Supporting Information

From Semi- to Full-Two-Dimensional Conjugated Side-Chain Design: A Way toward Comprehensive Solar Energy Absorption

Pengjie Chao,[†,∥] *Huan Wang,*[†] *Shiwei Qu*[†], *Daize Mo*[†], *Hong Meng,*[∥] *Wei Chen**[,‡,§] *and Feng He**[,†]

[†]Department of Chemistry, Southern University of Science and Technology, Shenzhen, 518055, P. R. China

[‡]Materials Science Division, Argonne National Laboratory, 9700 Cass Avenue, Lemont, Illinois, 60439, United States

[§]Institute for Molecular Engineering, The University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois, 60637, United States

[∥]School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, China

Corresponding Author

*E-mail: hef@sustc.edu.cn (F. H.); wchen@anl.gov (W. C.)

1. Materials and Methods

All starting reagents were obtained commercially as analytical grade and used directly without any purification unless stated otherwise. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithio-phene (3 in the Scheme 1) [1], 2,6- Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]-dithiophene (4 in the Scheme 1) [1], 3-Fluoro-4,6-dihydrothieno[3,4-b]thiophene-2-carboxylic acid[1, 2] and the polymer PTB7-Th[1, 3] were synthesized as reported in the literatures. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400/500 spectrometers. All chemical shifts (δ) are reported in *ppm* with TMS (tetramethylsilane) as the internal standards. The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet. Gel permeation chromatography (GPC) was performed on Agilent Technologies PL-GPC 220 using 1,2,4-trichlorobenzene as eluent at 150 ^{o}C. Solution and thin film optical absorption spectra were measured with a UV-Vis-IR spectrophotometer (Shimadzu, UV3600). The thin films of the polymers were spin-coated from their solutions in chlorobenzene, and then the film absorption spectra were measured. Cyclic voltammetry (CV) was performed on a CHI 660E potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd. China) to determine the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) levels of the polymers, in an acetonitrile solution of 0.1 mol L^{-1} tetrabutylammonium phosphorus hexafluoride (n-Bu_4NPF_6) at a potential scan rate of 100 mV s^{-1} with an Ag/Ag+ reference electrode and a platinum wire counter electrode under a argon atmosphere. Polymer films were deposited from chlorobenzene solutions on a glass carbon working electrode (2 mm in diameter) and

dried before measurements. The redox potential of ferrocene/ferrocene^{+} (Fc/Fc^{+}) under the same conditions is located at 0.41 V, which is assumed to have an absolute energy level of -4.8 eV to vacuum. The HOMO and LUMO levels were calculated by the following equation: $E_{HOMO} = -(\phi_{ox}+4.80)$ eV, $E_{LUMO} = -(\phi_{red}+4.80)$ eV, where ϕ_{ox} is the onset oxidation potential *vs* Ag/Ag^{+} and ϕ_{red} is the onset reduction potential *vs* Ag/Ag^{+}.

Tapping mode atom force microscopy (TM-AFM) images were taken on a NanoScope IIIa controller (Veeco Metrology Group/Digital Instruments, Sant a Barbara, CA), using built-in software (version V6.13R1) to capture images. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The X-ray diffraction spectra were taken on a Rigaku D/max 2500 X-ray diffractometer. All *J*–*V* curves were captured under an AAA solar simulator (SAN-EI) calibrated by a standard single-crystal Si photovoltaic cell (certificated by National Institute of Metrology).

2. Device Fabrication and Testing

The fabrication and measurement methods of PSC devices are as follows: After a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried in an oven for 1 min at 80 °C under vacuum. The ITO glass

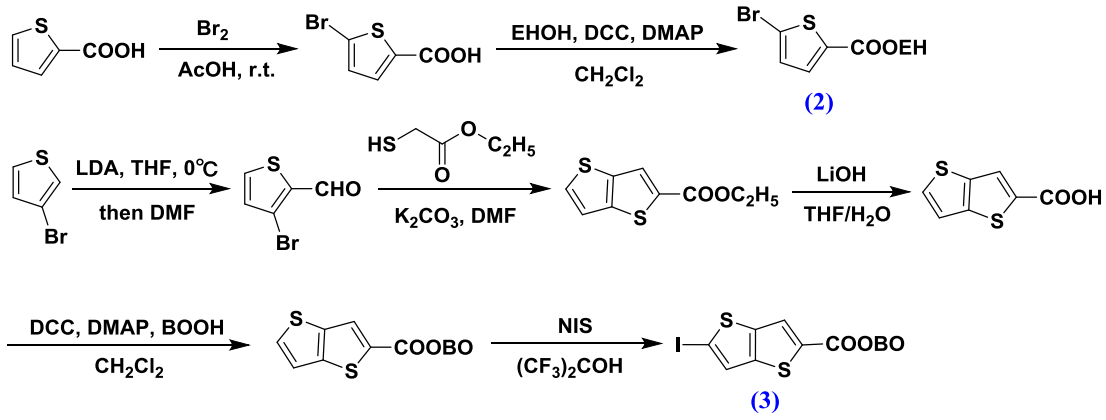
substrate was UV-ozone for 15 minutes and then the sol-gel-derived ZnO films was spin-coated onto the ITO sustrated followed by thermal treatment at 200 °C for 30 min. The concentration of the polymer:$PC_{71}BM$ blend solution in this study for spin-coating was 10 mg/mL (polymer/chlorobenzene), and chlorobenezene was used as the processing solvent. The additive 1,8-diiodooctane (DIO) was added into solution 30 min before spin-coating process. The blend was stirred at 80 °C in the glove box for overnight. The active layer was spin-coating at 2000 rpm for 60 s to get the blend film. A 10 nm MoO_3 layer and a 100 nm Ag layer were subsequently evaporated through a shadow mask to define the active area of the devices. The integrated device structure is ITO/ZnO/polymer:$PC_{71}BM$/MoO_3/Ag. The current-voltage curves were measured under 100 mW/cm^2 standard AM 1.5G spectrum (calibrated by 2 cm×2 cm monocrystalline silicon solar cell with a KG-3 filter). Light intensity was calibrated with a standard silicon solar cell. A shadow mask with a single aperture (4.15 mm^2) was placed onto the PSCs in order to accurately define the photoactive area. All EQE data were gained through the measurement of solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan). The hole mobility of the photosensitive layers was measured by the space charge limited current (SCLC) method using devices with the structure of ITO/PEDOT:PSS/polymer:$PC_{71}BM$(1:1.5, w/w)/MoO_3/Ag. The processing conditions used for the active layers were the optimized ones. Charge mobility was extracted by fitting the current density–voltage curves, recorded under dark conditions, with the Mott-Gurney equation.

Hole-only devices were fabricated with the device structure ITO/PEDOT:PSS/polymer:$PC_{71}BM$ (1:1.5, w/w)/MoO_3/Ag. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation

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

where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_{s.}$ The hole-mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

3. Synthesis and Characterization



Scheme S1. Synthetic routes of the compounds (2) and (3).

3-Fluoro-4,6-dihydrothieno[3,4-b]thiophene. To a solution of Methyl 3-fluoro-4,6-dihydro-thieno[3,4-b]thiophene-2-carboxylic acid (5.25 g, 25.71 mmol) and quinoline

(100 mL) was added Barium-promoted copper chromite (5.66 g, 18.20 mmol), and the mixture was heated at 200 °C to generate carbon dioxide gas. After 4 h of reaction, the solution was cooled to room temperature and extracted with ethyl acetate and washed thoroughly with 1 M HCl(aq). The organic layer was dried over magnesium sulfate. The crude product was purified by silica gel column chromatography (eluent: hexane) to afford a white solid (3.11 g, yield = 75.50%). ^{1}H NMR (400 MHz, $CHCl_3$-*d*) δ (ppm) 6.65 (s, 1H), 4.19–4.08 (m, 2H), 4.03–3.93 (m, 2H). ^{13}C NMR (101 MHz, $CHCl_3$-*d*) δ (ppm) 151.72, 138.90, 132.45, 106.75, 34.33, 31.58. HRMS: m/z=160.2166 [M^+].

