

Supporting Information

Synergistic Effect of Chlorination and Fully Two- Dimensional Design on Molecular Energy Level Modulation Toward Non-Fullerene Photovoltaics

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Materials and Methods

All starting reagents were obtained commercially as analytical grade and used directly without any purification unless stated otherwise. Toluene and THF were distilled over sodium/benzophenone and calcium hydride under N_2 prior to use. 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene (M3) ^[1], the polymer PTB7-Th^[2] and 3-chloro-4,6-dihydrothieno[3,4-b]thiophene-2-carboxylic acid ^[3] were synthesized as reported in the literatures. ¹H NMR and ¹³C 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 °C. Solution and thin film optical absorption spectra were measured with a UV-Vis 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*-Bu₄NPF₆) 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 0.44 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, Santa 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).

Device Fabrication and Testing

The inverted device structure was ITO/ZnO/donor:ITIC/MoO₃/Ag. ITO-coated glass substrates were cleaned with deionized water, acetone and isopropyl alcohol for 30 minutes once time and dried in the drying oven at 80 °C for 12 h before used. The ITO glass was then placed in the UV-ozone for 15 minutes and the sol-gel-derived ZnO films was spin-coated onto the ITO substrate followed by thermal treatment at 200 °C

for 30 min and cooled to room temperature under vacuum. The mixture of donor/ITIC (1:1 by wt/wt ratio) was dissolved in chlorobenzene (CB) with the addition of a small amount of DIO (0.25%, v/v) to obtain 8 mg ml⁻¹ of solution. The blend was stirred at 80 °C in the glove box for overnight. The active layer was spin-coating at 1000 rpm for 60 s to get the blend film. A 10 nm MoO₃ layer and a 100 nm Ag layer were subsequently evaporated through a shadow mask to define the active area of the devices. The power conversion efficiencies (PCEs) were tested under AM 1.5G irradiation with the intensity of 100 mW cm⁻² (Enli Technology Ltd., Taiwan) which was calibrated by a NREL certified standard silicon cell (4 cm²). The J-V curves were recorded with the computer-controlled Keithley 2400 sourcemeter in a dry box under an inert atmosphere. The external quantum efficiency (EQE) spectra were measured through the measurement of solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan).

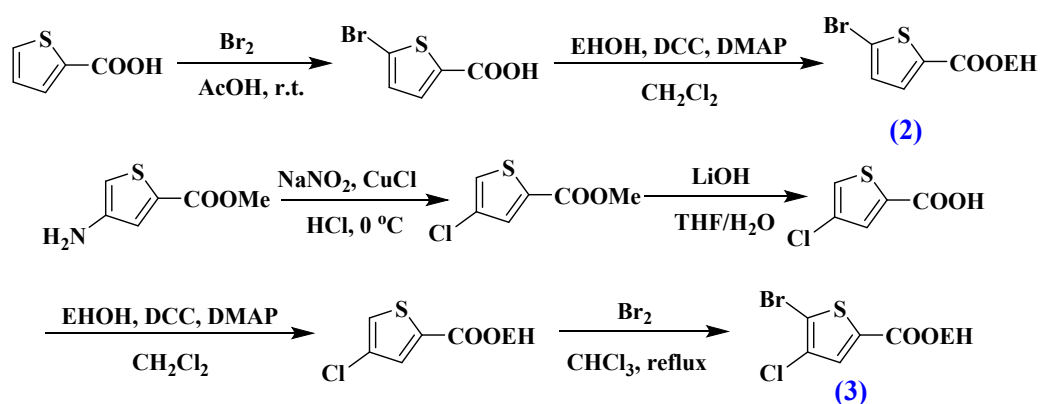
The hole mobilities of the photosensitive layers were measured by the space charge limited current (SCLC) method using the hole-only device with the structure of ITO/PEDOT:PSS/polymer:ITIC/MoO₃/Ag. The processing conditions used for the active layers were the optimized ones. Charge mobility was extracted by fitting the current density–voltage curves, recorded under dark conditions, with the Mott-Gurney equation. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{V^2}{d^3}$$

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.

Synthesis and Characterization



Scheme S1. The synthetic routes for compounds 2 and 3.

3-Chloro-4,6-dihydrothieno[3,4-b]thiophene. To a solution of Methyl 3-chloro-4,6-dihydro-thieno[3,4-b]thiophene-2-carboxylic acid (8.00 g, 36.41 mmol) and quinoline (80 mL) was added Barium-promoted copper chromite (5.66 g, 18.20 mmol), and 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 (5.07 g, yield = 78.85%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.09 (s, 1H), 4.24–4.20 (m, 2H), 4.04–3.98 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ (ppm) 141.76, 139.42, 123.36, 120.25, 34.44, 32.67.

2-Trimethyltin-3-chloro-4,6-dihydrothieno[3,4-b]thiophene (1). To a solution of 3-chloro-4,6-dihydrothieno[3,4-b]thiophene (4.14 g, 23.43 mmol) in tetrahydrofuran (50 mL) was added 2.4 M n-butyllithium (12.70 mL, 30.46 mmol) dropwise at $-78\text{ }^{\circ}\text{C}$. After stirring at $-78\text{ }^{\circ}\text{C}$ for 2 h, 1M trimethylstannyl chloride (35.15 ml, 35.15 mmol) was added to the mixture at $-78\text{ }^{\circ}\text{C}$, then keeping stirring at $-78\text{ }^{\circ}\text{C}$ 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 white needle crystal (6.80 g, yield = 85.49%). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 4.23–4.16 (m, 2H), 4.00–3.94 (m, 2H), 0.43 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 145.67, 143.98, 136.69, 127.02, 34.18, 32.35, -8.30. HRMS: $m/z=339.9257$ [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 ($20\text{ }^{\circ}\text{C}$) 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%). ¹H 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). ¹³C 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 CH₂Cl₂ (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 N₂ protection. The reaction mixture was poured to 100 mL of water and extracted with CH₂Cl₂. The organic phase was dried by sodium sulfate, and the solvent was removed. Column chromatography on silica gel using hexane/CH₂Cl₂ = 1/1 yielded the title compound as an oil (9.39 g, 71.95%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) δ 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⁺].

