Supporting Information

Boosted photovoltaic performance of indacenothiophene-based molecular acceptor via fusing a thiophene

Pengfei Wang,[ab] Xuechen Jiao,[cd] Shengjie Xu[a], Hao Wu[ab], Christopher R. McNeill,[c] Haijun Fan,*[a] and Xiaozhang Zhu*[ab]

[a]*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[b]*University of Chinese Academy of Sciences, Beijing 100049, China*
[c]*Department of Materials Science and Engineering, Monash University, Clayton, VIC 3800, Australia*
[d]*Australian Synchrotron, Clayton, Victoria 3800, Australia*

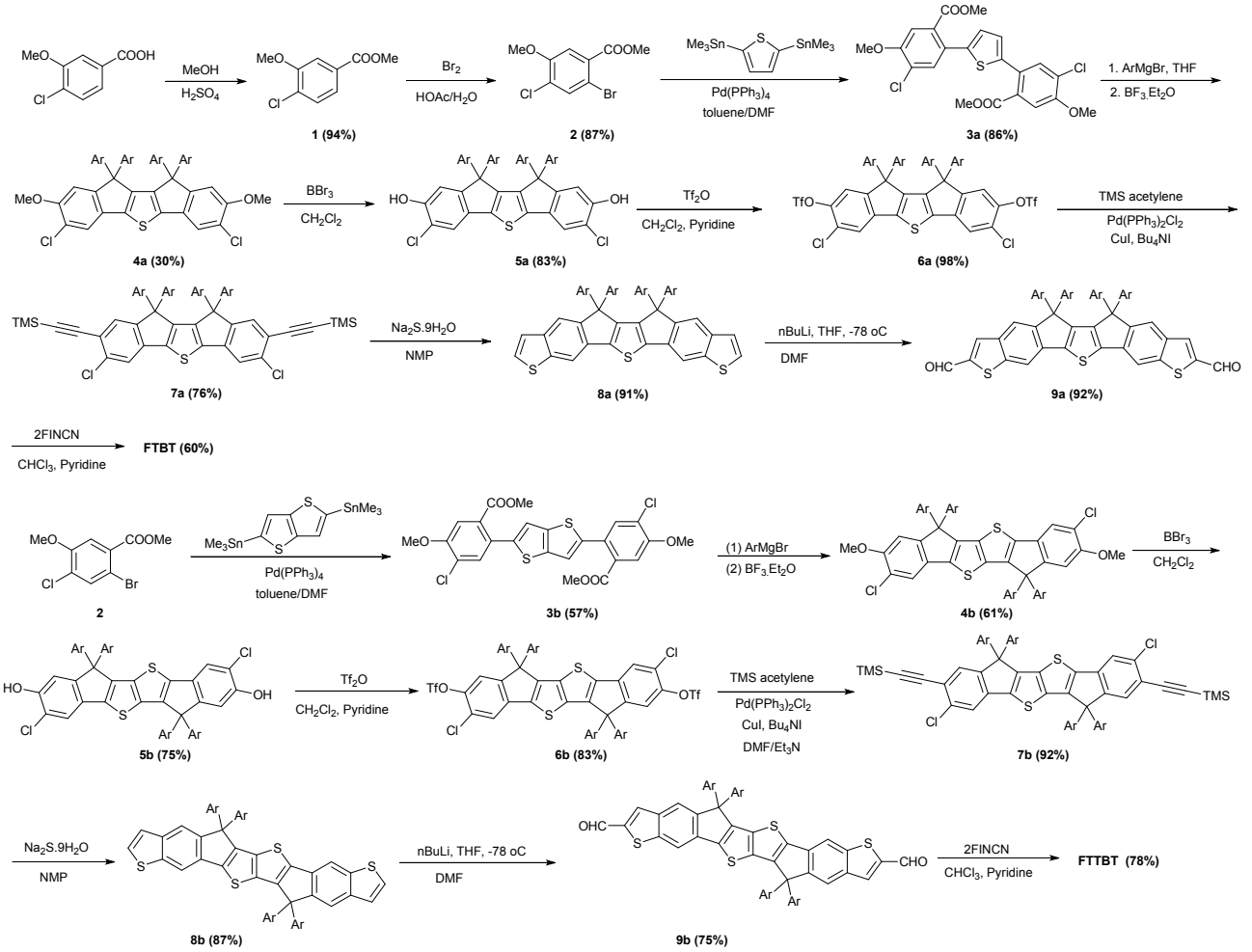
E-mail: fanhai2008@iccas.ac.cn; xzzhu@iccas.ac.cn

Materials and general methods

Unless otherwise stated, starting materials were obtained from commercial suppliers without further purification. Tetrahydrofuran (THF) was dried over Na/ benzophenone and freshly distilled prior to use. Dichloromethane (DCM) was dried over CaH_2 and freshly distilled prior to use. Super dry *N*,*N*-dimethylformamide (DMF) pyridine and acetonitrile was obtained from commercial suppliers. Polymer donor PM6 was prepared according to the reported literature.[1]

Hydrogen nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) were measured on Bruker Avance 400, Bruker Avance III 400 HD, and Bruker Avance 600 spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were recorded at 100 or 150 MHz. Chemical shifts for carbons are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: 77.0 ppm). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in Hertz (Hz), and integration. High-resolution mass spectra were measured from Bruker solariX or Thermo Scientific Exactive mass spectrometer by EI, APCI and MALDI ion source on TOF and FT analyzer. Elemental analyses were measured on Flash EA 1112 elemental analyzer. UV−vis spectra were recorded on a Jasco V-570 spectrometers. Cyclic voltammetry (CV) was performed on a CHI640D potentiostat in a conventional three-electrode cell configuration with glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, Ag/Ag+ as the reference electrode and calibrated with ferrocene/ferrocenium (Fc/Fc+) as an external potential marker in dry acetonitrile solution containing tetrabutylammonium phosphorus hexafluoride (n-Bu_4NPF_6, 0.1 M) as the supporting electrolyte, and the scan rate was 100 mV/s. Thermogravimetric analysis (TGA) measurement was performed on Netzsch STA 409 PC.

Synthesis details of FTBT and FTTBT



Scheme 1. Synthetic route of **FTBT** and **FTTBT**.

Methyl 4-chloro-3-methoxybenzoate (1)*:* A solution of 4-chloro-3-methoxybenzoic acid (3.732 g, 20 mmol) in MeOH (100 mL) and H_2SO_4 (2 mL) was refluxed overnight. After the completion of reaction, it was cooled to room temperature. Then the solution was washed with H_2O, and extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=1:1) to give the desired product **1** as a white solid (3.781 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.1 Hz, 2H), 7.42 (d, J = 8.5 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 154.9, 130.1, 129.8, 127.8, 122.5, 112.7, 56.3, 52.3. HRMS (EI) calcd for $C_9H_9O_3Cl[M]^+$ 200.0240, found: 200.0243.

Methyl 2-bromo-4-chloro-5-methoxybenzoate (2): A solution of compound **1** (3.483 g, 17.36 mmol) in HOAc (15 mL) and H_2O (15 mL) was slowly added Br_2 (1.3 mL, 1.5 equiv.) and then was allowed to stir at 60 ^{o}C overnight. After the completion of reaction, it was cooled to room temperature. Then the solution was washed with $Na_2S_2O_3.5H_2O$ aqueous solution and $NaHCO_3$ aqueous solution, and extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography

(PE:DCM=1:1) to give the desired product **2** as a white solid (4.229 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.38 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 154.1, 135.2, 130.7, 127.0, 114.3, 112.3, 56.5, 52.60. HRMS (EI) calcd for $C_9H_8O_3ClBr[M]^+$ 277.9345, found: 277.9341.

Dimethyl 6,6'-(thiophene-2,5-diyl)bis(4-chloro-3-methoxybenzoate) (3a): A mixture of 2,5-bis(trimethylstannyl)thiophene (866.2 mg, 2.114 mmol) and compound **2** (1.359 g, 2.3 equiv.) and tetrakis(triphenylphosphine)platinum (244.3 mg, 10 mol%) in dry toluene (16 mL) and *N*,*N*-dimethylformamide (4 mL) was degassed with nitrogen for 5 min, and then was stirred at 120 °C for 24 h. After the completion of reaction, it was cooled to room temperature. The mixture was washed with H_2O, extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=1:1 to 1:2) to give the desired product **3a** as a yellow solid (872.7 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.32 (s, 2H), 6.91 (s, 2H), 3.98 (s, 6H), 3.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 154.5, 141.2, 132.8, 130.6, 127.4, 126.5, 125.5, 112.9, 56.5, 52.4. HRMS (MALDI) calcd for $C_{22}H_{18}Cl_2O_6S$ $[M]^+$ 480.0196, found:480.0196

3,7-Dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-2,8-dimethoxy-10,11-dihydrodiindeno[1,2-b:2',1'-d]thiophene (4a): A solution of compound **3a** (721.5 mg, 1.5 mmol) in dry THF (20 mL) was added the freshly prepared 4-hexylphenyl-1-magnesium bromide that was prepared by slowly adding 1-bromo-4-hexylbenzene (4.341 g, 12 equiv.) to Mg (481.3 mg, 13.2 equiv.) in dry THF (20 mL), and then was refluxed for 3 h under a nitrogen atmosphere. Then the reaction was refluxed for 16 h and was cooled to room temperature. The mixture was quenched with H_2O under an ice bath, and extracted with diethyl ether. The organic phase was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue in dry dichloromethane (40 mL) was added $BF_3.Et_2O$ (3 mL) under an ice bath and a nitrogen atmosphere. The mixture was stirred for 1 h at room temperature and was poured into water. The organic phase was separated and dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=5:1) to give the desired product **4a** as a yellow solid (470.3 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 6.74 (d, J = 8.1 Hz, 8H), 6.60 (d, J = 8.2 Hz, 10H), 3.68 (s, 6H), 2.50 – 2.33 (m, 8H), 1.54 – 1.46 (m, 12H), 1.37 – 1.24 (m, 24H), 0.89 (t, J = 6.5 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 153.4, 150.5, 142.8, 140.7, 138.0, 129.9, 127.8, 127.4, 121.4, 119.3, 110.0, 64.2, 56.4, 35.5, 31.8, 31.0, 29.4, 22.7, 14.1. HRMS (MALDI) calcd for $C_{68}H_{78}Cl_2O_6S$ $[M]^+$ 1028.5094, found:1028.5095.

