

Supporting Information

Fine Turning of Open-Circuit Voltage by Chlorination in Thieno[3,4-*b*]thiophene-Benzodithiophene Terpolymers toward Enhanced Solar Energy Conversion

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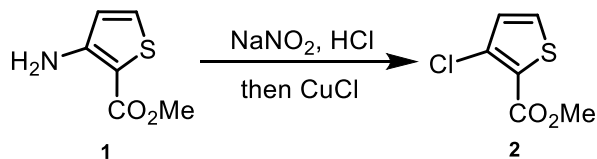
E-mail: hef@sustc.edu.cn; wchen@anl.gov

General Experimental:

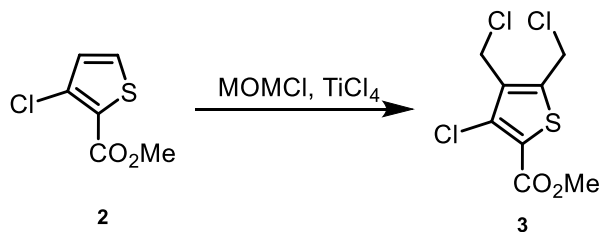
Non-aqueous reactions were carried out under inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents in oven-dried reaction vessels. Reagents were purchased from commercial sources and used without further purification. $\text{Pd(PPh}_3)_4$ was purchased from Strem Chemicals Inc. About solvents, THF (tetrahydrofuran) and toluene were distilled from Na/benzophenone prior to use; DCM (dichloromethane) and chloroform (anhydrous, Aladdin) were purified by solvent purification system (Innovative Technology, Inc.) prior to use, DMF (dimethylformamide) was purchased from J&K Scientific and used without further purification. Flash column chromatography was performed using the indicated solvents on E. Qingdao silica gel 60 (230 – 400 mesh ASTM). TLC was carried out using pre-coated sheets (Qingdao silica gel 60-F250, 0.2 mm) which, after development, were visualized at 254 nm, and/or staining in *p*-anisole, KMnO_4 , or phosphomolybdic acid solution followed by heating. NMR spectra were recorded on Bruker Avance 400 MHz or AV 500 MHz spectrometers. Chemical shifts were reported in parts per million (ppm), relative to either a tetramethylsilane (TMS) internal standard or the signals due to the solvent purchased from Cambridge Isotope Laboratories, Inc. Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad) and coupling constants (Hz). Gel permeation chromatography (GPC) was performed at 40 °C on a Malvern Viscotek 270max system equipped with a UV detector, using polystyrene as the standard and THF as the eluent.

Synthesis of Monomer and Polymers:

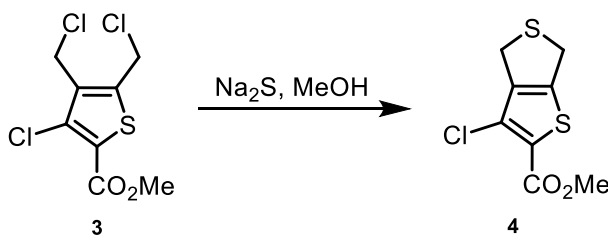
Units BDT-T and TT-F were synthesized according to reported procedures.¹⁻⁴



Methyl 3-chlorothiophene-2-carboxylate (2). Methyl 3-aminothiophene-2-carboxylate **1** (37.60 g, 240 mmol) was added gradually to a vigorously stirred 6M hydrochloric acid solution (100 mL). The reaction mixture was stirred for 30 min at room temperature and then cooled to $-20\text{ }^\circ\text{C}$ (ice-salt bath). It was diazotised with sodium nitrite (16.80 g, 240 mmol) in water (50 mL). The resulting diazonium salt was stirred for 1 h at $-20\text{ }^\circ\text{C}$ and was then poured into a well stirred solution of cuprous chloride (23.76 g, 240 mmol in concentrated hydrochloric acid (100 mL)) at $-20\text{ }^\circ\text{C}$. The reaction mixture was heated at $60\text{ }^\circ\text{C}$ for 1.5 h and cooled down, and then repeatedly extracted with ether ($3 \times 150\text{ mL}$). The product was washed with water and dried over magnesium sulfate and evaporated to dryness, and the residue was purified by crystallization to give **2** (37.84 g, 89%) as a white solid. **TLC:** $R_f = 0.6$ (silica gel, EtOAc/hexane = 1:4). **^1H NMR** (400 MHz, CDCl_3) δ 7.48 (d, $J = 5.3\text{ Hz}$, 1H), 7.02 (d, $J = 5.3\text{ Hz}$, 1H), 3.90 (s, 3H) ppm. **^{13}C NMR** (101 MHz, CDCl_3) δ 161.10, 131.71, 130.42, 130.22, 125.57, 52.24 ppm.

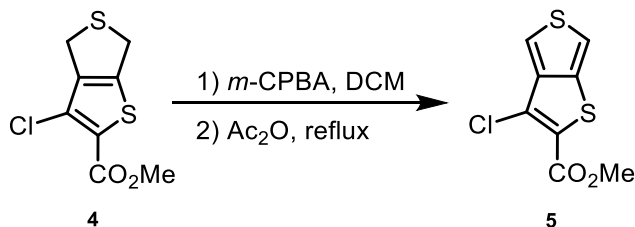


Methyl 3-chloro-4,5-bis(chloromethyl)thiophene-2-carboxylate (3). To a mixture of **2** (30.90 g, 175 mmol) and chloromethyl methyl ether (79.8 mL, 1050 mmol) was added dropwise TiCl_4 (30.7 mL, 280 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 5 h. The reaction was diluted with DCM (100 mL), washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4 (s). The organic phase was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, EtOAc/hexane = 1:10) to afford crude **3**, which was further purified by crystallization in n-hexane to give **3** (38.0 g, 79%) as a white solid. **TLC:** R_f = 0.6 (silica gel, EtOAc/hexane = 1:5). **^1H NMR** (400 MHz, CDCl_3) δ 4.80 (s, 2H), 4.64 (s, 2H), 3.92 (s, 3H) ppm. **^{13}C NMR** (101 MHz, CDCl_3): δ 160.42, 143.40, 135.57, 131.49, 125.72, 52.49, 37.40, 35.26 ppm.

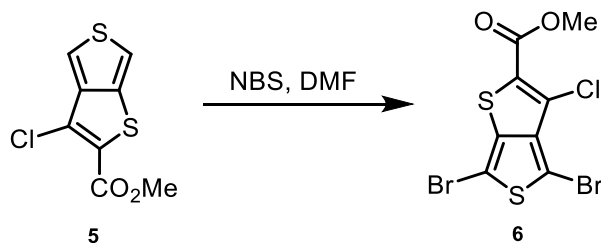


Methyl 3-chloro-4,6-dihydrothieno[3,4-b]thiophene-2-carboxylate (4). To a solution of **3** (35.6 g, 130 mmol) in 450 mL methanol was heated and kept mild boiling. Sodium sulfide (10.7 g, 136.5 mmol) in 900 mL methanol was added dropwise in 5 h. The reaction mixture was refluxed over night. After cooling to room temperature, the solvent was removed *in vacuo*. The residue was diluted with DCM (150 mL), washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4 (s). The organic phase was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, EtOAc/hexane = 1:10) to afford **4** (15.5 g, 51%) as a white solid. **TLC:** R_f = 0.6 (silica gel, EtOAc/hexane = 1:5). **^1H NMR** (400 MHz, CDCl_3) δ

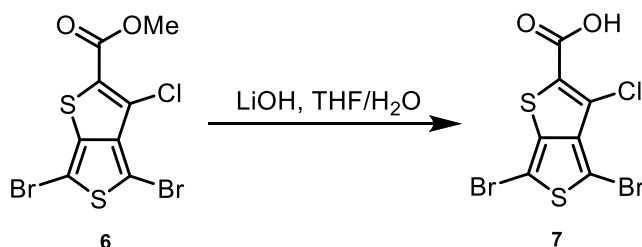
4.23 (t, $J = 3.1$ Hz, 2H), 4.02 (t, $J = 3.0$ Hz, 2H), 3.89 (d, $J = 0.9$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 160.99, 144.03, 143.94, 128.89, 126.41, 52.21, 34.57, 32.88 ppm.



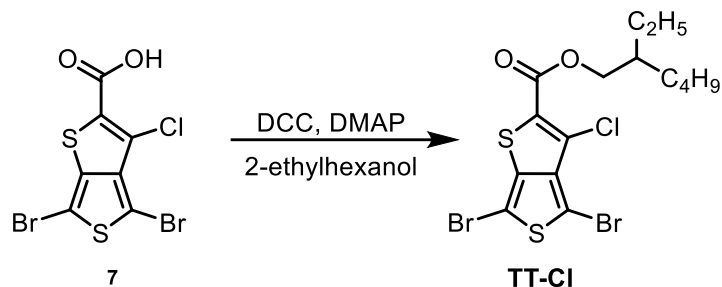
*Methyl 3-chlorothieno[3,4-*b*]thiophene-2-carboxylate (5).* To a solution of **4** (11.7 g, 50 mmol) in 250 mL DCM at -78 °C was added dropwise a solution of *m*-CPBA (8.72 g, 50 mmol) in 100 mL DCM. The reaction mixture was then warm to room temperature and stirred over night. The mixture was washed with *sat.* NaHCO_3 (aq.) (3×30 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 (s). The organic phase was concentrated *in vacuo* and the residue was refluxed in acetic anhydride for 5 h. After cooling to room temperature, the solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/hexane = 1:10) to afford **5** (10.3 g, 89%) as a white solid. TLC: $R_f = 0.6$ (silica gel, EtOAc/hexane = 1:4). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 2.8$ Hz, 1H), 7.33 (d, $J = 2.8$ Hz, 1H), 3.94 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3): δ 162.03, 145.21, 134.76, 130.35, 121.95, 117.15, 112.96, 52.56 ppm.



