Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Molecular Design of a Wide-band-gap Conjugated Polymer for Efficient Fullerene-free Polymer Solar Cells

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Experimental data

Materials

The monomer 2,6-bis(trimethyltin)-4,8-bis(5-(2-otylthio)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (M3) and 2,5-bis-trimethylstannanyl-thiophene were purchased from Solarmer Materials Inc. All other chemical reagents were used as received.

Synthesis

5-bromothiophene-3-carboxylic acid (1). To solution of thiophene-3-carboxylic acid (3.00 g, 23.4 mmol) in 30 mL of acetic acid was added slowly liquid bromine (Br_2) (23.5 mL, 46.8 mmol) in 30 mL acetic acid at room temperature, and the mixture was stirred for 4h. The reaction mixture was added to ice water and filtrated. The filter cake was recrystallized from -water to give 5-bromothiophene-3-carboxylic acid as an whiteness crystalline solid (3.63 g, 75%). MS (ESI): m/z 206.9. ^{1}H NMR (400 MHz, DMSO) δ(ppm): 12.9 (s, 1H), 8.28 (s, 1H, Ar H), 7.50 (S, 1H, Ar H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 162.0, 131.0, 128.3, 125.6, 108.6.

Ethylhexyl 5-bromo-3-thiophenecarboxylate (2). To solution of 5 (3.00 g, 14.5 mmol), Dicyclohexylcarbodiimide (DCC)(1.50 g, 7.25 mmol) and 4-dimethylaminopyridine (DMAP) (0.45 g, 3.62 mmol) in 20 mL of dry dichloromethane (CH_2Cl_2) was added slowly ethylhexyl alcohol (1.89 g, 14.5 mmol) and the mixture was stirred at room temperature for 24h. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. The organic layer was concentrated by vacuum evaporation, and the residue was purified by column chromatography on silica gel to give 3 (4.40, 95%) as a colourless liquid. MS (EI): m/z 320. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.96 (d, 2H, Ar H), 7.44 (d, 2H, Ar H), 4.17 (m, 4H, CH_2), 1.66 (m, 2H, CH), 1.43 (m, 4H, CH_2), 1.33 (m, 12H, CH_2), 0.94 (m, 12H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 161.7, 134.3, 133.6, 130.21, 112.83, 67.36, 38.89, 30.54, 28.98, 23.95, 22.97, 14.04, 11.06.

5,5’-dibromo-3,3’-dicarboxylic acid ethylhexyl ester-2,2’-bithiophene (M1). To solution of 6 (4.00 g, 12.5 mmol) in 15 mL of THF was added slowly 2 M diisopropylamide (LDA) in THF (6.2 mL, 12.5 mmol) at -78°C under argon, and the mixture was stirred at -78°C for 1h. Anhydrous copper chloride (2.53 g, 18.8 mmol) was added, and the solution was allowed to warm to room temperature over 2h. The organic layer was concentrated by vacuum evaporation, and the residue was purified by column chromatography on silica gel to give M1 (1.90 g, 24%) as a colourless liquid. MS (MALDI-TOF): m/z 659.3 (M+Na). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.47 (s, 2H, Ar H), 4.03(m, 4H, CH_2), 1.45 (m, 2H, CH), 1.25 (m, 4H, CH_2), 1.19 (m, 12H, CH_2), 0.88 (m, 12H, CH_3) ^{13}C NMR (400 MHz, $CDCl_3$, δ): 161.4, 139.2, 132.0,114.4, 68.2, 38.8, 30.2, 29.3, 23.6, 22.9, 14.0 10.9.

PB2T. M1 (0.1591 g, 0.25 mmol) and M3 (0.2422 g, 0.25 mmol) were dissolved into 6 mL of toluene in a two-neck roundbottom flask. The solution was flushed with argon for 5 min, and 15 mg of $Pd(PPh_3)_4$ was added into the flask subsequently. The mixture was flushed with argon for another 15 min and then allowed to stir at 110°C for 16h under an argon atmosphere. Then, the reactant was cooled down to room temperature, and the polymer was precipitated into 100 mL of methanol. The polymer was collected by filtration and further purified by silica gel chromatography by using chlorobenzene as eluent. The polymer was precipitated again in 100 mL of methanol and obtained as crimson solid with a yield of ~60%. $C_{60}H_{76}O_4S_8$ (PB2T): Calculated C: 64.47 H: 6.85. Found C: 64.85 H: 6.92.

2-bromothiophene-3-carboxylic acid (3). A solution of thiophene-3-carboxylic acid (3.00 g, 23.4 mmol) in 30 mL of tetrahydrofuran (THF) was added slowly to 2 M diisopropylamide (LDA) in THF (23.5 mL, 46.8 mmol) at -78°C under argon, and the mixture was stirred at -78°C for 1h. Carbon tetrabromide (CBr_4) (7.77 g, 23.4 mmol) in 20 mL of THF was added, and the solution was allowed to warm to room temperature over 1h. The reaction mixture was acidified with 1 M HCl and 250 mL of ether was added. The aqueous layer was extracted with ether and the combined organic layer was washed with water, dried ($MgSO_4$), and concentrated to give the crude product, which was recrystallized from ethanol-water (1:4) to give 2-bromothiophene-3-carboxylic acid as an gray crystalline solid (2.52 g, 52%). MS (ESI): m/z 206.8. ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 13.02 (s, 1H, COOH H), 7.67 (d, 1H, Ar H), 7.36 (d, 1H, Ar H). ^{13}C NMR (400 MHz, DMSO, δ): 163.2, 132.5, 130.7128.2, 119.0.

Ethylhexyl 2-bromo-3-thiophenecarboxylate (4). To solution of 2 (2.00 g, 9.66 mmol), Dicyclohexylcarbodiimide (DCC) (1.00 g, 4.83mmol) and 4-dimethylaminopyridine (DMAP) (0.30 g, 2.41 mmol) in 10 mL of dry dichloromethane (CH_2Cl_2) was added slowly ethylhexyl alcohol (1.26 g, 9.66 mmol) and the mixture was stirred at room temperature for 24h. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. The organic layer was concentrated by vacuum evaporation, and the residue was purified by column chromatography on silica gel to give 4 (2.93, 95%) as a colourless liquid. MS (EI): m/z 320. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.30 (d, 1H, Ar H), 7.15 (d, 1H, Ar H), 4.15 (m, 2H, CH_2), 1.63 (m, 1H, CH), 1.39 (m, 2H, CH_2), 1.27 (m, 6H, CH_2), 0.88 (m, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 162.1, 131.5, 129.5, 125.7, 119.3, 67.2, 38.8, 30.5, 28.9, 23.9, 22.9, 14.0, 11.0.

3,3’’- dicarboxylic acid ethylhexyl ester -2,2’:5’,2’’-trithiophene (5). In a 100 mL two-neck roundbottom flask, compound 3 (2 g, 6.94 mmol), 2,5-bis-trimethylstannanyl-thiophene (0.95 g, 2.31 mmol), and $Pd(PPh_3)_4$ (200 mg) were mixed in 40 mL of toluene under argon protection. The solution was stirred at 110°C for 24h. The organic layer was concentrated by vacuum evaporation, and the residue was purified by column chromatography on silica gel to give 5 (1.16, 90%) as a yellow oil. MS (MALDI-TOF): m/z 583.3 (M+Na). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.48 (d, 2H, Ar H), 7.39 (s, 2H, Ar H), 7.21 (d, 2H, Ar H), 4.16 (m, 4H, CH_2), 1.63 (m, 2H, CH), 1.39 (m, 4H, CH_2), 1.27 (m, 12H, CH_2), 0.88 (m, 12H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 163.2, 142.4, 135.9, 130.5, 129.1, 128.3, 124.1, 67.2, 38.7, 30.4, 28.9, 23.8, 22.9, 14.0, 11.0.

5,5’’-dibromo-3,3’’-dicarboxylic acid ethylhexyl ester-2,2’:5’,2’’-terthiophene (M2). In a 100 mL two-neck roundbottom flask, compound 4 (1 g, 1.78 mmol) and N-Bromosuccinimide (NBS) (0.63 g, 3.56 mmol) were mixed in 10 mL of chloroform under argon protection. The solution was stirred at room temperature for 24h. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. The organic layer was concentrated by vacuum evaporation, and the residue was purified by column chromatography on silica gel to give M2 (1.15, 90%) as luminous yellow oil. MS (MALDI-TOF): m/z 718.3 (M+). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 7.42 (s, 2H, Ar H), 7.33 (s, 2H, Ar H), 4.16 (m, 4H, CH_2), 1.63 (m, 2H, CH), 1.39 (m, 4H, CH_2), 1.27 (m, 12H, CH_2), 0.88 (m, 12H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 162.0, 143.5, 135.3, 132.7, 129.4, 128.7, 111.1, 67.6, 38.8, 30.9, 30.4, 29.8, 28.9, 23.8, 22.9, 14.0, 11.0.