3,7-Dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-10,11-dihydrodiindeno[1,2-b:2',1'-d]thiophene-2,8-diol (5a): A solution of compound **4a** (440.3 mg, 0.4273 mmol) in dry dichloromethane (30 mL) was added boron tribromide (247 μL, 6 equiv.) under an ice bath and a nitrogen atmosphere, and then was stirred overnight. The reaction mixture was poured into water under an ice bath. The organic phase was separated, and the aqueous phase was extracted with dichloromethane. The combined organic phase dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=2:1) to give the desired product **5a** as a yellow solid (352.9 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 2H), 6.72 (d, J = 7.8 Hz, 10H), 6.59 (d, J = 8.1 Hz, 8H), 5.35 (s, 2H), 2.49 – 2.33 (m, 8H), 1.57 –1.45 (m, 8H), 1.39 – 1.26 (m, 24H), 0.89 (t, J = 6.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 150.5, 149.5, 142.8, 140.7, 137.8, 130.2, 127.8, 127.4, 118.5, 117.7, 113.8, 64.0, 35.5, 31.8, 31.1, 29.4, 22.7, 14.1. HRMS (MALDI) calcd for

$C_{66}H_{74}Cl_2O_2S$ $[M]^+$ 1000.4781, found:1000.4781.

3,7-Dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-10,11-dihydrodiindeno[1,2-b:2',1'-d]thiophene-2,8-diyl bis(trifluoromethanesulfonate) (6a): Compound **5a** (329.9 mg, 0.3292 mmol) in dry dichloromethane (25 mL) and super dry pyridine (1 mL) was added trifluoromethanesulfonic anhydride(165 μL, 3 equiv.) under an ice bath and a nitrogen atmosphere. The reaction mixture was then stirred for 3 h at room temperature. After the reaction completion, the reaction mixture was poured into H_2O under an ice bath. The organic phase was separated, and aqueous phase was extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=5:1) to give the desired product **6a** as a yellow solid (410.1 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 6.97 (s, 2H), 6.69 (d, *J* = 8.2 Hz, 8H), 6.63 (d, *J* = 8.2 Hz, 8H), 2.49 – 2.34 (m, 8H), 1.55 – 1.43 (m, 8H), 1.35 – 1.24 (m, 24H), 0.88 (t, *J* = 6.5 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.1, 143.8, 143.5, 141.6, 136.8, 136.2, 127.8, 127.6, 126.2, 120.2, 120.1, 118.5 (q, *J* = 320.9 Hz), 64.5, 35.5, 31.7, 31.1, 29.3, 22.6, 14.1. HRMS (APCI) calcd for $C_{68}H_{72}Cl_2F_6O_6S_3$ $[M]^+$ 1264.3767, found: 1264.3759.

((3,7-dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-10,11-dihydrodiindeno[1,2-b:2',1'-d]thiophene-2,8-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (7a): A mixture of compound **6a** (393.1 mg, 0.31 mmol), bis(triphenylphosphine)palladium(II) chloride (26.1 mg, 12 mol%) and copper(1) iodide (17.7 mg, 30 mol%) and tetrabutylammonium iodide (343.5 mg, 3 equiv.) in *N*,*N*-dimethylformamide (10 mL) and triethylamine (2 mL) was degassed with nitrogen for 10 min, and then ethynyltrimethylsilane (131, 3 equiv.) was added. The mixture was allowed to stir at 75 °C overnight. After the completion of reaction, the mixture was cooled to room temperature. The mixture was washed with water and extracted with chloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=10:1) to give the desired product **7a** as a yellow solid (275.3 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.14 (s, 2H), 6.70 (d, *J* = 8.1 Hz, 8H), 6.60 (d, *J* = 8.1 Hz, 8H), 2.50 – 2.32 (m, 8H), 1.58 – 1.45 (m, 8H), 1.31 (s, 24H), 0.90 (t, *J* = 6.5 Hz, 12H), 0.20 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 152.8, 144.6, 141.0, 137.5, 137.0, 135.6, 129.8, 127.8, 127.5, 120.0, 118.7, 102.2, 100.2, 63.9, 35.5, 31.8, 31.1, 29.4, 22.7, 14.1, -0.2. HRMS (MALDI) calcd for $C_{76}H_{90}Cl_2SSi_2$ $[M]^+$ 1160.5673, found: 1160.5673.

The synthesis of 8a: Sodium sulfide nonahydrate (201.1 mg, 4 equiv.) in *N*-methylpyrrolidone (6 mL) was degassed with nitrogen at 10 min, then compound **7a** (243.6 mg, 0.2095 mmol) was added. The mixture was stirred at 190 °C for 12 h. After the completion of reaction, the mixture was cooled to room temperature. The mixture was washed with water, and extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography ($CHCl_3$) to give the desired product **8a** as a yellow solid (190.7 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.45 (s, 2H), 7.28 (d, *J* = 5.4 Hz, 2H), 7.11 (d, *J* = 5.4 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 8H), 6.59 (d, *J* = 8.2 Hz, 8H), 2.47 – 2.34 (m, 8H), 1.56– 1.44 (m, 8H), 1.37 – 1.24 (m, 24H), 0.88 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.3, 144.7, 140.4, 138.9, 138.2, 134.0, 128.0, 127.3, 125.4, 124.3, 120.3, 111.2, 63.6, 35.5, 31.8, 31.1, 29.5, 22.7, 14.1. HRMS (MALDI) calcd for $C_{70}H_{76}S_3$ $[M]^+$ 1012.5104, found: 1012.5096.

The synthesis of 9a*:* To the solution of compound **8a** (89.2 mg, 0.088 mmol) in dry THF (8 mL) was added n-butyllithium (0.14 mL, 2.5 equiv.) and stir at -78 °C for 1.5 h, and *N,N*-dimethylformamide (19.3 mg, 3 equiv.) was added. The mixture continued to stirring at -78 °C for 1 h and then was allowed to stir at room temperature for 1 h, which was quenched with water. The mixture was extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=1:1 to 1:2) to give the desired product **9a** as a yellow solid (85.8 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 2H), 7.87 (s, 2H), 7.77 (s, 2H), 7.55 (s, 2H), 6.80 (d, *J* = 8.2 Hz, 8H), 6.62 (d, *J* = 8.2 Hz, 8H), 2.48 – 2.33 (m, 8H), 1.56 – 1.45 (m, 8H), 1.36 – 1.23 (m, 24H), 0.88 (t, *J* = 6.7 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 156.1, 152.7, 145.9, 142.63, 142.58, 141.0, 138.0, 137.5, 137.4, 134.8, 127.9, 127.5, 122.6, 112.1, 63.7, 35.5, 31.8, 31.1, 29.4, 22.6, 14.1. HRMS (MALDI) calcd for $C_{72}H_{76}O_2S_3$ $[M]^+$ 1068.5002, found: 1068.4996.

The synthesis of FTBT: A solution of compound **9a** (48.1 mg, 0.045 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (51.8 mg, 5 equiv.) in chloroform (10 mL) and pyridine (0.2 mL) was degassed with nitrogen at 5 min, and then the mixture was stirred at room temperature for 15 h. The mixture was washed with water, and extracted with chloroform. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography ($CHCl_3$) to give the desired product **FTBT** as a black solid (40.6 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 2H), 8.51 – 8.57 (m, 2H), 7.94 (s, 2H), 7.78 (s, 2H), 7.72 (t, *J* = 7.4 Hz, 2H), 7.53 (s, 2H), 6.82 (d, *J* = 7.9 Hz, 8H), 6.65 (d, *J* = 8.0 Hz, 8H), 2.49 – 2.35 (m, 8H), 1.51 (m, 12H), 1.31 (m, 24H), 0.87 (t, *J* = 6.3 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 157.8, 156.7, 154.7 (dd, *J* = 266.9 Hz, *J* = 13.6 Hz), 154.6 (dd, *J* = 257.4 Hz, *J* = 14.1 Hz), 153.8, 148.1, 147.4, 143.2, 141.3, 138.8, 138.6, 137.8, 137.4, 136.8, 136.6 (d, *J* = 10.7 Hz), 134.6 (d, *J* = 6.2 Hz), 128.1, 127.7, 123.4, 122.2, 114.9 (d, *J* = 21.3 Hz), 113.9, 113.7, 112.9 (d, *J* = 18.9 Hz), 111.3, 63.7, 35.6, 31.8, 31.2, 29.4, 22.6, 14.1.^{19}F NMR (377 MHz, $CDCl_3$) δ -121.52 (d, *J* = 18.9 Hz, 1F), -122.80 (d, *J* = 18.7 Hz, 1F). HRMS (MALDI) calcd for $C_{96}H_{80}F_4N_4O_2S_3$ $[M]^+$ 1492.5374, found: 1492.5380. Anal. calcd for $C_{96}H_{80}F_4N_4O_2S_3$ (%): C, 77.18; H, 5.40; N, 3.75; found: C, 76.88; H, 5.44; N, 3.94;

Dimethyl 6,6'-(thieno[3,2-b]thiophene-2,5-diyl)bis(4-chloro-3-methoxybenzoate) (3b)*:*A mixture of 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (1.863 g, 4 mmol) and compound **2** (2.572 g, 2.3 equiv.) and tetrakis(triphenylphosphine)platinum (462.2 mg, 10 mol%) in dry toluene (20 mL) and *N*,*N*-dimethylformamide (5 mL) was degassed with nitrogen for 5 min, and then sealed, stirred at 120 °C for 24 h. After the completion of reaction, it was cooled to room temperature. The mixture was washed with H_2O, extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=1:2 to DCM) to give the desired product **3b** as a yellow solid (1.232 g, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.34 (s, 2H), 7.14 (s, 2H), 3.99 (s, 6H), 3.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 154.7, 141.9, 139.3, 133.0, 130.6, 127.7, 125.6, 118.7, 112.9, 56.5, 52.5. HRMS (MALDI) calcd for $C_{24}H_{18}Cl_2O_6S_2$ $[M]^+$ 535.9916, found: 535.9916.

3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-2,8-dimethoxy-6,12-dihydroindeno[1,2-b]indeno[2',1':4,5] thieno[2,3-d]thiophene (4b)*:*To a solution of compound **3b** (806.1 mg, 1.5 mmol) dissolved in dry THF (20 mL) was added the freshly prepared 4-hexylphenyl-1-magnesium bromide that was prepared by slowly adding 1-bromo-4-hexylbenzene (4.341 g, 12 equiv.) to Mg (481.3 mg,

13.2 equiv.) in dry THF (20 mL), and then was refluxed for 3 h under a nitrogen atmosphere. Then the reaction was refluxed for 16 h and was cooled to room temperature. The mixture was quenched with H_2O under an ice bath, and extracted with diethyl ether. The organic phase was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue in dry dichloromethane (40 mL) was added $BF_3.Et_2O$ (3 mL) under an ice bath and a nitrogen atmosphere. The mixture was stirred for 1 h at room temperature and was poured into water. The organic phase was separated and dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (n-hexane:DCM=1:1) to give the desired product **4b** as a yellow solid (0.990 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.13 (d, *J* = 8.2 Hz, 8H), 7.08 (d, *J* = 8.2 Hz, 8H), 6.98 (s, 2H), 3.83 (s, 6H), 2.56 (t, *J* = 8.0 Hz, 8H), 1.67 – 1.54 (m, 8H), 1.46 – 1.19 (m, 24H), 0.86 (t, *J* = 6.4 Hz, 12H).^{13}C NMR (100 MHz, $CDCl_3$) δ 153.30, 153.26, 146.4, 141.9, 140.9, 140.0, 135.6, 131.4, 128.5, 127.9, 121.9, 120.3, 110.7, 63.4, 56.5, 35.6, 31.7, 31.2, 29.1, 22.6, 14.1. HRMS (MALDI) calcd for $C_{70}H_{78}Cl_2O_2S_2$ $[M]^+$ 1084.4815, found:1084.4811.