Methyl 4-chlorothiophene-2-carboxylate. Methyl 4-aminothiophene-2-carboxylate (5.00 g, 31.81 mmol) was added gradually to a vigorously stirred 6 M hydrochloric acid solution (60 mL), Then the reaction mixture was stirred for 30 min at room temperature and then cooled to -20 °C (ice-salt bath). It was diazotised slowly with sodium nitrite

(2.41 g, 34.99 mmol) in water (10 mL). The resulting diazonium salt was stirred for 1 h at -20 °C and then poured into a well stirred solution of cuprous chloride (3.78 g, 38.17 mmol in concentrated hydrochloric acid (100 ml)) at -20 °C. The reaction mixture was heated at 60 °C for 1.5 h and cooled down, and then repeatedly extracted with ether (3×150 mL). The product was washed with water and dried over magnesium sulfate and evaporated to remove the solvent, and the residue was purified by silic gel chromatography to obtain a white solid (3.66 g, yield =65.24%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.66 (t, *J* = 1.4 Hz, 1H), 7.35 (s, 1H), 3.92 (d, *J* = 1.0 Hz, 3H). GC-MS: *m/z*=175.9763 [M]⁺.

4-Chlorothiophene-2-carboxylic acid. To a solution of Methyl 4-chloro-thiophene-2-carboxylate (2.00 g, 11.32 mmol) in tetrahydrofuran (20 mL) and deionized water (20 mL) was added lithium hydroxide (1.36 g, 56.62 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 (1.47 g, yield = 79.89%). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm) 13.50 (s, 1H), 7.93 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 1.7 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ (ppm) 162.38, 135.89, 132.72, 128.69, 124.79. HRMS: *m/z*=162.9611 [M⁺].

2-Ethylhexyl 4-chlorothiophene-2-carboxylate. To a 250 ml round-bottom flask with CH₂Cl₂ (100 mL) was added the raw materials of 4-chlorothiophene-2-carboxylic acid (2.56 g, 15.73 mmol), DCC (4.86 g, 23.59 mmol), and DMAP (2.31 g, 18.87 mmol). 2-

ethylhexan-1-ol (20.49 g, 157.30 mmol) was added to the flask and then stirred for 48 h under N₂ protection. The reaction mixture was poured to 100 mL of water and extracted with CH₂Cl₂. The organic phase was dried by sodium sulfate, and the solvent was removed. Column chromatography on silica gel using hexane/CH₂Cl₂ = 1/1 yielded the title compound as an oil (3.22 g, 74.49%). ¹H NMR (400 MHz, CDCl₃) δ(ppm) 7.64 (d, *J* = 1.6 Hz, 1H), 7.34 (d, *J* = 1.6 Hz, 1H), 4.24 (dd, *J* = 5.7, 2.6 Hz, 2H), 1.70 (q, *J* = 6.1 Hz, 1H), 1.44 (td, *J* = 7.5, 6.4 Hz, 2H), 1.40–1.31 (m, 6H), 0.94 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 161.34, 134.36, 132.74, 126.62, 126.05, 67.96, 38.85, 30.49, 28.95, 23.91, 22.96, 14.06, 11.08.

2-Ethylhexyl 5-bromo-4-chlorothiophene-2-carboxylate (3). To a 250 ml two-necked round-bottom flask with 2-ethylhexyl 4-chlorothiophene-2-carboxylate (2.70 g, 9.82 mmol) in CHCl₃ (50 ml) was added dropwise the bromine (5ml, 98.23 mmol) and the mixture was heated to reflux for 3 h. The reaction mixture was cooled down to room temperature and treated with saturated sodium sulfite solution, and the color was changed into colorless from dark red, then the reaction mixture was extracted with CHCl₃, the organic phase was dried by sodium sulfate, the solvent was removed and the residue was purified by silic gel chromatography to obtain colorless liquid (3.30 g, yield =94.97 %). ¹H NMR (400 MHz, CDCl₃) δ (ppm)7.56 (s, 1H), 4.23 (dd, *J* = 5.7, 3.2 Hz, 2H), 1.69 (p, *J* = 6.1 Hz, 1H), 1.48–1.39 (m, 2H), 1.34 (s, 6H), 0.99–0.88 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 160.56, 133.48, 132.52, 128.00, 116.32, 68.16, 38.83, 30.44, 28.93, 23.88, 22.95, 14.06, 11.07. HRMS: *m/z*=353.3411[M⁺].

3-Chloro-4,6-dihydrothieno[3,4-b]thiophene-2-carboxylic acid. To a solution of

Methyl 3-chloro-4,6-dihydrothieno[3,4-b]thiophene-2-carboxylate (19.64 g, 83.67 mmol) in tetrahydrofuran (200 mL) and deionized water (200 mL) was added lithium hydroxide (10.02 g, 418.37 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 (18.26 g, yield = 99.35%). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm) 13.49 (s, 1H), 4.29–4.25 (m, 2H), 4.01 (t, *J* = 3.2 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ (ppm) 161.76, 144.36, 143.83, 130.40, 124.72, 34.51, 32.52. HRMS: *m/z*=220.9309 [M⁺].

2-Ethylhexyl 5-(3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate. To a solution of (3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)trimethylstannane (1.00 g, 2.95 mmol), 2-ethylhexyl 5-bromothiophene-2-carboxylate (1.41 g, 4.42 mmol) in toluene (30 mL) and DMF (6 ml) was added Pd(PPh₃)₄ (340.50 mg, 0.29 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 2-ethylhexyl 5-(3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate as yellow solid (1.11 g, yield = 90.98%). ¹H NMR (500 MHz, CDCl₃) δ

(ppm) 7.67 (d, $J= 3.9$ Hz, 1H), 7.22 (d, $J= 3.9$ Hz, 1H), 4.22 (d, $J= 5.9$ Hz, 2H), 4.19–4.12 (m, 2H), 4.00–3.90 (m, 2H), 1.71 (m, 1H), 1.44 (m, 3.3 Hz, 2H), 1.40–1.29 (m, 6H), 0.93 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 162.10, 143.11, 140.70, 137.14, 133.17, 132.99, 132.94, 125.31, 117.77, 67.71, 38.87, 34.59, 33.21, 30.54, 28.98, 23.97, 23.02, 14.11, 11.12. HRMS: $m/z=415.0609$ [M^+].