PB3T. M2 (0.1796 g, 0.25 mmol) and M3 (0.2422 g, 0.25 mmol) were dissolved into 6 mL of toluene in a two-neck round bottom flask. The solution was flushed with argon for 5 min, and 15 mg of $Pd(PPh_3)_4$ was added into the flask subsequently. The mixture was flushed with argon for another 15 min and then allowed to stir at 110°C for 16h under an argon atmosphere. Then, the reactant was cooled down to room temperature, and the polymer was precipitated into 100 mL of methanol. The polymer was collected by filtration and further purified by silica gel chromatography by using chlorobenzene as eluent. The polymer was precipitated again in 100 mL of methanol and obtained as crimson solid with a yield of ~70%. $C_{64}H_{78}O_4S_9$ (PB3T): Calculated C: 64.06 H: 6.55. Found C: 63.06 H: 6.25.

Instrumentation

The number-average molecular weight (M_n) and polydispersity index (PDI) was measured on Inc. Gel permeation chromatography (GPC) by using dichlorobenzene as eluent at 145^{o}C. TGA measurement was performed on TGA-2050 from TA Instruments, Inc. UV-vis absorption spectroscopy was performed on a Hitachi UH4150 spectrophotometer. Cyclic voltammetry was conducted on Chenhua, Inc., electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, and Ag/AgCl electrode as the reference electrode with a scanning rate of 20 mV/s in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu4NPF6) solution, and the potential of Ag/Ag+ reference electrode was internally calibrated by using ferrocene/ferroncenium (Fc/Fc+) as the redox couple. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 HD spectrometer. MALDI-TOF mass spectra were determined by Bruker BIFLEX III. Elemental analysis was performed on a flash EA1112 analyzer. Atomic Force Microscopy (AFM) was measured by using Bruker Vecoo, Inc., V. Transmission electron microscopy (TEM) was performed using a JEOL 2200FS instrument. The current density-voltage (J-V) characteristics were measured with a Keithley 2400 measure unit. The power conversion efficiencies were conducted under 1 sun, AM 1.5G (air mass 1.5 global) (100 mW/cm^{2}) using a XES-70S1 solar simulator (SAN-EI Electric Co., Ltd.,AAA grade, 70 mm×70 mm photo-beam size). 20 mm×20 mm monocrystalline silicon reference cell with KG3 filter (Enli Tech Co. Ltd., Taiwan) was selected for accurately measuring the PSCs according to our recent work.[S3] The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Fabrication of polymer solar cells

Photovoltaic devices were fabricated with the structure of ITO/PEDOT:PSS/polymer:IT-M/PFN-Br/Al. Specific process is as follows: patterned ITO-coated glass was cleaned by oxygen plasma for 20 min and then PEDOT:PSS (Bayer baytron 4083) anode buffer layer was spin-cast onto the ITO substrate. Afterwards, the glass was dried at 150°C for 15 min. Then the active layer was spin-coated on top of the PEDOT:PSS layer. Finally, 5 nm PFN-Br and 80 nm Al layer were successively deposited by evaporation under a pressure of ca. 3×10^{-4} Pa. The concentrations of chlorobenezene solution of polymer:IT-M, anisole solution of PB3T:IT-M and chlorobenezene solution of polymer:PCBM were 9, 8, and 10 mg/mL, respectively. Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen drybox containing less than 5 ppm oxygen and moisture. The thickness of the active layer was measured on an Bruker Dektak. The *J-V* curves of the PV devices were measured under 100 mW/cm^2 of the standard AM 1.5G spectrum. The devices areas are 0.04 cm^2.The spectral mismatch factor was calibrated to be unity via a National Institute of Metrology (NIM) certificated silicon reference cell with a KG3 filter. All EQE curves were measured through the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

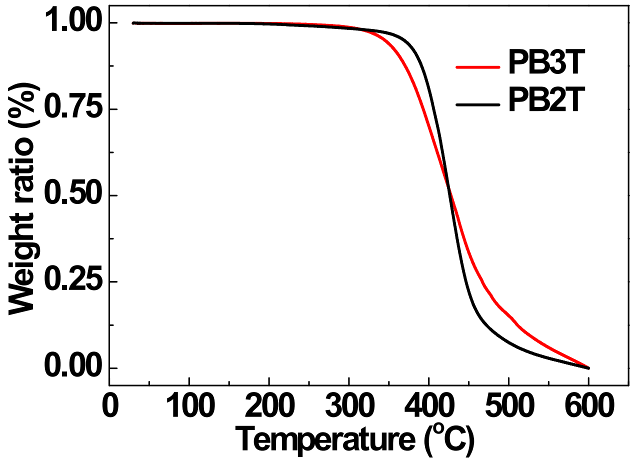

Fig. S1 TGA plots of polymers with a heating rate of 10°C/min under nitrogen.

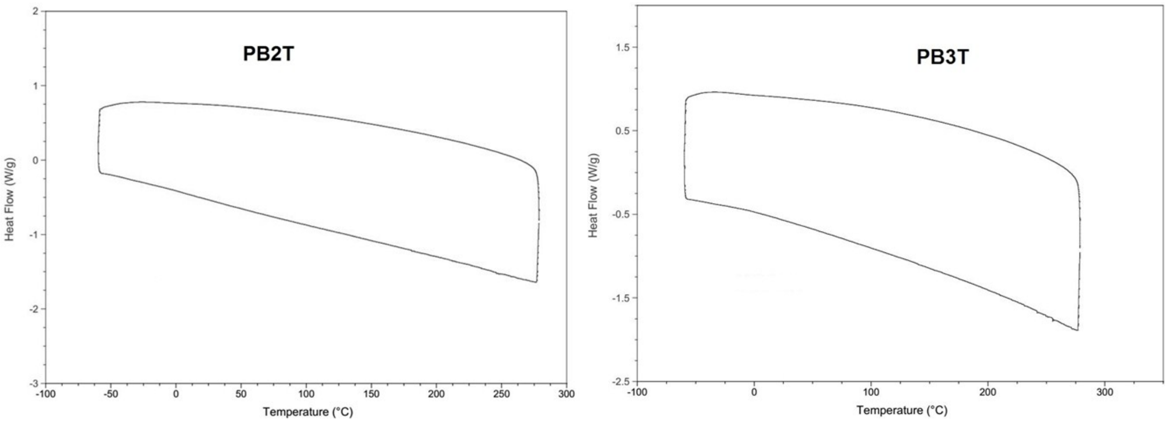

Fig. S2 DSC thermograms of PB2T and PB3T in nitrogen at a heating rate of 10°C/min.

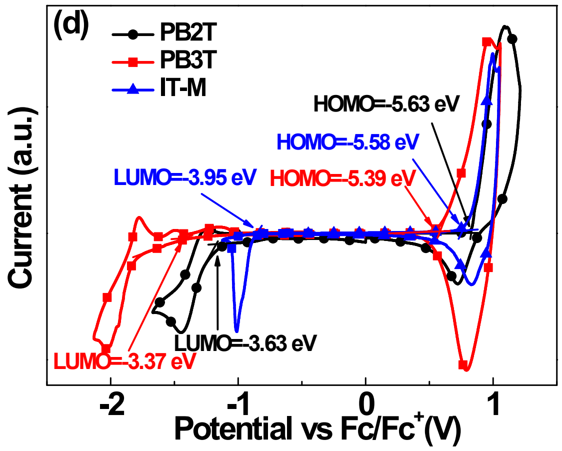

Fig. S3 The cyclic voltammograms for PB2T, PB3T and IT-M.

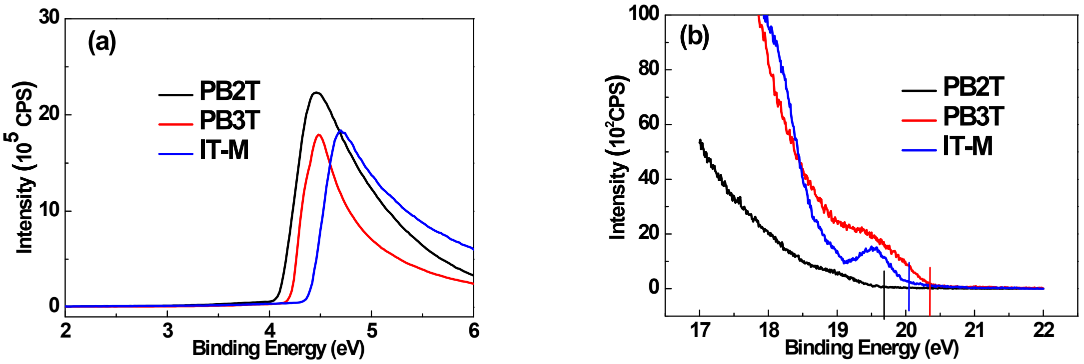

Fig. S4 UPS spectra of the onset (a) and the secondary edge region (b) of PB2T, PB3T and IT-M.

Table S1. Frontier orbital energy levels of polymers.

Polymer	HOMO (eV)[a]	LUMO (eV)[a]	HOMO (eV)[b]	LUMO (eV)[b]
PB2T	-5.23	-2.18	-5.64	-3.40
PB3T	-5.02	-2.50	-5.17	-3.16
IT-M	-5.50	-3.35	-5.56	-3.96

[a] Energy levels evaluated by DFT calculation. [b] HOMO Energy levels evaluated by UPS, and the LUMO were determined by adding optical band gap to the HOMO levels.