2-Trimethyltin-3-fluoro-4,6-dihydrothieno[3,4-b]thiophene (1). To a solution of 3-fluoro-4,6-dihydrothieno[3,4-b]thiophene (3.00 g, 18.72 mmol) in tetrahydrofuran (50 mL) was added 2.4 M n-butyllithium (10.2 mL, 30.46 mmol) dropwise at −78 °C. After stirring at −78 °C for 4 h, 1M trimethyltin chloride (28.1 ml, 28.09 mmol) was added to the mixture at −78 °C, then keeping stirring at −78 °C for 1 h, the mixture was gradually warmed up to room temperature. After stirring for 4 h, the reaction was quenched with ultrapure water (50 mL). The mixture was extracted with ether, and the organic layer was washed with ultrapure water 10 times, then dried over sodium sulfate. Removing the solvent under reduced pressure gave a yellow solid and recrystallized from isopropanol to afford a light yellow needle crystal (4.83 g, yield = 79.87%). ^{1}H NMR (500 MHz, $CHCl_3$-*d*) δ (ppm) 4.17–4.07 (m, 2H), 4.00–3.88 (m, 2H), 0.38 (s, 3H). ^{13}C NMR (126 MHz, $CHCl_3$-*d*) δ (ppm) 156.81, 145.85, 133.66, 117.32, 34.06, 31.07, -8.36. HRMS: m/z=322.9521 [M^+].

5-Bromothiophene-2-carboxylic acid. To a 250 ml round-bottomed flask fitted with an efficient stirrer was added thiophene-2-carboxylic acid (20.00g, 156.06 mmol) and 150ml of AcOH. The mixture was stirred at room temperature (20 °C) and 8.42 ml (163.88 mmol) of Br_2 was added dropwise over about two hours. The mixture was stirred vigorously overnight, The terminal point of the reaction is monitored by TLC. The reaction mixture was poured into water and stirred for 20 min until the mixture turned from yellow to white. The mixture was filtered through a Brandt funnel and rinsed with water. The cake was dissolved in ethyl acetate and washed with water. The organic phase was dried over anhydrous sodium sulfate, filtered and concentrated to remain about 20 ml of ethyl acetate. Then 50 mL of petroleum ether was added. The resulting mixture was stirred at 50 °C for 30 minutes and then cooled to room temperature slowly. Some precipitate appeared. Filtration and drying in vacuo afforded white solid (16.47 g, 50.94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 13.39 (s, 1H), 7.56 (d, J = 4.0 Hz, 1H), 7.33 (d, J = 4.0 Hz, 1H).^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 162.24, 136.59, 134.36, 132.35, 119.34. HRMS: m/z 206.9108 [M^+].

2-Ethylhexyl 5-Bromothiophene-2-carboxylate (2). To a 250 ml round-bottom flask with CH_2Cl_2 (100 mL) was added the raw materials of 5-bromothiophene-2-carboxylic acid (8.47 g, 40.89 mmol), DCC (25.29 g, 122.70 mmol), and DMAP (9.99 g, 81.78 mmol). 2-ethylhexan-1-ol (26.63 g, 204.50 mmol) was added to the flask and then stirred for 48 h under N_2 protection. The reaction mixture was poured to 100 mL of water and extracted with CH_2Cl_2. The organic phase was dried by sodium sulfate,

and the solvent was removed. Column chromatography on silica gel using hexane/CH_2Cl_2 = 1/1 yielded the title compound as an oil (9.39 g, 71.95%). ^{1}H NMR (400 MHz, $CHCl_3$-*d*) δ (ppm) 7.54 (d, *J* = 3.9 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 1H), 4.20 (dd, *J* = 5.7, 3.0 Hz, 2H), 1.67 (p, *J* = 6.0 Hz, 1H), 1.48–1.38 (m, 2H), 1.37–1.28 (m, 5H), 0.94–0.85 (m, 11H). ^{13}C NMR (126 MHz, $CHCl_3$-*d*) δ (ppm) 161.28, 135.15, 133.43, 130.88, 120.02, 67.76, 38.86, 30.50, 28.95, 23.93, 22.97, 14.07, 11.09. HRMS: m/z=319.0355 [M^+].

3-Bromothiophene-2-carbaldehyde. 3-bromothiophene (5.00 g, 30.67 mmol) was added dropwise to a solution of lithium diisopropylamide(16.1 ml, 32.20 mmol) at 0℃. After stirring the mixture for 2 h, dimethylformamide (DMF) (2.6 mL, 33.73 mmol) was added to the mixture at 0℃ and the mixture was warmed up to room temperature. After stirring fo r 4 h, water (100 mL) was added to the mixture and extracted with ethyl acetate three times. The organic layer was dried over magnesium sulfate and further purified by silic gel chromatography. Evaporating in vacuo to afford a brightly yellow liquid (4.81 g, 25.18 mmol, yield = 82.22%). ^{1}H NMR (500 MHz, $CHCl_3$-*d*) δ (ppm) 9.99 (s, 1H), 7.72 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 5.1 Hz, H). ^{13}C NMR (126 MHz, $CHCl_3$-*d*) δ (ppm) 183.07, 136.93, 134.85, 132.04, 120.37.

Ethyl thieno[3,2-b]thiophene-2-carboxylate. 3-bromothiophene-2-carbaldehyde (4.81 g, 25.33 mmol) was added to a mixture of potassium carbonate (5.25 g, 38.00 mmol) and ethyl 2-mercaptoacetate (3.35 g, 27.87 mmol) in dimethylformamide (50 mL) at room temperature. After stirring for 3 days at room temperature, the mixture was poured into water (100 mL) and extracted with dichloromethane. The organic

layer was dried over magnesium sulfate. The crude product was purified by silica gel column chromatography (eluent: petroleum ether/ dichloromethane=8:1-5:1) to afford a colorless liquid (4.21 g, yield = 78.29%). ^{1}H NMR (500 MHz, $CHCl_3$-*d*) δ (ppm) 7.99 (s, 1H), 7.58 (d, *J* = 5.3 Hz, 1H), 7.28 (d, *J* = 5.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CHCl_3$-*d*) δ (ppm) 162.70, 143.89, 138.73, 135.21, 131.62, 125.59, 119.76, 61.40, 14.39. HRMS: m/z 213.0035 [M^+].

Thieno[3,2-b]thiophene-2-carboxylic Acid. A solution of ethyl thieno[3,2-b]-thiophene-2-carboxylate (4.21 g, 19.83 mmol) and lithium hydroxide (2.37 g, 99.16 mmol) in tetrahydrofuran (50 mL) and water (50 mL) was refluxed at 100 ℃ for 4 h. After the reaction, the solvent was evaporated, and concentrated HCl was added to the residue. The precipitate was extracted with chloroform and water. The organic layer was dried over magnesium sulfate. Removing the solvent under reduced pressure gave a white solid (3.59 g, yield= 98.37%). ^{1}H NMR (400 MHz, $CHCl_3$-*d*) δ (ppm) 8.12 (s, 1H), 7.93 (d, *J* = 5.3 Hz, 1H), 7.51 (d, *J* = 5.3 Hz, 1H). HRMS: m/z 183.9604 [M^+].

2-Butyloctyl thieno[3,2-b]thiophene-2-carboxylate. To a 250 ml round-bottom flask with CH_2Cl_2 (100 mL) were added the raw materials of Thieno[3,2-b]-thiophene-2-carboxylic Acid (3.90 g, 21.17 mmol), DCC (13.09 g, 63.51 mmol), and DMAP (5.17 g, 42.34 mmol). 2-butyloctan-1-ol (19.73 g, 105.90 mmol) was added to the flask and then stirred for 48 h under N_2 protection at room temperature. The reaction mixture was poured to 100 mL of water and extracted with CH_2Cl_2. The organic phase was dried by sodium sulfate, and the solvent was removed. Column chromatography on silica gel using hexane/CH_2Cl_2 = 1/1 yielded the title compound

as an oil (5.61 g, 75.20%). ^{1}H NMR (500 MHz, $CHCl_3$-*d*) δ (ppm) 7.98 (s, 1H), 7.59 (d, *J* = 5.3 Hz, 1H), 7.28 (d, *J* = 5.2 Hz, 1H), 4.23 (d, *J* = 5.6 Hz, 2H), 1.87–1.66 (m, 1H), 1.44–1.21 (m, 16H), 0.89 (m, 6H). ^{13}C NMR (126 MHz, $CHCl_3$-*d*) δ (ppm) 162.82, 143.90, 138.75, 135.30, 131.58, 125.46, 119.75, 68.12, 37.43, 31.83, 31.40, 31.08, 29.65, 28.98, 26.75, 23.01, 22.68, 14.13, 14.09. HRMS: m/z 353.1598 [M^+].