2-Ethylhexyl 5-(3-chlorothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate. A solution of 2-ethylhexyl 5-(3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (1.11 g, 2.67 mmol) in 20 mL of methylene dichloride was stirred and cooled in a dry ice bath, and then 3-chloroperbenzoic acid (*m*-CPBA) (570.15 mg, 2.81 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-chlorothieno[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 (0.78 g, 70.98%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (ppm) 7.90 (d, $J= 2.8$ Hz, 1H), 7.84 (dd, $J= 3.3, 2.0$ Hz, 2H), 7.58 (d, $J= 4.0$ Hz, 1H), 4.21 (dd, $J= 5.9, 2.5$ Hz, 2H), 1.74 – 1.59 (m, 1H), 1.46 – 1.18 (m, 8H), 0.89 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 162.20, 145.40, 140.67, 134.61, 133.91, 133.01, 132.93, 127.38, 113.94, 112.72, 112.60, 67.87, 38.89, 30.55, 28.99, 23.96, 23.00, 14.10, 11.11. HRMS: $m/z=412.8566$ [M^+].

2-Ethylhexyl 5-(4,6-dibromo-3-chlorothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (M1). To a solution of 2-ethylhexyl 5-(3-chlorothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (0.78 g, 1.90 mmol) in 15 mL of THF was added dropwise a solution of NBS (0.84 g, 4.75 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 (0.87 g, 80.56%). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.74 (d, *J* = 4.0 Hz, 1H), 7.39 (d, *J* = 4.0 Hz, 1H), 4.25 (d, *J* = 5.0 Hz, 2H), 1.72 (m, *J* = 6.1 Hz, 1H), 1.52–1.28 (m, 8H), 0.94 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 162.03, 139.90, 139.72, 135.78, 135.45, 135.20, 132.73, 128.03, 113.15, 100.19, 97.83, 67.97, 38.88, 30.54, 28.99, 23.96, 23.00, 14.10, 11.12. HRMS: *m/z*=570.9641 [M⁺].

2-Ethylhexyl 4-chloro-5-(3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate. To a solution of (3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)trimethylstannane (1.62 g, 4.48 mmol), 2-ethylhexyl 5-bromo-4-chlorothiophene-2-carboxylate (4) (1.30 g, 3.68 mmol) in toluene (30 mL) and DMF (6 mL) was added Pd(PPh₃)₂Cl₂ (257.98 mg, 0.36 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 2-ethylhexyl 4-chloro-5-(3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate as yellow solid (1.13 g, yield = 56.39%). ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.64 (s, 1H), 4.29 – 4.25 (m, 2H), 4.23 (dd, *J* = 5.7, 1.9 Hz, 2H), 4.11 – 3.98 (m, 2H), 1.70 (p, *J* = 6.1 Hz, 1H), 1.43 (p, *J* = 7.4 Hz, 2H), 1.39 – 1.28 (m, 6H), 1.00 – 0.80 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ(ppm) 161.19, 142.42, 139.95, 133.32, 133.24, 132.68, 128.89, 124.59, 120.59, 68.13, 38.85, 34.70, 33.28, 30.48, 28.96, 23.90, 22.98, 14.08, 11.08. HRMS: *m/z*=449.0221 [M⁺].

2-Ethylhexyl 4-chloro-5-(3-chlorothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate. A solution of 2-ethylhexyl 4-chloro-5-(3-chloro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (0.98 g, 2.19 mmol) in 20 mL of methylene dichloride was stirred and cooled in a dry ice acetone bath, and then *m*-CPBA (466.70 mg, 2.29 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 4-chloro-5-(3-chlorothieno[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 (0.92 g, 93.88%). ¹H NMR (500 MHz, CDCl₃) δ(ppm) 7.66 (s, 1H), 7.52 (d, *J* = 2.2 Hz, 1H), 7.31 (d, *J* = 2.3 Hz, 1H), 4.24 (dd, *J* = 5.7, 2.5 Hz, 2H), 1.71 (m, 1H), 1.44 (m, 2H), 1.39–1.30 (m, 6H), 0.93 (m, 6H). ¹³C NMR (126 MHz, CDCl₃)

δ (ppm) 162.20, 145.40, 140.67, 134.61, 133.91, 133.01, 132.93, 127.38, 113.94, 112.72, 112.60, 67.87, 38.89, 30.55, 28.99, 23.96, 23.00, 14.10, 11.11. HRMS: $m/z=447.6457$ [M^+].

2-Ethylhexyl 4-chloro-5-(4,6-dibromo-3-chlorothiopheno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (M2). To a solution of 2-ethylhexyl 5-(3-chlorothiopheno[3,4-b]thiophen-2-yl)thiophene-2-carboxylate (0.92 g, 2.05 mmol) in 15 mL of THF was added dropwise a solution of NBS (0.91 g, 5.13 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 (0.84 g, 67.37%). ^1H NMR (500 MHz, CDCl_3) δ (ppm) 7.66 (s, 1H), 4.25 (dd, $J = 5.7, 3.2$ Hz, 2H), 1.71 (m, 1H), 1.44 (m, 2H), 1.40–1.29 (m, 6H), 0.93 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm) 160.94, 139.08, 136.89, 134.78, 133.45, 132.31, 132.29, 126.60, 116.52, 100.60, 97.85, 68.31, 38.85, 30.47, 28.96, 23.90, 22.97, 14.08, 11.08. HRMS: $m/z=602.8273$ [M^+].

Polymerization of polymer 2D-PBTCl.

To a 25 mL flask, compound M3 (155.84 mg, 0.18 mmol), compound M1 (100.00 mg, 0.18 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (8.10 mg, 0.007 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 (2.8 mL) and DMF (0.7 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 chlorobenzene fraction by precipitation from methanol. The solid was dried under vacuum. Yield: 148.13 mg (85.59%). GPC: $M_w=66.16$ KDa; $M_n=41.37$ KDa; PDI=1.59. The polymer was thermally stable up to 361 °C (5% weight loss by TGA).