3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydroindeno[1,2-b]indeno[2',1':4,5]thieno[2,3-d]thiophene-2,8-diol (5b)*:* Compound **4b** (760.2 mg, 0.7 mmol) was dissolved in dry dichloromethane (40 mL) under a nitrogen atmosphere, and was added boron tribromide (405 μL, 6 equiv.) under an ice bath. Then the mixture was stirred overnight. After the completion of the reaction, the reaction mixture was poured into water under an ice bath. The organic phase was separated, and the aqueous phase was extracted with dichloromethane. The combined organic phase dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (n-hexane:DCM=1:1) to give the desired product **5b** as a light yellow solid (553.6 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 7.12 (d, *J* = 8.0 Hz, 8H), 7.07 (d, *J* = 8.4 Hz, 10H), 5.48 (s, 2H), 2.55 (t, *J* = 7.8 Hz, 8H), 1.63 – 1.52 (m, 8H), 1.37 – 1.23 (m, 24H), 0.87 (t, *J* = 6.3 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.4, 146.3, 141.9, 140.9, 139.9, 135.7, 131.6, 128.5, 127.9, 118.9, 118.7, 114.6, 63.2, 35.6, 31.7, 31.2, 29.1, 22.6, 14.1. HRMS (MALDI) calcd for $C_{68}H_{74}Cl_2O_2S_2$ $[M]^+$ 1056.4502, found:1056.4500.

3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydroindeno[1,2-b]indeno[2',1':4,5]thieno[2,3-d]thiophene-2,8-diyl bis(trifluoromethanesulfonate) (6b)*:* Compound **5b** (501.3 mg, 0.4737 mmol) was dissolved in dry dichloromethane (25 mL) and super dry pyridine (1 mL) under a nitrogen atmosphere, and trifluoromethanesulfonic anhydride(239 μL, 3 equiv.) was added under an ice bath. The reaction mixture was then stirred for 3 h at room temperature. After the completion of reaction, the reaction mixture was poured into H_2O under an ice bath. The organic phase was separated, and aqueous phase was extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (PE:DCM=10:1) to give the desired product **6b** as a light yellow solid (410.1 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.33 (s, 2H), 7.14 – 7.04 (m, 16H), 2.57 (t, *J* = 7.8 Hz, 8H), 1.63 – 1.52 (m, 8H), 1.38 – 1.23 (m, 24H), 0.86 (t, *J* = 6.3 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 149.1, 143.2, 142.7, 140.8, 138.52, 138.47, 137.3, 128.8, 127.6, 126.8, 120.9, 120.7, 118.6 (*q*, *J* = 320.9 Hz), 63.6, 35.5, 31.7, 31.2, 29.1, 22.6, 14.0. HRMS (APCI) calcd for $C_{70}H_{72}Cl_2F_6O_6S_4$ $[M]^+$ 1320.3498, found:1320.3498.

((3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydroindeno[1,2-b]indeno[2',1':4,5]thieno[2,3-d]thiophene-2,8-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (7b)*:* A mixture of comound **6b** (500.7 mg, 0.3786 mmol), bis(triphenylphosphine)palladium(II) chloride (31.9

mg, 12 mol%) and copper(1) iodide (21.6 mg, 30 mol%) and tetrabutylammonium iodide (419.5 mg, 3 equiv.) in dimetilformamide (12 mL) and triethylamine (2.4 mL) was degassed with nitrogen for 10 min, and then ethynyltrimethylsilane (161 μL, 3 equiv.) was added. The mixture was allowed to stir at 75 °C overnight. After the completion of reaction, the mixture was cooled to room temperature. The mixture was washed with water and extracted with chloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (n-hexane:DCM=20:1) to give the desired product **7b** as a yellow solid (422.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 2H), 7.36 (s, 2H), 7.14 – 7.05 (m, 16H), 2.56 (t, *J* = 7.8 Hz, 8H), 1.64 – 1.52 (m, 8H), 1.39 – 1.26 (m, 24H), 0.87 (t, *J* = 6.7 Hz, 6H), 0.26 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 148.9, 142.2, 141.7, 139.2, 139.1, 137.1, 136.2, 130.4, 128.6, 127.9, 119.59, 119.57, 102.2, 100.6, 63.0, 35.6, 31.7, 31.2, 29.1, 22.6, 14.1, -0.1. HRMS (MALDI) calcd for $C_{78}H_{90}Cl_2S_2Si_2$ $[M]^+$ 1216.5394, found:1216.5395

The synthesis of 8b*:* Sodium sulfide nonahydrate (316.8 mg, 4 equiv.) in *N*-methylpyrrolidone (8 mL) was degassed with nitrogen at 10 min, then compound **7b** (402.2 mg, 0.33 mmol) was added. The mixture was stirred at 190 °C for 12 h. After the completion of reaction, the mixture was cooled to room temperature. The mixture was washed with water, and extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography ($CHCl_3$) to give the desired product **8b** as a yellow solid (305.4 mg, 87% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.84 (s, 2H), 7.78 (s, 2H), 7.39 (d, *J* = 5.4 Hz, 2H), 7.26 (d, *J* = 5.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 8H), 7.08 (d, *J* = 7.9 Hz, 8H), 2.53 (t, *J* = 7.8 Hz, 8H), 1.60 – 1.48 (m, 8H), 1.36 – 1.19 (m, 24H), 0.83 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 147.2, 142.5, 141.7, 140.8, 139.5, 137.8, 136.3, 135.2, 128.4, 128.1, 125.7, 124.2, 121.1, 112.3, 62.7, 35.6, 31.7, 31.3, 29.1, 22.6, 14.1. HRMS (MALDI) calcd for $C_{72}H_{76}S_4$ $[M]^+$ 1068.4824, found:1068.4828.

The synthesis of 9b*:* To the solution of compound **8b** (128.4 mg, 0.12 mmol) in dry THF (10 mL) was added n-butyllithium (0.19 mL, 2.5 equiv.) and stir at -78 °C for 1.5 h and *N*,*N*-dimethylformamide (26.3 mg, 3 equiv.) was added. The mixture continued to stirring at -78 °C for 1 h and then was allowed to stir at room temperature for 1 h, which was quenched with water. The mixture was extracted with dichloromethane. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography (n-hexane:DCM=2:1) to give the desired product **9b** as a yellow solid (100.7 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 2H), 7.91 (s, 2H), 7.88 (s, 2H), 7.81 (s, 2H), 7.19 (d, *J* = 8.1 Hz, 8H), 7.10 (d, *J* = 8.1 Hz, 8H), 2.56 (t, J =7.8 Hz, 8H), 1.65 – 1.54 (m, 8H), 1.39 – 1.20 (m, 24H), 0.86 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 151.8, 148.8, 143.2, 142.9, 142.7, 142.2, 140.0, 138.9, 137.5, 136.9, 134.7, 128.6, 127.9, 123.3, 112.9, 62.8, 35.6, 31.7, 31.2, 29.1, 22.6, 14.1. HRMS (MALDI) calcd for $C_{74}H_{76}O_2S_4$ $[M]^+$ 1124.4723, found:1124.4725.

The synthesis of FTTBT: A solution of compound **9b** (73.2 mg, 0.065 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (74.8 mg, 5 equiv.) in chloroform (10 mL) and pyridine (0.2 mL) was degassed with nitrogen at 5 min, and then the mixture was stirred at room temperature for 22 h. The mixture was washed with water, and extracted with chloroform. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica-gel column chromatography ($CHCl_3$) to give the desired product **FTTBT** as a black solid (78.9 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 2H), 8.53 –

8.59(m, 2H), 8.08 (s, 2H), 7.86 (s, 2H), 7.81 (s, 2H), 7.73 (t, J = 7.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 8H), 7.11 (d, J = 8.1 Hz, 8H), 2.57 (t, J = 7.6 Hz, 8H), 1.63 – 1.51 (m, 8H), 1.39 – 1.21 (m, 24H), 0.86 (t, J = 6.4 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.6, 158.1, 154.72 (dd, J = 259.5 Hz, J = 13.6 Hz), 154.66 (dd, J = 263.8 Hz, J = 13.8 Hz), 152.3, 150.0, 148.7, 143.9, 143.1, 142.4, 140.1, 139.7, 138.8, 138.4, 136.9, 136.7, 134.6 (d, J = 4.5 Hz), 128.7, 127.9, 123.7, 122.9, 115.0 (d, J = 22.5 Hz), 114.0, 113.7, 112.9 (d, J = 19.5 Hz),112.2, 71.3, 62.8, 35.6, 31.7, 31.2, 29.1, 22.6, 14.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -121.50 (d, J = 19.2 Hz, 1F), -122.77 (d, J = 19.0 Hz, 1F). HRMS (MALDI) calcd for $C_{98}H_{80}F_4N_4O_2S_4$ $[M]^+$ 1548.5095, found:1548.5090. Anal. calcd for $C_{98}H_{80}F_4N_4O_2S_4$ (%): C, 75.94; H, 5.20; N, 3.61; found: C, 75.78; H, 4.94; N, 3.66;

Solar cell fabrication and characterization

Indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment with detergent, deionized water, acetone, and ethanol for 20 min each, and were then UV/ozone treated. A thin layer of PEDOT:PSS (Baytron P VP Al 4083) was spin-coated at 3000 r.p.m. for 30 s and then baked at 150 °C for 20 min. The substrates were then transferred to a nitrogen-filled glove box. A blend solution of PM6:**FTBT** and PM6:**FTTBT** (1:1 weight ratio, 7 mg/mL in donor weight concentration) in chloroform was spin-coated at different spin rates on the top of the substrate. After spin-coating a thin layer (~10 nm) of PDINO at 3000 r.p.m. for 40 s on the top of the active layer, ca 80 nm Al layer was deposited under a vacuum of 10^{-4} Pa. The active area of the solar cells was 0.04 cm^2. For photovoltaic measurement, the *J-V* curve was recorded by a Precision Source/Measure Unit (B2912A, Agilent Technologies) and an AAA grade solar simulator (XES-70S1, SAN-EI Electric Co. Ltd, 7 ×7 cm^2 beam size) coupled with AM 1.5G solar spectrum filters was taken as the light source. The light power on the surface of the sample was calibrated to be 100 mW cm^{-2} in use of a standard monocrystalline silicon reference cell (SRC-1000-TC-QZ, VLSI Standards Inc., 2 × 2 cm^2). The external quantum efficiency (EQE) was measured by a Solar Cell Spectral Response Measurement System (QE-R3011, Enlitech Co. Ltd) with the light intensity at each wavelength also calibrated by a standard single crystal Si photovoltaic cell.