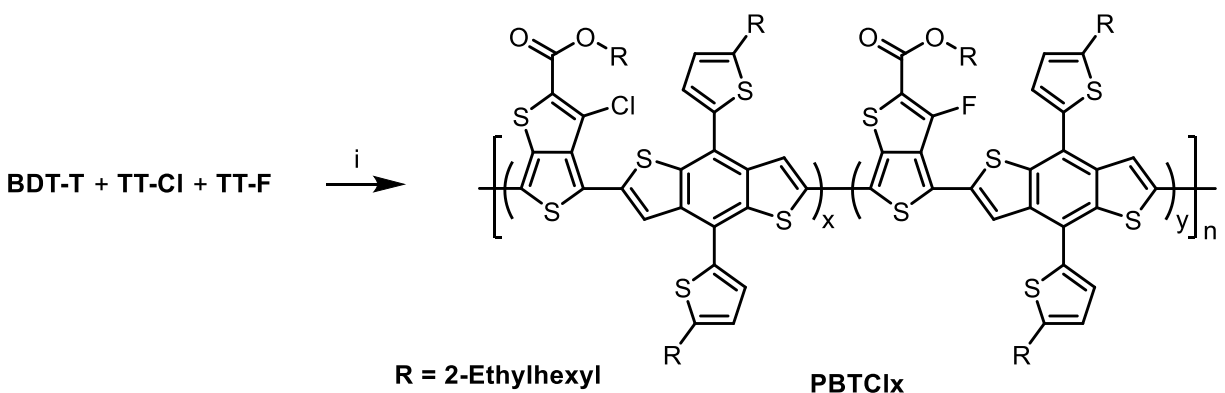
*Methyl 4,6-dibromo-3-chlorothieno[3,4-*b*]thiophene-2-carboxylate (6).* To a solution of **5** (7.50 g, 32.4 mmol) in 500 mL THF at room temperature was added dropwise a solution of NBS (14.40 g, 81.0 mmol) in 140 mL DMF under nitrogen protection at dark. The reaction mixture was heated up to 40 °C and stirred for 24 h. Then it was cooled down and poured to *sat.* NaHSO₃ (aq.) at 0 °C. The mixture was extracted with DCM (2 × 60 mL), washed with brine (50 mL), dried over anhydrous Na₂SO₄ (s). The organic phase was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, DCM/hexane = 1:2) to afford **6** (11.56 g, 91%) as a white solid. TLC: R_f = 0.3 (silica gel, DCM/hexane = 1:2). ¹H NMR (400 MHz, CDCl₃) δ 3.94 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 161.38, 139.58, 136.96, 131.97, 122.70, 103.68, 98.29, 52.80 ppm.



*4,6-dibromo-3-chlorothieno[3,4-*b*]thiophene-2-carboxylic acid (7).* To a solution of **6** (10.53 g, 26.96 mmol) in THF/H₂O (570 mL, 2/1) was added LiOH (3.23 g, 134.79 mmol) at room temperature. The reaction mixture was refluxed for 4 h. After cooling to room temperature, the THF was removed *in vacuo*. The residue was acidified with 1N HCl and filtered to afford **7** (10.05 g, 99%) as a white solid. ¹³C NMR (101 MHz, DMSO-*d*₆): δ 162.10, 139.48, 136.34, 134.65, 120.54, 104.13, 99.42 ppm.



*2-ethylhexyl 4,6-dibromo-3-chlorothiopheno[3,4-*b*]thiophene-2-carboxylate (TT-Cl).* To a solution of **7** (376.5 mg, 1.0 mmol), DCC (247.4 mg, 1.2 mmol) and DMAP (146.6 mg, 1.2 mmol) in DCM (5 mL) was added 2-ethylhexan-1-ol (0.79 mL, 5 mmol) at room temperature. The reaction mixture was stirred for 24 h under Ar protection. The reaction was diluted with DCM (30 mL), washed with water (10 mL) and brine (10 mL), dried over anhydrous Na₂SO₄ (s). The organic phase was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, DCM/hexane = 1:10) to afford TT-Cl (317.6 mg, 65%) as a yellow oil. **TLC:** *R_f* = 0.2 (silica gel, hexane). **¹H NMR** (400 MHz, CDCl₃) δ 4.33 – 4.22 (m, 2H), 1.70 (m, 1H), 1.51 – 1.28 (m, 8H), 0.99 – 0.86 (m, 6H) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 161.18, 139.69, 135.99, 132.75, 122.25, 103.49, 98.22, 68.31, 38.80, 30.46, 28.95, 23.90, 22.97, 14.08, 11.11 ppm.



Synthesis of the copolymers PBTClx by Stille Coupling. Units BDT-T (162.8 mg, 0.18 mmol), TT-F and TT-Cl were weighted into a 25 mL one-neck round-bottom flask. Pd(PPh₃)₄ (8.3 mg, 0.0072 mmol) was added. The flask was subjected to three successive cycles of vacuum followed by refilling with argon. Then anhydrous DMF (0.54 mL) and anhydrous toluene (2.7 mL) were added via a syringe. The polymerization was carried out at 120 °C for 24 h under argon protection. The raw product was precipitated into methanol and collected by filtration. The precipitate was dissolved in chloroform and filtered through Celite to remove the metal catalyst. The crude polymer was washed with methanol, acetone and *n*-hexanes in a Soxhlet apparatus to remove the oligomers. Finally the polymer was extracted with chloroform. The polymer solution was condensed to about 5 mL and slowly poured in methanol (150 mL). The precipitate was collected and dried *in vacuo* overnight to yield PBTClx as dark purple solid.

The unit ratios of TT-Cl to TT-F are 100:0, 75:25, 50:50, 25:75, 20:80, 10:90 and 0:100, and the corresponding copolymers were named **PBTCl**, **PBTCl75**, **PBTCl50**, **PBTCl25**, **PBTCl20**, **PBTCl10** and PTB7-Th respectively.

PBTCl: Yield (97.5%). GPC: $M_n = 24.0$ kDa, $M_w = 103.3$ kDa, PDI = 4.3. ¹H NMR (400 MHz, CDCl₂CDCl₂, 80 °C) δ 7.38 (b, 1H), 7.21 (b, 1H), 6.87 – 6.73 (b, 2H), 6.44 – 6.26 (b, 2H), 3.71 (b, 2H), 2.41 – 2.18 (b, 4H), 1.25 – 1.06 (b, 3H), 0.92 – 0.73 (b, 28H), 0.37 (b, 14H) ppm.

PBTCl75: Yield (93.2%). GPC: $M_n = 58.6$ kDa, $M_w = 117.4$ kDa, PDI = 2.0. ¹H NMR (400 MHz, CDCl₂CDCl₂, 80 °C) δ 7.38 (b, 1H), 7.20 (b, 1H), 6.81 (b, 2H), 6.38 (b, 2H), 3.70 (b, 2H), 2.32 (b, 4H), 1.15 (b, 3H), 0.83 (b, 32H), 0.44 – 0.23 (b, 10H) ppm.

PBTCl50: Yield (99.0%). GPC: $M_n = 90.1$ kDa, $M_w = 271.4$ kDa, PDI = 3.0. ^1H NMR (400 MHz, $\text{CDCl}_2\text{CDCl}_2$, 80 °C) δ 7.41 (b, 1H), 7.20 (b, 1H), 6.81 (b, 2H), 6.39 (b, 2H), 3.71 (b, 2H), 2.34 (b, 4H), 1.16 (b, 3H), 0.83 (b, 24H), 0.45 – 0.28 (b, 18H) ppm.

PBTCl25: Yield (99.0%). GPC: $M_n = 98.4$ kDa, $M_w = 348.4$ kDa, PDI = 3.5. ^1H NMR (400 MHz, $\text{CDCl}_2\text{CDCl}_2$, 80 °C) δ 7.40 (b, 1H), 7.19 (b, 1H), 6.80 (b, 2H), 6.38 (b, 2H), 3.70 (b, 2H), 2.27 (b, 4H), 1.16 (b, 3H), 0.84 (b, 24H), 0.47 – 0.21 (b, 18H) ppm.

PBTCl20: Yield (99.0%). GPC: $M_n = 75.2$ kDa, $M_w = 236.4$ kDa, PDI = 3.1. ^1H NMR (400 MHz, $\text{CDCl}_2\text{CDCl}_2$, 80 °C) δ 7.42 (b, 1H), 7.19 (b, 1H), 6.80 (b, 2H), 6.38 (b, 2H), 3.70 (b, 2H), 2.35 (b, 4H), 1.16 (b, 3H), 0.84 (b, 24H), 0.38 (b, 18H) ppm.

PBTCl10: Yield (99.0%). GPC: $M_n = 60.7$ kDa, $M_w = 197.4$ kDa, PDI = 3.3. ^1H NMR (400 MHz, $\text{CDCl}_2\text{CDCl}_2$, 80 °C) δ 7.42 (b, 1H), 7.19 (b, 1H), 6.80 (b, 2H), 6.38 (b, 2H), 3.70 (b, 2H), 2.35 (b, 4H), 1.16 (b, 3H), 0.83 (b, 29H), 0.37 (b, 14H) ppm.

PTB7-Th^[4]: Yield (99.0%). GPC: $M_n = 58.3$ kDa, $M_w = 249.2$ kDa, PDI = 4.3.

