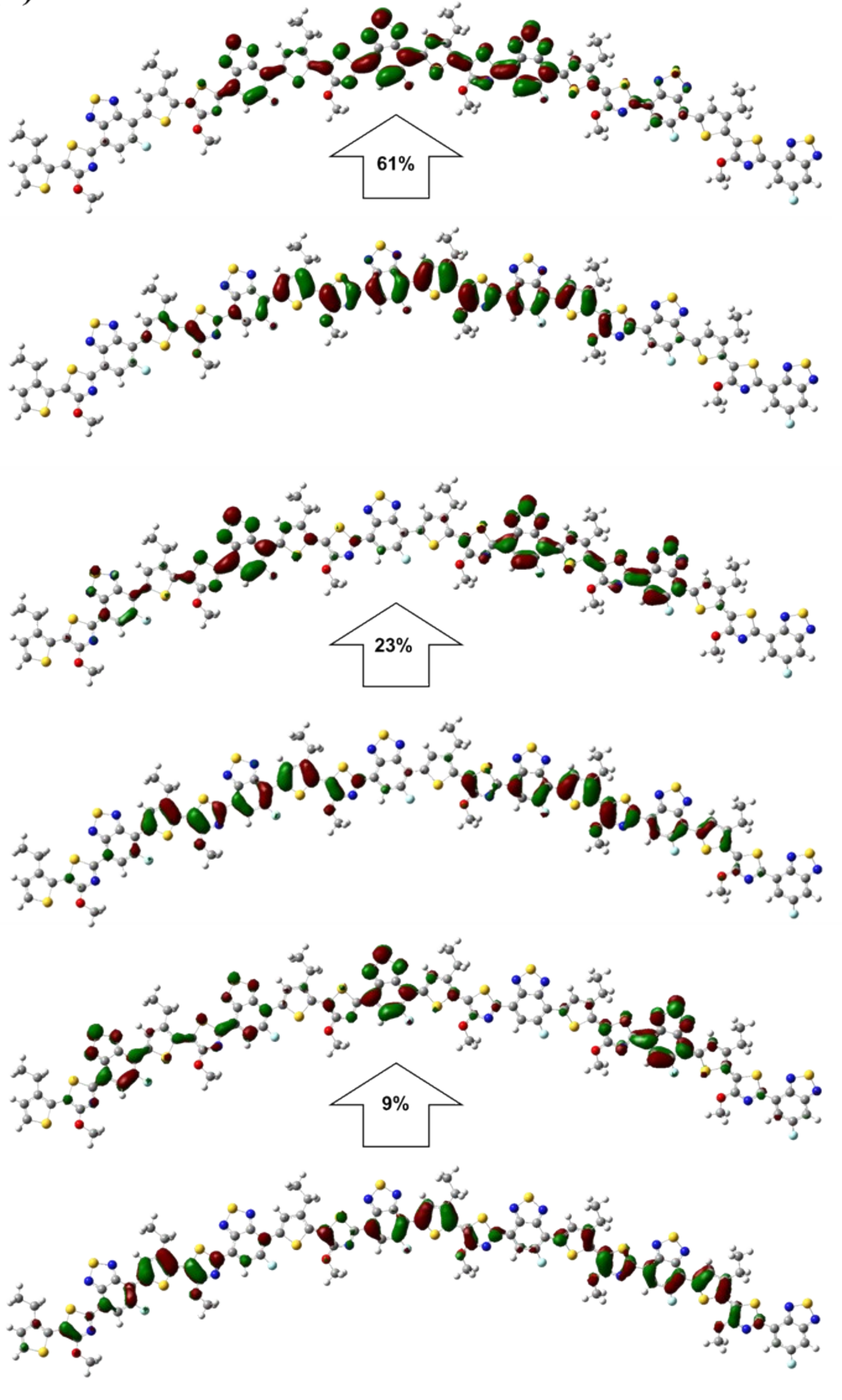


Figure S3. Optimized geometries in both top and side views for the hexamers of the repeat units of (a) P1, (b) P2, and (c) P3. The calculation was conducted at the DFT//B3LYP/6-31(d,p) level.

(a)



(b)



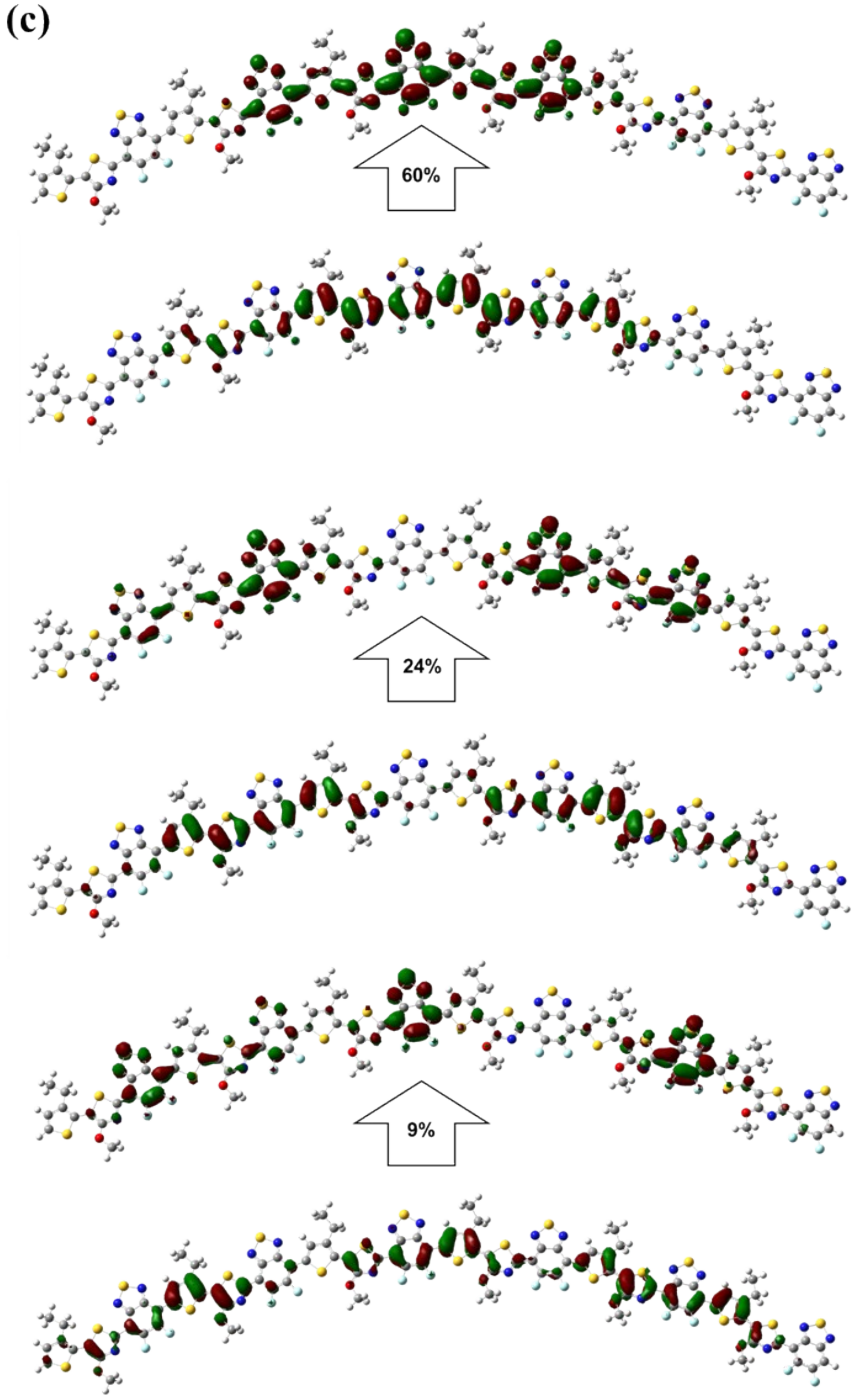


Figure S4. Natural transition orbitals with the largest contribution to the S_0–S_1 transitions for (a) P1, (b) P2, and (c) P3. (top: electron wave function; bottom: hole wave function). The calculation was conducted at TD-DFT//(tuned)-ωB97X-D/6-31G(d,p) level using hexamers of the polymer repeat units.