Space charge-limited current (SCLC) method was employed to examine the hole and electron mobilities of the blend film. The hole mobility was measured with a device configuration of ITO/PEDOT:PSS/active layer/ Au while the electron-only device taking an ITO/ZnO/active layer/PDINO/Al configuration. The active layers for charge-transportion devices spin-coated were followed the same condition as that of the real solar cell device. The mobilities were calculated by fitting the dark current to a SCLC model which is described as:

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

where J is the current density, ε_0 is the permittivity of the free space, ε_r is the relative permittivity of the material, μ is the zero-field mobility, L is the thickness of the active layer, and V is the effective voltage in the devices, and $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images of the thin films were obtained on a Bruker Dimension Icon with Scanasyst operating in tapping mode.

GIXD characterization

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement was performed at the small and wide angle X-ray scattering beamline at Australian Synchrotron.[2] A Pilatus 1M 2-dimentional detector with 0.172 mm × 0.172 mm active pixels was utilised in integration mode. The detector was positioned approximately 300 mm downstream from the sample location. The precise sample-to-detector distance was determined with a silver behenate standard. 11 KeV incident X-ray with approximately a 0.25 mm × 0.1 mm spot was used to provide large enough q space. The 2-dimentional raw data was reduced and analyzed with a modified version of Nika.[3] GIWAXS patterns shown have been corrected to represent real Qz and Qxy axes with considering missing wedge. Critical incident angle was determined by the maximized scattering intensity from sample scattering with negligible contribution from underneath layer scattering. All data were collected with integration time of 1 s to minimize beam damage.

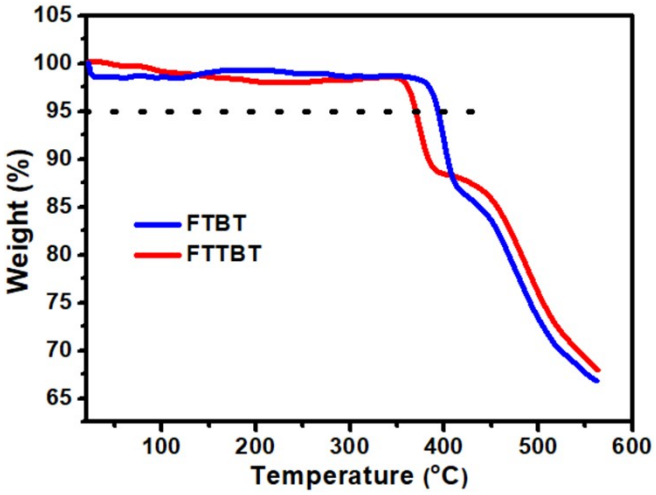


Figure S1. TGA curves of **FTBT** and **FTTBT**.

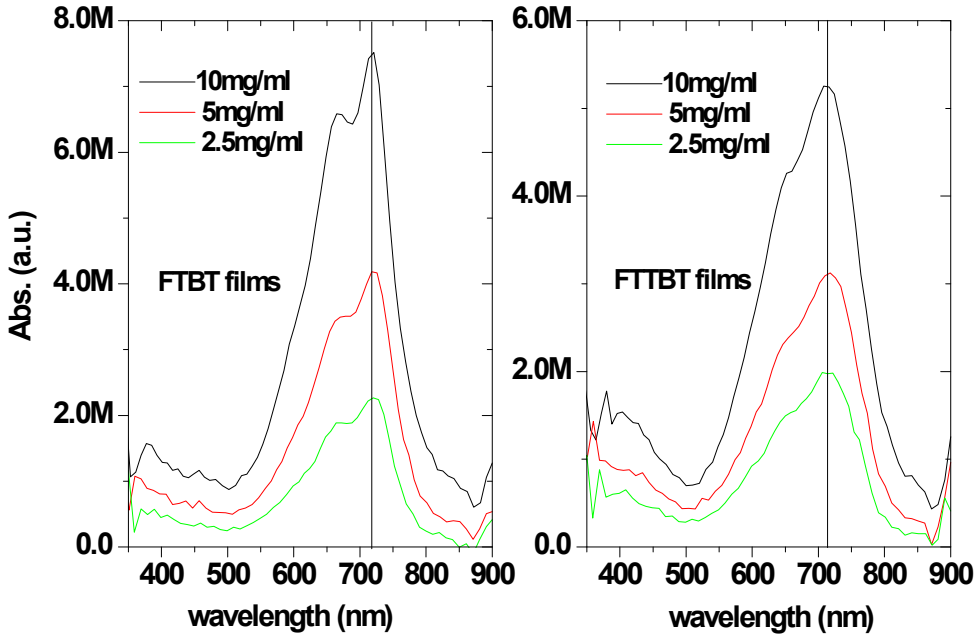


Figure S2. UV absorption of **FTBT** and **FTTBT** films spin-coated from diluted solutions.

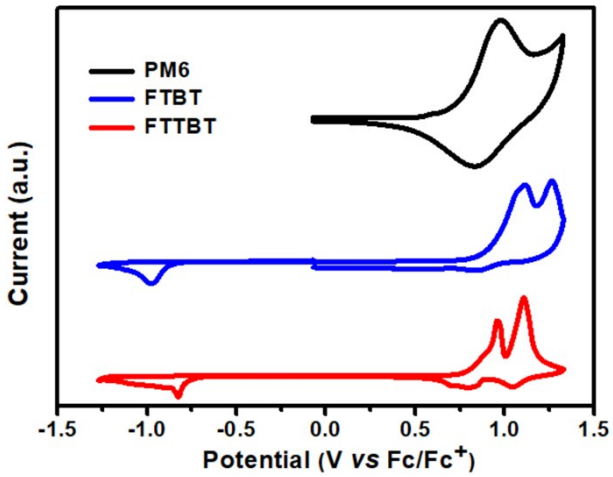


Figure S3. CV curves of PM6, **FTBT** and **FTTBT**.

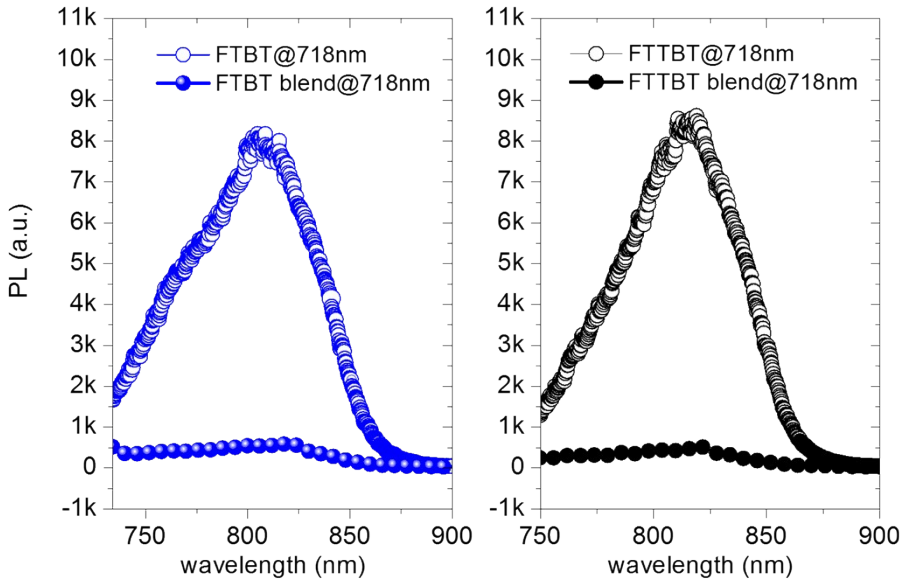


Figure S4. Photoluminescence spectra of **FTBT** and **FTTBT** pristine and their respective blend films, all excited at 718 nm.

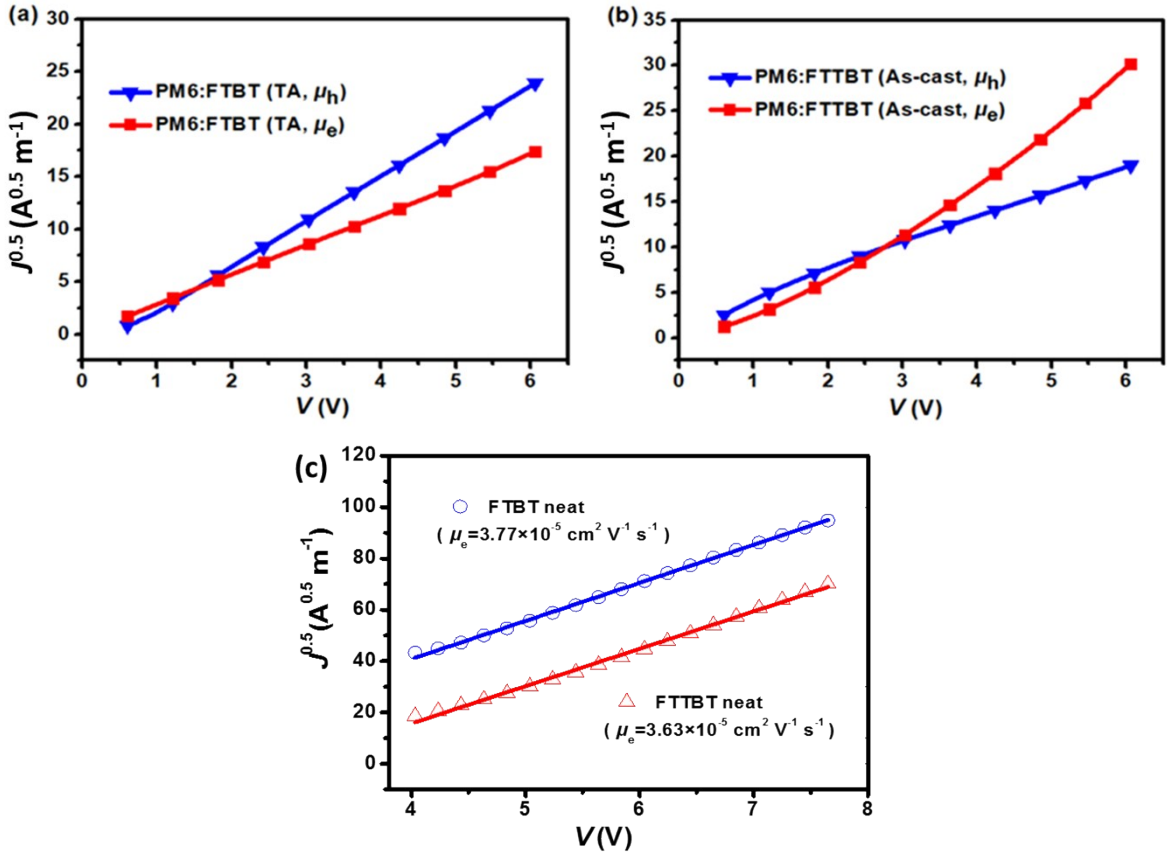


Figure S5. $J^{1/2}$- V characteristics of (a) PM6:**FTBT** blend film, (b) PM6:**FTTBT** blend film, and (c) pristine films of **FTBT** and **FTTBT**.