Measurements:

Thermal Analysis: Thermal gravimetric analysis (TGA) was performed using a TA Instruments at a heating rate of 10 °C/min using 1-3 mg of sample in a 100 μL platinum pan (under nitrogen).

Absorption Spectra: The absorption spectra were measured with a UV-Vis-IR spectrophotometer (Shimadzu, UV3600). The solutions that were used for the UV-visible spectroscopy measurements were dissolved in chloroform at a concentration of 10 $\mu\text{g mL}^{-1}$. The films were drop-coated from the chloroform solution onto a quartz substrate.

Cyclic Voltammetry (CV) Measurements: The Cyclic Voltammetry (CV) measurements were carried out using an electrochemical workstation (CHI600E) to determine the HOMO and LUMO levels of the polymers and fullerene derivatives. Polymer films were dip-coated from chloroform solutions on a Pt working electrode (2 mm in diameter). CV curves were measured under an argon atmosphere using solutions in CH₃CN containing 0.1 M Bu₄NPF₆ with a Pt wire as the counter electrode and Ag/Ag⁺ as the reference electrode. The redox potential of ferrocene/ferrocene⁺ (Fc/Fc⁺) under the same conditions is located at 0.044 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:

$$E_{\text{HOMO}} = -E_{\text{ox}} + [(-4.8)+0.044](\text{eV}) \quad (1)$$

$$E_{\text{LUMO}} = -E_{\text{red}} + [(-4.8)+0.044](\text{eV}) \quad (2)$$

Device Fabrication and Characterization: The inverted device structure was ITO/ZnO/PBTClx:PC₇₁BM /MoO₃/Ag. The ITO-coated glass substrates were cleaned in deionized water, acetone and isopropyl alcohol for 15 minutes and dried in the drying oven. The ITO glass substrate was UV-ozone for 15 minutes and then the sol-gel-derived ZnO films was spin-coated onto the ITO substrated followed by thermal treatment at 200 °C for 30 min. The mixture of PBTClx/PC₇₁BM(1:1.5 by wt/wt ratio) was dissolved in chlorobenzene(CB) with the addition of a small of DIO (97:3, v/v) to obtain 10 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 2000 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.

Power conversion efficiencies (PCEs) were tested under the illumination of AM 1.5 G at 100 mW/cm⁻² using the computer-controlled Keithley 2400 sourcemeter in a dry box under an inert atmosphere. The light intensity was calibrated by a standard silicon solar cell(certified by NREL) before testing, giving a value of 100 mW cm⁻² during the test. The current density voltage (*J-V*) characteristic of hole-only devices were conducted on computer-controlled a Keithley 236 sourcemeter under dark. The external quantum efficiency (EQE) spectra was measured using a commercial EQE measurement system (Beijing, Zolix, DSR 100UV-B).

Hole mobility of the polymers PBTC1x was determined by fitting the dark current to the model of a single carrier SCLC using the device structure ITO/PEDOT:PSS/polymers/MoO₃/Ag. The SCLC method 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 density, ε_0 is the permittivity of the free space, ε_r is the dielectric constant of the polymers, μ_h is the zero-field mobility, and d is the thickness of the active layer.

AFM and TEM characterization: The film morphology was measured using the atomic Force microscopy (AFM) studies with the tapping mode from Asylum Reserach. The film samples were spin-coated onto the ITO substrate following the method of fabrication of the polymers. Bright-field transmission electron microscopy studies were performed with a techai F30 instrument. The TEM samples were prepared directly from the films which were spincoated on PEDOT:PSS. The substrate were immersed in the deionized water. The active layer thin films were floated and subsequently transferred to a lacey carbon TEM grid (Emcn.inc).

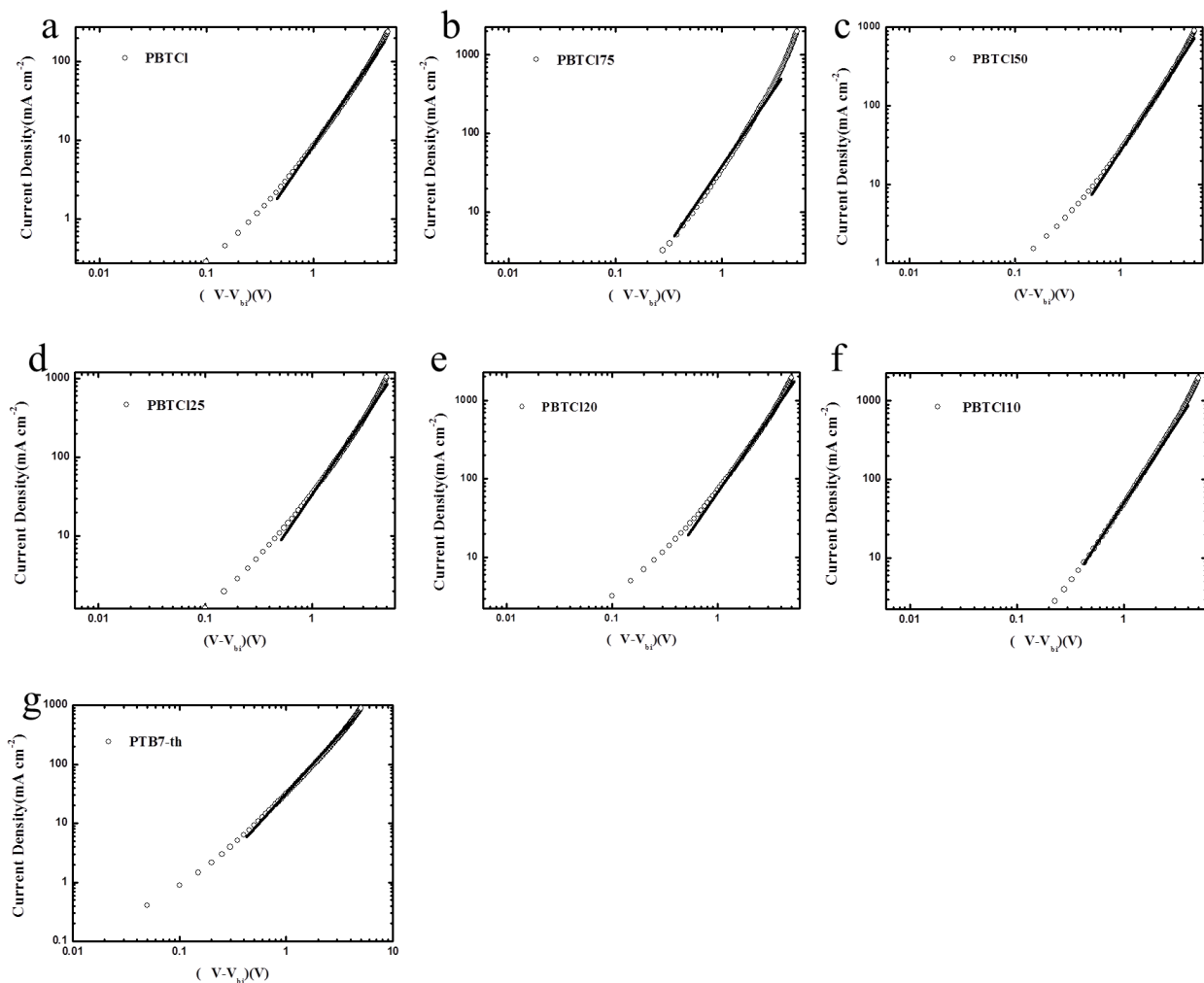


Figure S1. Plots obtained from the hole-only devices based on polymer:PC₇₁BM blend films: (a) **PBTCl:PC₇₁BM**, (b) **PBTCl75:PC₇₁BM**, (c) **PBTCl50:PC₇₁BM**, (d) **PBTCl25:PC₇₁BM**, (e) **PBTCl20:PC₇₁BM**, (f) **PBTCl10:PC₇₁BM**, (g) **PTB7-Th:PC₇₁BM**.

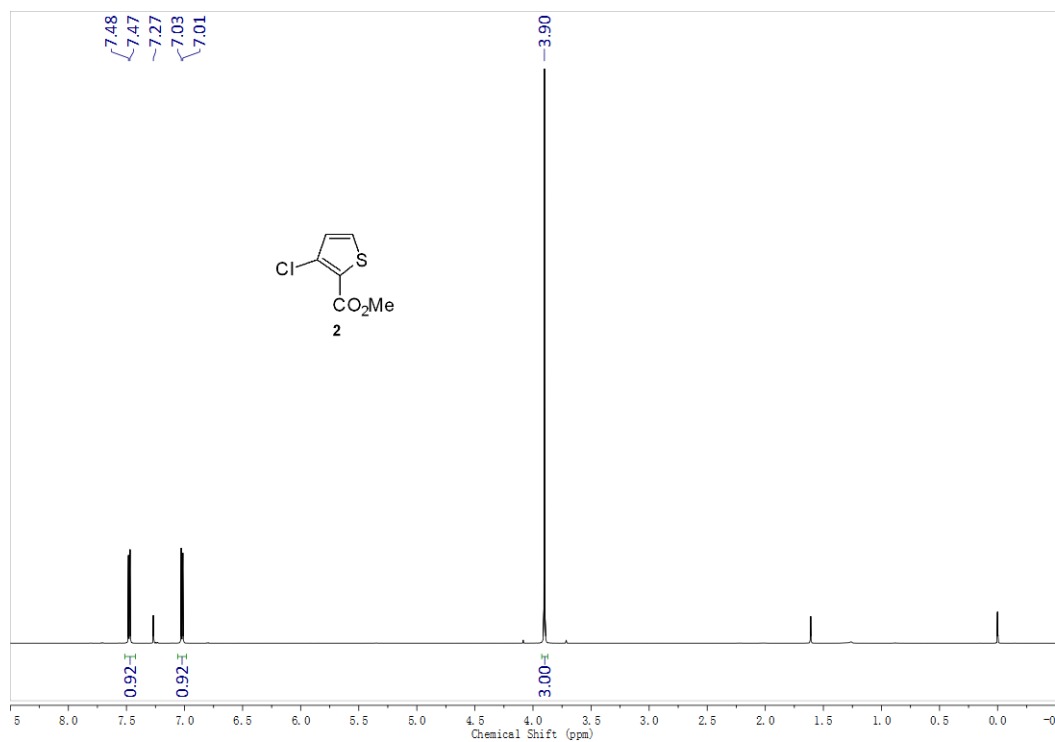


Figure S2. ¹H NMR spectrum of compound **2**.