5 OTFT Device Fabrication and Characterization

Bottom-gate/top-contact (BG/TC) device configuration was used for OTFTs. P-doped silicon with 300 nm thermally grown oxide layer was used as substrate, which was cleaned by sequential sonication in acetone and isopropanol, followed by warm bath in SC–1 solution (H_2O:ammonium hydroxide:hydrogen peroxide, 5:1:1, volume ratio) at 55–65 °C to remove particles and organic residuals. The cleaned silicon oxide surface was functionalized with self-assemble monolayer (SAM) to reduce surface energy and promote optimal molecular packing during semiconductor coating step. Prior to SAM growth, the silicon substrates were treated with UV-Ozone for 30 min and oxygen plasma for 10 min. Octadecyltrimethoxysilane (OTMS) monolayer was spin-coated on top of the SiO_2 surface from trichloroethylene solution (concentration: 3 mM), which was then exposed to saturated ammonium vapor for 15 h to complete the hydrolysis reaction. After sonication cleaning in toluene, isopropanol, and deionized water in sequence, the OTMS-treated SiO_2/Si substrate was found to have water contact angle around 108°–110°. The polymer semiconductor layers were spin-coated on top from chloroform solutions (3 mg mL^{-1}) at 3000 rpm, then thermally annealed at different temperatures (100, 150, 200, and 250 ºC) for 10 min and cooled to room temperature. At last, 40 nm Au was evaporated through shadow mask onto the semiconducting layer as the source and drain electrodes. The channel length is 100 µm and the channel width is 1 mm. The transistor devices were characterized with Keithley S4200 semiconductor analyzer in a nitrogen-filled glove box. For mobility calculation, standard equation in the saturation regime was used: $I_{SD} = \frac{WC_i}{2L}\mu(V_G - V_T)^2$, where W is the channel length, L is the channel length, I_{SD} is gate leakage-corrected source to drain current, C_i is the capacitance per unit area of the SiO_2 layer, μ is the saturation mobility, V_G is the gate voltage, and V_{th} is the gate threshold voltage.

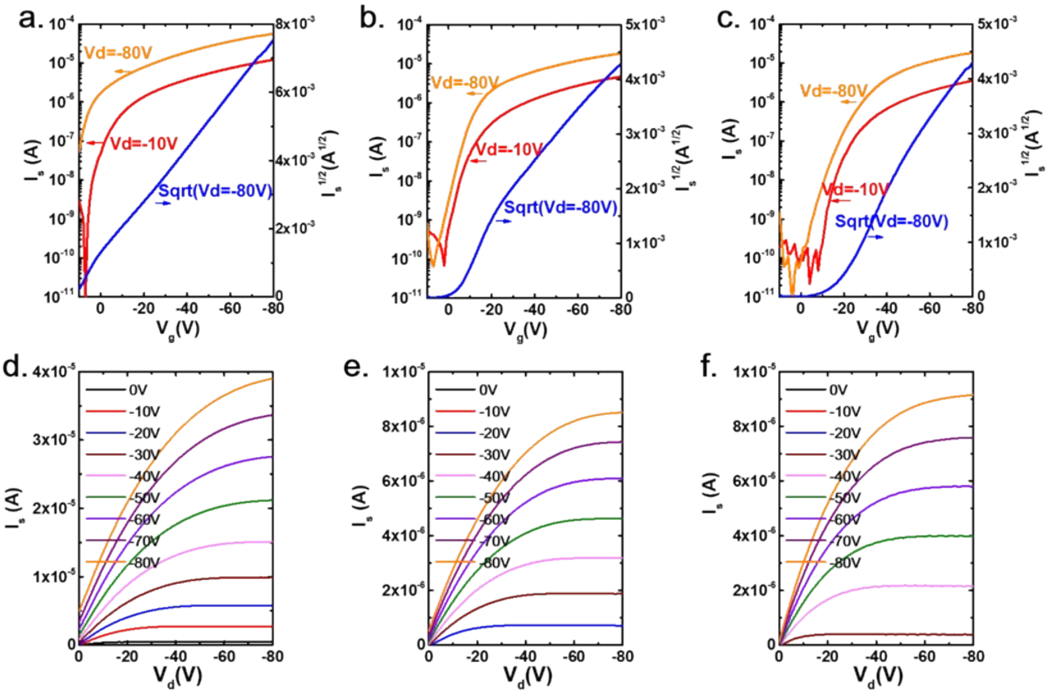


Figure S5. BG/TC OTFT transfer and output characteristics of (a, d) P1, (b, e) P2, and (c, f) P3. On the basis of the transfer characteristics, the transistors show gate-dependent mobility. The origin of this problem has been assigned to contact resistance[5,6] or dielectric induced interface charge trapping[7,8]. For our case, we suspect that it could be due to dielectric induced interface charge trapping since the contact resistance for hole injection is minimal. Nonetheless, for mobility calculation, we deliberately avoided the low V_g region where the kink problem happened. All mobility values were extracted from high V_g region (−70 to −80 V) to ensure the reliability of the results.

Table S1. BG/TC OTFT performance parameters of TRTzOR-based polymer semiconductors P1–P3. All mobility values were extracted from high V_g region (−70 to −80 V).

Polymer	T_{anneal} [ºC]	μ_{lin} [cm^2 V^{-1} s^{-1}]	μ_{sat} [cm^2 V^{-1} s^{-1}]	V_{th} [V]	I_{on}/I_{off}
P1	100	0.023 (0.018)	0.022 (0.017)	8.4	10^4
	150	0.063 (0.053)	0.058 (0.048)	3.3	10^5
	200	0.15 (0.13)	0.13 (0.12)	2.9	10^5
	250	0.13 (0.11)	0.10 (0.098)	1.0	10^4
P2	100	0.021 (0.017)	0.013 (0.010)	−6.2	10^4
	150	0.027 (0.021)	0.025 (0.021)	−6.0	10^4
	200	0.048 (0.037)	0.051 (0.039)	−10.0	10^4
	250	0.041 (0.039)	0.035 (0.032)	−5.6	10^4
P3	100	0.023 (0.022)	0.048 (0.033)	−25.8	10^5
	150	0.045 (0.038)	0.051 (0.046)	−19.9	10^5
	200	0.074 (0.066)	0.076 (0.067)	−15.9	10^5
	250	0.082 (0.075)	0.092 (0.081)	−22.5	10^5

6 Polymer Solar Cell Fabrication and Characterization

Polymer solar cells (PSCs) were fabricated using conventional architecture of ITO/PEDOT:PSS/Polymer:$PC_{71}BM$/ETL/Al. Glasses with pre-patterned ITO layer (sheet resistance: 10 Ω per square) were used as substrates, which were cleaned by sonication in detergent bath, deionized water, acetone, and isopropanol for 30 min each, followed by baking in oven for 3 h. After UV-Ozone exposure for 15 min, the PEDOT:PSS layer (Clevios P VP A1 4083, ~30 nm) was spin-coated on top of ITO at a spinning rate of 3000 rpm for 25 s, then annealed at 150 °C for 15 min in air. Subsequently, the substrates were transferred into a nitrogen-filled glove box for following steps. Polymer (7 mg mL^{-1}):$PC_{71}BM$ solutions (1:1.5, w/w) were prepared in chloroform with 3% (volume ratio) diphenyl ether (DPE) as the additive. To completely dissolve the polymers, the solutions were stirred at room temperature for at least 3 h before performing the active layer deposition step. Various spin-casting conditions were tested to search for the optimal performance. Finally, PDINO electron transport layer (ETL, 10 nm) was spin-casted from ethanol solution (1.5 mg mL^{-1}) at 3000 rpm for 25 s, followed by Al cathode (100 nm) evaporation at a high vacuum level (1E−4 Pa) using shadow mask to complete the device fabrication.