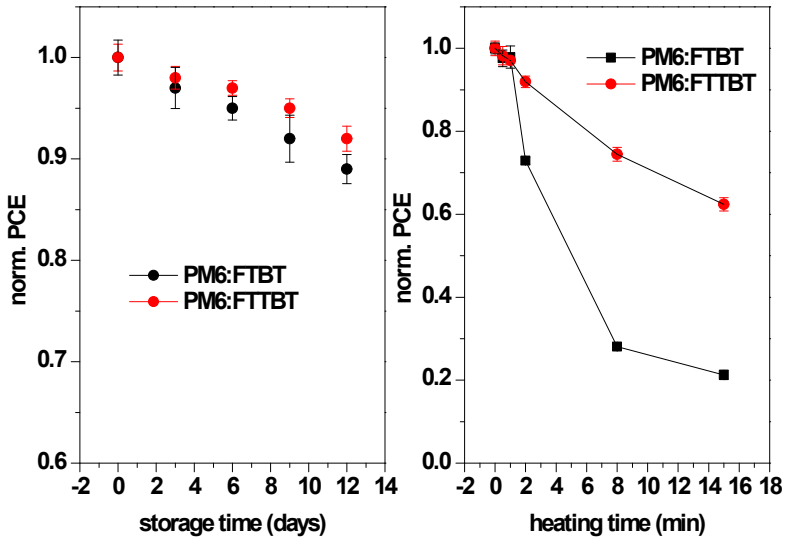


Figure S6. Normalized PCE decay of PM6:**FTBT** and PM6:**FTTBT** devices after 12 days storage (a) or being heated at 150 °C (b). All devices were measured in a glove box without being encapsulated after fabrication. The normalization of PCE was based on the average of eight devices under identically processing condition.

Figure S7. Contact angles of ethanol (EA) droplets on PM6, FTBT and FTTBT pristine films.

Table S1. The optical and electrochemical properties of **FTBT** and **FTTBT**.

Materials	λ_{max}^{abs} (sol., nm)	ε ($\times 10^5$ M^{-1} cm^{-1})	λ_{max}^{abs} (film., nm)	λ_{onset}^{abs} (film, nm)	E_g^{opt} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
FTBT	678	1.71	718	778	1.59	-5.67	-3.95
FTTBT	686	1.82	718	804	1.54	-5.57	-4.02
PM6[a]			620	670	1.85	-5.52	-3.67

[a] $E_{LUMO} = E_g^{opt} - E_{HOMO}$.

Table S2. Photovoltaic parameters for PM6:**FTBT** and PM6:**FTTBT** solar cells.

Blend	Treatment	V_{oc} (V)	J_{sc} (mA cm^{2-})	FF (%)	PCE (%)
PM6:**FTBT**[a]	—	0.978	7.26	42.52	3.02
	TA (120 °C)	0.962	7.82	46.12	3.47
	0.5%1-CN	0.937	6.80	39.67	2.53
PM6:**FTTBT**[b]	—	0.934	16.01	65.49	9.79
	TA (120 °C)	0.905	15.49	65.53	9.19
	0.5%1-CN	0.938	16.30	62.84	9.60

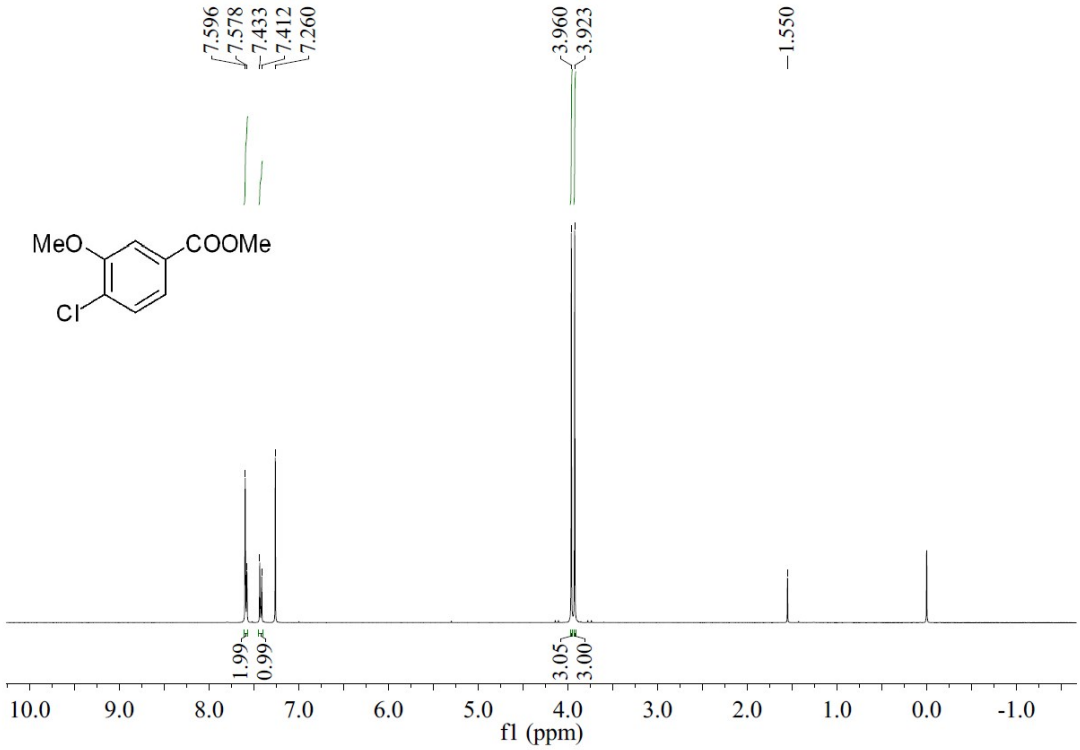
[a]The thickness of PM6:**FTBT** layers is ~80 nm. [b]The thickness ofPM6:FTTBT layers is ~80 nm.

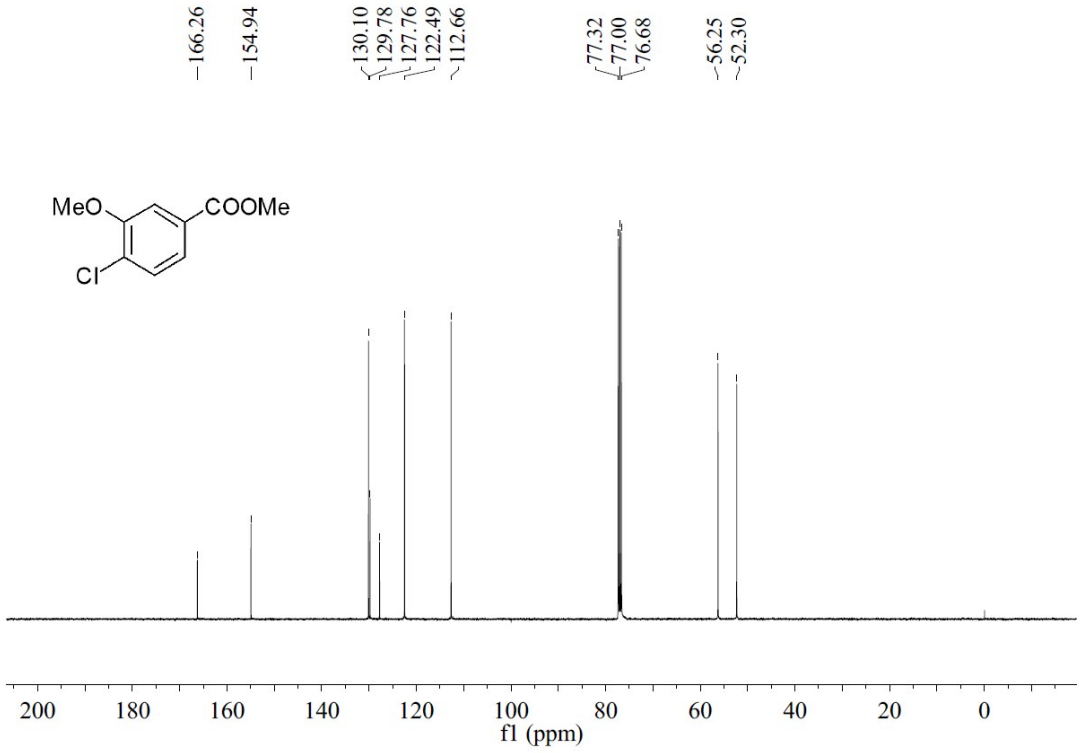
Table S3. J_{ph}/J_{sat} value and SCLC mobility of PM6:**FTBT** and PM6:**FTTBT** devices.

Blend film	J_{ph}/J_{sat}	μ_h (cm^2 $V^{-1}s^{-1}$)	μ_e (10^{-5} cm^2 $V^{-1}s^{-1}$)	μ_e/μ_h
FTBT, neat (~80 nm)	-	-	3.8×10^{-5}	-
FTTBT, neat (~80 nm)	-	-	3.6×10^{-5}	-
PM6:**FTBT** (~ 80 nm)	68%	8.2×10^{-5}	3.3×10^{-5}	0.40
PM6:**FTTBT**(~ 80 nm)	65%	3.6×10^{-5}	1.1×10^{-4}	3.05