Polymerization of 2D-PBTC12. 2D-PBTC12 was prepared using the same procedure as 2D-PBTC1. Yield: 155.80 mg (92.22%). GPC: $M_w=80.30$ KDa; $M_n=41.86$ KDa; PDI=1.91. The polymer was thermally stable up to 385 °C (5% weight loss by TGA).

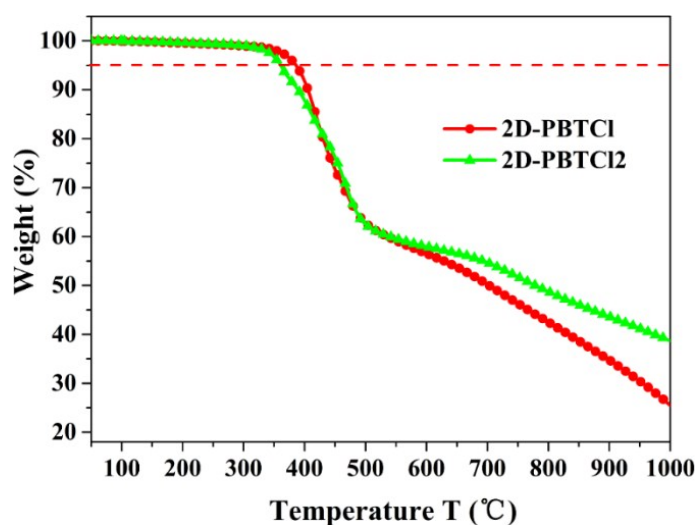


Figure S1. Thermogravimetric analysis (TGA) of the polymers.

Table S1. The optimized details and the corresponding performing parameters of the PSCs based on 2D-PBTC1: ITIC with different D/A ratios under the illumination of AM 1.5G, 100 mW cm⁻².

D/A Ratio	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (PCE _{ave}) (%)
1.5:1	0.89	14.42	54.67	7.03 (6.91)
1.25:1	0.91	14.77	58.40	7.82 (7.67)

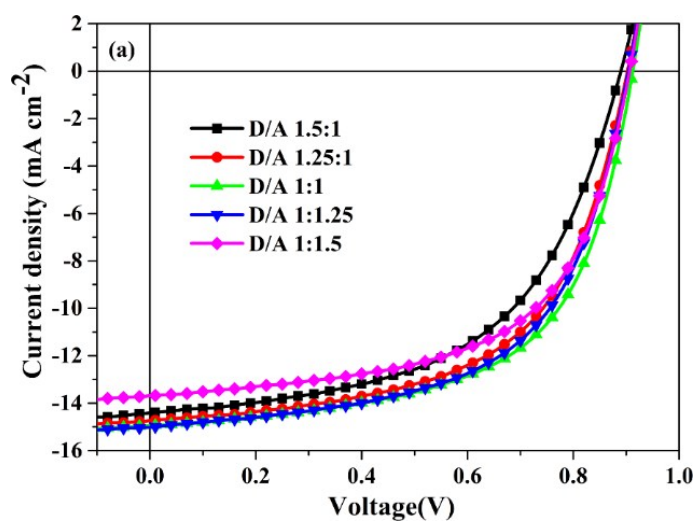
1:1	0.90	15.33	61.40	8.42 (8.31)
1:1.25	0.90	14.93	59.08	8.00 (7.89)
1:1.5	0.91	13.75	59.45	7.45 (7.31)

^aThe average device PCE obtained from more than 15 devices.

Table S2. The optimized details and the corresponding performing parameters of the PSCs based on 2D-PBTCl: ITIC with different DIO volume under the illumination of AM 1.5G, 100 mW cm⁻².

DIO (v%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	$PCE(PCE_{ave})$ (%)
0%	0.91	15.01	59.95	8.22(8.09)
0.25%	0.90	15.27	61.64	8.48(8.32)
0.5%	0.88	15.59	57.78	7.94(7.81)
0.75%	0.86	14.91	52.40	6.72(6.61)
1%	0.86	13.95	50.08	6.02(5.88)

^aThe average device PCE obtained from more than 15 devices.



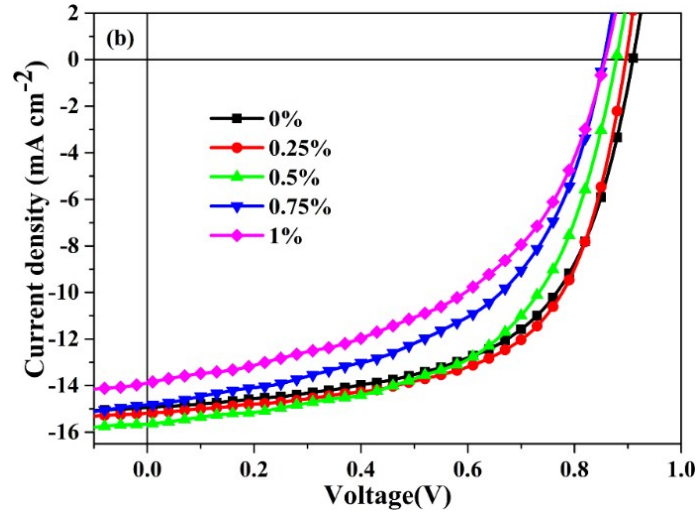


Figure S2. The J - V curves for the PSCs based on 2D-PBTCl a) with different D/A ratios and b) different DIO contents under the illumination of AM 1.5G (100 mW cm^{-2}).