2-Butyloctyl 5-iodothieno[3,2-b]thiophene-2-carboxylate(3). To a 100 ml round-bottom flask with 20 ml $(CF_3)_2COH$ were added 2-butyloctyl thieno[3,2-b]-thiophene-2-carboxylate (3.00 g, 8.51 mmol) and NIS(2.49 g, 11.06 mmol), and kept stirring under Ar atmosphere protection at room temperature in the dark overnight. Saturated sodium sulphite solution (50 mL) was added to the mixture, extracted with ethyl acetate, washed by bring. The organic layer was dried over magnesium sulfate and further purified by flash column. Evaporating in vacuo to afford a brightly colorless liquid(3.66 g, 89.93%). ^{1}H NMR (500 MHz, $CHCl_3$-*d*) δ (ppm) 7.90 (s, 1H), 7.47 (s, 1H), 4.24 (d, *J* = 5.6 Hz, 2H), 1.77 (q, *J* = 6.0 Hz, 1H), 1.49–1.20 (m, 16H), 0.91 (dt, *J* = 12.9, 6.7 Hz, 5H). ^{13}C NMR (126 MHz, $CHCl_3$-*d*) δ (ppm) 162.80, 143.98, 143.35, 134.99, 128.76, 124.33, 80.54, 68.27, 37.41, 31.82, 31.38, 31.06, 29.63, 28.96, 26.74, 23.00, 22.68, 14.13, 14.09. HRMS: m/z=479.0562 [M^+].

3-Fluoro-4,6-dihydrothieno[3,4-b]thiophene-2-carboxylic acid. To a solution of Methyl 3-fluoro-4,6-dihydrothieno[3,4-b]thiophene-2-carboxylate (6.00 g, 27.49 mmol) in THF (80 mL) and deionized water (80 mL) was added lithium hydroxide (3.29 g, 137.40 mmol), and kept stirring at room temperature for 5 h. After the reaction, the solvent was evaporated, then 2M HCl solution was added to the residue.

The precipitate was extracted with chloroform and water. The organic layer was dried over magnesium sulfate. Removing the solvent under reduced pressure gave a white solid (5.57 g, yield = 99.31%). ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 13.30 (s, 1H, broad), 4.22 (t, J = 3.2 Hz, 2H), 4.03 (t, J = 3.2 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 161.63, 153.16, 144.72, 133.47, 116.94, 34.57, 31.19. HRMS: m/z=204.9786 [M^+].

2-Ethylhexyl 5-(3-fluoro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate. To a solution of 2-trimethyltin-3-fluoro-4,6-dihydrothieno[3,4-b]thiophene (1.00 g, 3.09 mmol), 2-ethylhexyl 5-bromothiophene-2-carboxylate **(2)** (1.48 g, 4.64 mmol) in toluene (30 mL) and DMF (6 ml) was added $Pd(PPh_3)_4$ (357.90 mg, 0.31 mmol) after degassing and purging with nitrogen for 3 times, and then the mixture was stirred at 120 °C for 24 hours under N_2 protection. After cooling down to room temperature, the mixture was poured into water and extracted with ethyl acetate, the organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The obtained crude dark red solid was purified by silica gel chromatography with petroleum ether/dichloromethane (20: 1 to 5: 1)as eluent, affording 2-ethylhexyl 5-(3-fluoro-4,6-dihydro- thieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate as yellow solid (1.23 g, yield = 96.45%). ^{1}H NMR (500 MHz, $CHCl_3$-d) δ (ppm) 7.70 (d, J = 3.9 Hz, 1H), 7.13 (d, J = 3.9 Hz, 1H), 4.22 (dd, J = 5.8, 2.3 Hz, 2H), 4.17 (t, J = 3.2 Hz, 2H), 4.04 (t, J = 3.2 Hz, 2H), 1.70 (p, J = 6.1 Hz, 1H), 1.48–1.29 (m, 8H), 0.93 (m, 6H). ^{13}C NMR (126 MHz, $CHCl_3$-d) δ (ppm) 162.22 , 148.43, 139.43, 136.94, 133.57, 133.20, 132.38, 124.15, 119.08, 67.68, 38.88, 33.22, 29.76, 23.94,

22.99, 14.08, 11.10. HRMS: m/z=399.0909 [M^+].

2-Ethylhexyl 5-(3-fluorothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate. A solution of 2-ethylhexyl 5-(3-fluoro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (1.01 g, 2.53 mmol) in 20 mL of methylene dichloride was stirred and cooled in a dry ice bath, and then 3-chloroperbenzoic acid (m-CPBA) (527.47 mg, 2.59 mmol) in 20 mL of methylene dichloride was added dropwise. After the addition, the mixture was kept stirring in dry ice bath overnight. Removal of solvent under vacuum produced a yellow solid. The residue contained a crude product of 2-ethylhexyl 5-(3-fluorothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate and m-CPBA. The obtained solid was refluxed in 20 mL of acetic anhydride for 2 h. Then the mixture was cooled down, and solvent was removed under vacuum. Column chromatography on silica gel using hexanes as eluent yielded the title compound as light yellow solid (0.90 g, 89.70%). ^{1}H NMR (400 MHz, $CHCl_3$-*d*) δ (ppm) 7.74 (d, *J* = 4.0 Hz, 1H), 7.44 (d, *J* = 2.7 Hz, 1H), 7.25–7.20 (m, 2H), 4.23 (dd, *J* = 5.8, 1.3 Hz, 2H), 1.71 (p, *J* = 6.0 Hz, 1H), 1.50–1.29 (m, 8H), 0.93 (m, 6H). ^{13}C NMR (101 MHz, $CHCl_3$-*d*) δ (ppm) 162.17, 145.34, 142.64, 139.33, 136.44, 133.90, 133.40, 131.86, 125.71, 119.26, 113.46, 67.78, 38.90, 30.55, 29.00, 23.96, 23.00, 14.08, 11.11. HRMS: m/z=397.0748 [M^+].

2-Ethylhexyl 5-(4,6-dibromo-3-fluorothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (M1). To a solution of 2-ethylhexyl 5-(3-fluorothieno[3,4-b]thiophen-2-yl)-thiophene-2-carboxylate (0.42 g, 1.05 mmol) in 15 mL of THF was added dropwise a solution of NBS (0.47 g, 2.65 mmol) in 10 mL of DMF under nitrogen protection in

the dark in ice bath, and the reaction mixture was kept stirring overnight. Then it was poured to saturated sodium sulfite solution at ice-water bath, and extracted with ethyl acetate. The organic phase was collected and dried by anhydrous sodium sulfate. Removal of the solvent and column purification on silica gel using hexane as eluent yielded the target product (0.45 g, 76.27%). ^{1}H NMR (500 MHz, $CHCl_3$-*d*) δ (ppm) 7.74 (d, *J* = 3.8 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 1H), 4.31–4.15 (m, 2H), 1.71 (p, *J* = 6.1 Hz, 1H), 1.49–1.29 (m, 8H), 0.93 (dt, *J* = 17.5, 7.2 Hz, 5H). ^{13}C NMR (126 MHz, $CHCl_3$-*d*) δ (ppm) 161.95, 144.08, 141.90, 138.20, 134.85, 134.74, 133.37, 126.36, 121.27, 98.97, 98.45, 67.86, 38.89, 30.52, 29.00, 23.95, 23.00, 14.10, 11.12. HRMS: calculated for $C_{19}H_{20}O_2Br_2FS_3$ [M^+]=554.8950; found m/z=554.8935[M^+].

2-Butyloctyl 5-(3-fluoro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thieno[3,2-b]thiophene-2-carboxylate. To a solution of 2-trimethyltin-3-fluoro-4,6-dihydrothieno-[3,4-b]thiophene (1.00 g, 3.09 mmol), 2-butyloctyl 5-iodothieno[3,2-b]thiophene-2-carboxylate(2) (1.56 g, 3.25 mmol) in toluene (30 mL) and DMF (6 ml) was added Pd(PPh3)4 (357.86 mg, 0.31 mmol) after degassing and purging with nitrogen for 3 times, and then the mixture was stirred at 120 °C for 24 hours under N2 protection. After cooling down to room temperature, the mixture was poured into water and extracted with ethyl acetate, the organic layer was dried with MgSO4 and concentrated under reduced pressure. The obtained crude dark red solid was purified by silica gel chromatography with petroleum ether/dichloromethane (20: 1 to 5: 1) as eluent, affording light yellow solid (1.25 g, yield =78.88%). ^{1}H NMR (500 MHz, CH_2Cl_2-d_2) δ (ppm) 7.90 (s, 1H), 7.36 (s, 1H), 4.21 (d, *J* = 5.7 Hz, 2H), 4.17 (s, 2H),

4.04 (s, 2H), 1.77 (p, *J* = 5.9 Hz, 1H), 1.45–1.21 (m, 16H), 0.90 (dt, *J* = 13.6, 6.8 Hz, 6H). ^{13}C NMR (126 MHz, CH_2Cl_2-d_2) δ (ppm) 162.31, 149.24, 147.14, 144.06, 138.67, 137.42, 135.11, 133.26, 125.15, 119.25, 116.03, 68.10, 37.42, 34.52, 31.83, 31.79, 31.36, 31.04, 29.63, 28.96, 26.71, 23.01, 22.67, 13.89, 13.85. HRMS: calculated for $C_{25}H_{33}O_2FS_4$ [M^+]=512.7754; found m/z=512.1283[M^+].