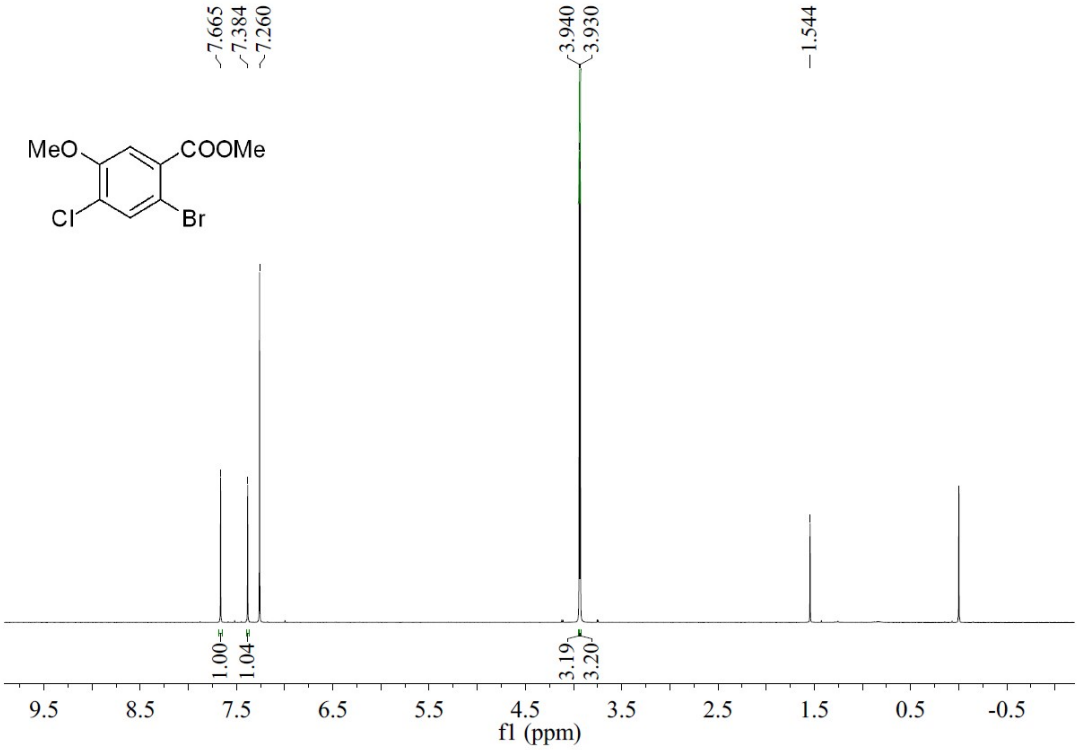
NMR Charts

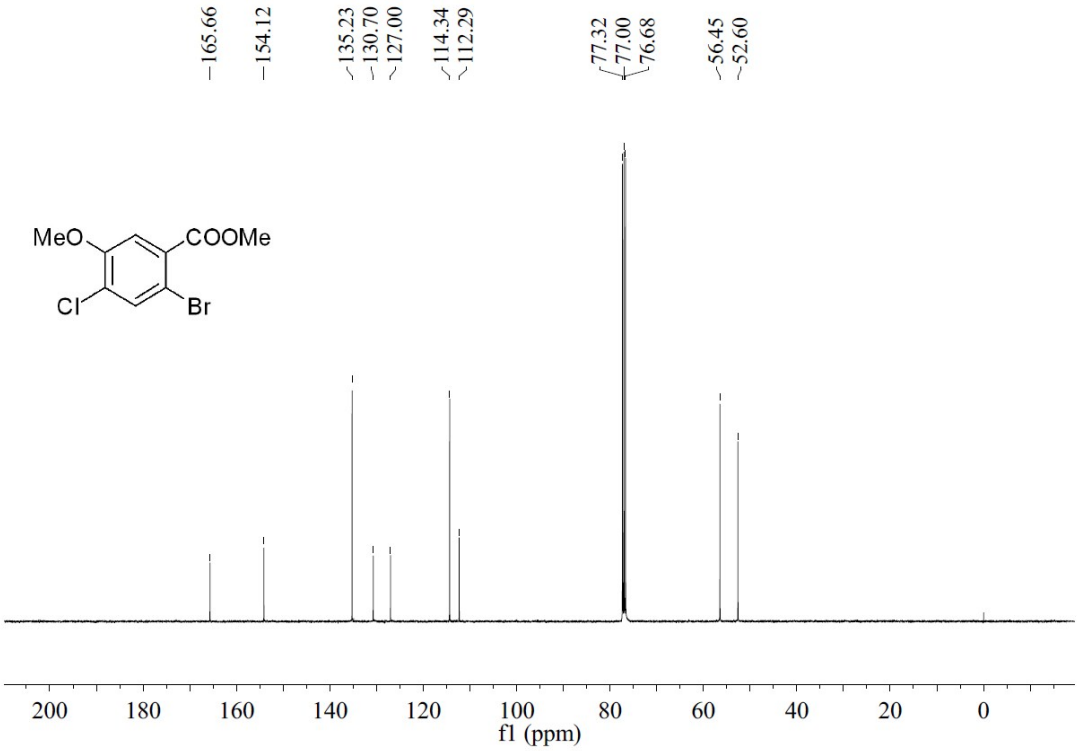
Methyl 4-chloro-3-methoxybenzoate (1)



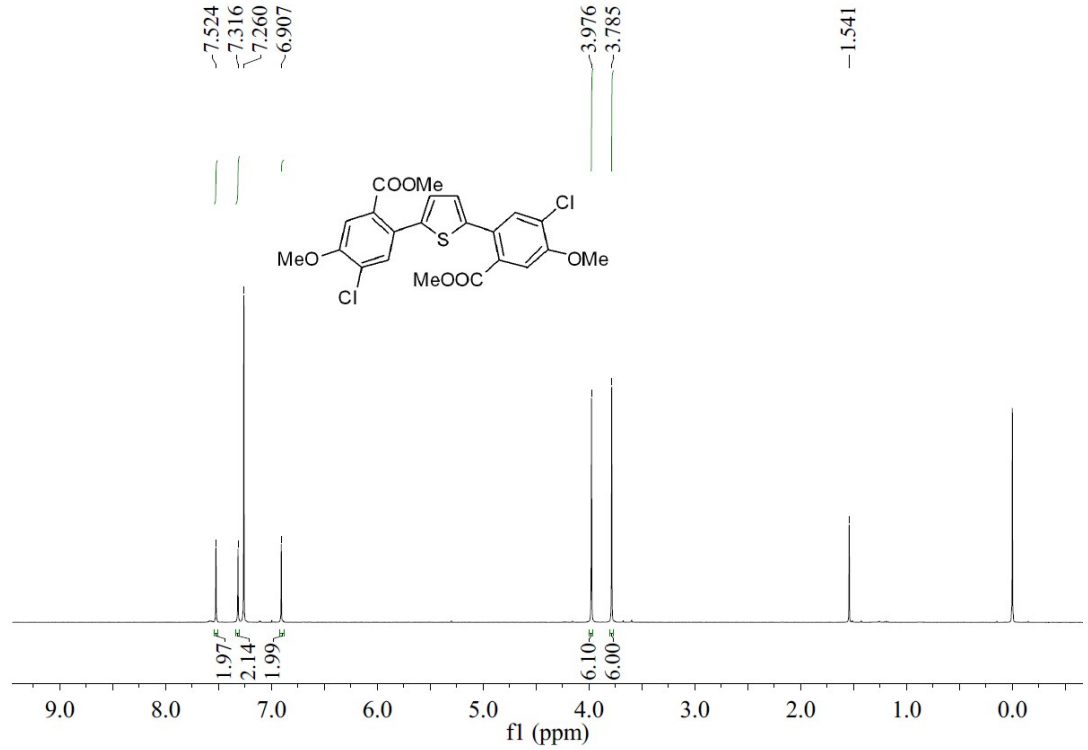


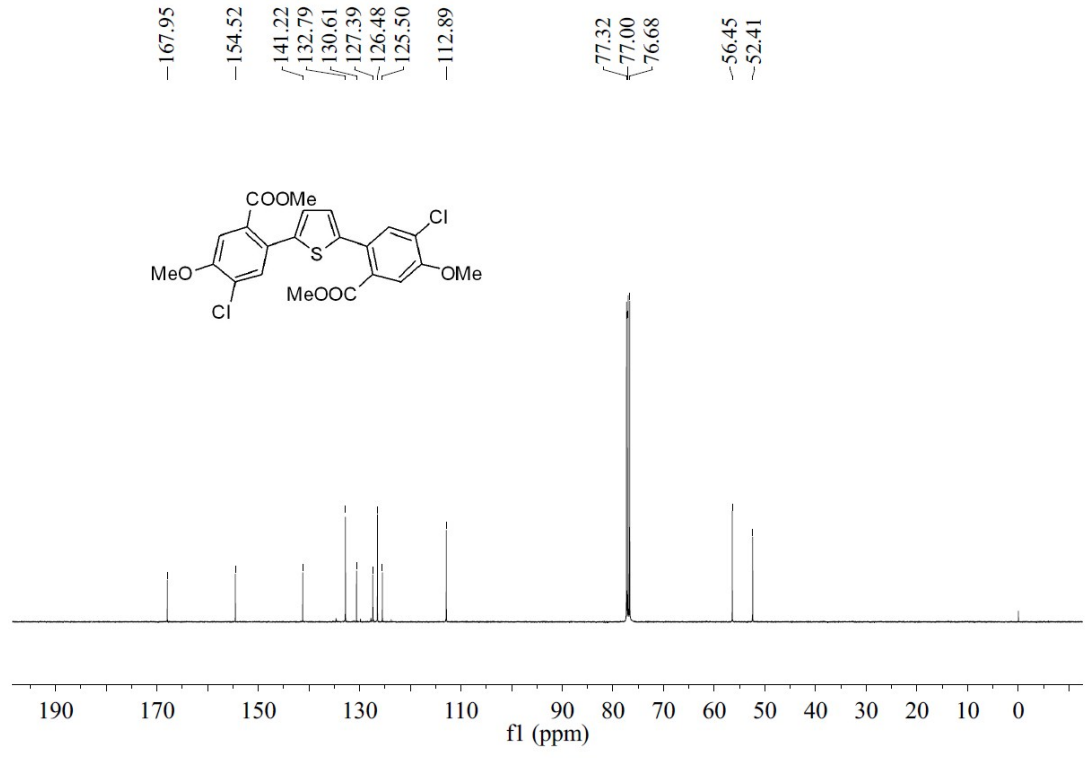
Methyl 2-bromo-4-chloro-5-methoxybenzoate (2)