J-V curves were collected in a nitrogen-filled glove box using a Xe lamp-based SS-F5-3A Solar Simulator (Enli Technology, Inc.) under simulated AM1.5G light (100 mW cm^{-2}). The light intensity was controlled with NREL-calibrated Si solar cell with a KG-5 filter. External quantum efficiency (EQE) curves were measured in air with a QE-R3011 measurement system (Enli Technology, Inc.)

Table S2. PSC Device performance parameters with various amount of DPE additive, using device architecture of ITO/PEDOT:PSS/Polymer:PC$_{71}$BM/PDINO/Al. Data from the best performing devices are presented here.

Polymer	Additive	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
P1	w/o	0.57	13.31	56.97	4.19
	1% DPE	0.57	14.31	58.30	4.74
	3% DPE	0.56	18.22	63.07	6.46
P2	w/o	0.65	11.23	62.41	4.41
	1% DPE	0.63	15.14	58.01	5.64
	3% DPE	0.64	17.04	57.24	6.27
P3	w/o	0.77	3.97	56.68	1.72
	1% DPE	0.77	13.82	53.89	5.70
	3% DPE	0.76	14.55	54.47	6.09

Table S3. PSC Device performance parameters with various solvents, using device architecture of ITO/PEDOT:PSS/Polymer:PC$_{71}$BM/PDINO/Al and 3% DPE additive. Data from the best performing devices are presented here.

Polymer	Solvent	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
P1	CF	0.56	18.22	63.07	6.46
	DCB	0.55	17.28	59.97	5.68
P2	CF	0.64	17.04	57.24	6.27
	DCB	0.63	15.14	58.01	5.64
P3	CF	0.76	14.55	54.47	6.09
	CB	0.76	11.11	50.55	4.28
	DCB	0.76	11.00	54.35	4.52
	o-DCB/CB (1:1)	0.76	10.91	53.39	4.35

Table S4. PSC device performance parameters with various electron transport layers (ETLs), using device architecture of ITO/PEDOT:PSS/Polymer:$PC_{71}BM$/ETL/Al and 3% DPE additive. Data from the best performing devices are presented.

Polymer	Electron injection layer	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
P1	PDINO	0.56	18.22	63.07	6.46
	LiF	0.56	14.84	60.37	5.02
	Ca	0.54	16.26	62.39	5.50
P2	PDINO	0.64	17.04	57.24	6.27
	LiF	0.60	6.11	43.30	1.58
	Ca	0.63	15.14	58.01	5.64
P3	PDINO	0.76	14.55	54.47	6.09
	LiF	0.76	13.38	49.86	5.07
	Ca	0.73	9.96	59.28	4.31

7 SCLC Mobility Characterization

Space charge limited current (SCLC) mobilities of polymer:$PC_{71}BM$ blend films were measured using both hole-only and electron-only devices. The device architecture is ITO/PEDOT:PSS/polymer:$PC_{71}BM$/MoO_3/Ag for hole-only device, and it is ITO/ZnO/Polymer:$PC_{71}BM$/PDINO/Al for electron-only device. The SCLC mobilities were extracted from the current-voltage curves by the Mott-Gurney equation: [9]

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, ε_0 is vacuum permittivity (8.85×10^{-12} F m^{-1}), ε_r is the relative dielectric constant of the active layer, μ is the SCLC mobility and d is the thickness of the active layer. $V = V_{app} - V_{bi}$ is the voltage drop across the active layer, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in voltage coming from the work function difference between the electrodes (neglected in the hole-only and electron-only devices).

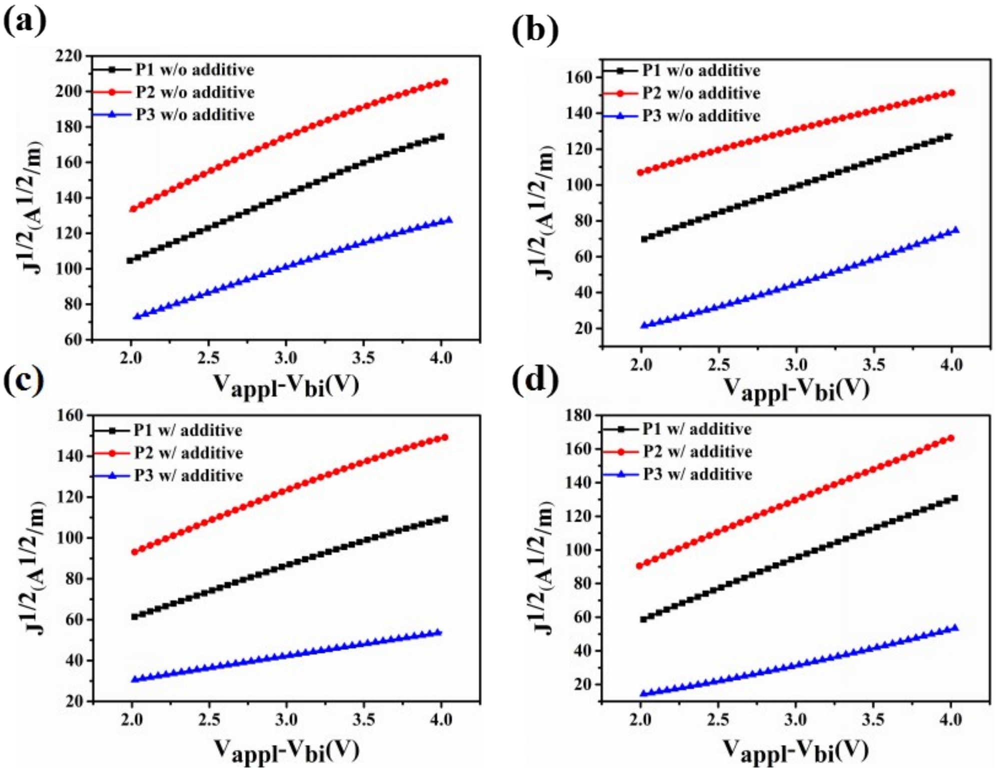


Figure S6. $J^{1/2}$–V curves of (a, c) hole-only and (b, d) electron-only devices using polymer:PC$_{71}$BM blend films with or without 3% DPE additive, measured in dark at room temperature.

Table S5. SCLC mobilities of the polymer:PC$_{71}$BM blend films with or without 3% DPE additive, measured in dark at room temperature.

Polymer	Additive	$\mu_{h,SCLC}$ [cm^2 V^{-1} s^{-1}]	$\mu_{e,SCLC}$ [cm^2 V^{-1} s^{-1}]	μ_h/μ_e
P1	n	8.60×10^{-4}	2.16×10^{-4}	3.98
	y	8.14×10^{-4}	7.79×10^{-4}	1.04
P2	n	7.99×10^{-4}	1.23×10^{-4}	6.50
	y	7.40×10^{-4}	2.89×10^{-4}	2.56
P3	n	5.74×10^{-4}	1.46×10^{-4}	3.92
	y	3.65×10^{-4}	7.60×10^{-4}	0.48

8 Film Morphology Characterization

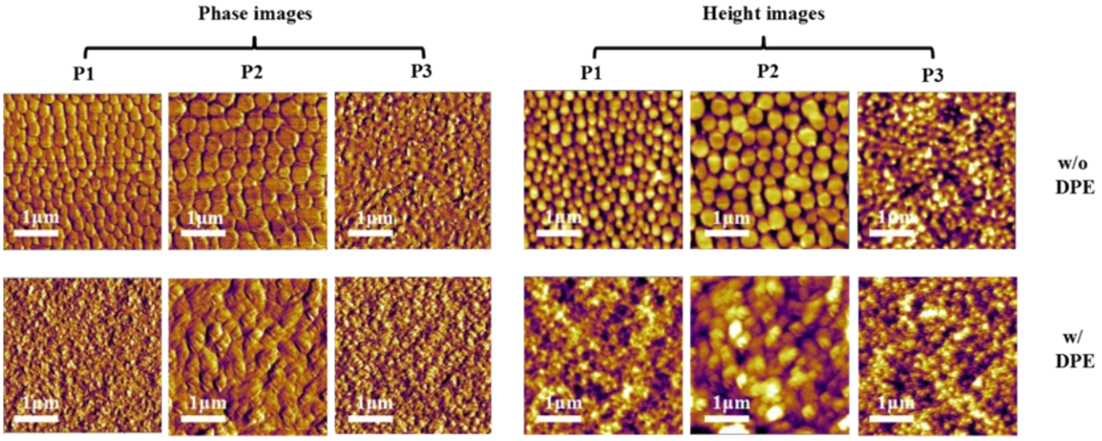


Figure S7. Tapping-mode AFM phase and height images of polymer:PC$_{71}$BM blend films prepared under the same conditions for the best-performing PSC devices.