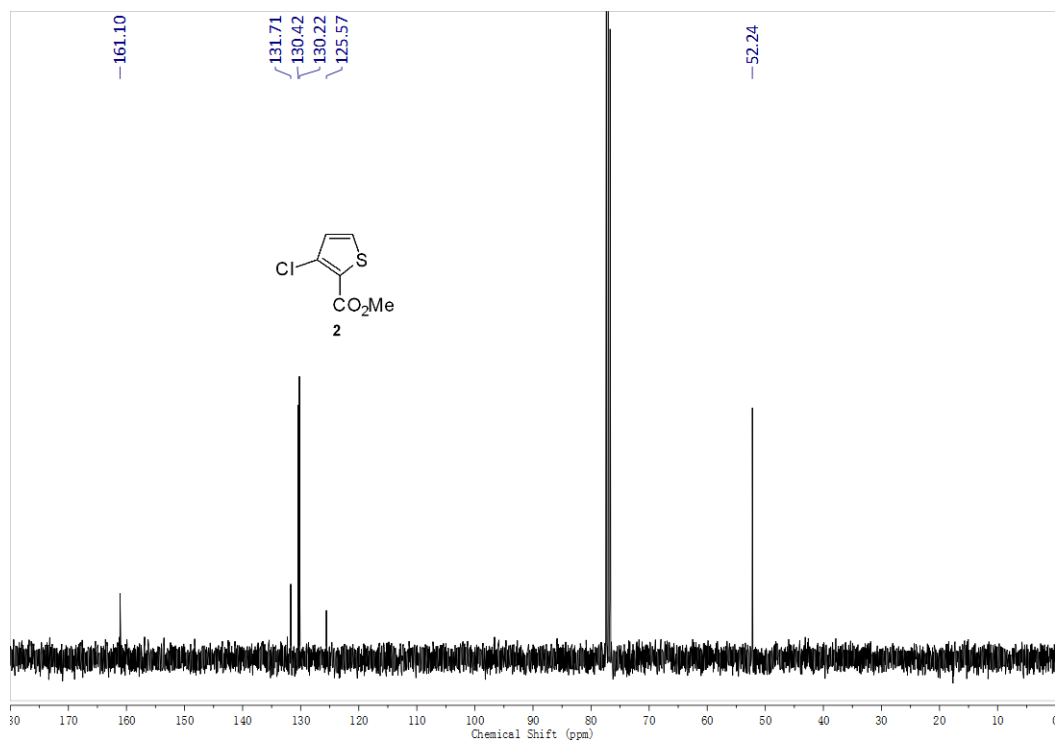


Figure S3. ¹³C NMR spectrum of compound **2**.

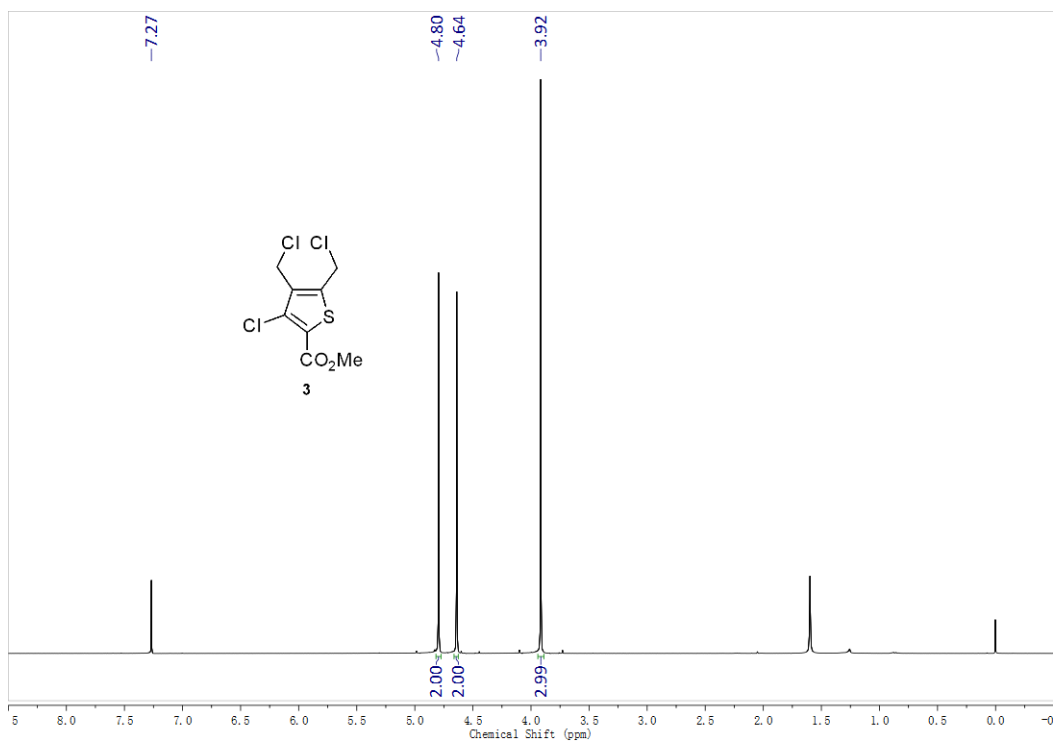


Figure S4. ¹H NMR spectrum of compound **3**.

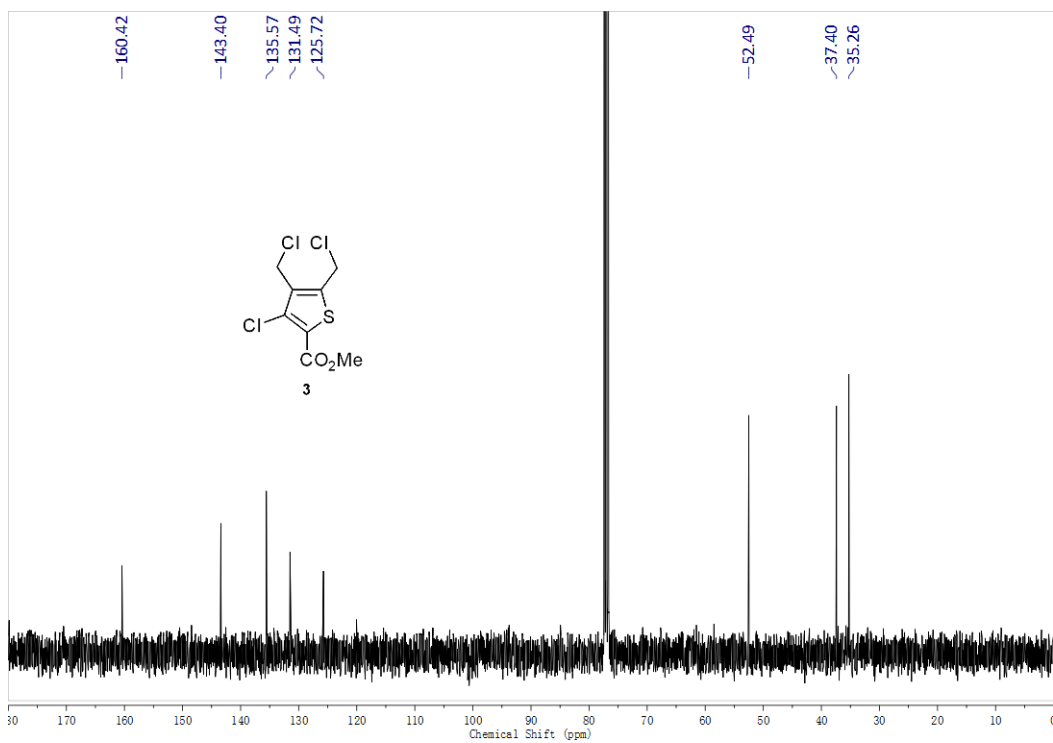


Figure S5. ¹³C NMR spectrum of compound **3**.