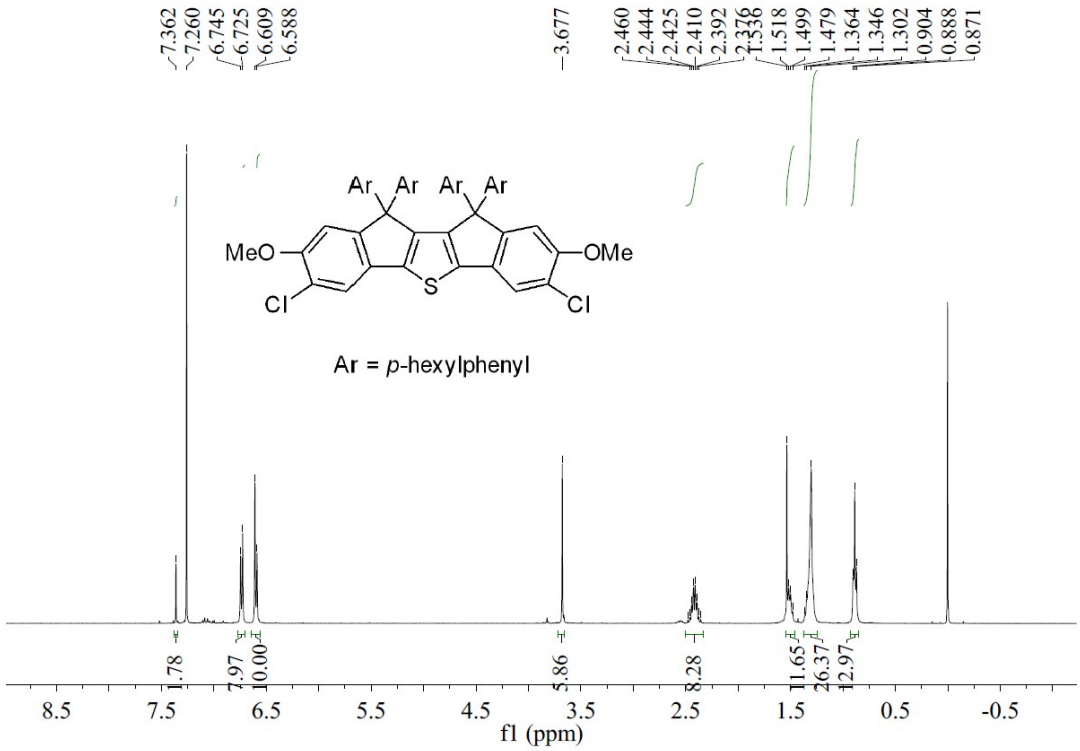


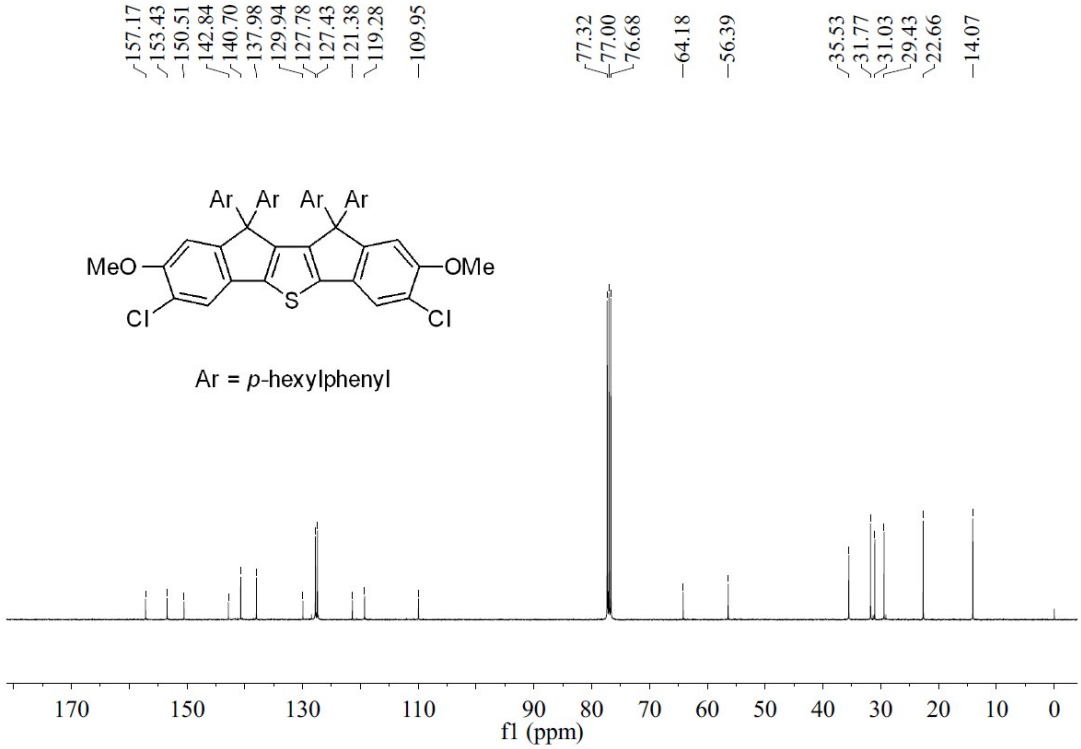
Dimethyl 6,6'-(thiophene-2,5-diyl)bis(4-chloro-3-methoxybenzoate) (3a)



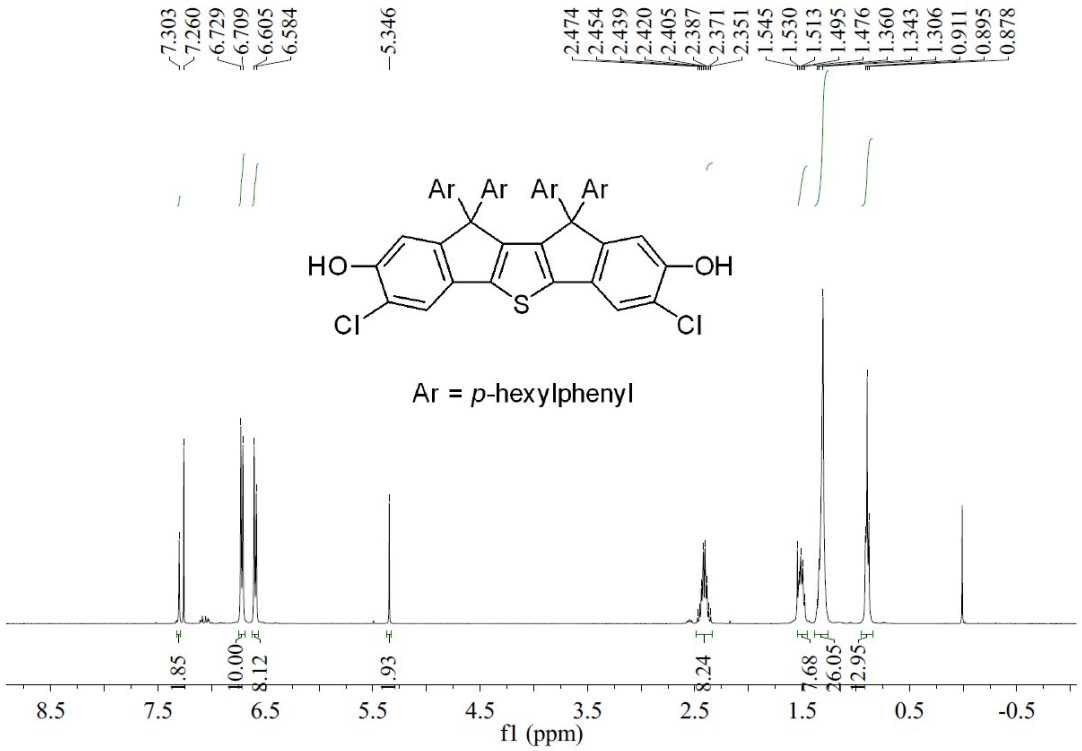


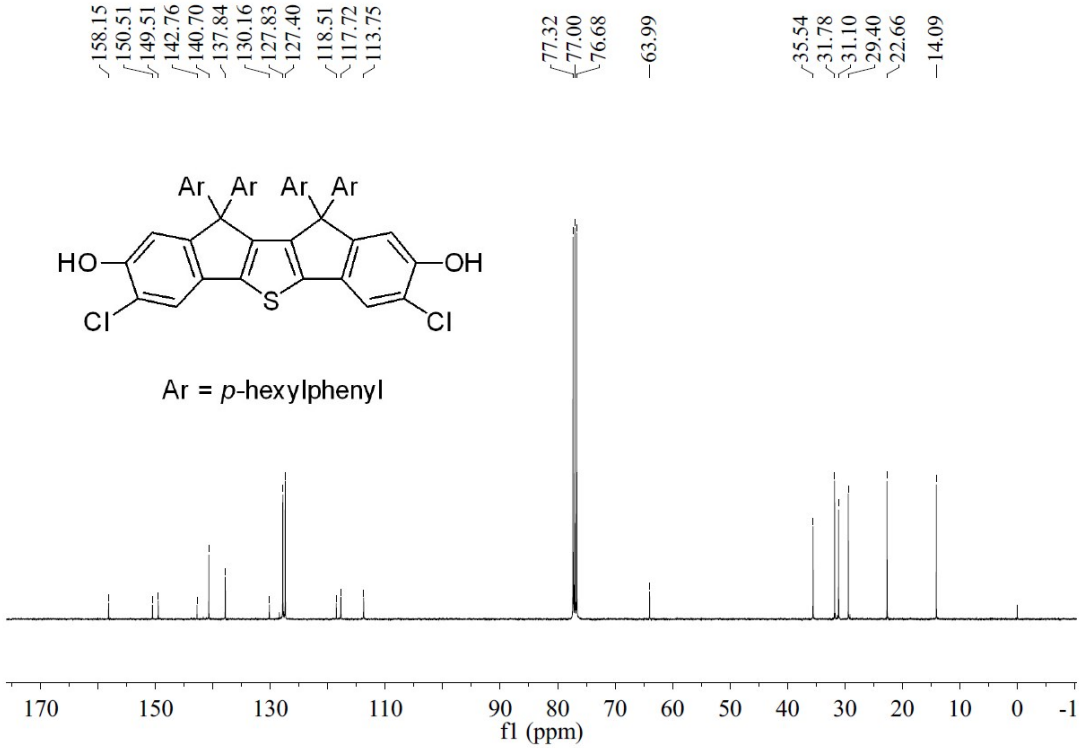
3,7-Dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-2,8-dimethoxy-10,11-dihydrodiindeno[1,2-*b*:2',1'-*d*]thiophene (4a)