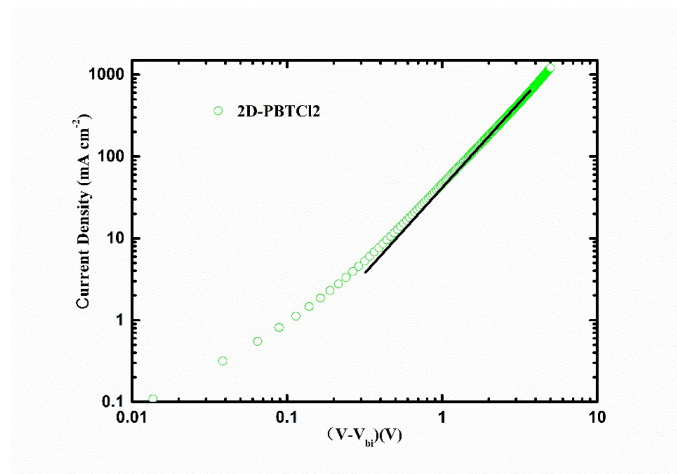
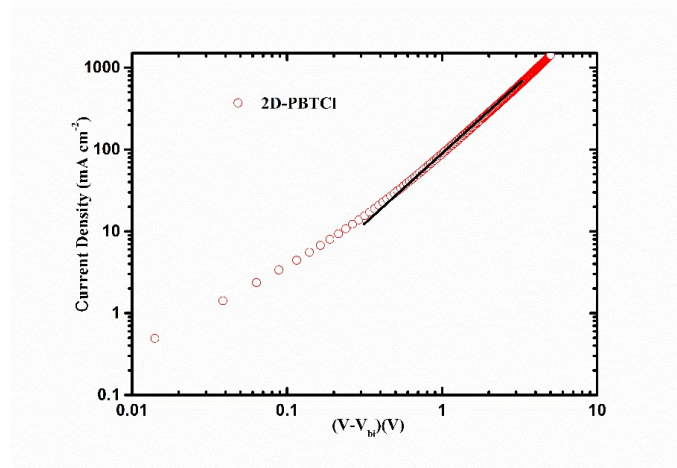


Figure S3. J - V plots for the devices ITO/PEDOT:PSS/polymer:ITIC/MoO₃/Ag. 2D-PBTCl and 2D-PBTCl2. (The symbols are experimental data for transport of hole, and

the black lines are fitted according to the space-charge-limited-current model).

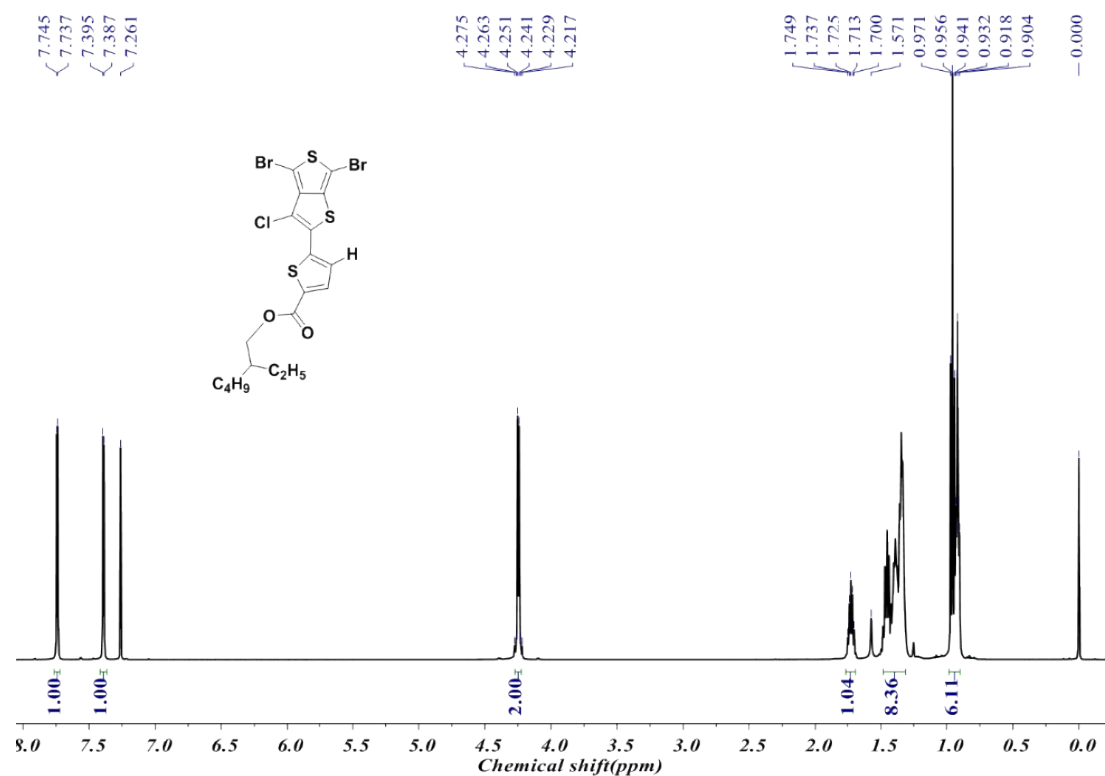


Figure S4. ¹H NMR spectrum of compound M1.