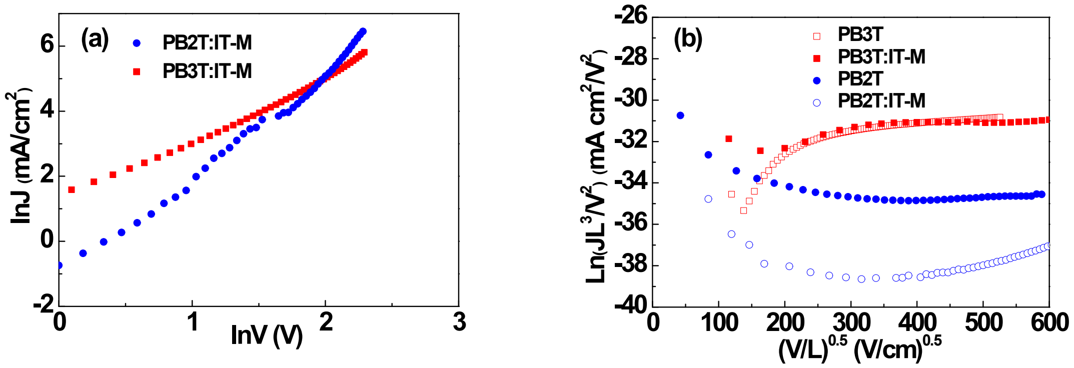

Fig. S5 (a) The electron mobility and (b) the hole mobility of the corresponding devices films measured by SCLC method. Please check the data (right side).

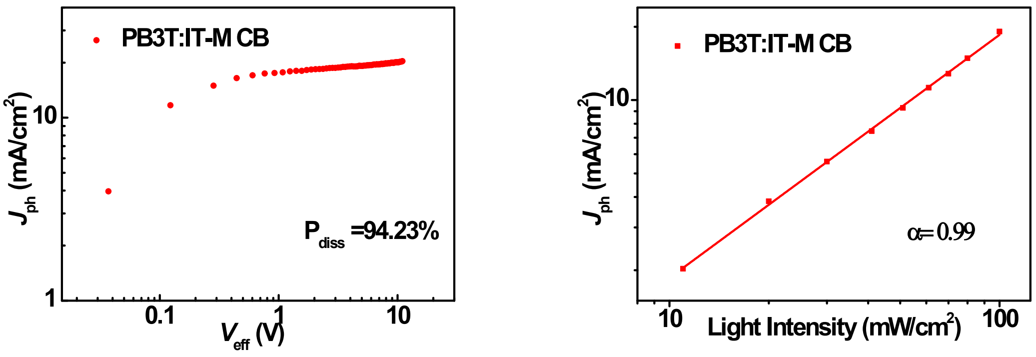

Fig. S6 The plots of photocurrent density (J_{ph}) versus effective voltage (V_{eff}) or light intensity (P_{in}) .

Table S2. Photovoltaic properties of PB3T:IT-M devices with different thermal annealing temperature. (under AM 1.5G illumination, 100 mW/cm^2)

Active layer	Temperature [°C]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF	PCE [%]
PB3T:IT-M (1.5:1, w/w)	90	1.01	18.1	0.58	10.6
	120	1.01	18.4	0.59	11.0
	150	1.00	19.2	0.61	11.7
	160	0.99	17.2	0.63	10.7
	180	0.95	13.6	0.58	7.49

Table S3. Photovoltaic properties of PB3T:IT-M devices annealed at 150°C for different time. (under AM 1.5G illumination, 100 mW/cm^2)

Active layer	Annealed time [min]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF	PCE [%]
PB3T:IT-M (1.5:1, w/w)	0	1.02	17.6	0.60	10.7
	5	1.00	18.0	0.64	11.5
	10	1.00	19.2	0.61	11.7
	20	1.00	18.7	0.62	11.6
	40	0.99	19.1	0.59	11.1
	60	0.98	18.1	0.61	10.8

Table S4. Photovoltaic parameters of PB3T:IT-M and PB2T:IT-M devices. (under AM 1.5G illumination, 100 mW/cm^2)

Active layer[a]	D/A ratio [wt/wt]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF	PCE [%]
PB3T:PC$_{71}$BM	60:40	0.99	11.0	0.44	4.91
PB3T:PC$_{71}$BM	50:50	0.99	10.1	0.51	5.08
PB3T:PC$_{71}$BM	40:60	0.98	9.73	0.68	6.48
PB3T:PC$_{71}$BM	30:70	0.97	10.1	0.66	6.39
PB3T:PC$_{61}$BM	40:60	0.98	10.4	0.71	7.24
PB2T:PC$_{61}$BM	40:60	0.82	0.09	0.36	0.03
PB2T:PC$_{71}$BM	40:60	0.85	0.27	0.29	0.07

[a] *As-cast film*

NMR

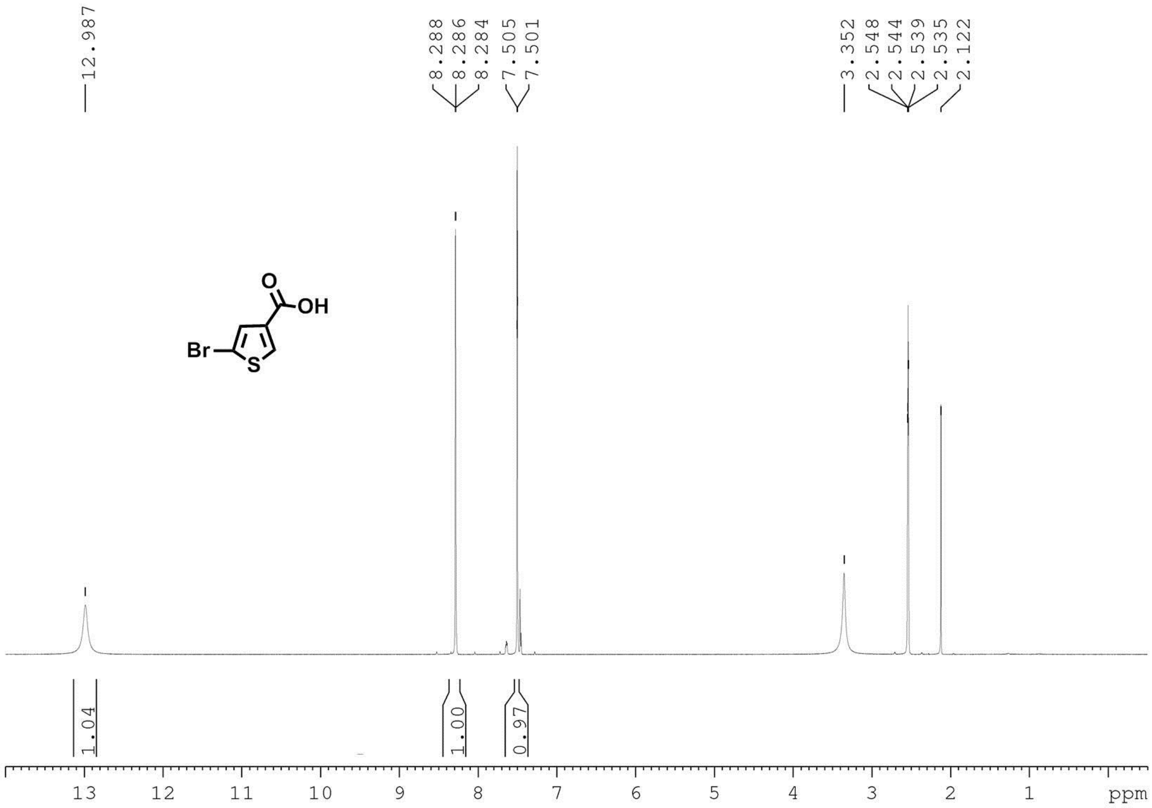

Figure S7. ^{1}H NMR spectrum of compound 1.