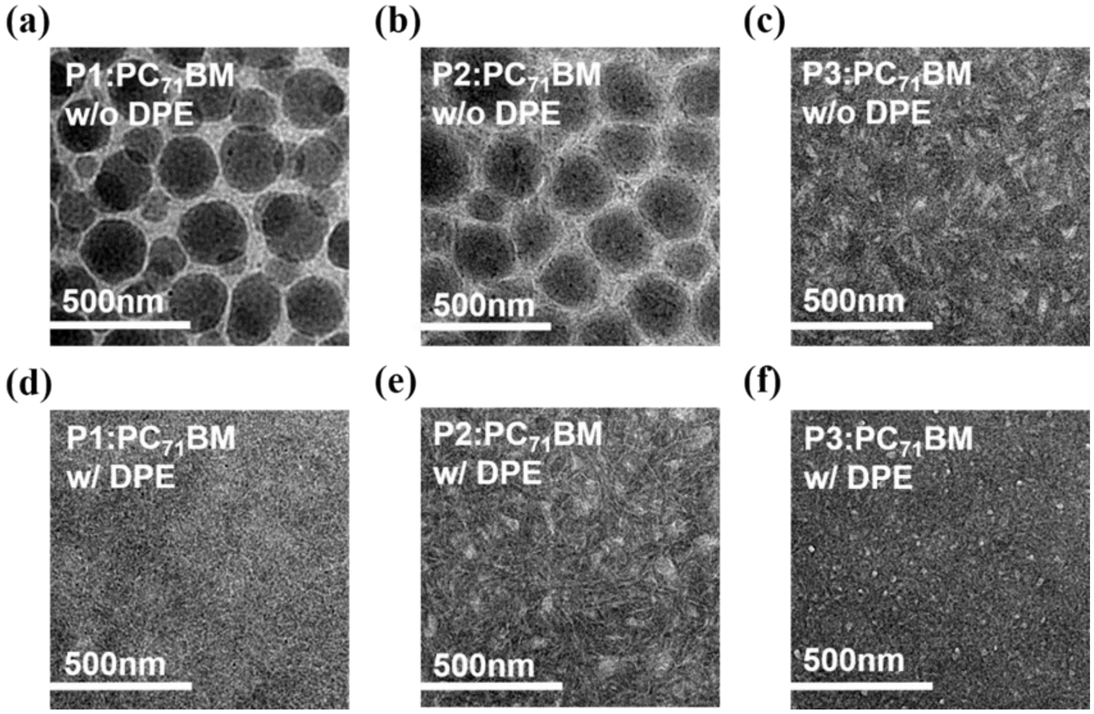


Figure S8. TEM images of polymer:PC$_{71}$BM blend films without (a-c) and with (d-f) DPE additive. The films were prepared under the same conditions for the best-performing PSC devices.

Table S6. AFM measured root-mean-square (RMS) roughness values of polymers:$PC_{71}BM$ blend films.

Blend	w/o DPE [nm]	w/ DPE [nm]
P1: $PC_{71}BM$	3.44	1.88
P2: $PC_{71}BM$	3.68	1.99
P3: $PC_{71}BM$	1.85	2.37

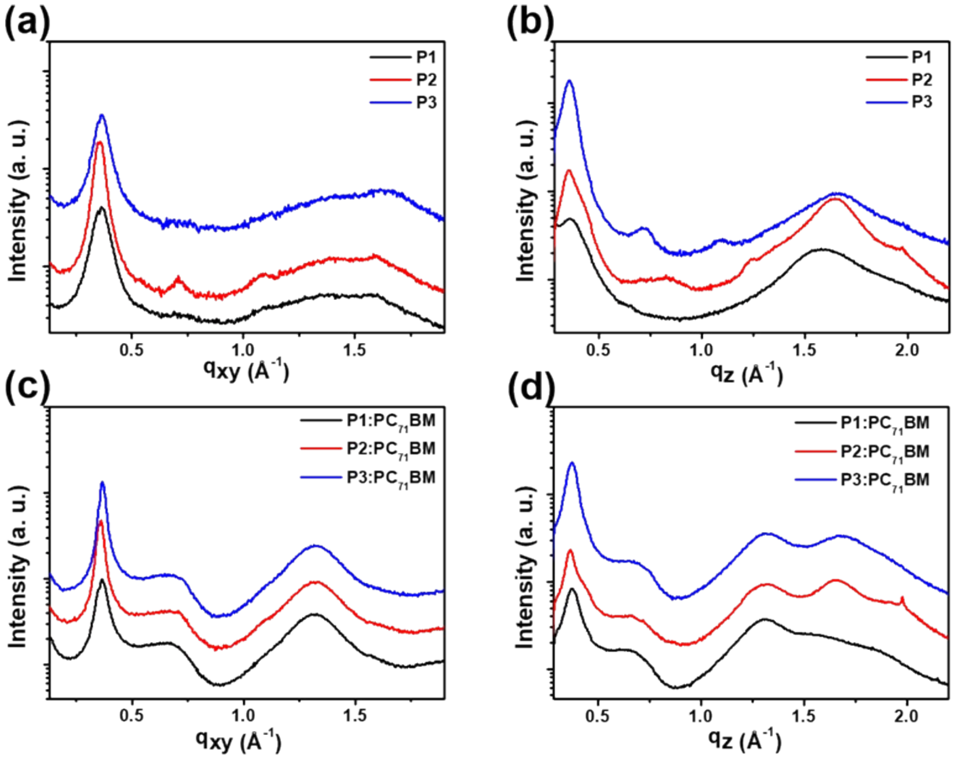


Figure S9. Out-of-plane (q_z) and in-plane (q_{xy}) line cuts of the GIWAXS for neat films (a, b) and blended films (c, d).

Table S7. Summary of packing parameters of P1-P3 pristine and blend films. [a] IP: in-plane; OOP: out-of-plane.

Film	Plane [a]	Direction	Lamellar spacing		Direction	π-π stack	
			q (Å^{-1})	d-spacing (Å)		q (Å^{-1})	d-spacing (Å)
P1	IP	(100)	0.3625	17.32			
	OOP	(100)	0.3623	17.33	(010)	1.576	3.98
P2	IP	(100)	0.3558	17.65			
		(200)	0.7069	17.77			
		(300)	1.087	17.33			
	OOP	(100)	0.3556	17.66	(010)	1.651	3.80
P3	IP	(100)	0.3647	17.22			
	OOP	(100)	0.3601	17.44	(010)	1.66	3.78
		(200)	0.7209	17.42			
		(300)	1.091	17.27			
P1:PC$_{71}$BM	IP	(100)	0.3625	17.32	PC$_{71}$BM	1.32	4.76
	OOP	(100)	0.3779	16.62	PC$_{71}$BM	1.313	4.78
P2:PC$_{71}$BM	IP	(100)	0.3558	17.65	PC$_{71}$BM	1.322	4.75
	OOP	(100)	0.365	17.21	PC$_{71}$BM	1.313	4.78
					(010)	1.656	3.79
P3:PC$_{71}$BM	IP	(100)	0.367	17.11	PC$_{71}$BM	1.322	4.75
	OOP	(100)	0.3757	16.72	PC$_{71}$BM	1.319	4.76
					(010)	1.684	3.73

Table S8. Summary of coherence crystalline length (CCL) parameters of P1-P3 pristine and blend films.