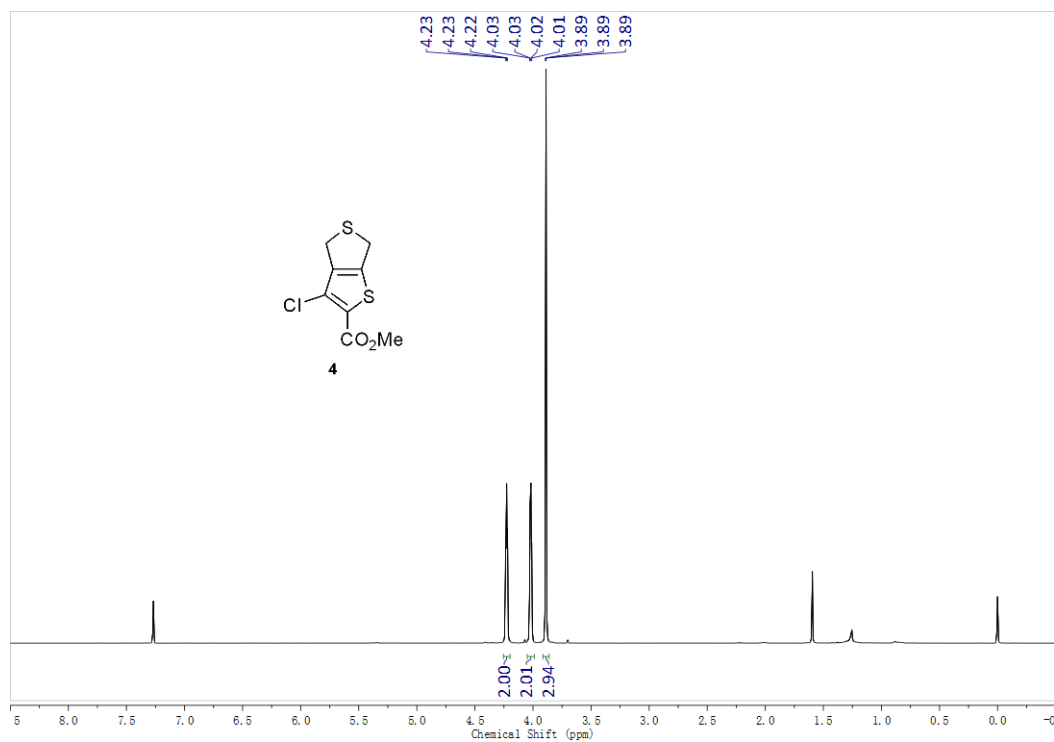


Figure S6. ¹H NMR spectrum of compound **4**.

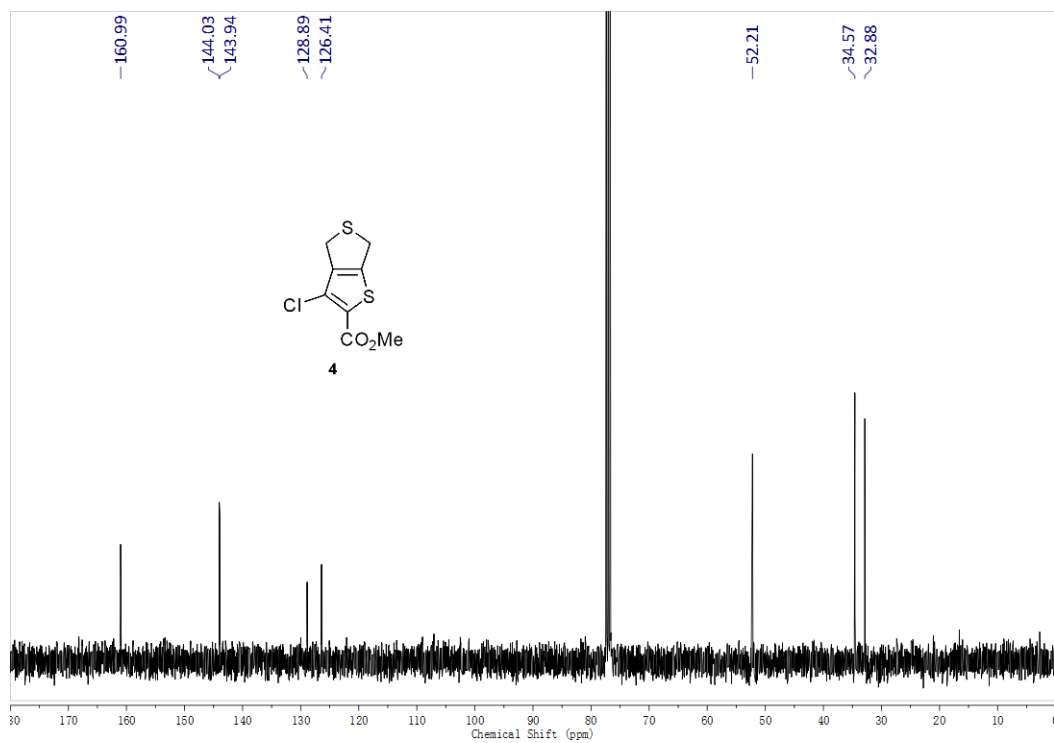


Figure S7. ¹³C NMR spectrum of compound **4**.

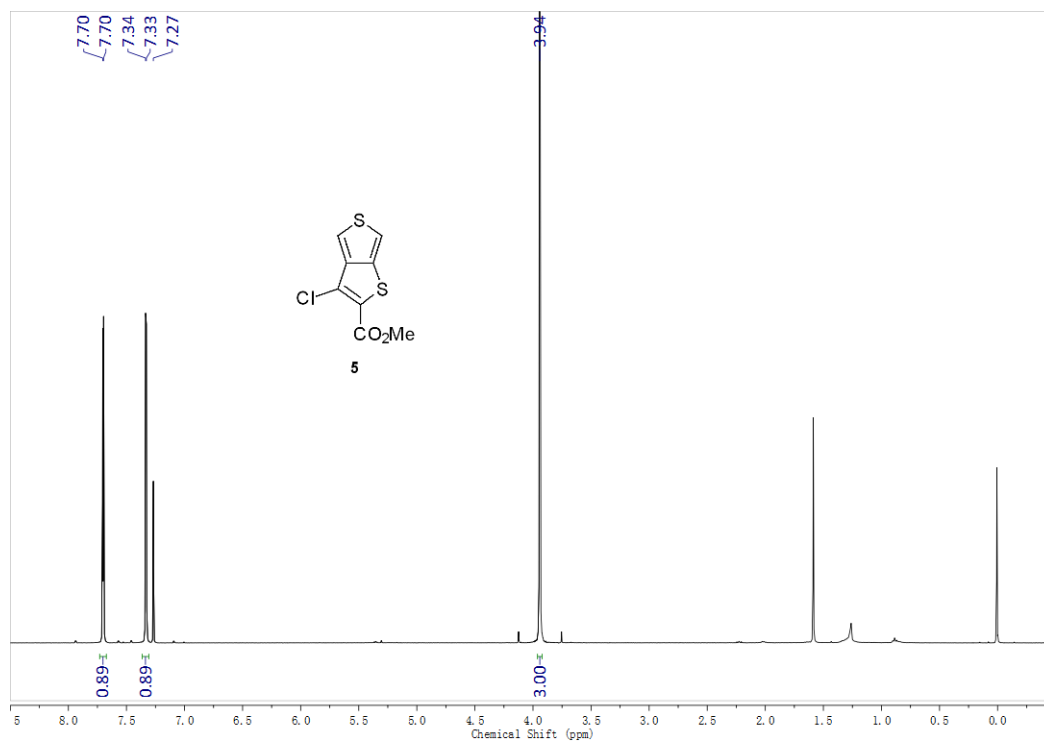


Figure S8. ^1H NMR spectrum of compound **5**.

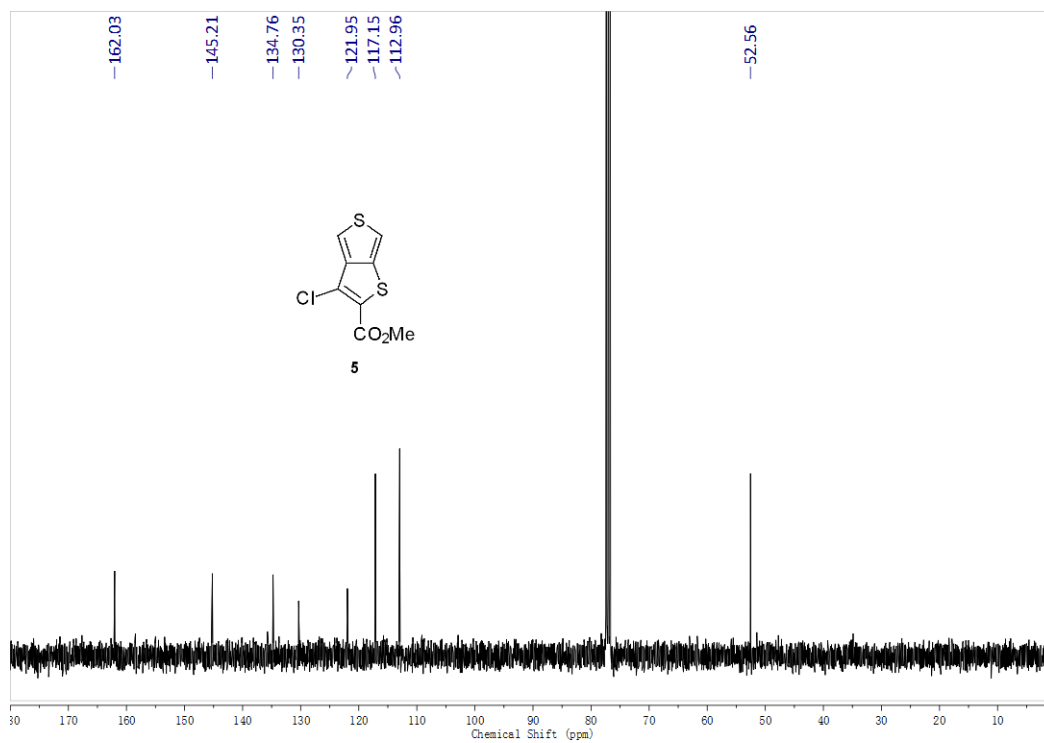


Figure S9. ^{13}C NMR spectrum of compound **5**.