2-Butyloctyl 5-(3-fluorothieno[3,4-b]thiophen-2-yl)thieno[3,2-b]thiophene-2-carboxylate. A solution of 2-butyloctyl 5-(3-fluoro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thieno[3,2-b]thiophene-2-carboxylate (1.23 g, 2.41 mmol) in 20 mL of methylene dichloride was stirred and cooled in a dry ice bath, and m-CPBA (513.36 mg, 2.53 mmol) in 20 mL of methylene dichloride was added dropwise. After the addition, the mixture was kept stirring in dry ice bath overnight. Removal of solvent under vacuum produced a yellow solid. The residue contained a crude product of 2-butyloctyl 5-(3-fluorothieno[3,4-b]thiophen-2-yl) thieno[3,2-b]thiophene-2-carboxylate and m-CPBA. The obtained solid was refluxed in 20 mL of acetic anhydride for 2 h. Then the mixture was cooled down, and solvent was removed under vacuum. Column chromatography on silica gel using hexanes as eluent yielded the title compound as light yellow solid (1.12 g, 91.41%). ^{1}H NMR (500 MHz, CH_2Cl_2-d_2) δ (ppm) 7.94 (s, 1H), 7.48 – 7.42 (m, 2H), 7.32 – 7.26 (m, 1H), 4.22 (d, *J* = 5.7 Hz, 2H), 1.77 (q, *J* = 6.0 Hz, 1H), 1.48 – 1.19 (m, 16H), 0.90 (dt, *J* = 14.3, 6.9 Hz, 6H). ^{13}C NMR (126 MHz, CH_2Cl_2-d_2) δ (ppm) 162.29, 144.76, 143.85, 142.61, 138.82, 136.47, 135.80, 131.69, 125.17, 119.51, 118.39, 113.21, 112.58, 68.17, 37.42, 31.83, 31.36, 31.04, 29.63, 28.96, 26.71, 23.01, 22.68, 13.89, 13.85. HRMS: calculated for $C_{25}H_{29}O_2FS_4$

[M^+]=508.7434; found m/z= 509.1104[M^+].

2-Butyloctyl 5-(4,6-dibromo-3-fluorothieno[3,4-b]thiophen-2-yl)thieno[3,2-b]thiophene-2-carboxylate (M2). To a solution of 2-butyloctyl 5-(3-fluorothieno-[3,4-b]thiophen-2-yl)thieno[3,2-b]thiophene-2-carboxylate (1.13 g, 2.22 mmol) in 15 mL of THF was added dropwise a solution of NBS (0.79 g, 4.44 mmol) in 10 mL of DMF under nitrogen protection in the dark in ice bath, and the reaction mixture was kept stirring overnight. Then it was poured to saturated sodium sulfite solution at ice-water bath, and extracted with ethyl acetate. The organic phase was collected and dried by anhydrous sodium sulfate. Removal of the solvent and column purification on silica gel using hexane as eluent yielded the target product (0.45 g, 76.27%). ^{1}H NMR (400 MHz, $CHCl_3$-*d*) δ (ppm) 7.80 (s, 1H), 7.23 (s, 1H), 4.15 (d, *J* = 5.7 Hz, 2H), 1.75 – 1.63 (m, 1H), 1.26 (m, 16H), 0.83 (dt, *J* = 12.5, 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CHCl_3$-*d*) δ (ppm) 161.27, 142.67, 140.15, 138.47, 136.52, 135.18, 133.55, 132.19, 124.02, 120.50, 117.04, 97.83, 97.12, 67.28, 36.39, 30.81, 30.37, 30.04, 28.63, 27.94, 25.72, 21.99, 21.66, 13.11, 13.08. HRMS: calculated for $C_{25}H_{27}Br_2O_2FS_4$ [M^+]=666.5354; found m/z=666.9284[M^+].

Polymerization of PBT-Th. To a 25 mL flask, compound 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene (88.60 mg, 0.11 mmol), compound M1 (63.60 mg, 0.11 mmol) and $Pd(PPh_3)_4$ (5.3 mg, 0.0046 mmol) were added under argon, then the reaction container was purged with argon for 20 min to remove O_2. After the addition of toluene (3 mL) and DMF (0.6 ml), the reactant mixture was heated to reflux and maintained at the same temperature for 18 h. After

cooling to room temperature, the mixture was poured into methanol (200 ml), then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, acetone, hexane and chloroform. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. Yield: 65.28 mg (56.66%).GPC:M_w=124.72 KDa; M_n=55.95 KDa; PDI=2.22. T_d=336 ^oC (5% weight loss by TGA). **^{1}H NMR** (400 MHz, $CDCl_2CDCl_2$, 80 ^oC) δ (ppm) 7.25 (br, ArH), 6.86 (br, ArH), 4.19-4.02 (b, O-CH_2), 2.85 (br, CH_2), 1.93 (br, CH), 1.82-1.57 (br, CH), 1.54-1.07 (br, CH_2), 1.05-0.24 (br, CH_3).

Polymerization of 2D-PTB-Th. 2D-PTB-Th was prepared using the same procedure as PBT-Th. Yield: 312.10 mg (76.20%). GPC:M_w=87.42 KDa; M_n=49.45 KDa; PDI=1.76. T_d=383 ^oC (5% weight loss by TGA). **^{1}H NMR** (400 MHz, $CDCl_2CDCl_2$, 80 ^oC) δ (ppm) 8.23-6.17 (br, ArH), 4.21 (b, O-CH_2), 2.88 (br, CH_2), 2.05-1.12 (br, CH and CH_2), 1.10-0.51 (br, CH_3).

Polymerization of 2D-PTB-TTh. 2D-PTB-TTh was prepared using the same procedure as PBT-Th. Yield: 101.50 mg (93.76%).GPC:M_w=40.15 KDa; M_n=22.51 KDa; PDI=1.78. T_d=386 ^oC (5% weight loss by TGA). **^{1}H NMR** (400 MHz, $CDCl_2CDCl_2$, 80 ^oC) δ (ppm) 8.36-6.27 (br, ArH), 4.18 (b, O-CH_2), 2.88 (br, CH_2), 2.38-1.14 (br, CH and CH_2), 1.13-0.38 (br, CH_3).

4. TGA curves

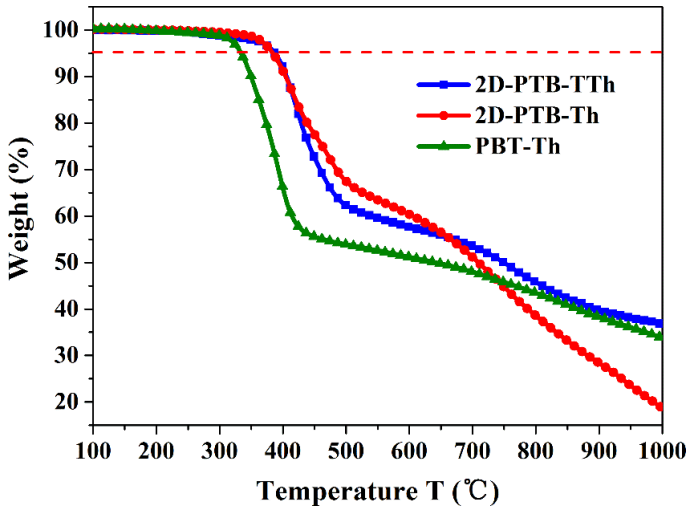


Figure S1. Thermogravimertic analysis (TGA) of the polymers.