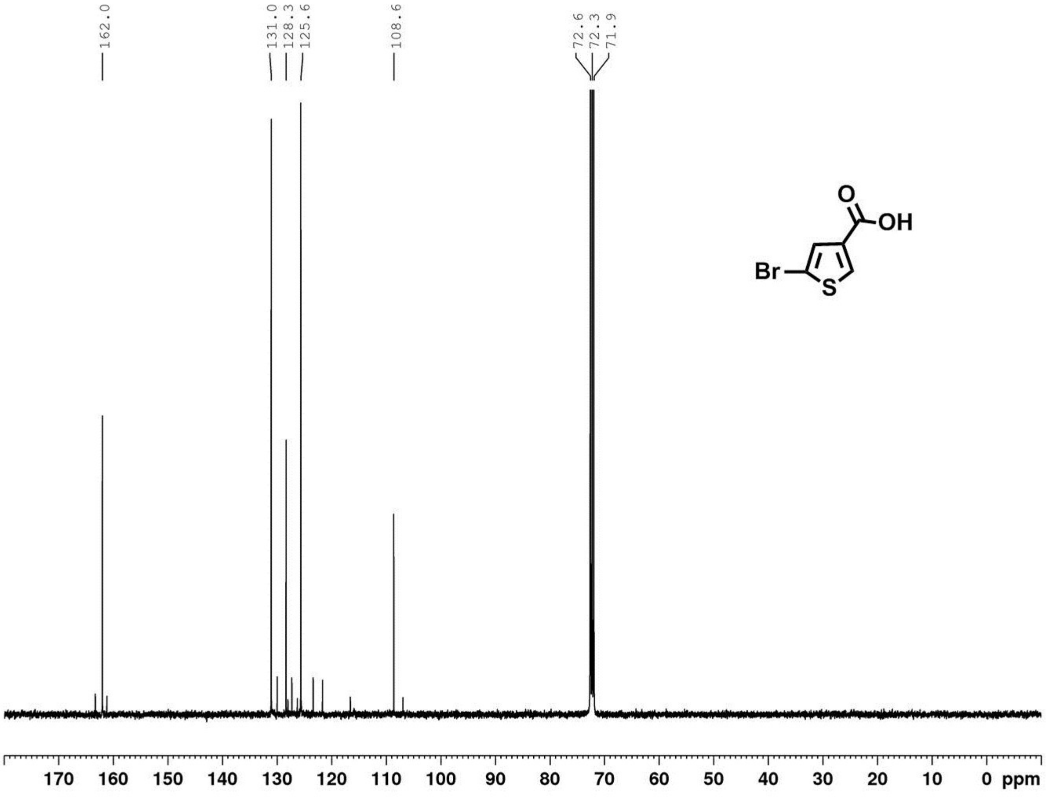

Figure S8. ^{13}C NMR spectrum of compound 1.

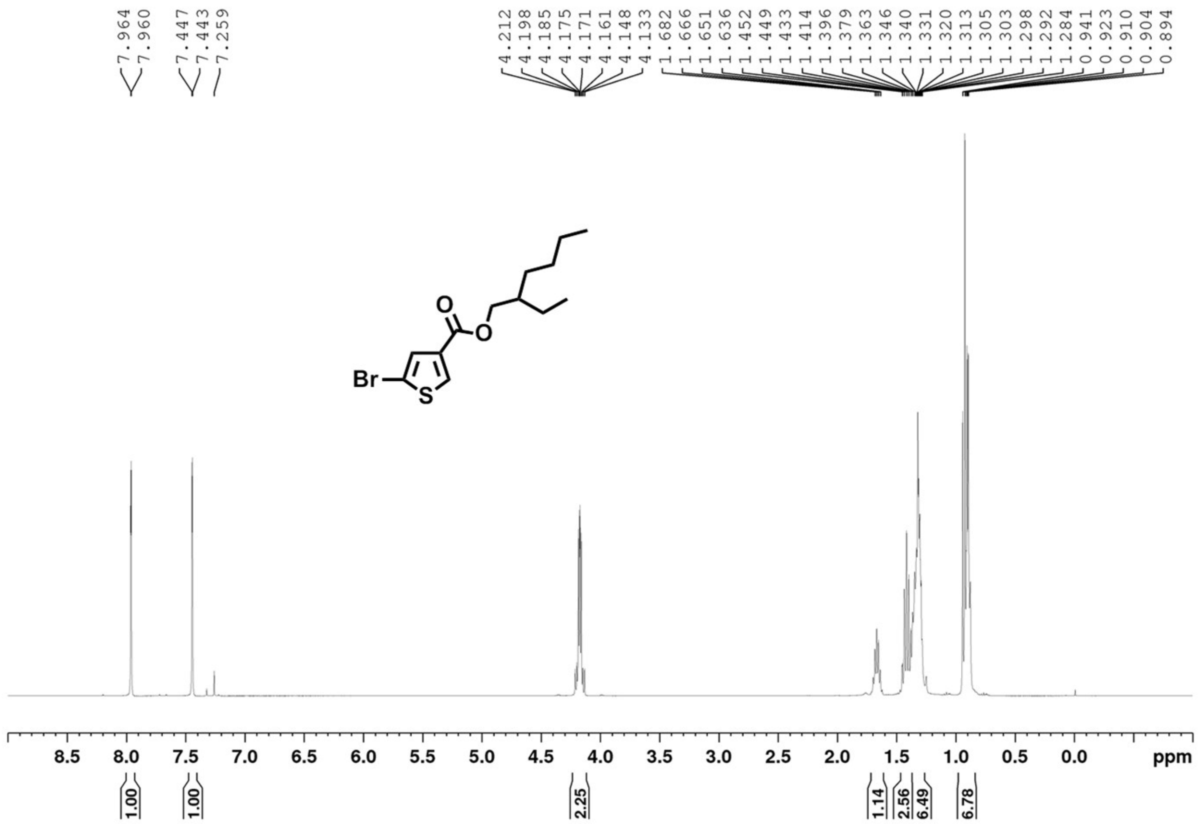

Figure S9. ^{1}H NMR spectrum of compound 2.

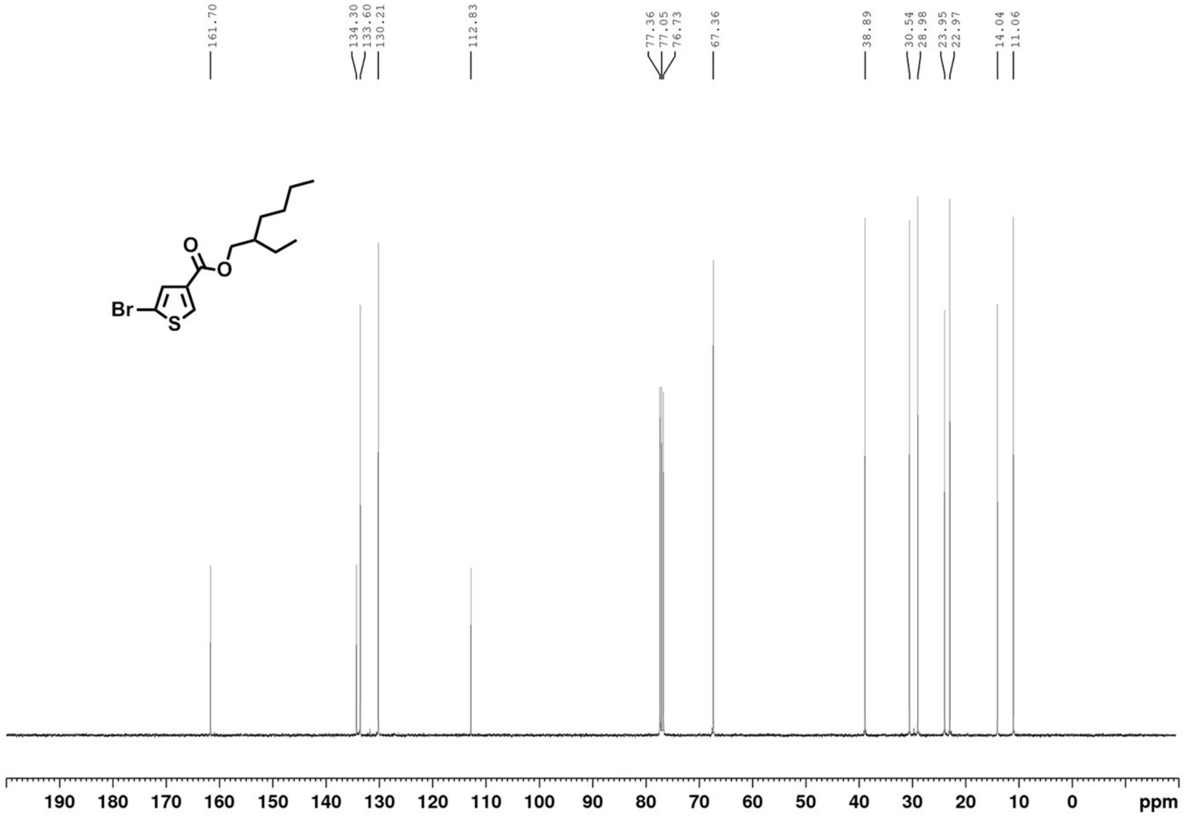

Figure S10. ^{13}C NMR spectrum of compound 2.