Crystallographic parameters			P1	P2	P3
Pristine	From q_{xy} profile (100)	q (Å^{-1})	0.362	0.356	0.365
		d-spacing (Å)	17.36	17.66	17.23
		FWHM (Å^{-1})	0.090	0.057	0.081
		Coherence length (Å)	63.1	99.4	70.0
Crystallographic parameters			P1:PC$_{71}$BM	P2:PC$_{71}$BM	P3:PC$_{71}$BM
Blend	From q_{xy} profile (100)	q (Å^{-1})	0.363	0.356	0.367
		d-spacing (Å)	17.33	17.66	17.12
		FWHM (Å^{-1})	0.067	0.045	0.046
		Coherence length (Å)	84.1	124.9	123.1

9 ^{1}H NMR, ^{13}C NMR, and HRMS Spectra of Compounds

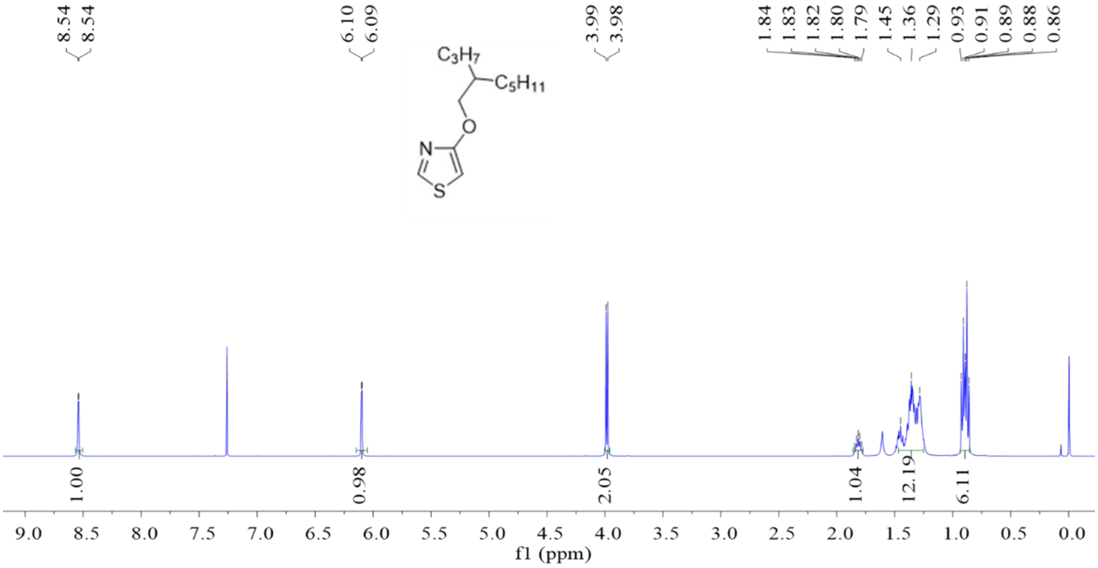


Figure S10. The ^{1}H NMR spectrum of compound **5**.

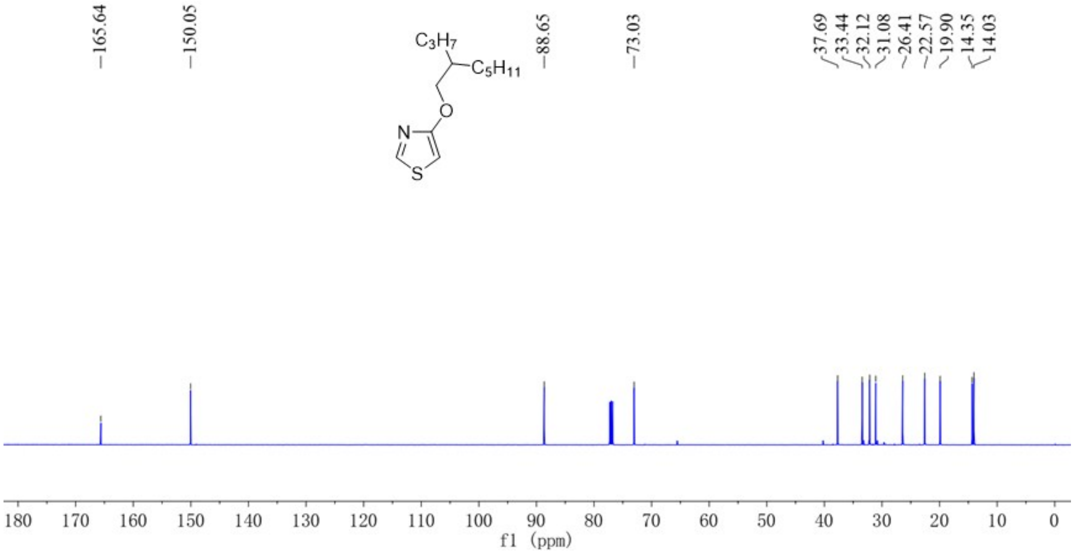


Figure S11. The ^{13}C NMR spectrum of compound **5**.

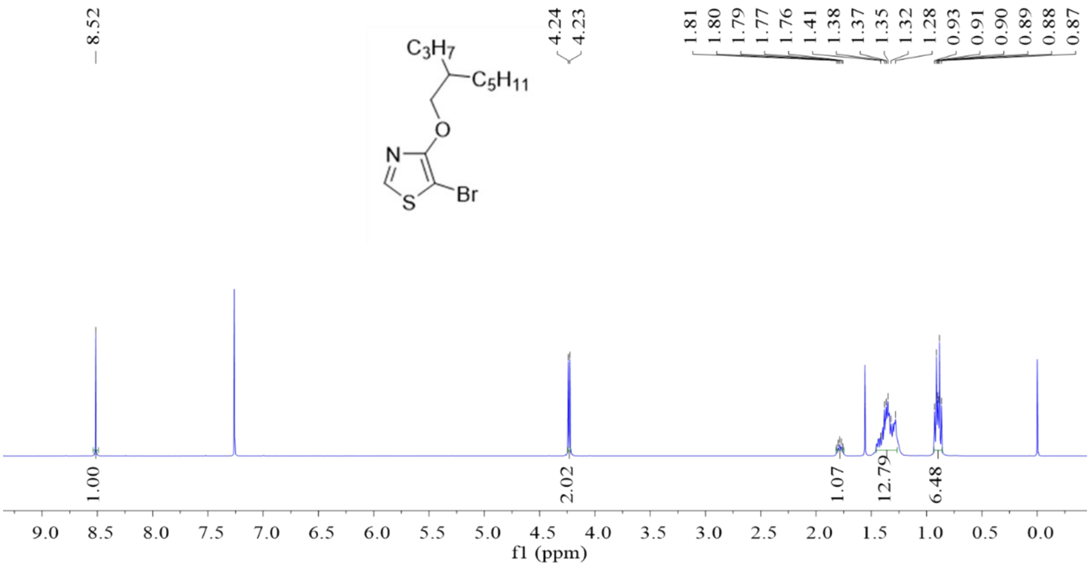


Figure S12. The ^{1}H NMR spectrum of compound **6**.