5. Hole mobility measurement

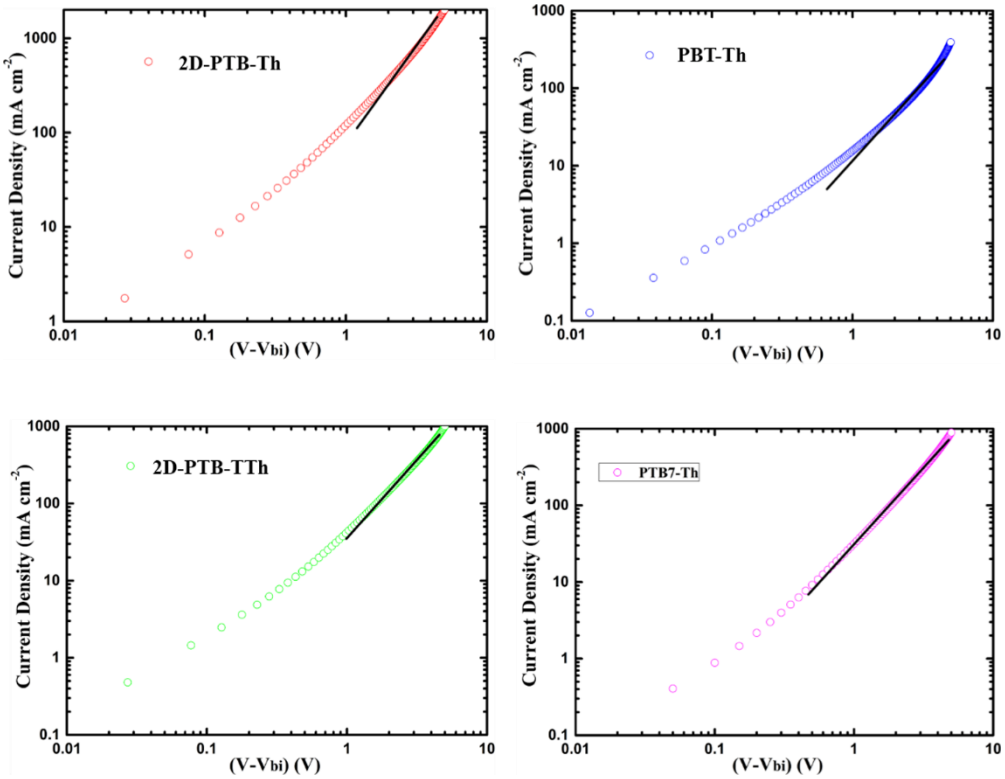


Figure S2. J-V plots for the devices ITO/ZnO/polymer:PC 71 BM/Ag. (a) 2D-PTB-Th, (b) 2D-PTB-TTh, (c) PBT-Th and (d) PTB7-Th. (The symbols are experimental data for transport of hole, and the black lines are fitted according to the space-charge-limited-current model).

6. NMR Spectra

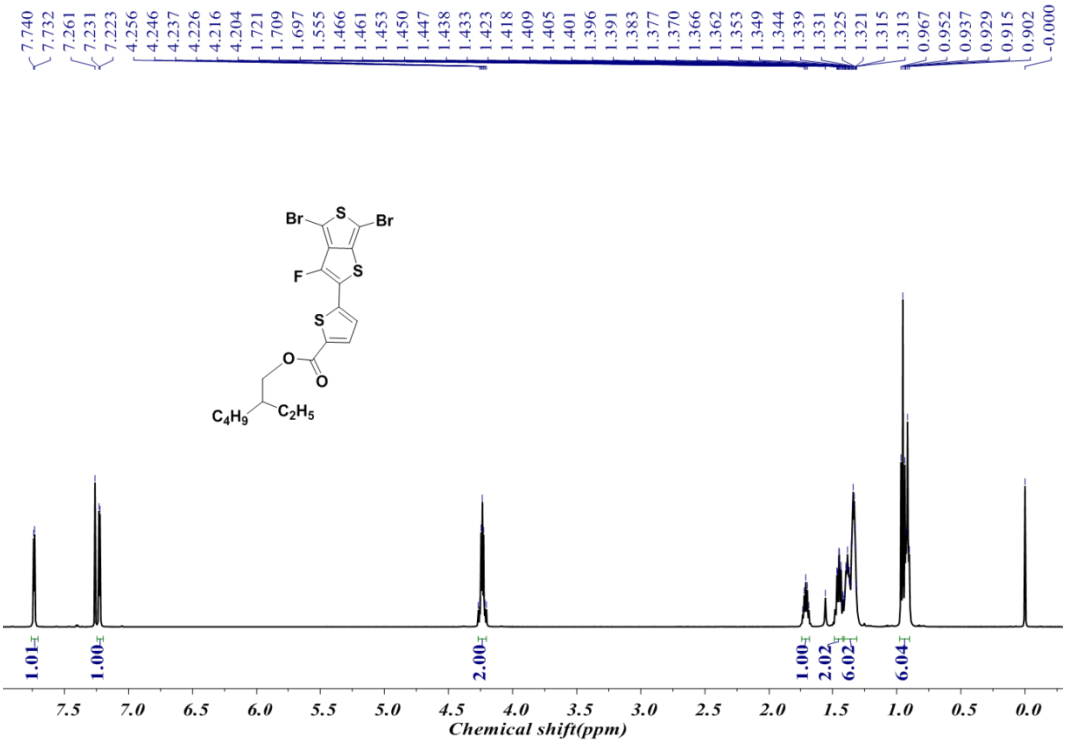


Figure S3. ^{1}H NMR spectrum of compound M1.

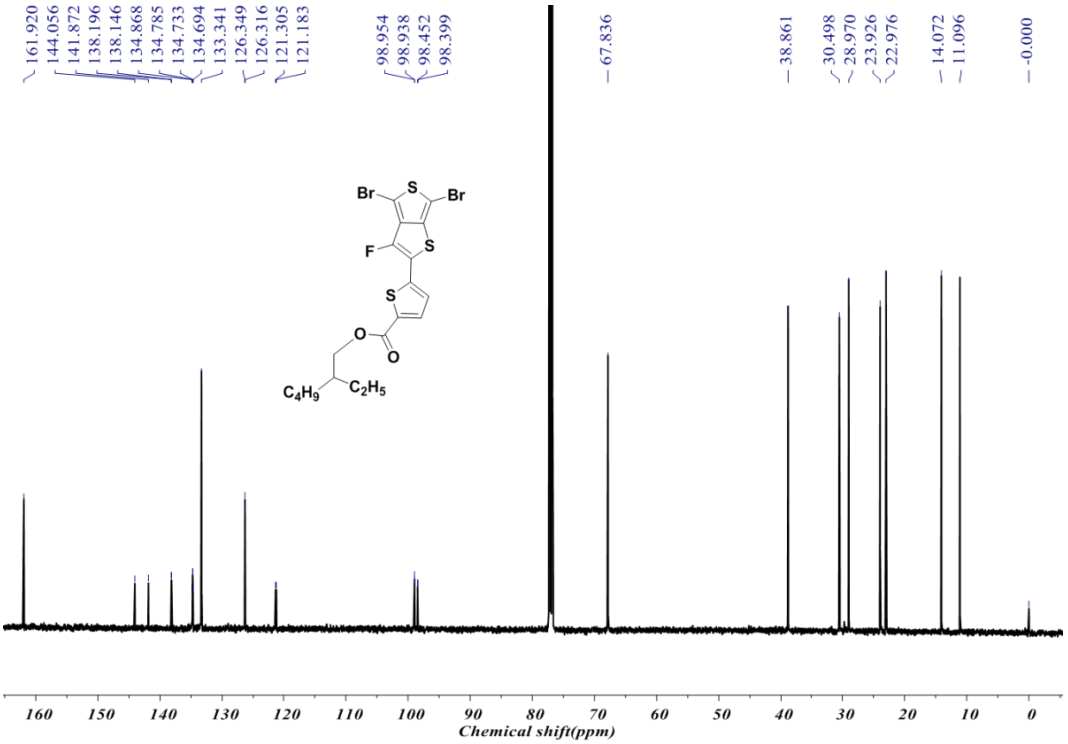


Figure S4. ^{13}C NMR spectrum of compound M1.