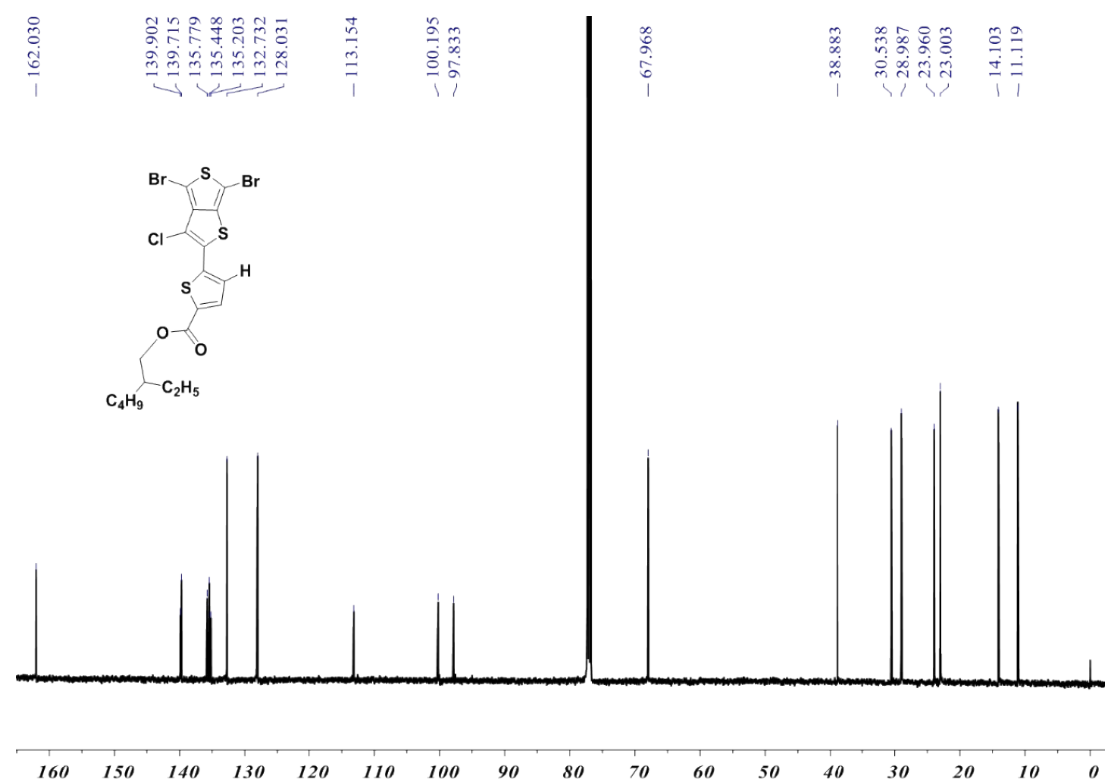


Figure S5. ¹³C NMR spectrum of compound M1.

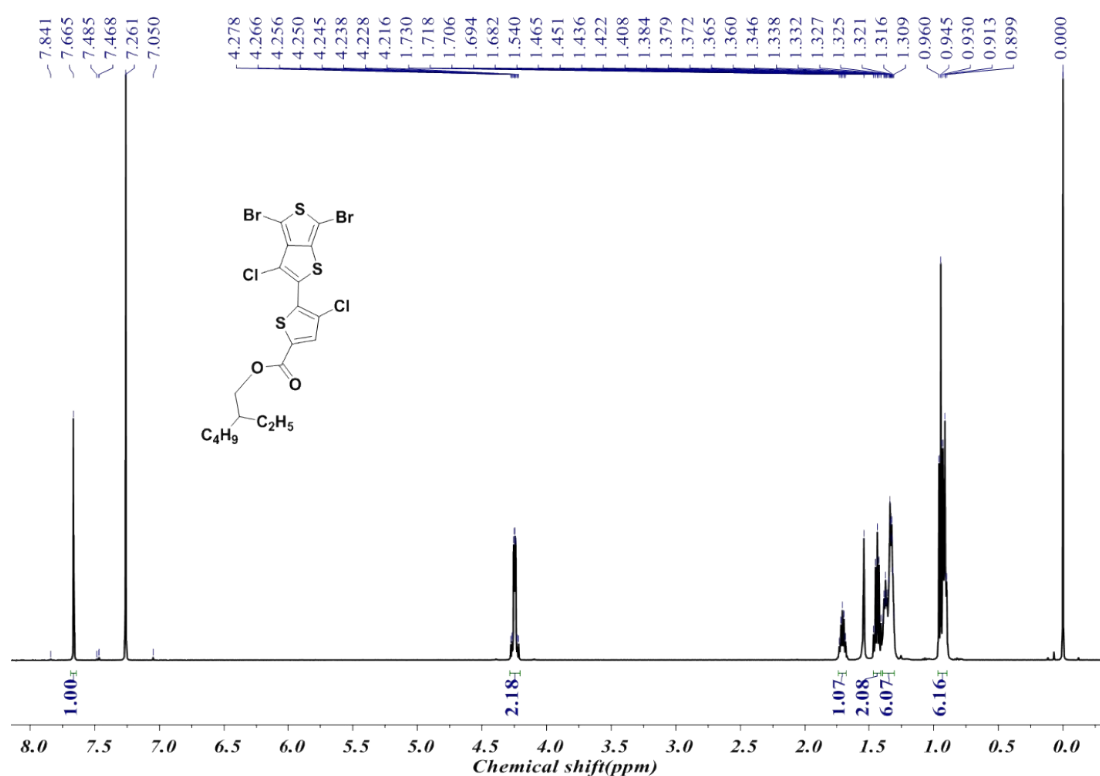


Figure S6. ^1H NMR spectrum of compound M2.

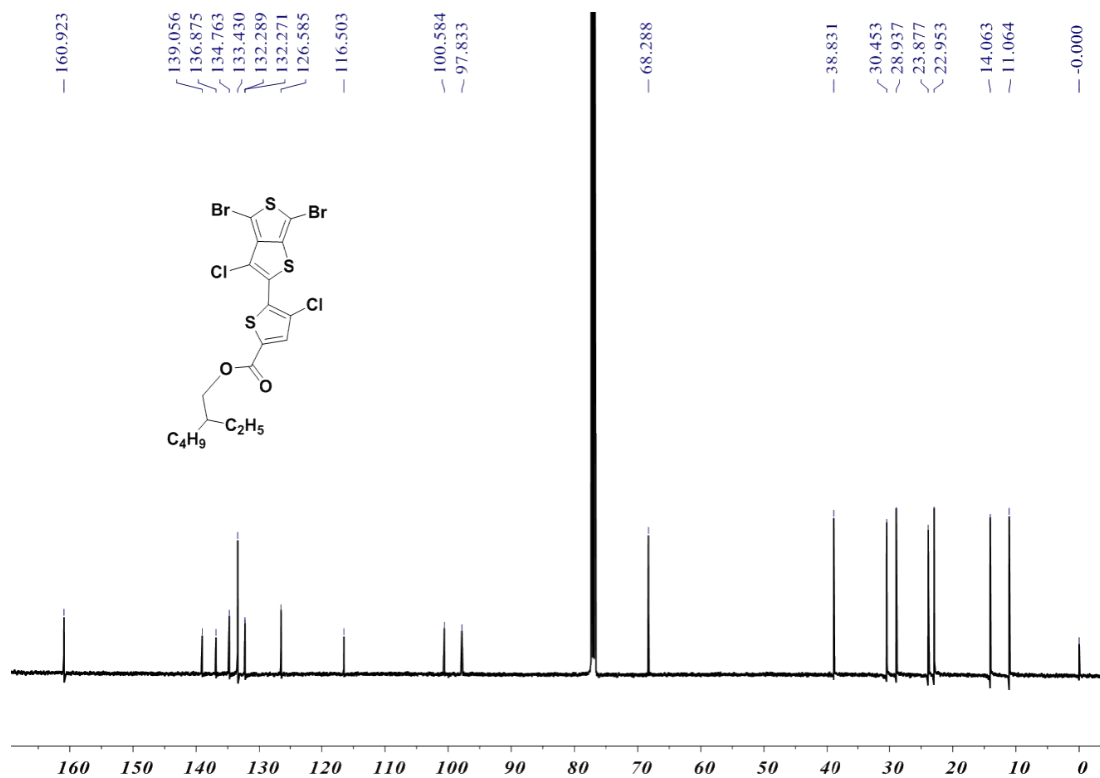


Figure S7. ^{13}C NMR spectrum of compound M2.