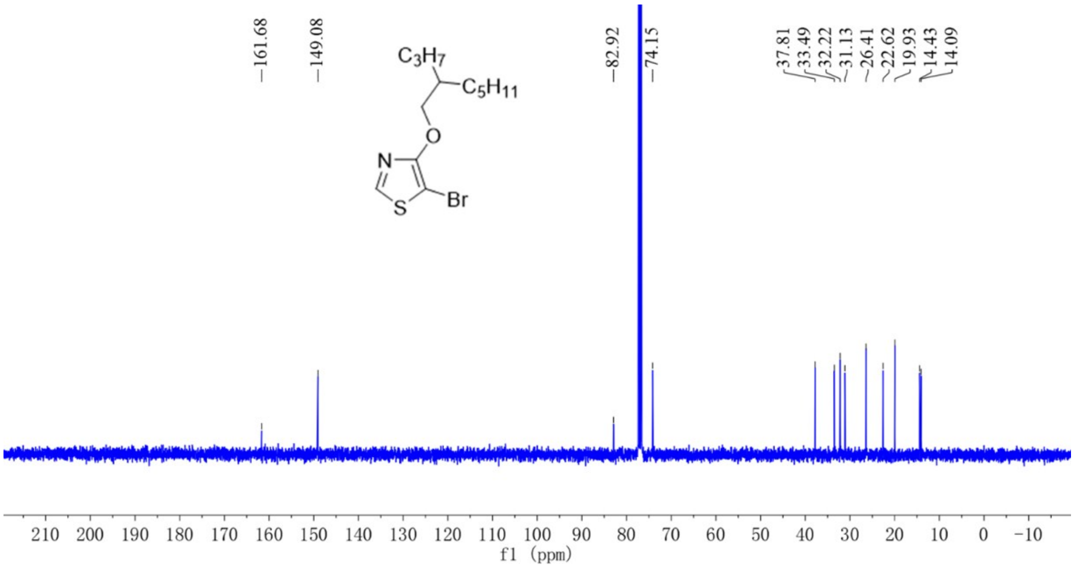


Figure S13. The ^{13}C NMR spectrum of compound **6**.

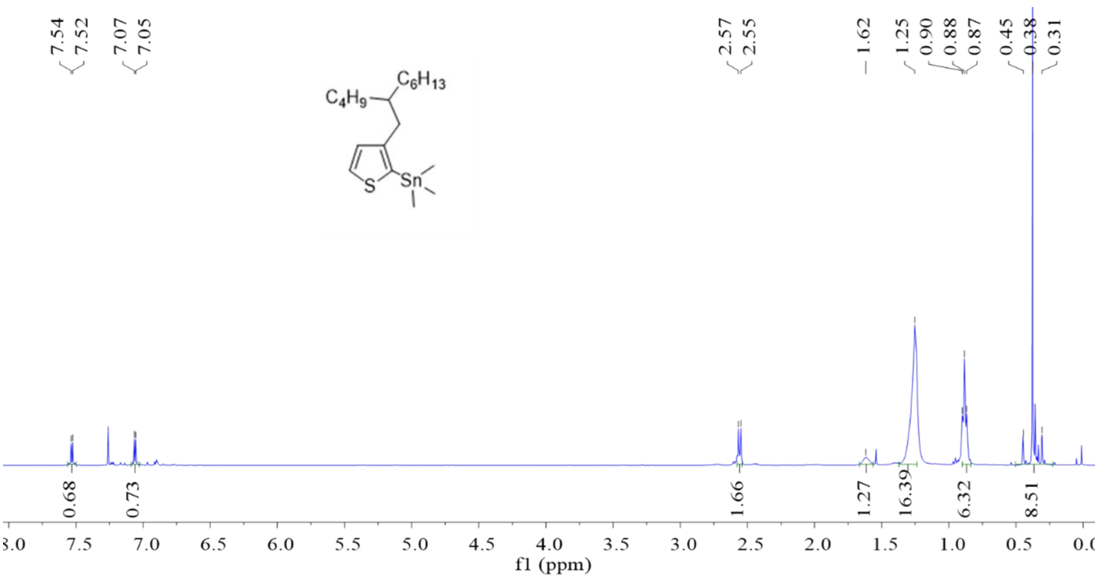


Figure S14. The ^{1}H NMR spectrum of compound **4**.

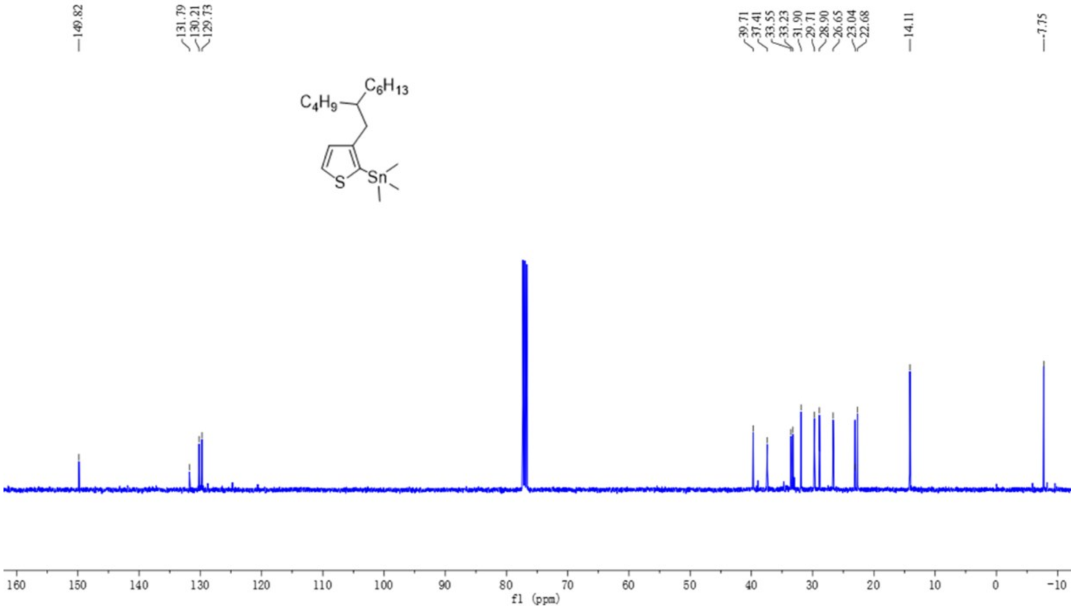


Figure S15. The ^{13}C NMR spectrum of compound **4**.

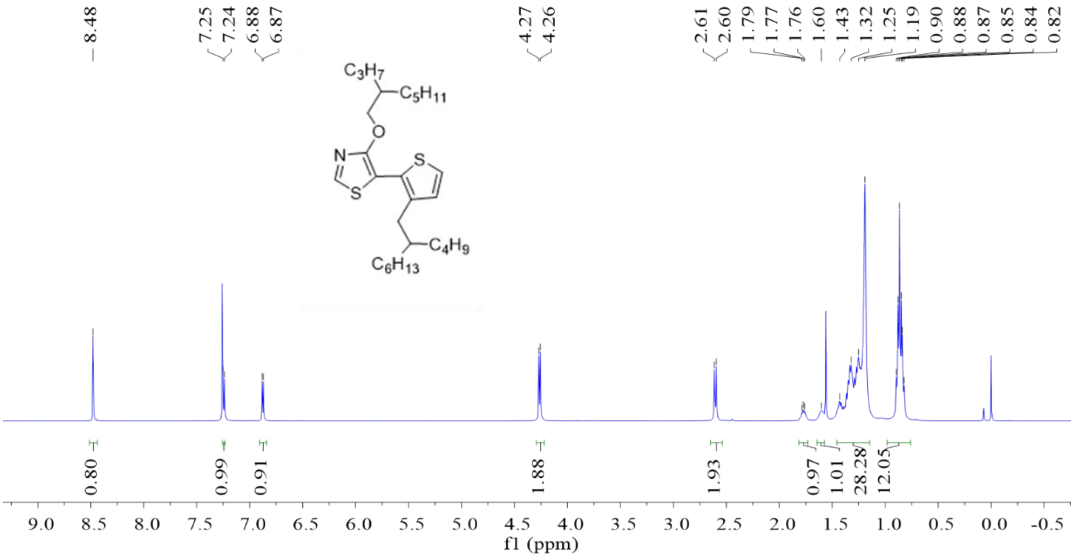


Figure S16. The ^{1}H NMR spectrum of compound **7**.