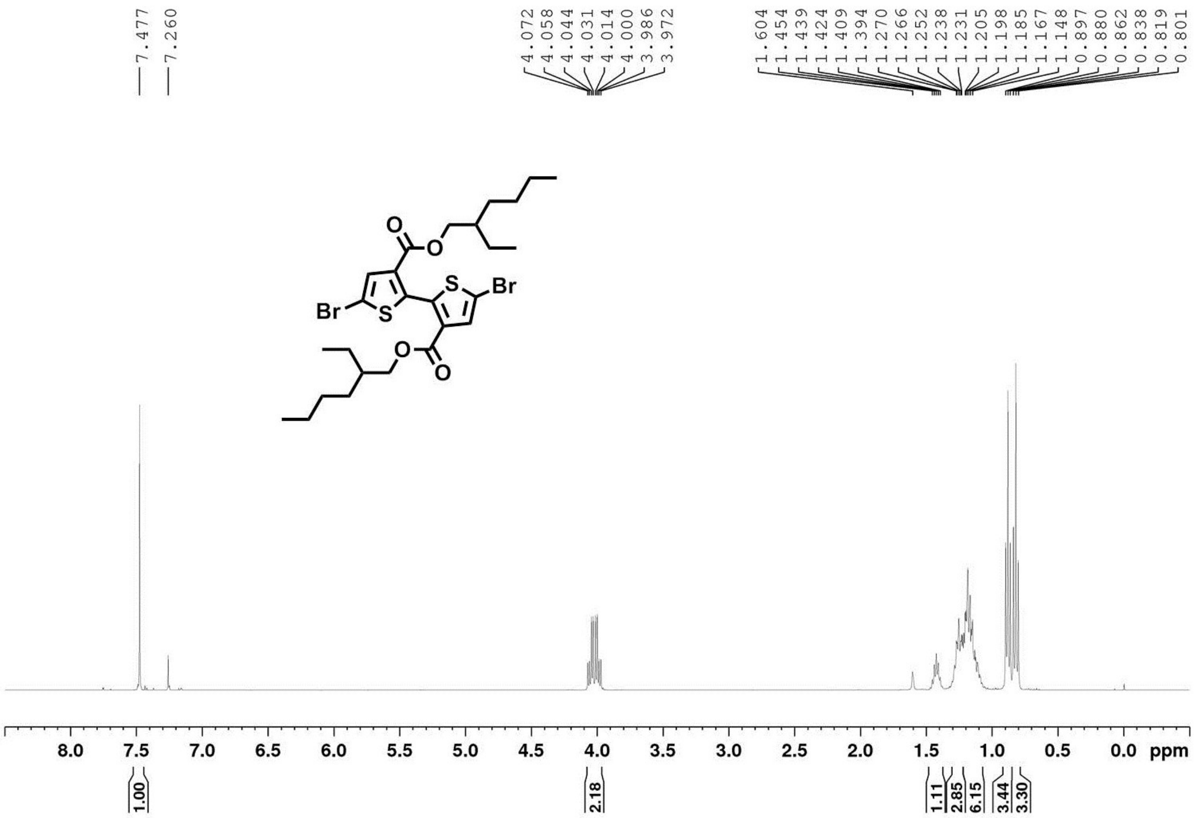

Figure S11. ^{1}H NMR spectrum of monomer M1.

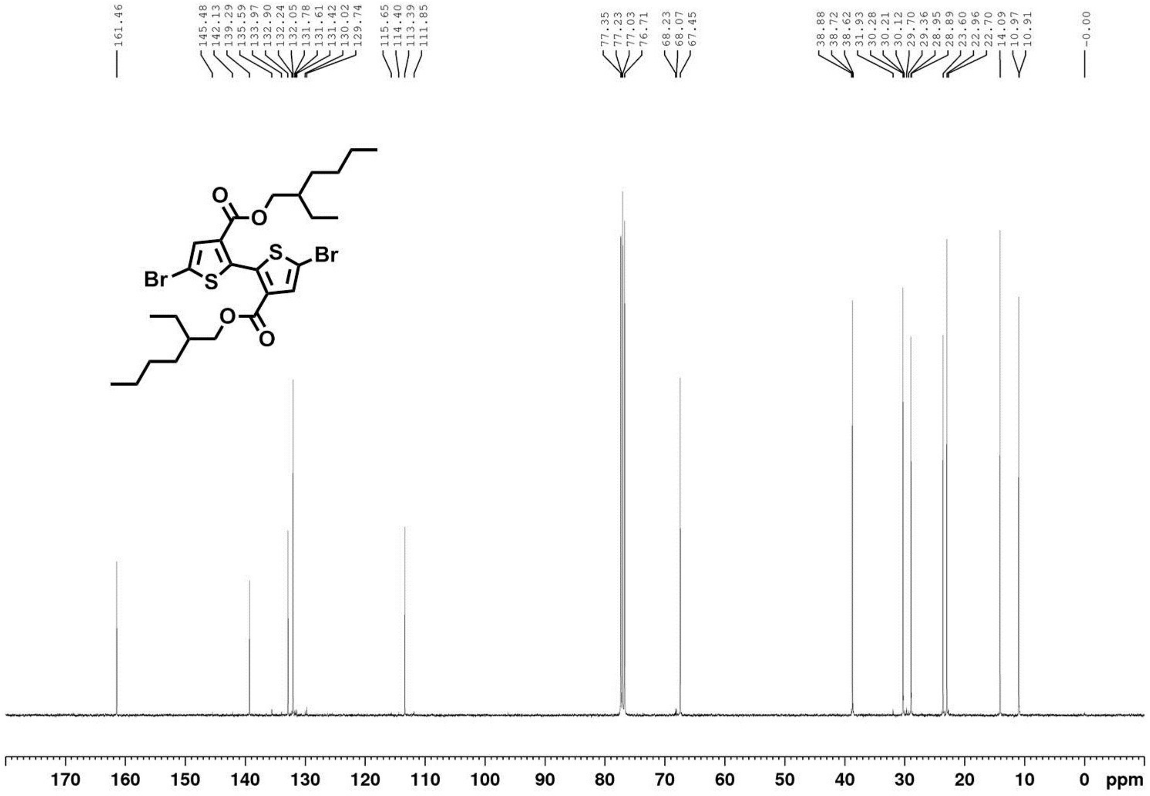

Figure S12. ^{13}C NMR spectrum of monomer M1.

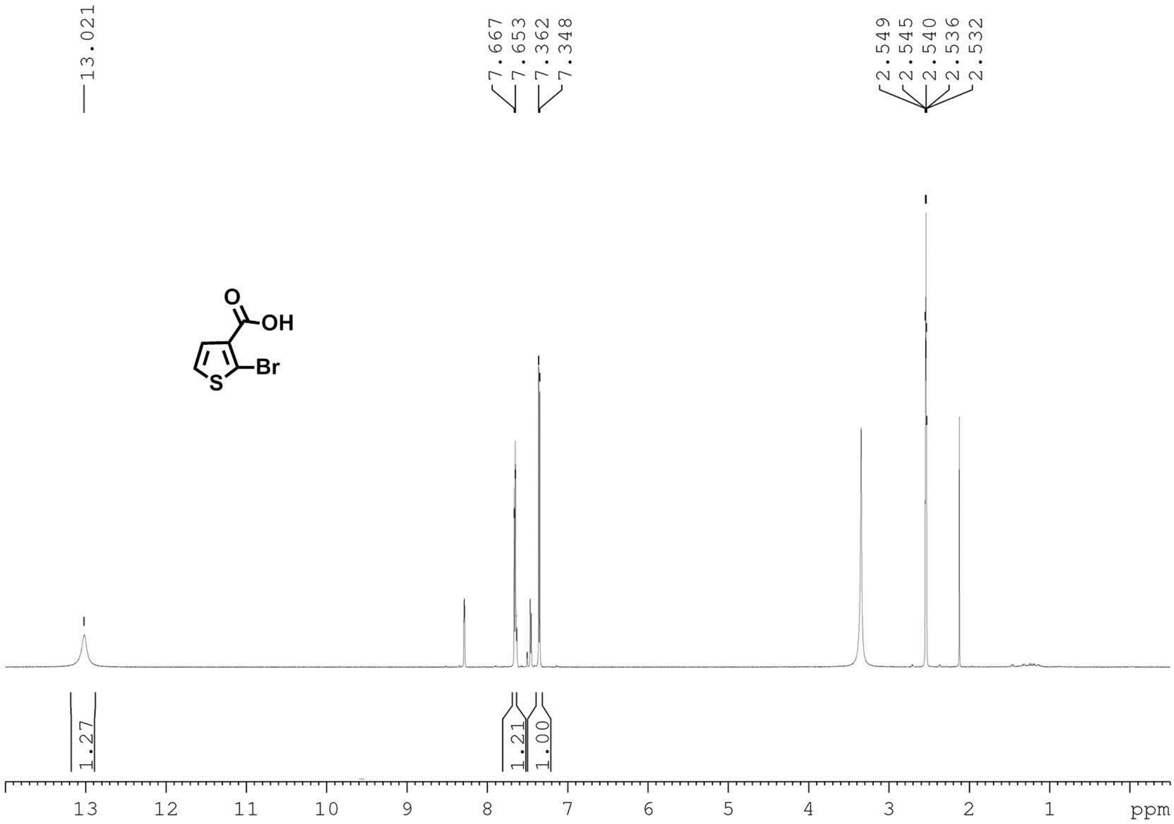

Figure S13. ^{1}H NMR spectrum of compound 3.