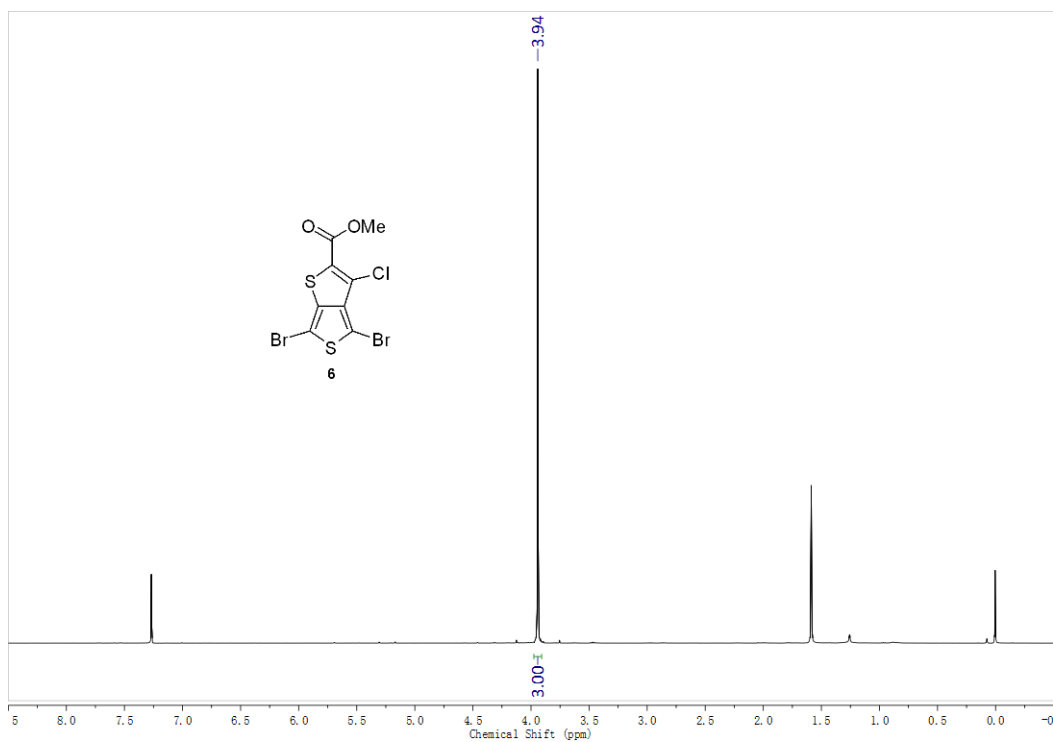


Figure S10. ¹H NMR spectrum of compound **6**.

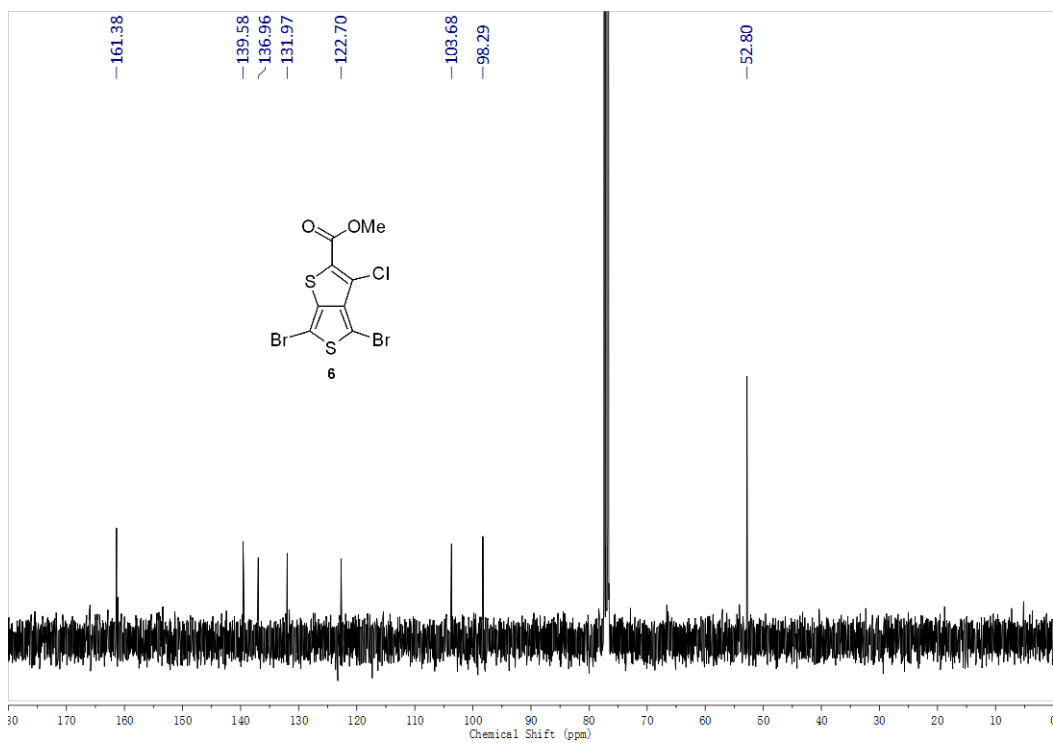


Figure S11. ¹³C NMR spectrum of compound **6**.

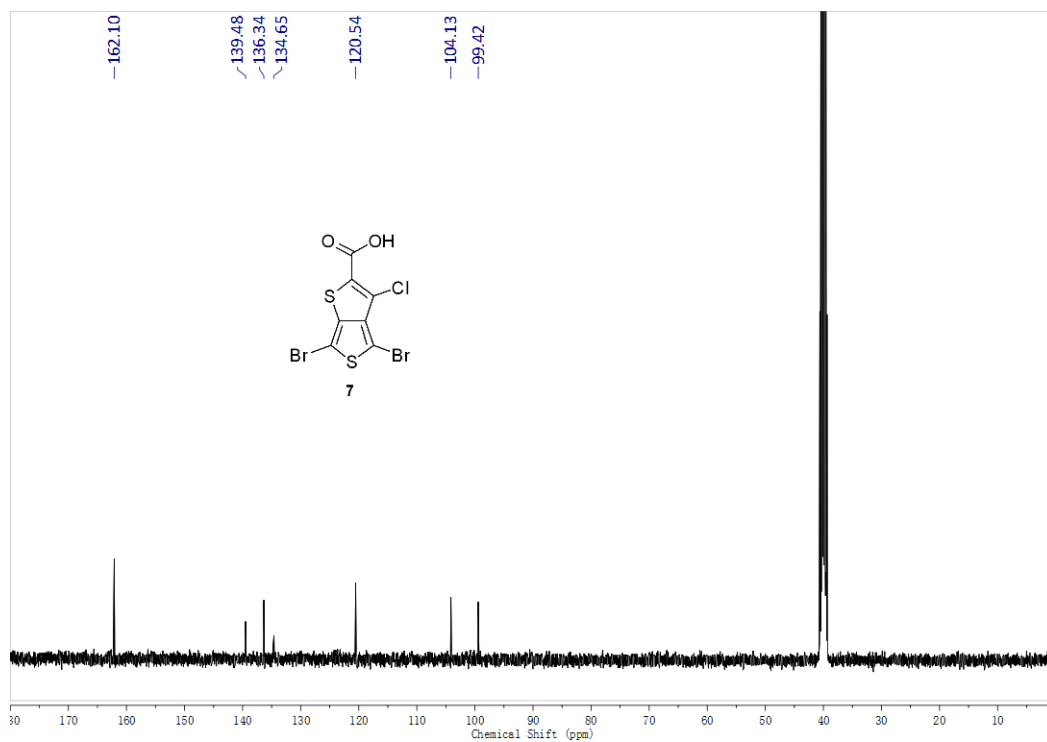


Figure S12. ¹³C NMR spectrum of compound **7**.

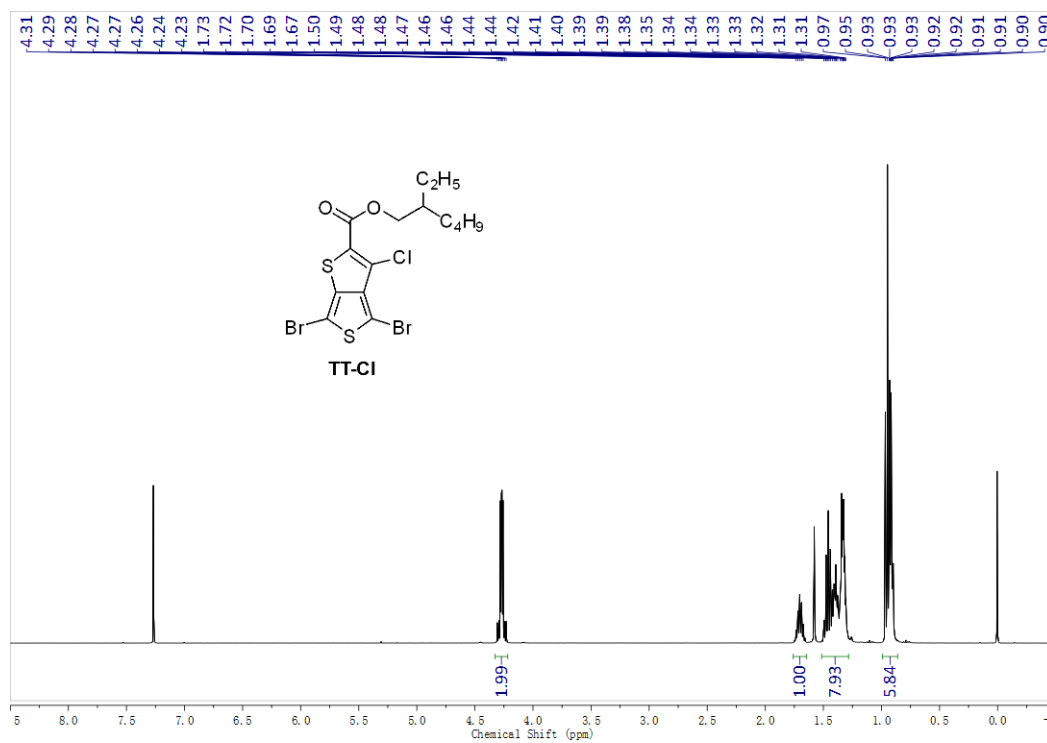


Figure S13. ¹H NMR spectrum of compound **TT-Cl**.