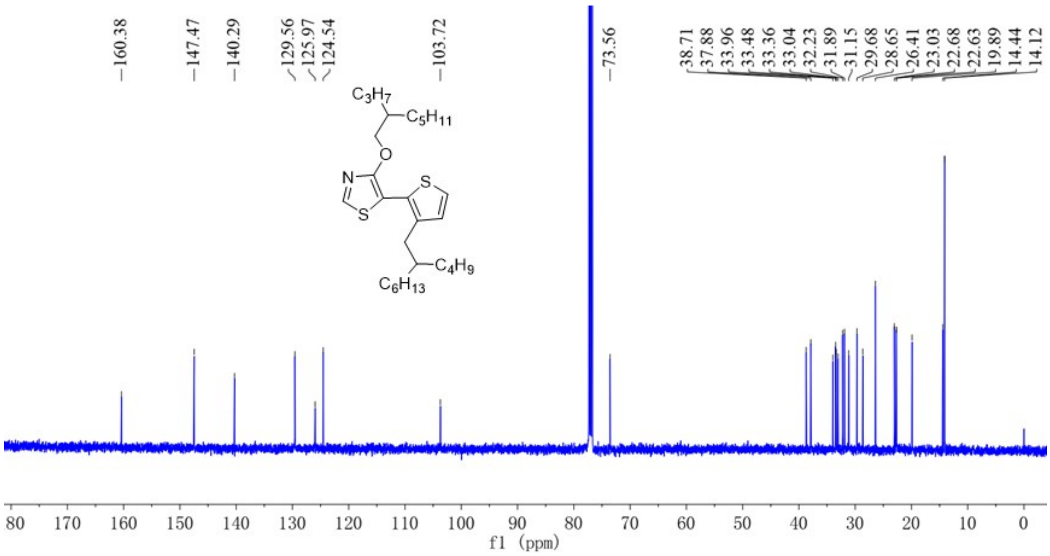


Figure S17. The ^{13}C NMR spectrum of compound **7**.

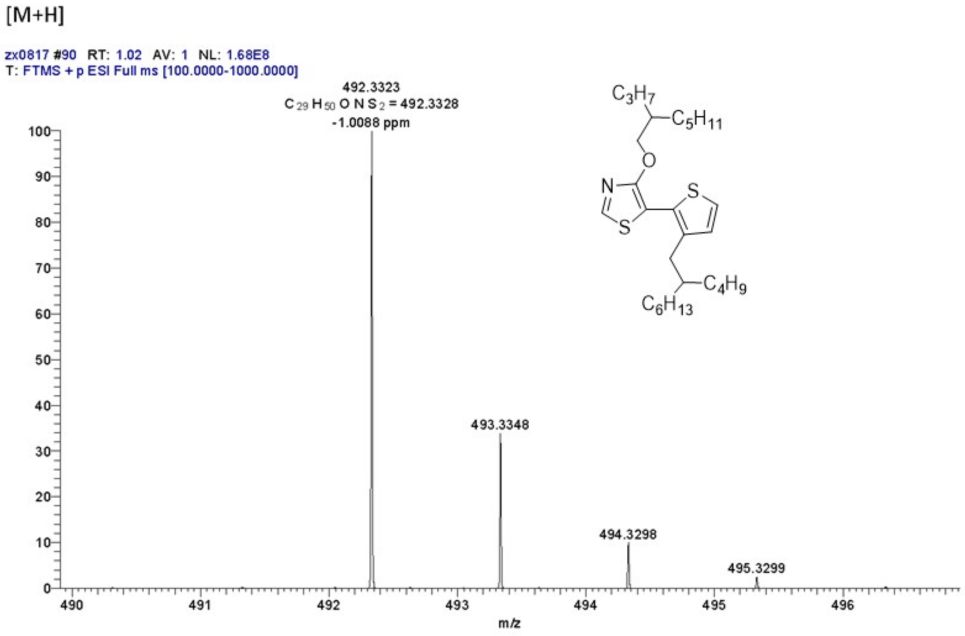


Figure S18. The HRMS spectrum of compound **7**.

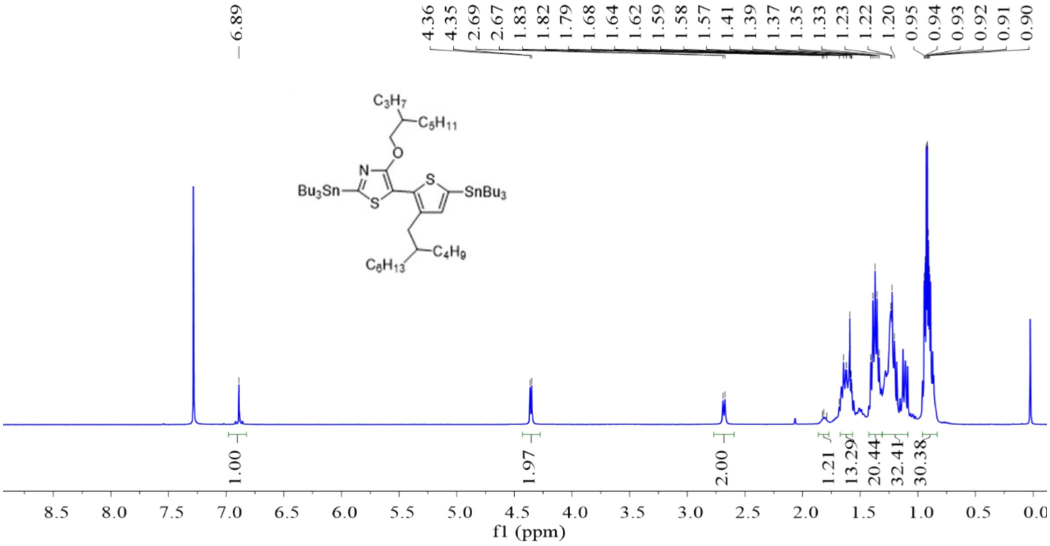


Figure S19. The ^{1}H NMR spectrum of compound **8**.

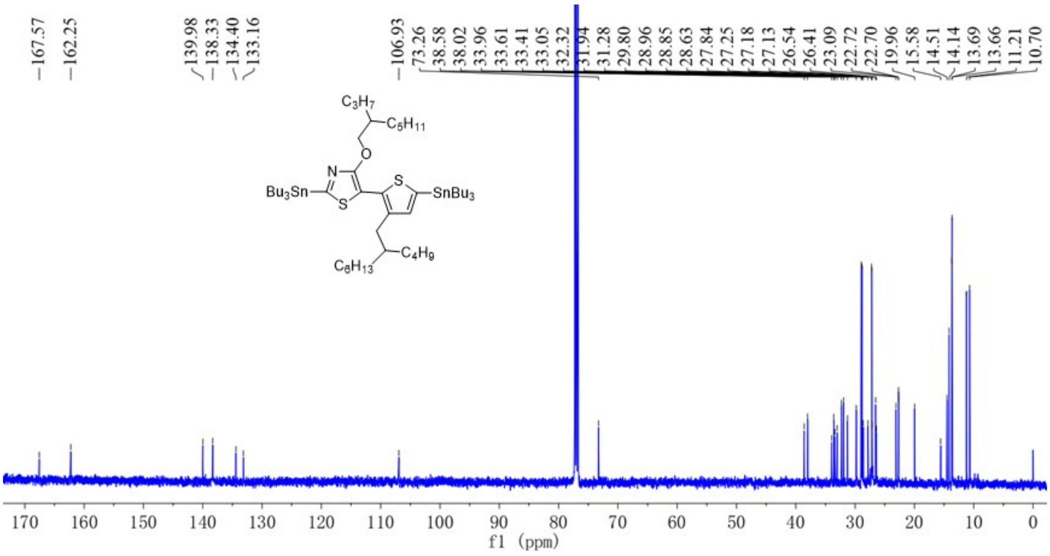


Figure S20. The ^{13}C NMR spectrum of compound **8**.