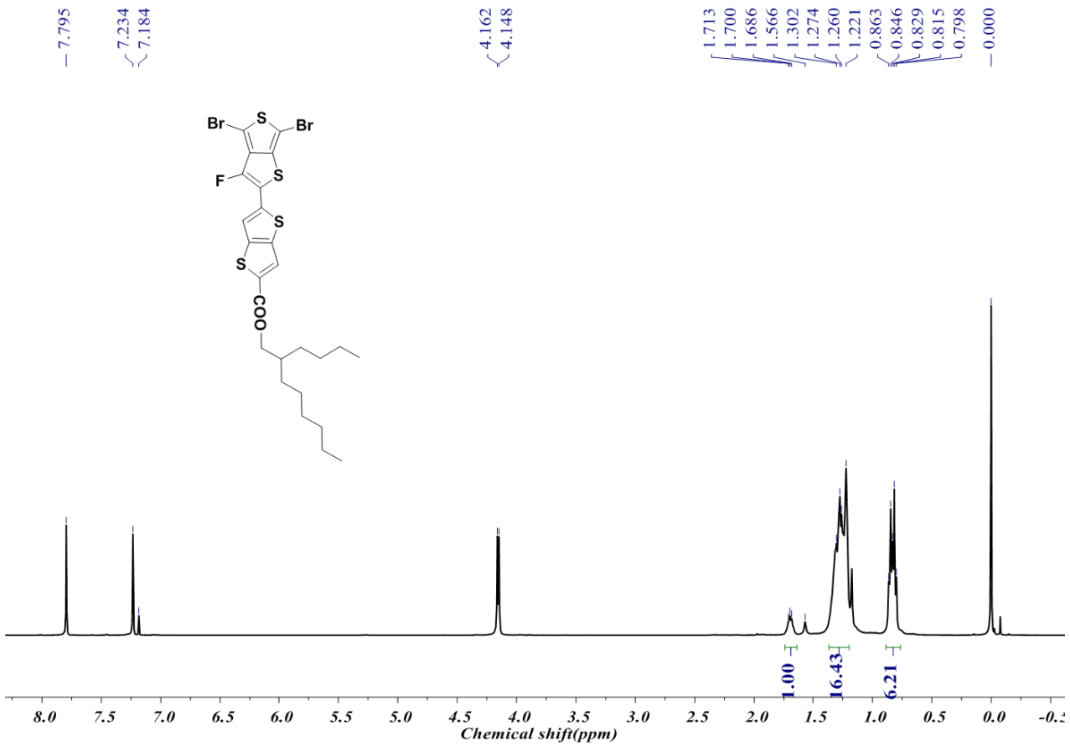


Figure S5. ^{1}H NMR spectrum of compound M2.

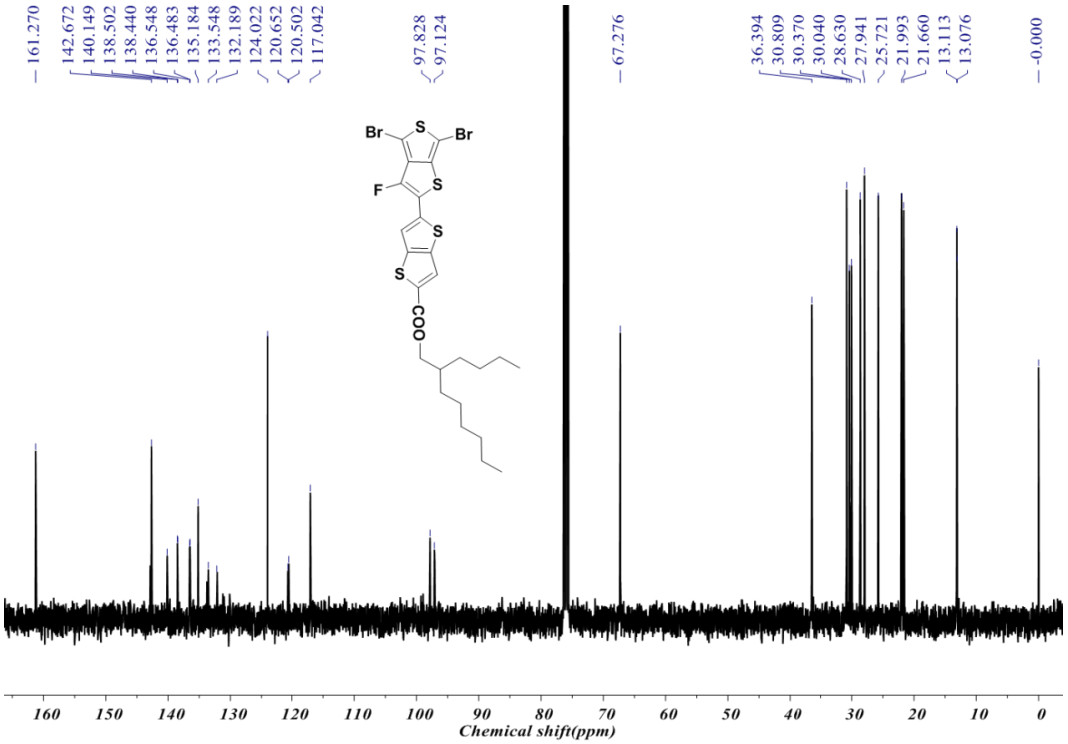


Figure S6. ^{13}C NMR spectrum of compound M2.

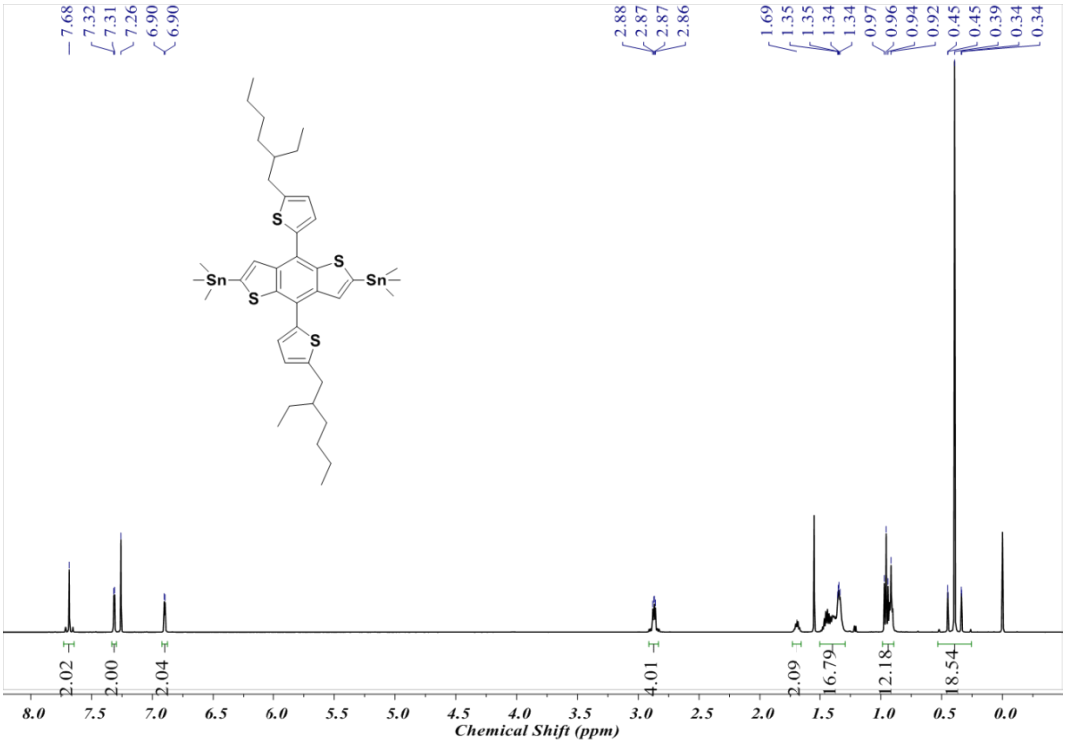


Figure S7. ^{1}H NMR spectrum of compound M3.