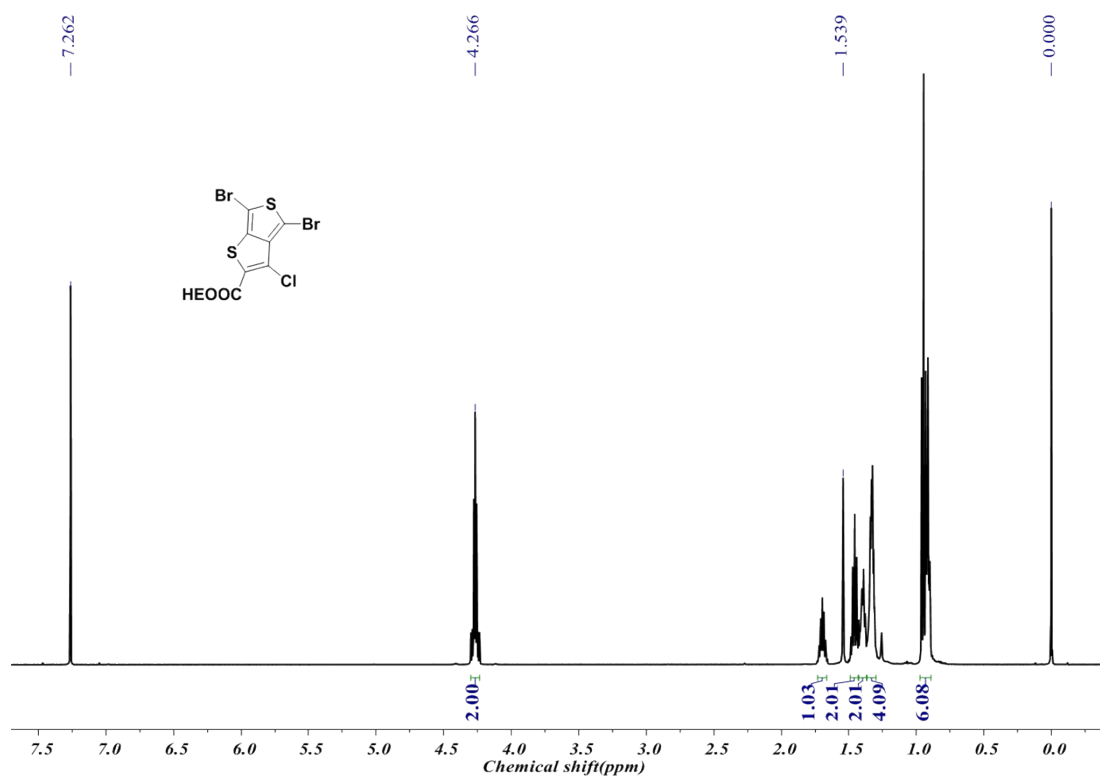


Figure S8. ^1H NMR spectrum of compound M3.

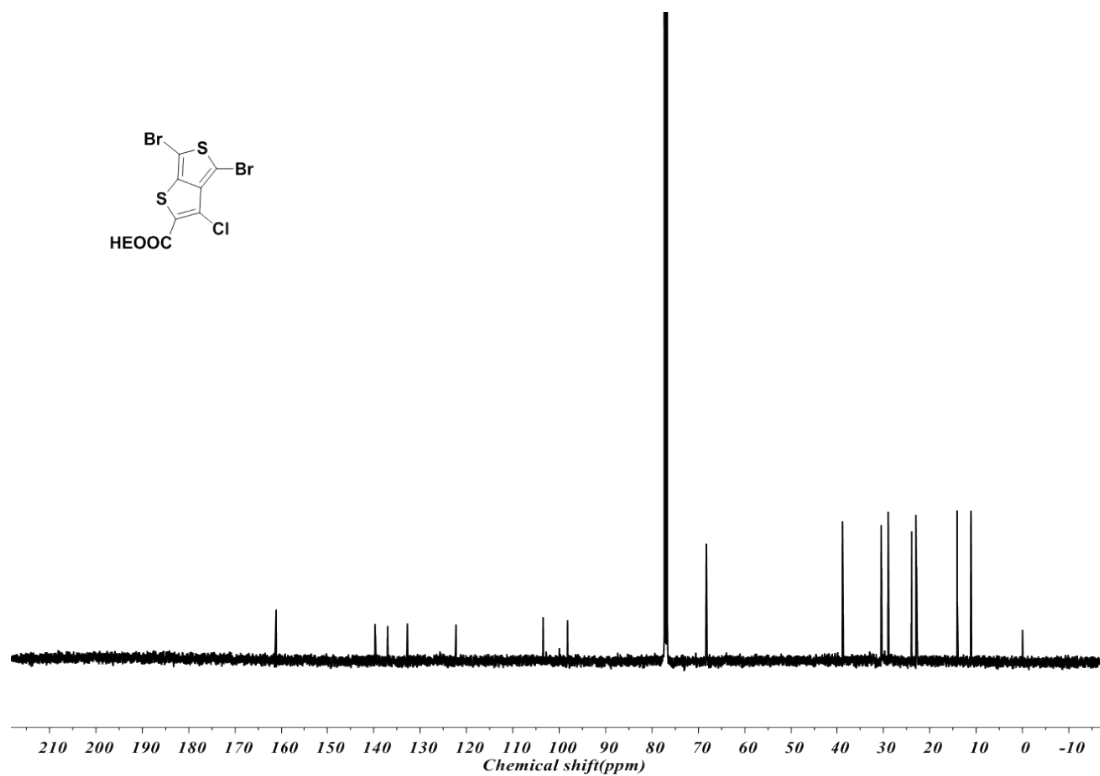


Figure S9. ^{13}C NMR spectrum of compound M3.