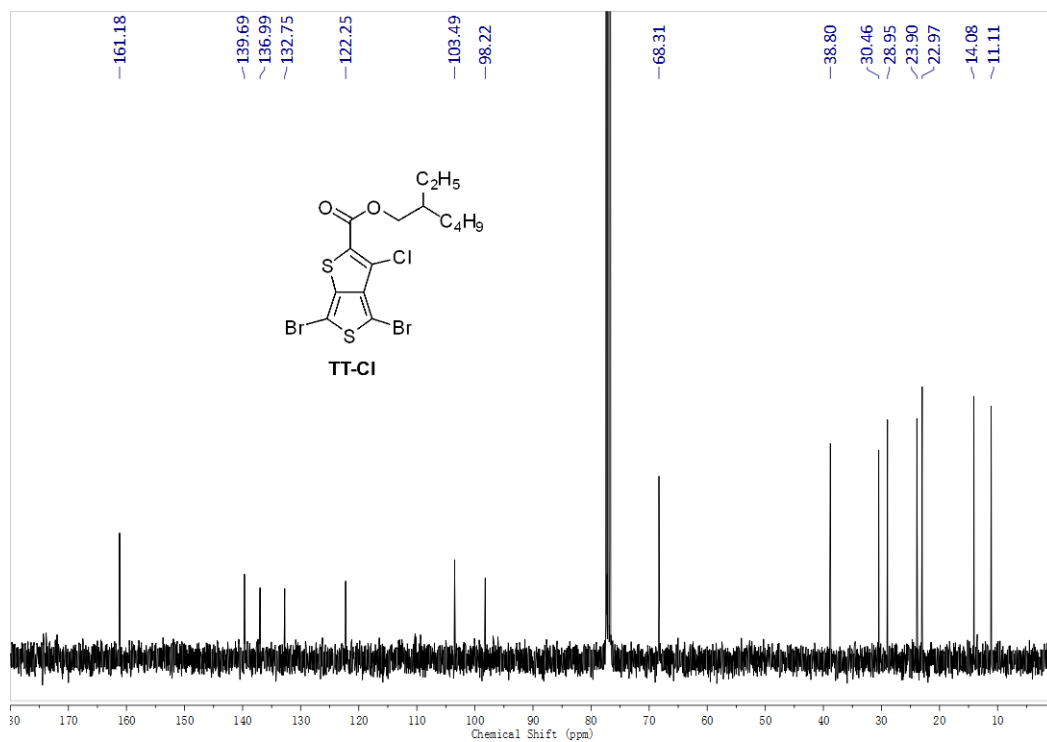


Figure S14. ^{13}C NMR spectrum of compound **TT-Cl**.

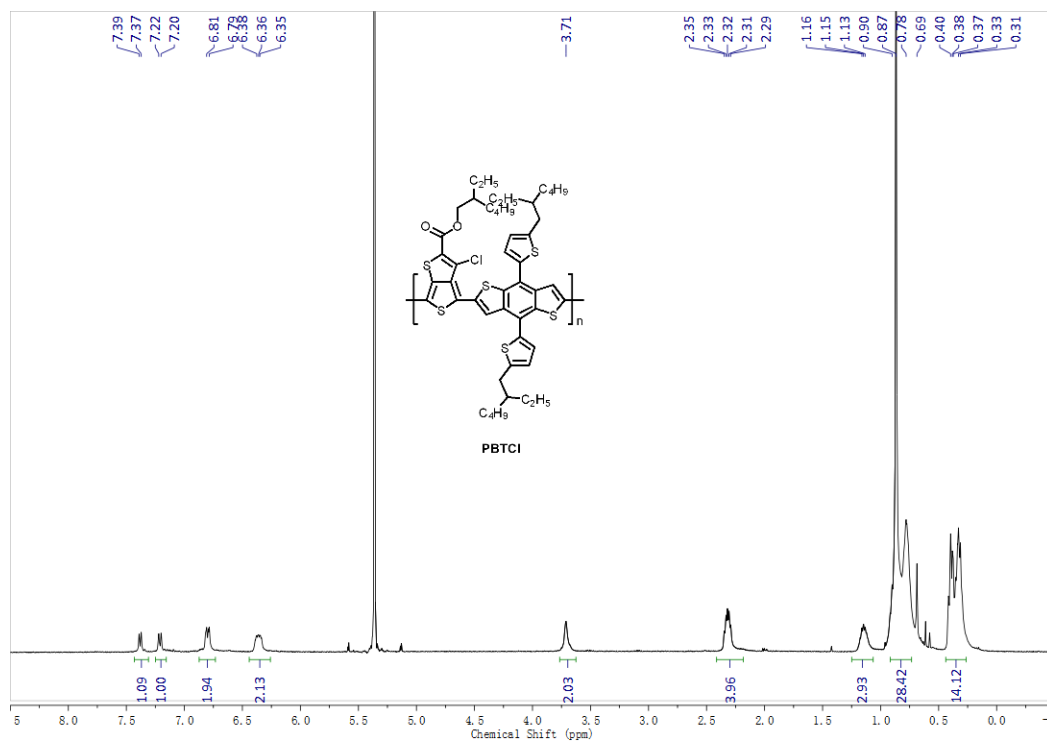


Figure S15. ^1H NMR spectrum of compound **PBTCl**.

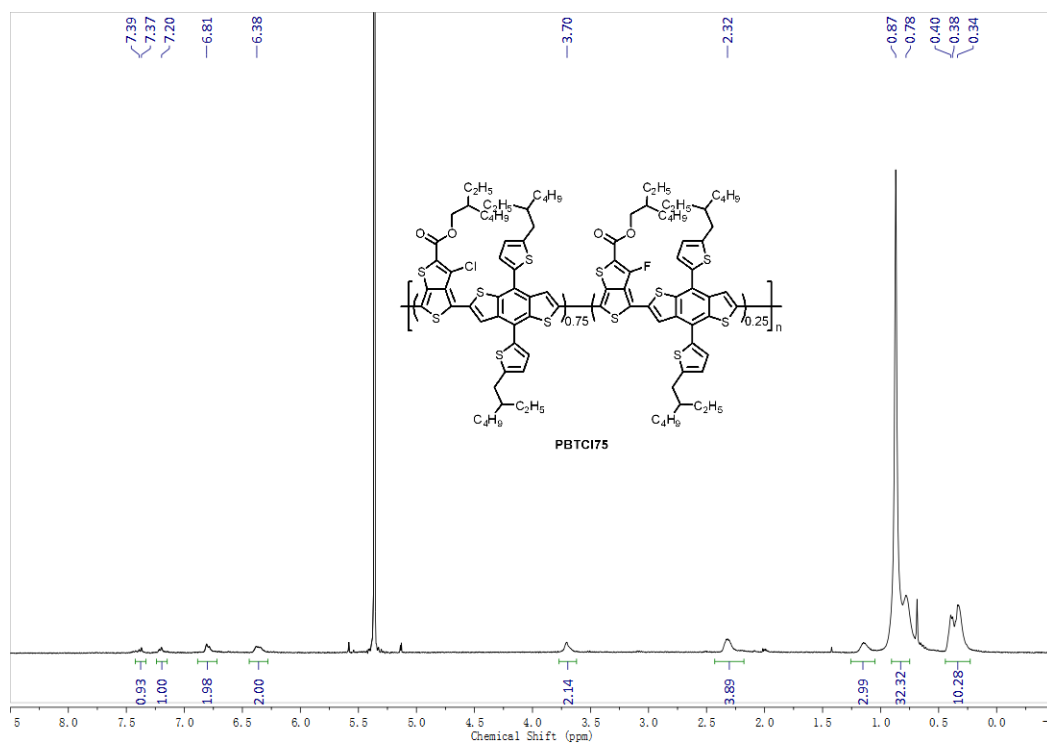


Figure S16. ^1H NMR spectrum of compound **PBTCI75**.