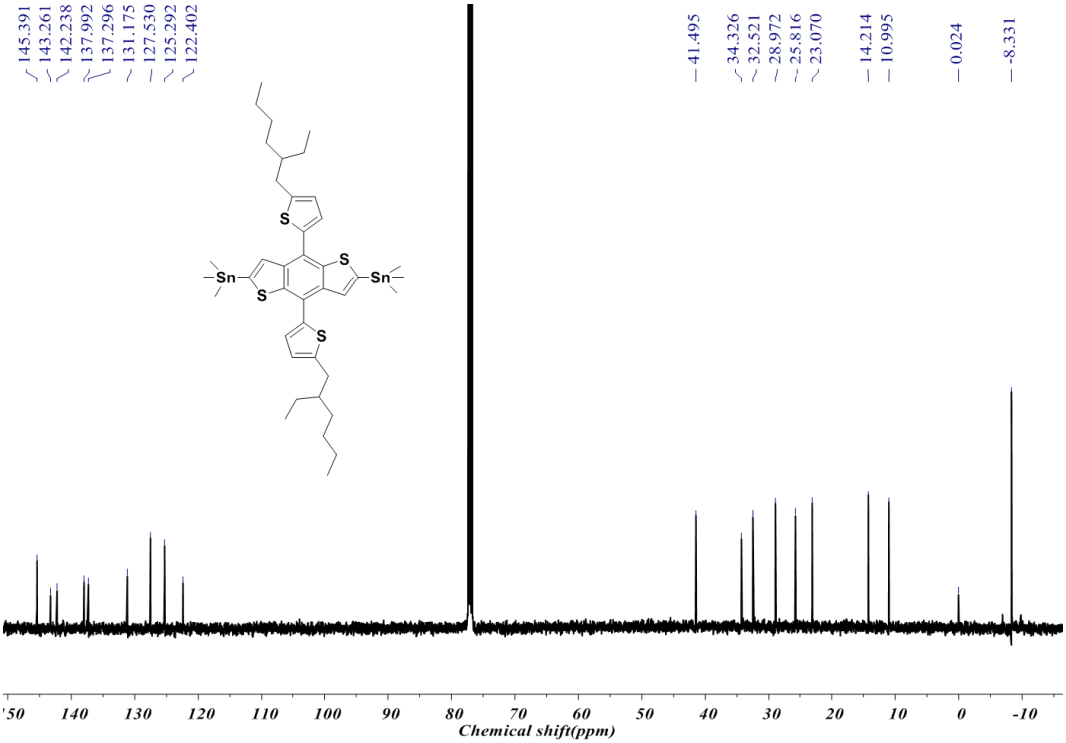


Figure S8. ^{13}C NMR spectrum of compound M3.

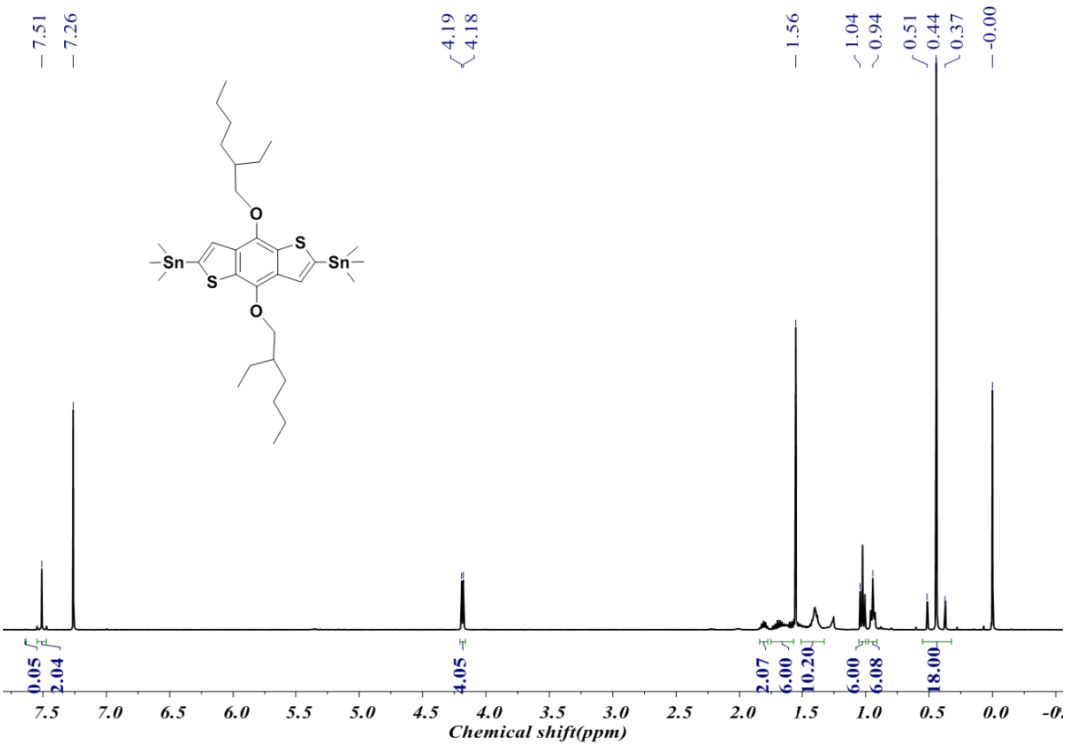


Figure S9. ^{1}H NMR spectrum of compound M4.

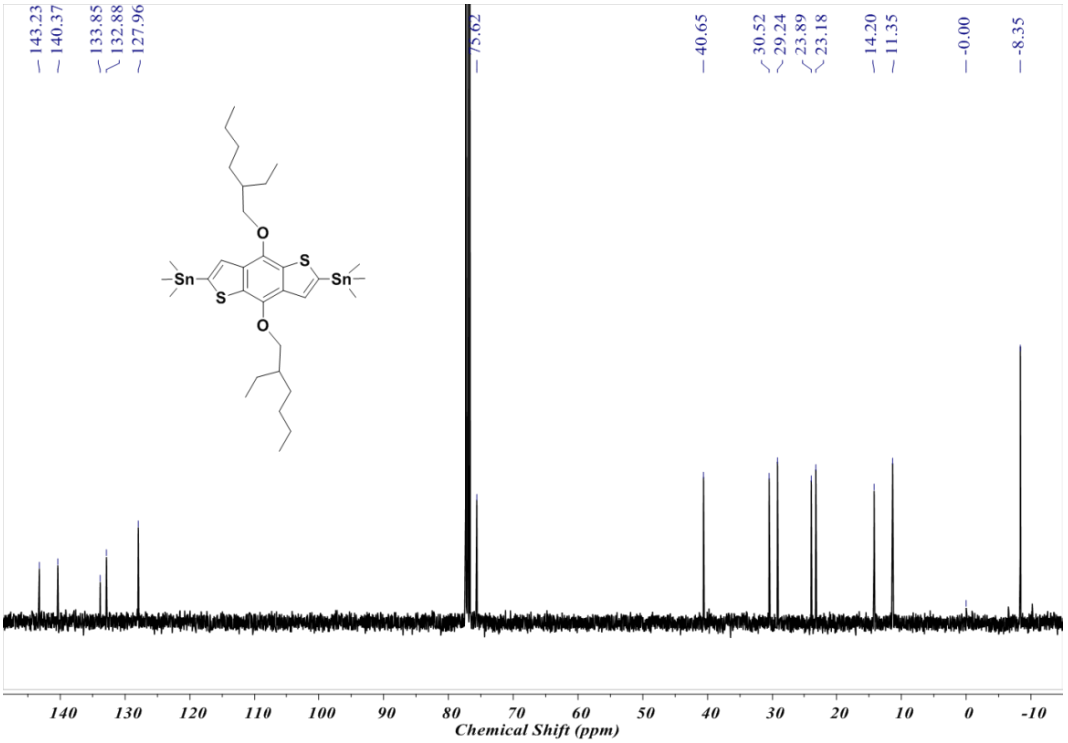


Figure S10. ^{13}C NMR spectrum of compound M4.