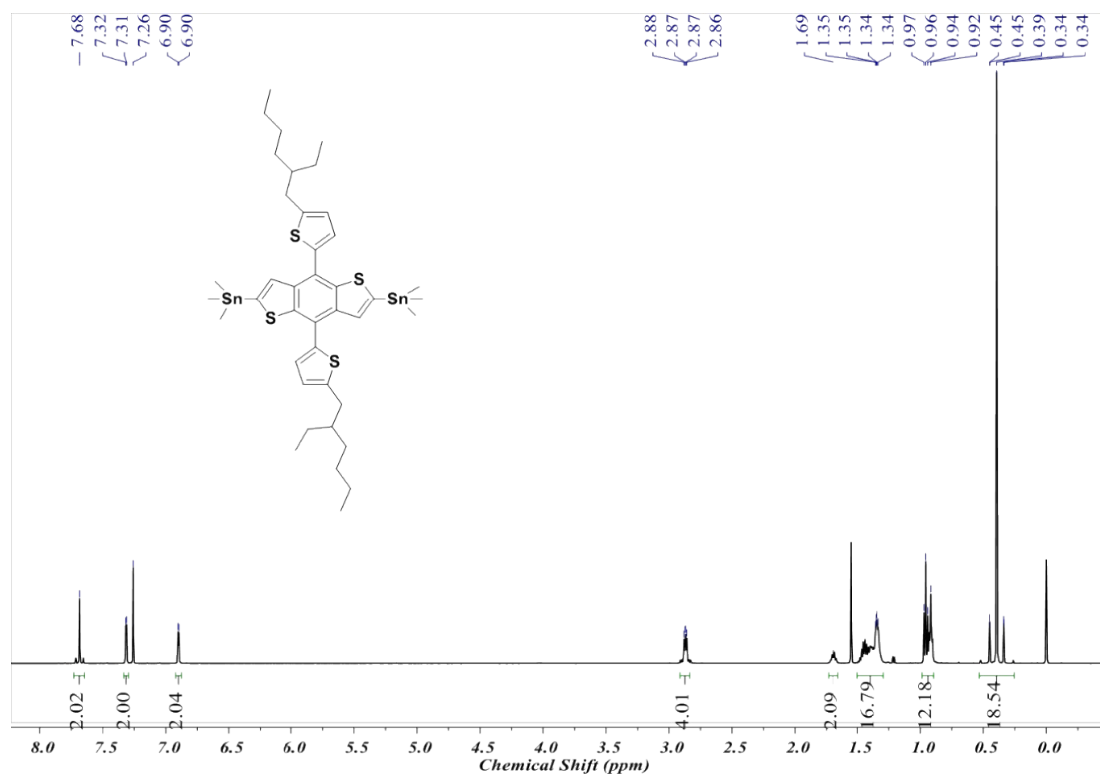


Figure S10. ^1H NMR spectrum of compound M4.

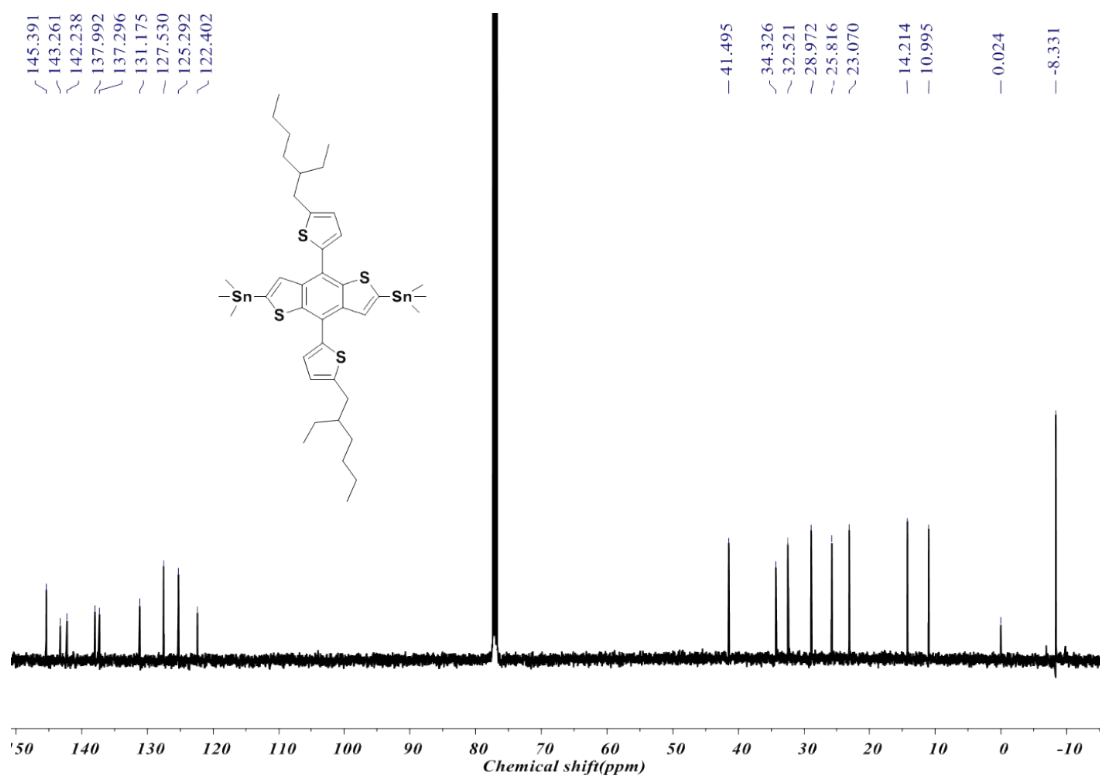


Figure S11. ^{13}C NMR spectrum of compound M4.

Reference

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