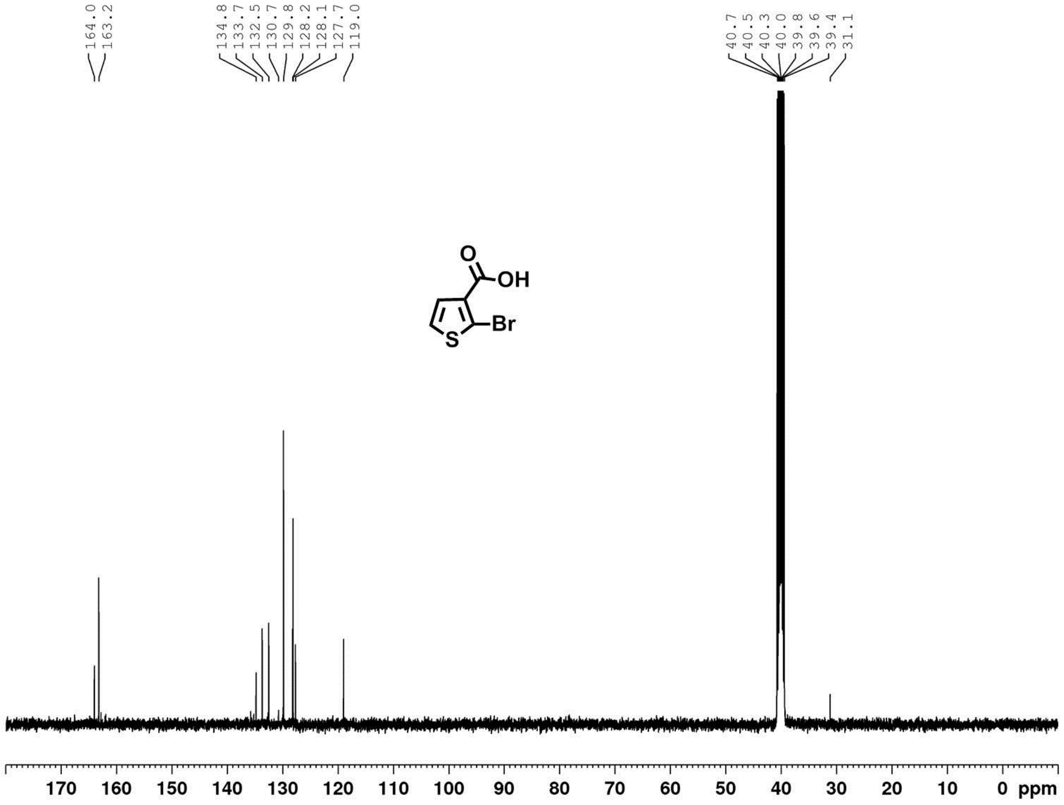

Figure S14. ^{13}C NMR spectrum of compound 3.

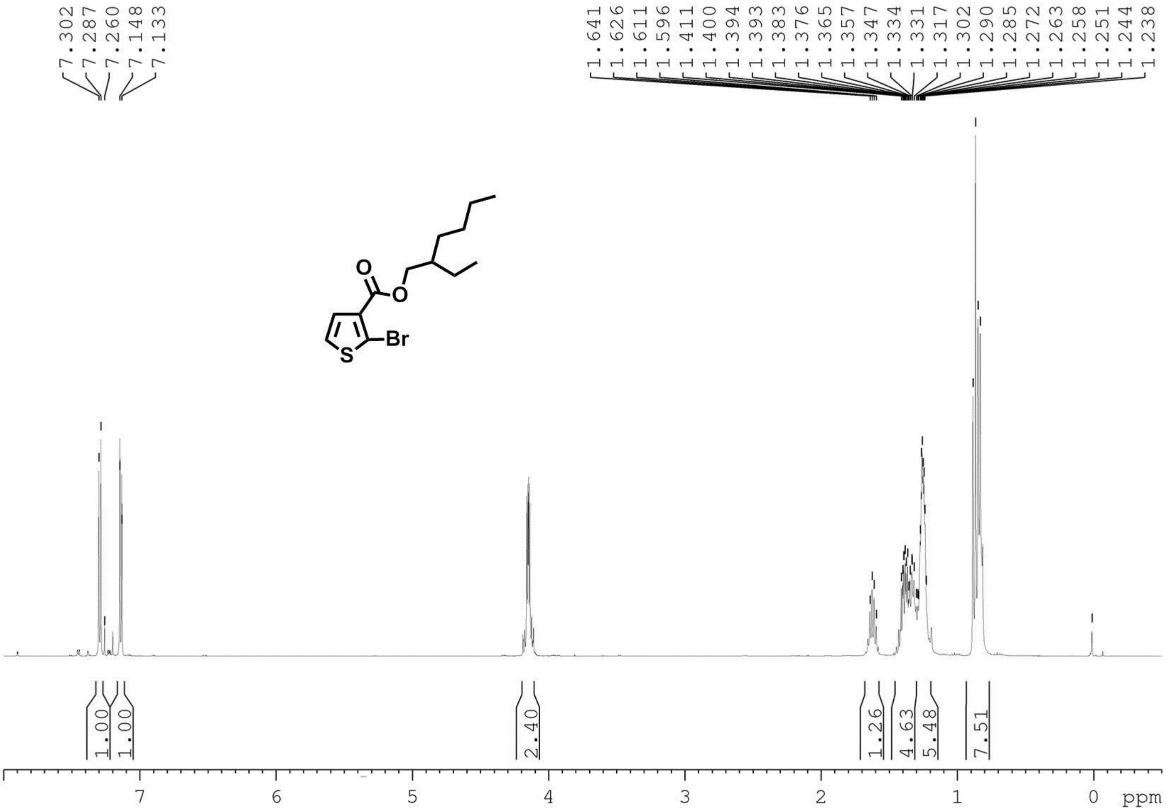

Figure S15. ^{1}H NMR spectrum of compound 4.

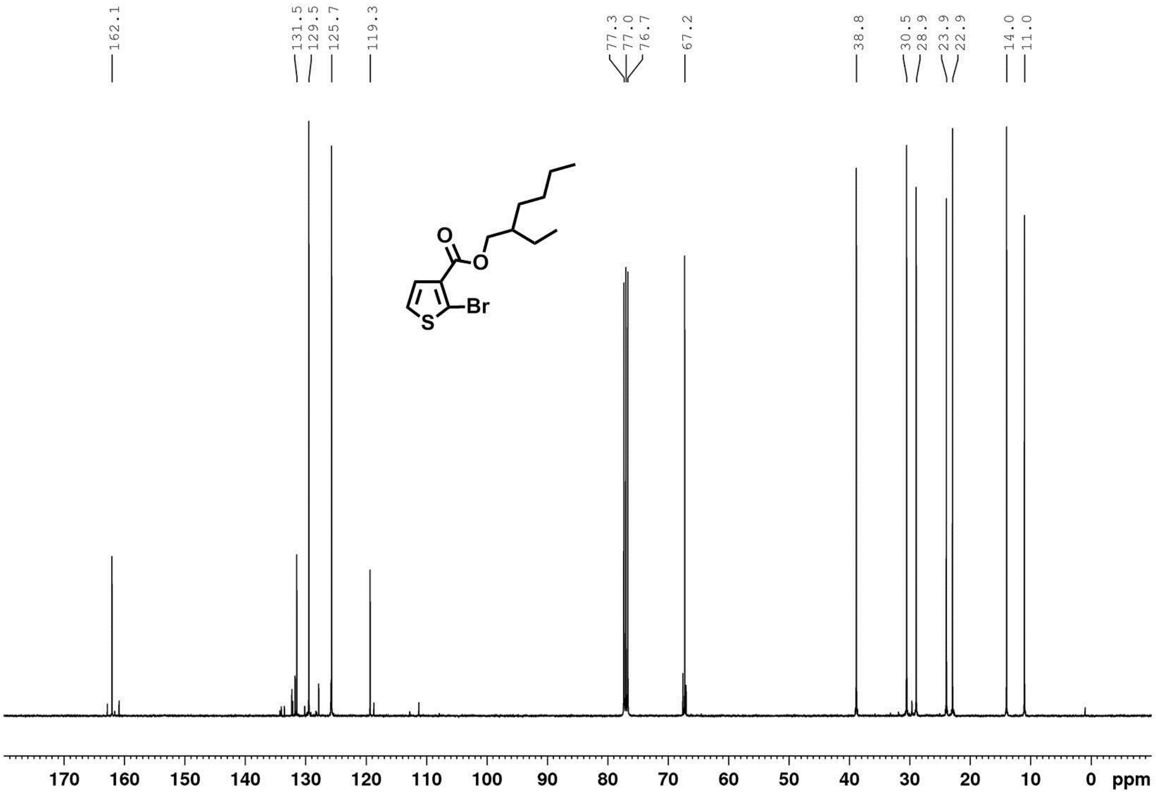

Figure S16. ^{13}C NMR spectrum of compound 4.