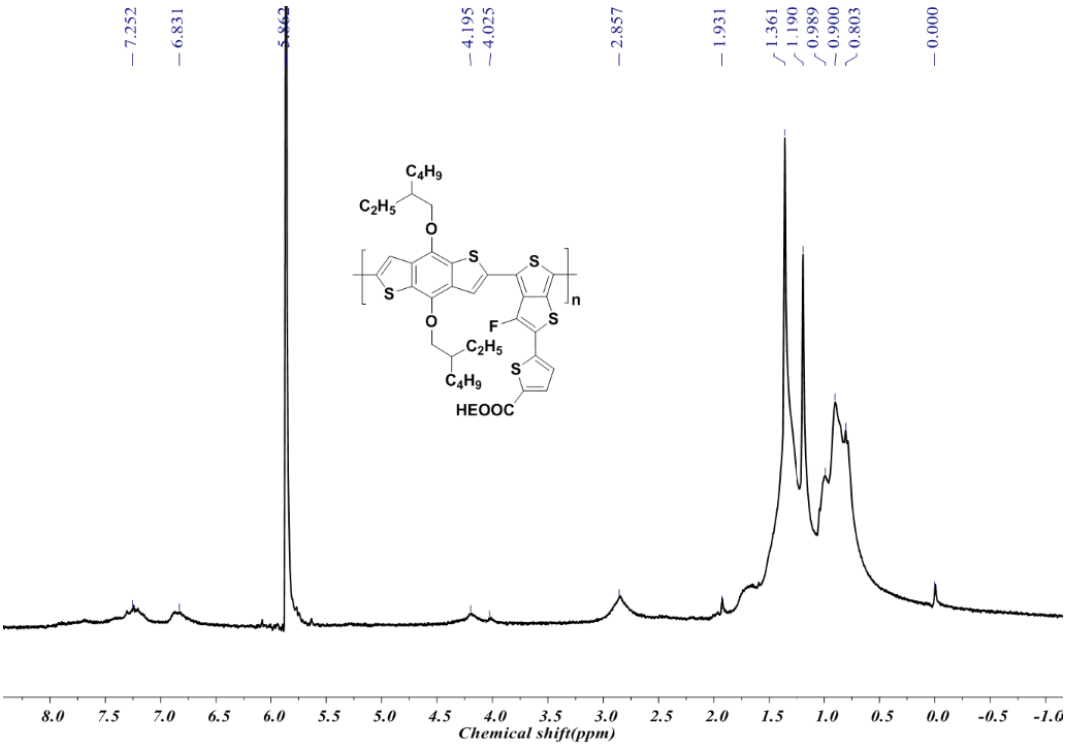


Figure S11. [1]H NMR spectrum of compound PBT-Th.

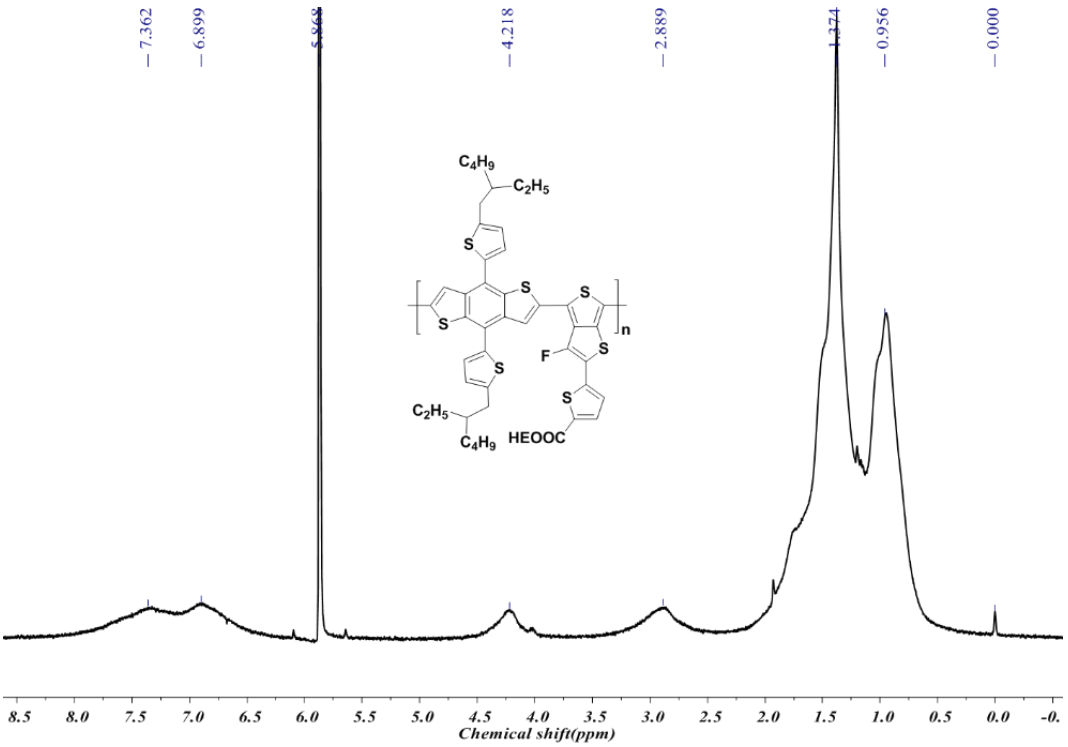


Figure S12. [1]H NMR spectrum of compound 2D-PTB-Th.

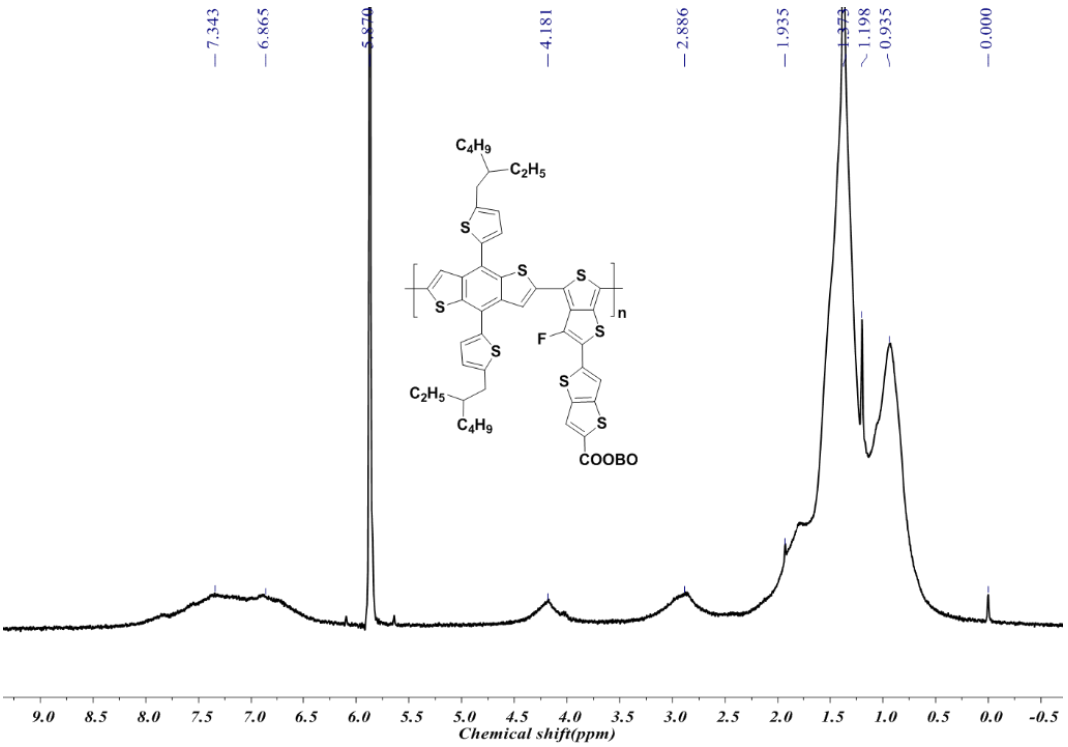


Figure S13. ^{1}H NMR spectrum of compound 2D-PTB-TTh.

7. References

[1] a) Yongye Liang, Danqin Feng, Yue Wu, Szu-Ting Tsai, Gang Li, Claire Ray, L. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 7792; b) Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater*. **2010**, *22*, E135; c) Y. Liang, D. Feng, J. Guo, J. M. Szarko, C. Ray, L. X. Chen, L. Yu, *Macromolecules* **2009**, *42*, 1091; d) H. J. Son, W. Wang, T. Xu, Y. Liang, Y. Wu, G. Li, L. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 1885.

[2] a) L. Ye, S. Zhang, W. Zhao, H. Yao, J. Hou, *Chem. Mater.* **2014**, *26*, 3603; b) L. Huo, T. Liu, X. Sun, Y. Cai, A. J. Heeger, Y. Sun, Adv. Mater. **2015**, *27*, 2938; c) D. Liu, Q. Zhu, C. Gu, J. Wang, M. Qiu, W. Chen, X. Bao, M. Sun, R. Yang, *Adv. Mater.* **2016**, *28*, 8490.

[3] a) S.-H. Liao, H.-J. Jhuo, Y.-S. Cheng, S.-A. Chen, Advanced Materials 2013, 25, 4766; b) P. Chao, R. Gu, X. Ma, T. Wang, Y. Zhao, *Polym. Chem.* **2016**, *7*, 5147; c) P. Chao, Y. Li, X. Gu, D. Han, X. Jia, M. Wang, T. Zhou, T. Wang, *Polym. Chem.* **2015**, *6*, 2977.