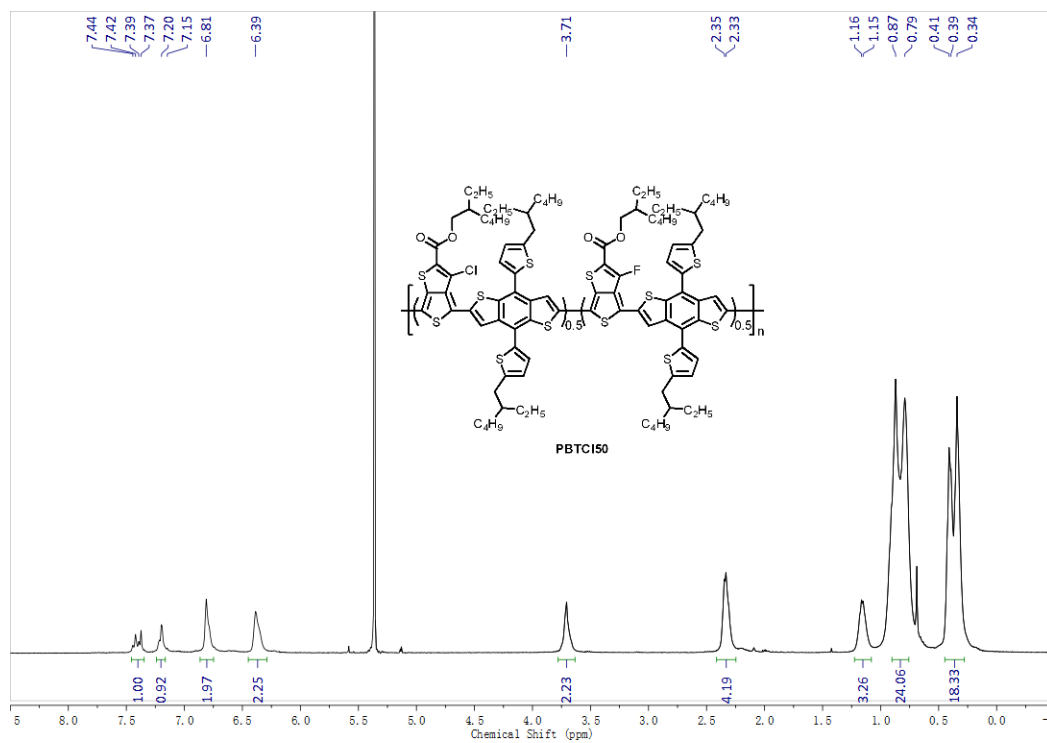


Figure S17. ^1H NMR spectrum of compound **PBTCI50**.

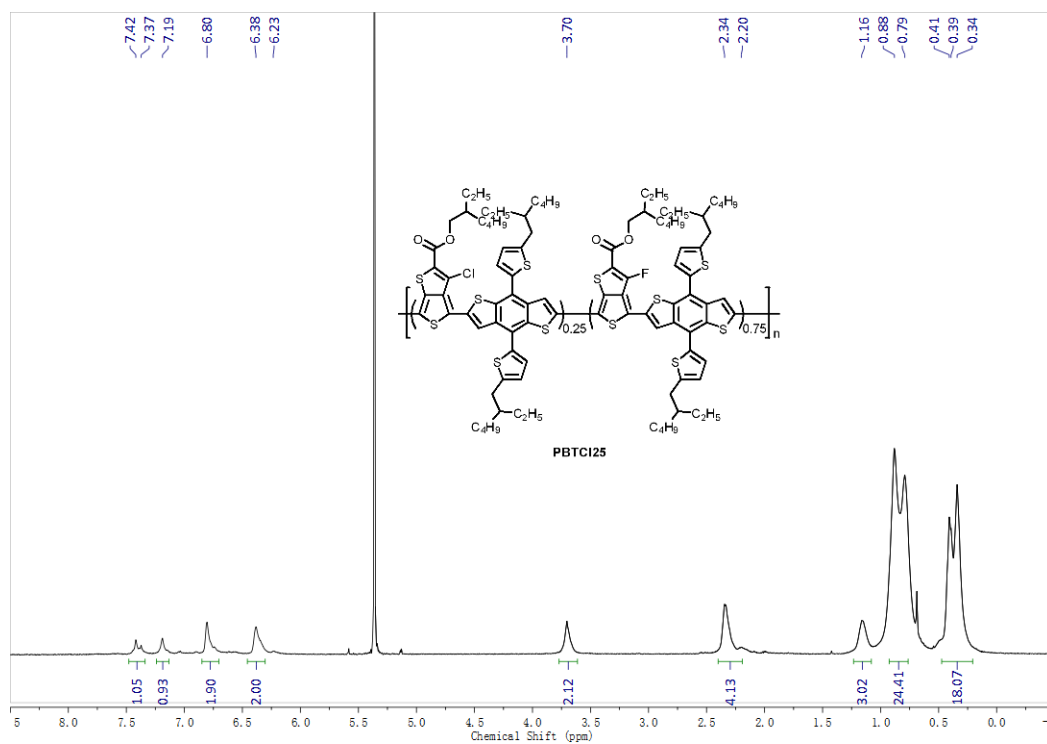


Figure S18. ¹H NMR spectrum of compound **PBTCl25**.

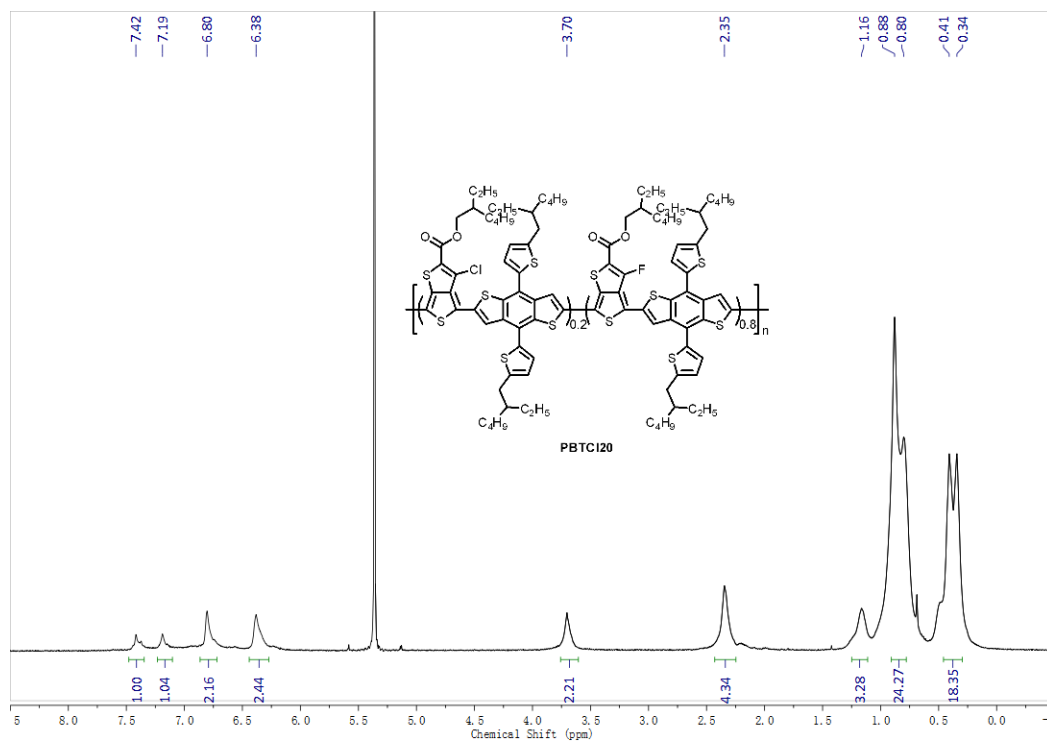


Figure S19. ¹H NMR spectrum of compound **PBTCl20**.

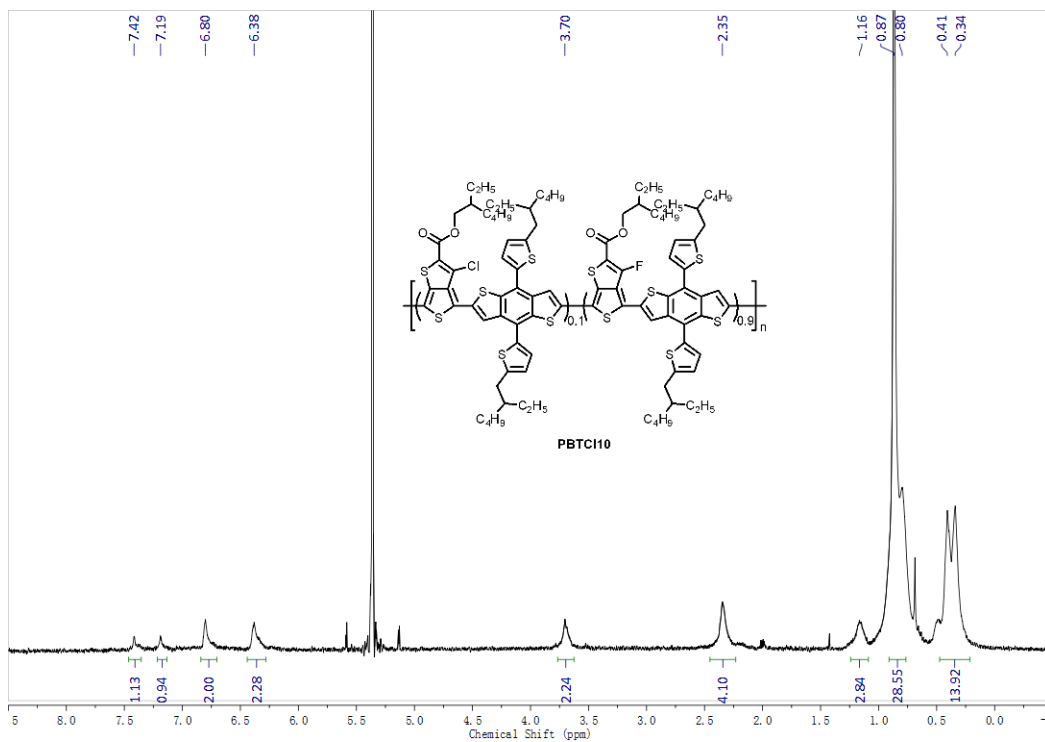


Figure S20. ^1H NMR spectrum of compound **PBTCl10**.

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