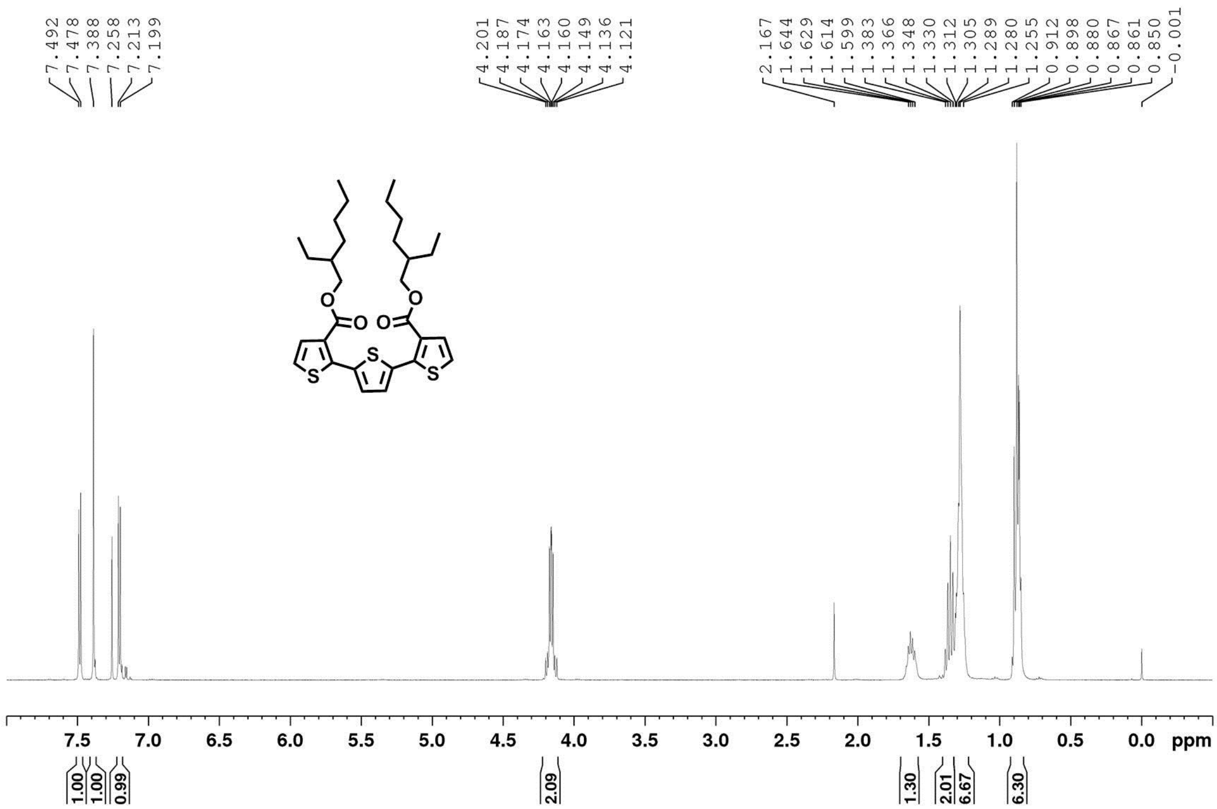

Figure S17. ^{1}H NMR spectrum of compound 5.

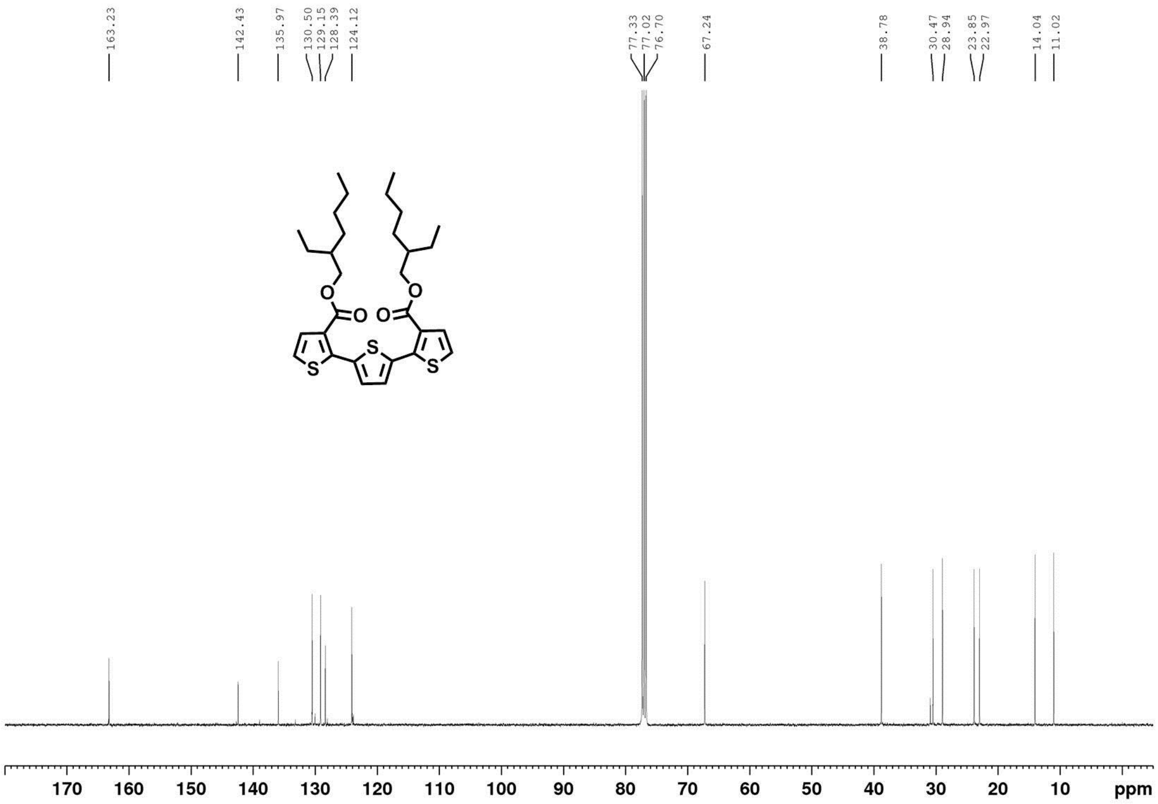

Figure S18. ^{13}C NMR spectrum of compound 5.

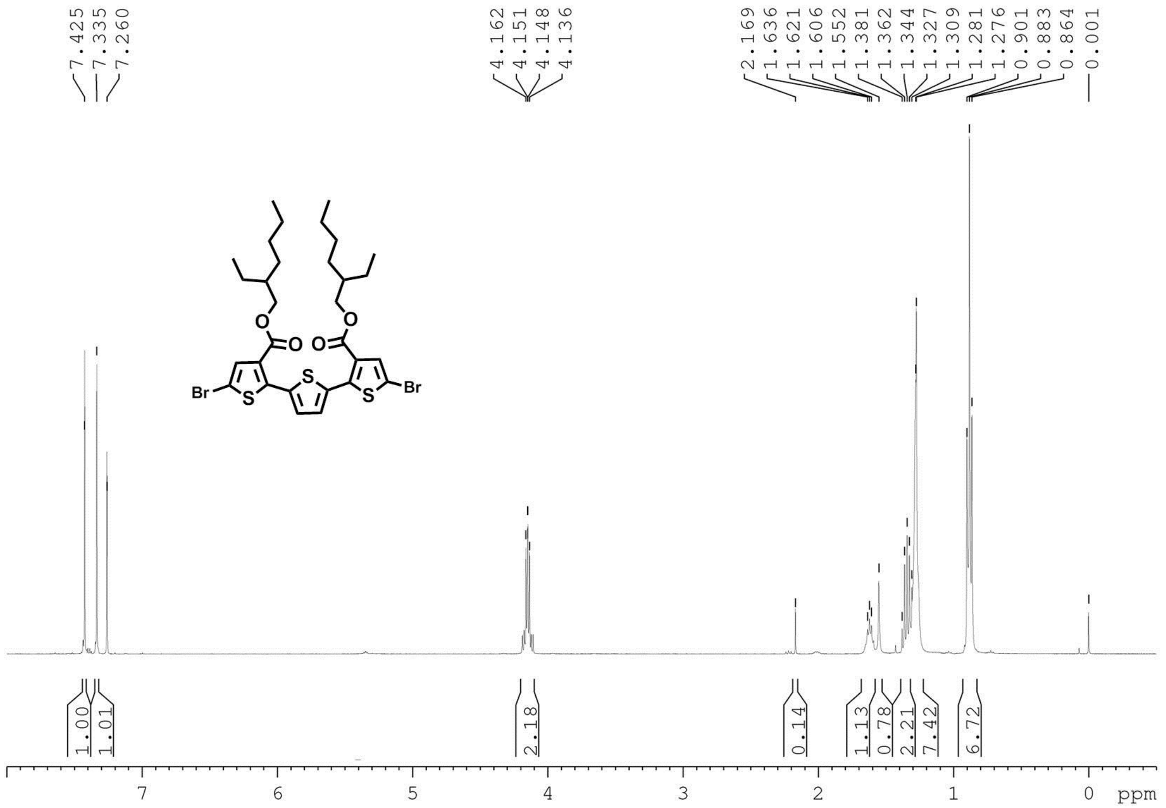

Figure S19. ^{1}H NMR spectrum of compound M2.