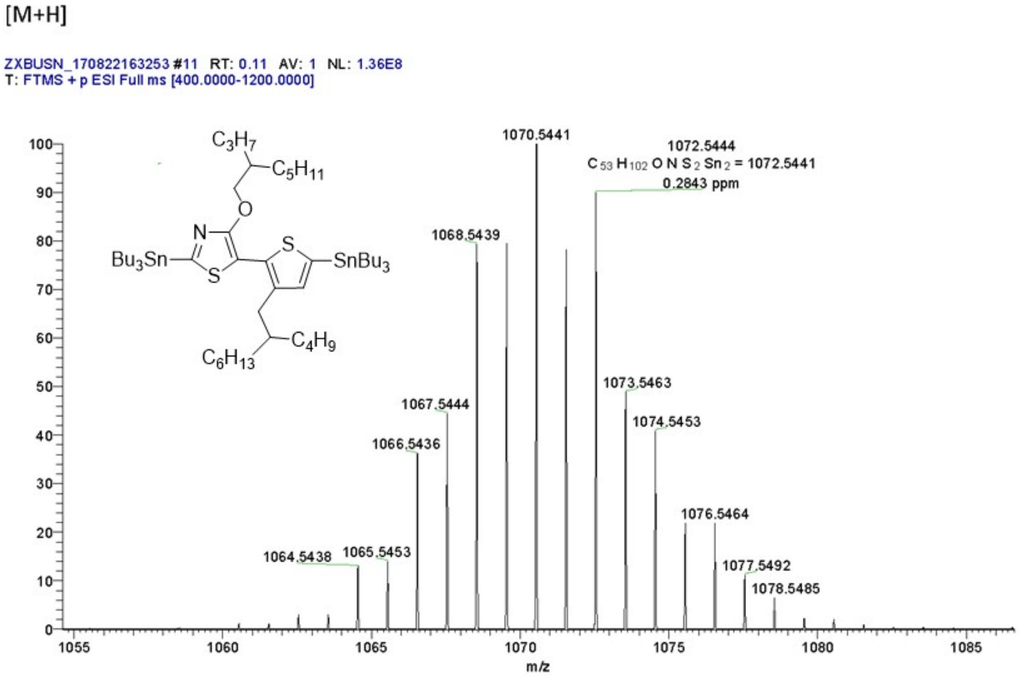


Figure S21. The HRMS spectrum of compound **8**.

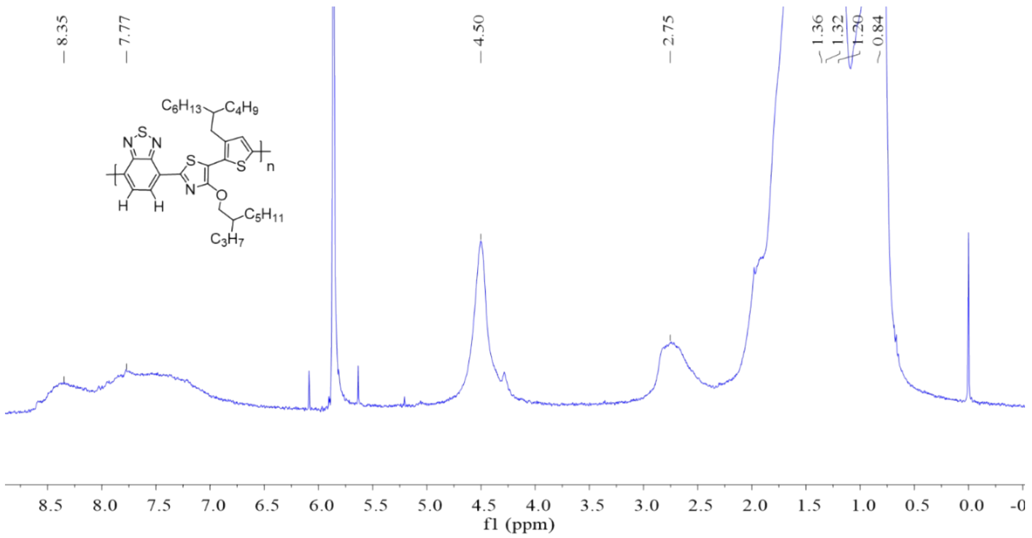


Figure S22. The 1H NMR spectrum of **P1** at 80 ºC in $C_2D_2Cl_4$.

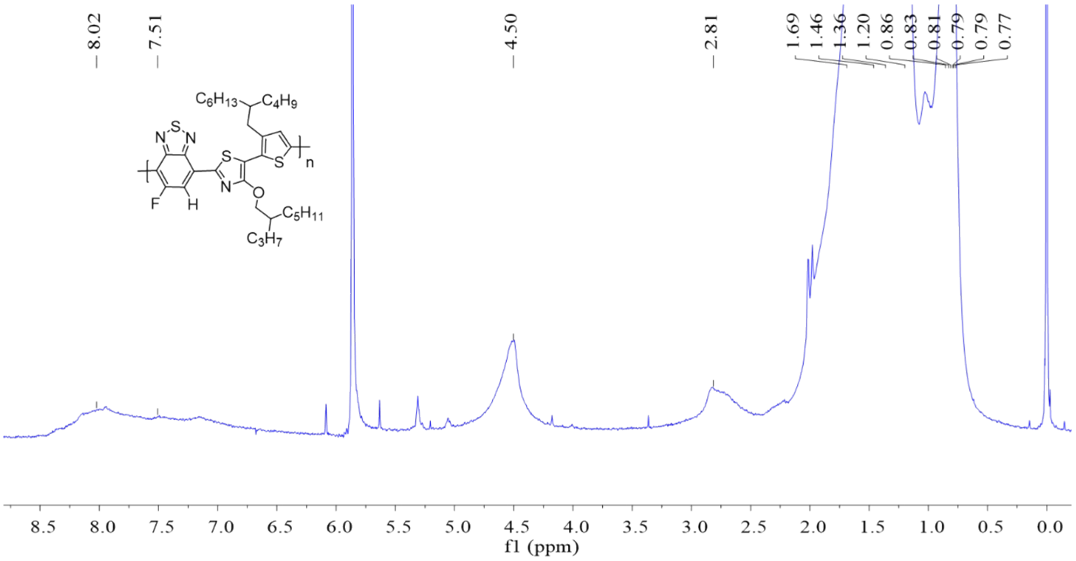


Figure S23. The ^{1}H NMR of **P2** at 80 ºC in $C_2D_2Cl_4$.

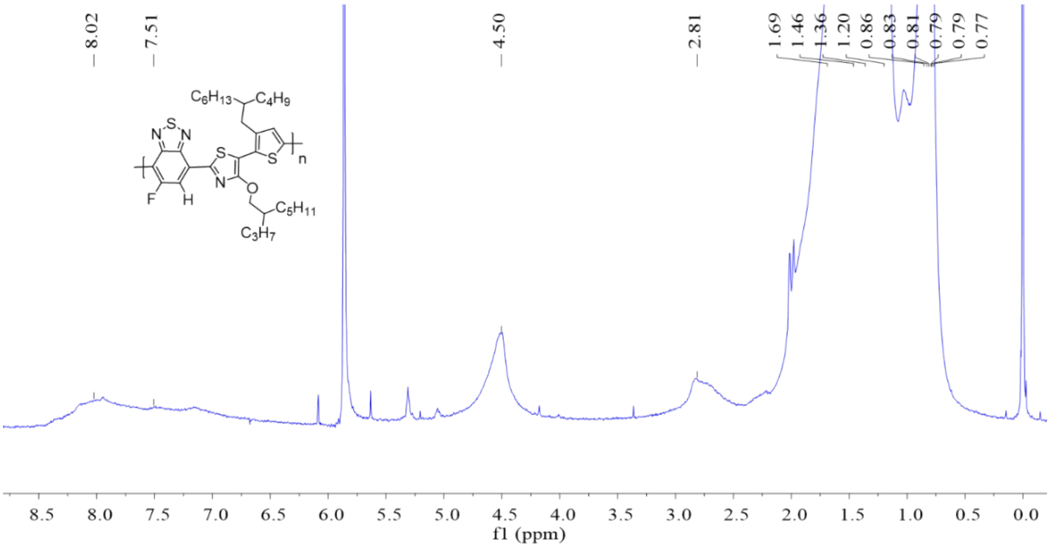


Figure S24. The ^{1}H NMR of **P3** at 80 ºC in $C_2D_2Cl_4$.

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