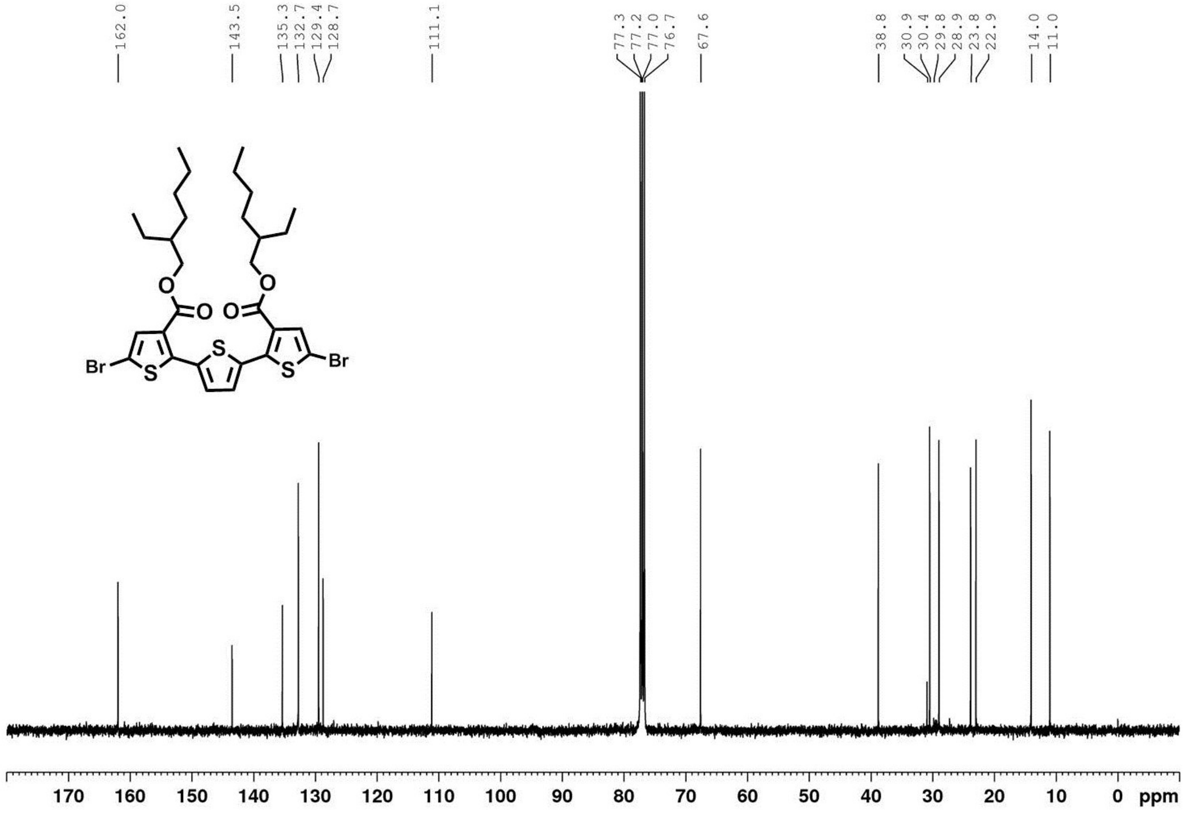

Figure S20. ^{13}C NMR spectrum of monomer M2.

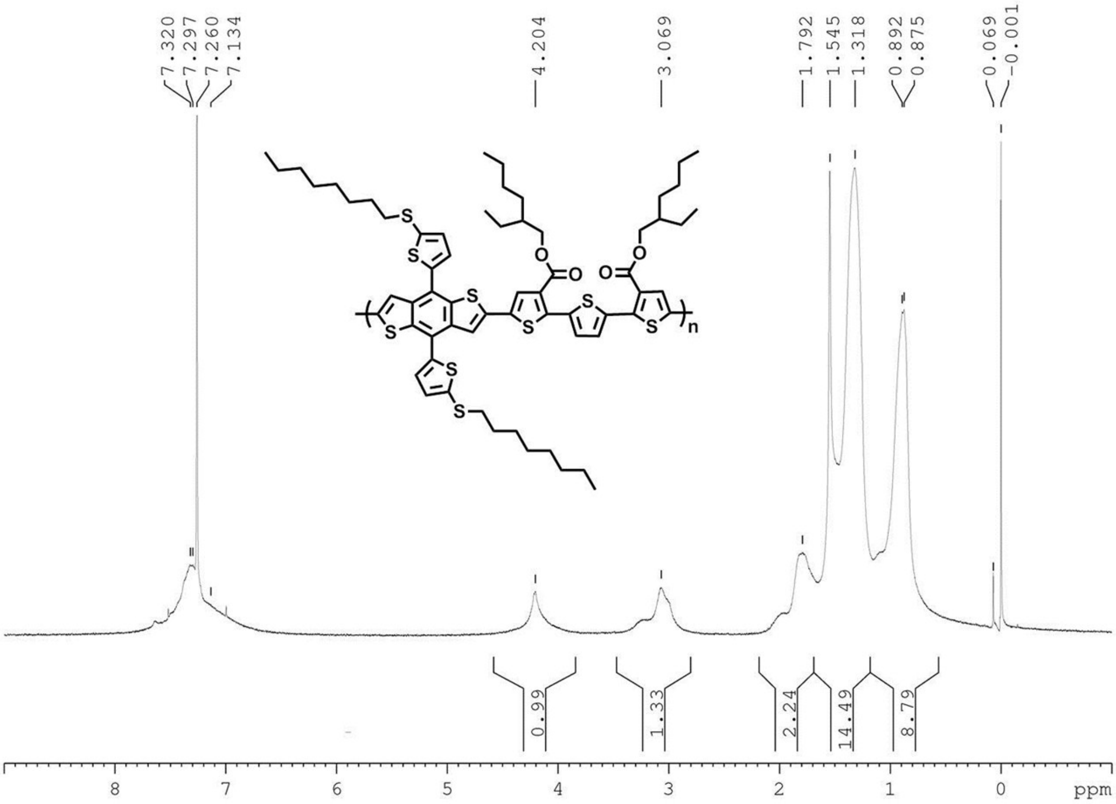

Figure S21. ^{1}H NMR spectrum of polymer PB3T.

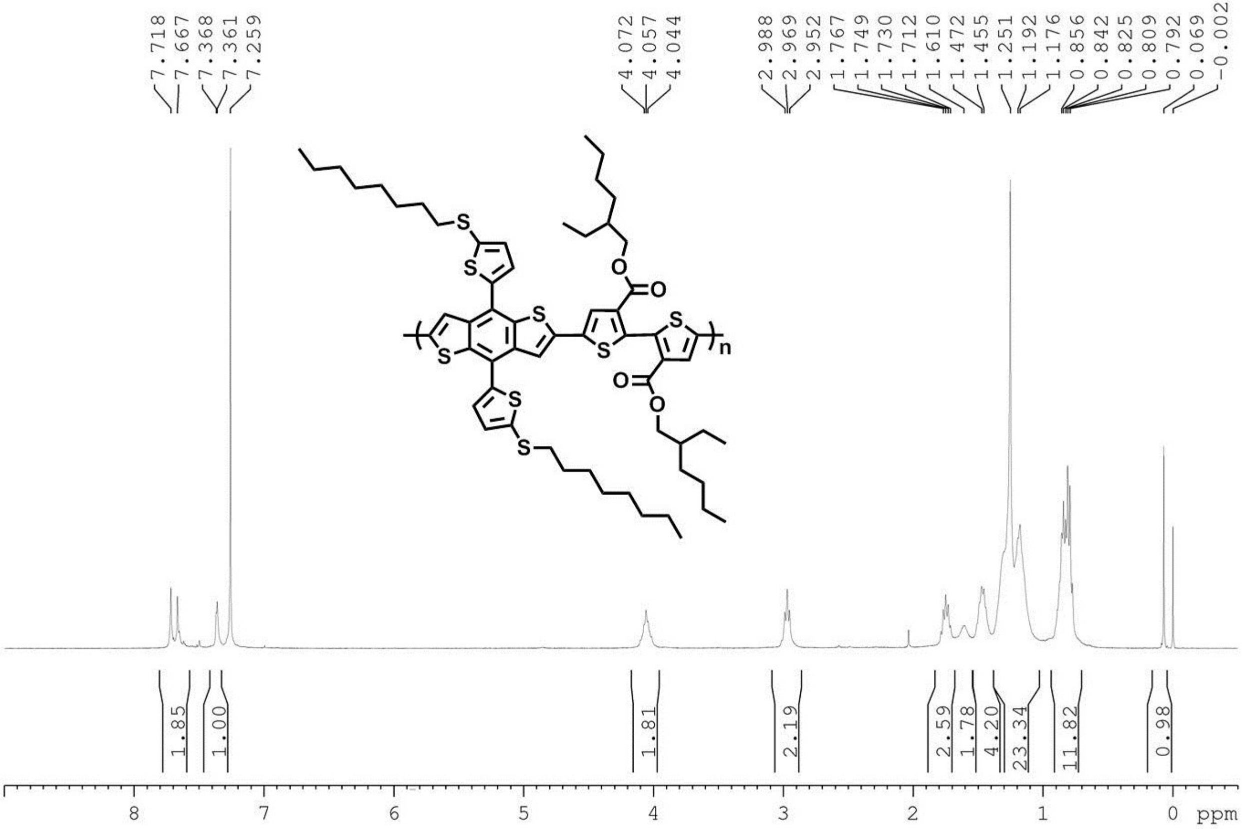

Figure S22. ^{1}H NMR spectrum of polymer PB2T.