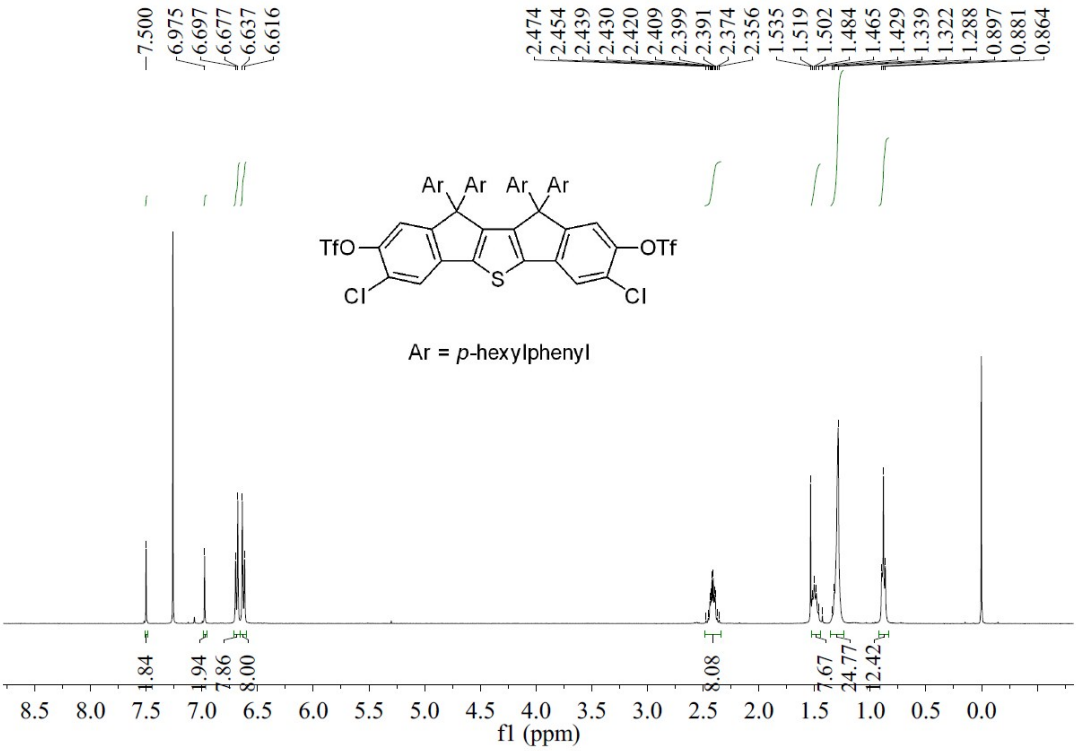


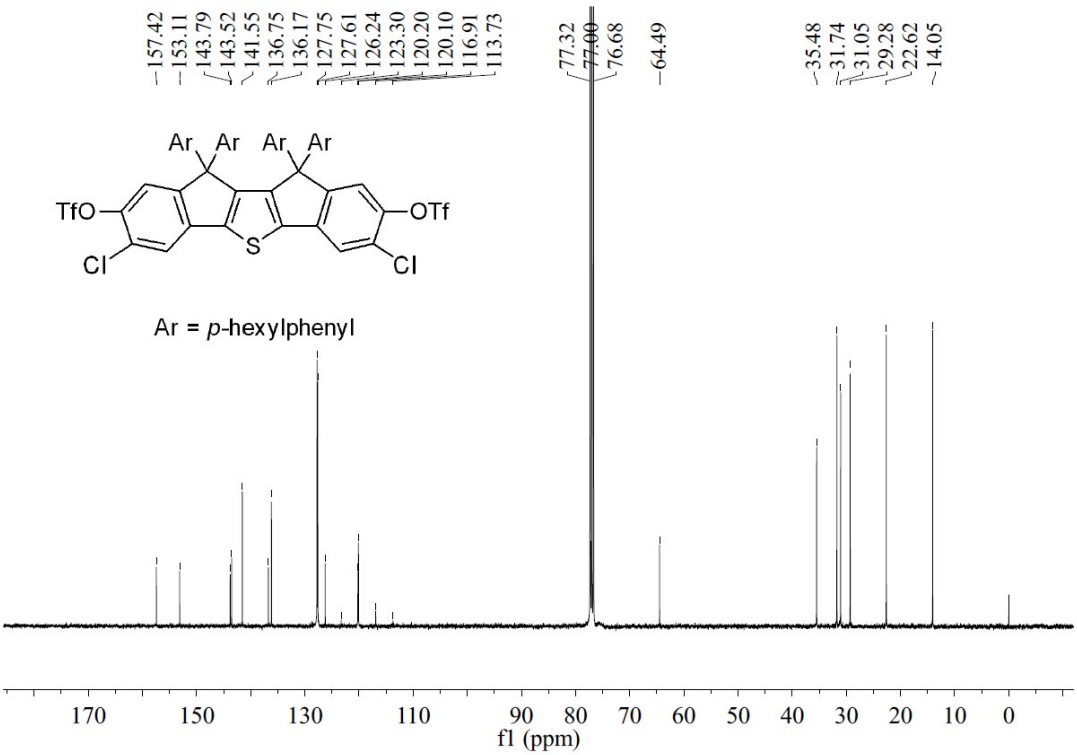
3,7-Dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-10,11-dihydrodiindeno[1,2-*b*:2',1'-*d*]thiophene-2,8-diol (5a)



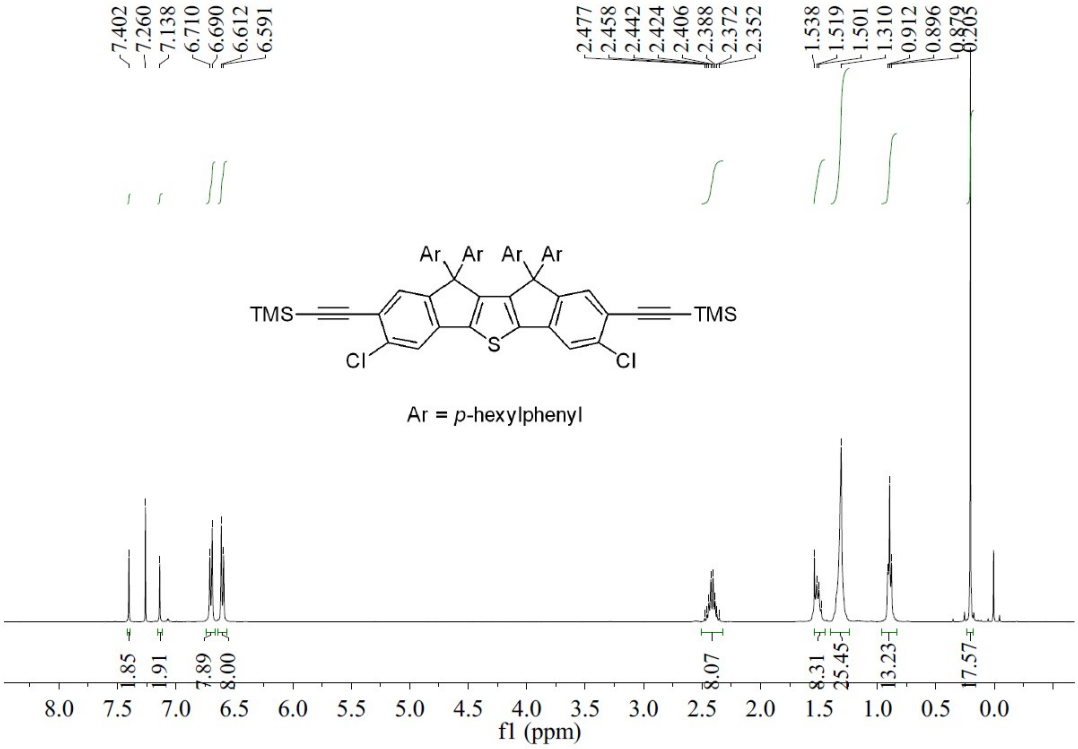


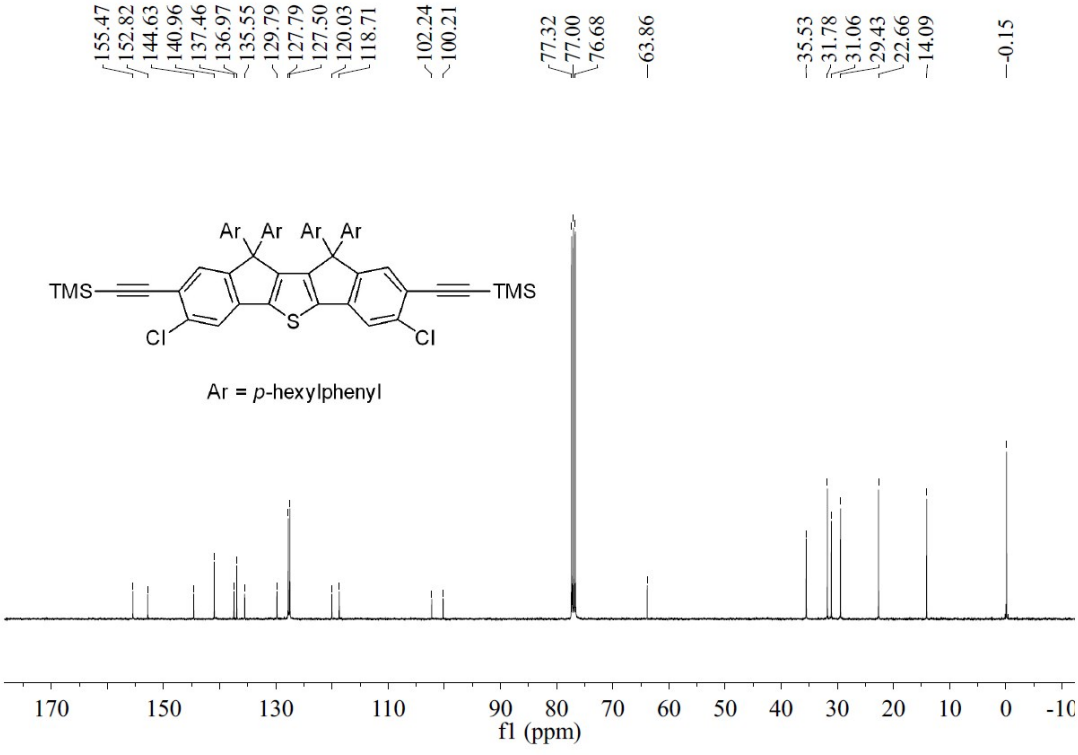
3,7-Dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-10,11-dihydrodiindeno[1,2-*b*:2',1'-*d*]thiophene-2,8-diyl bis(trifluoromethanesulfonate) (6a)



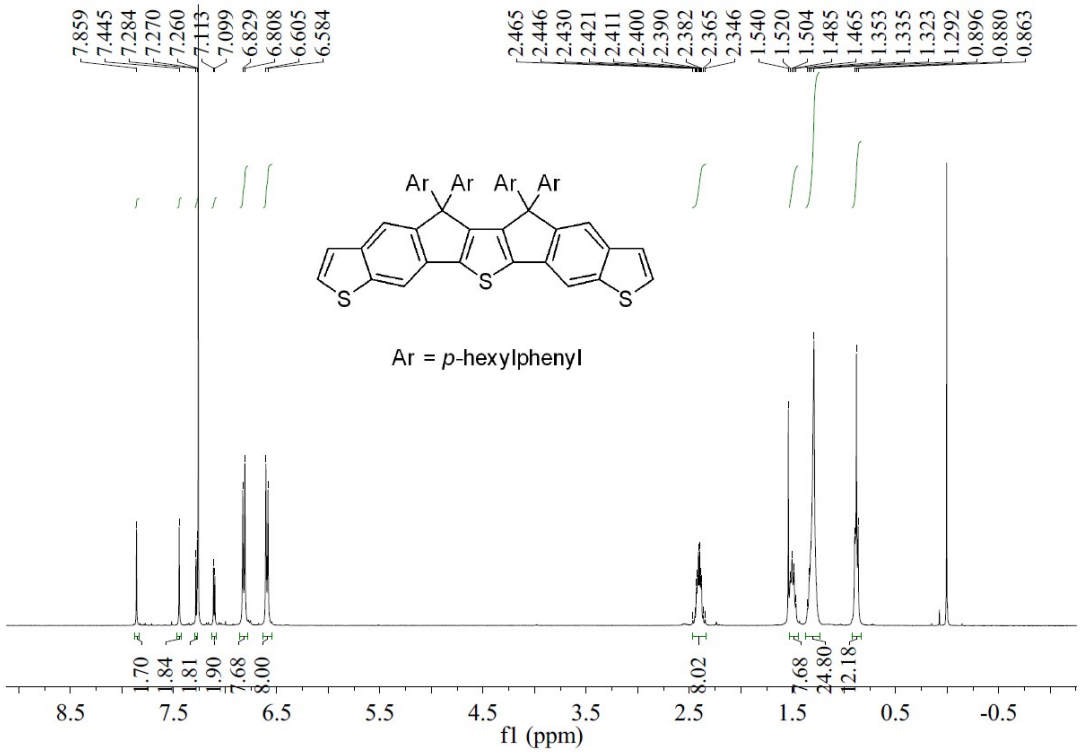


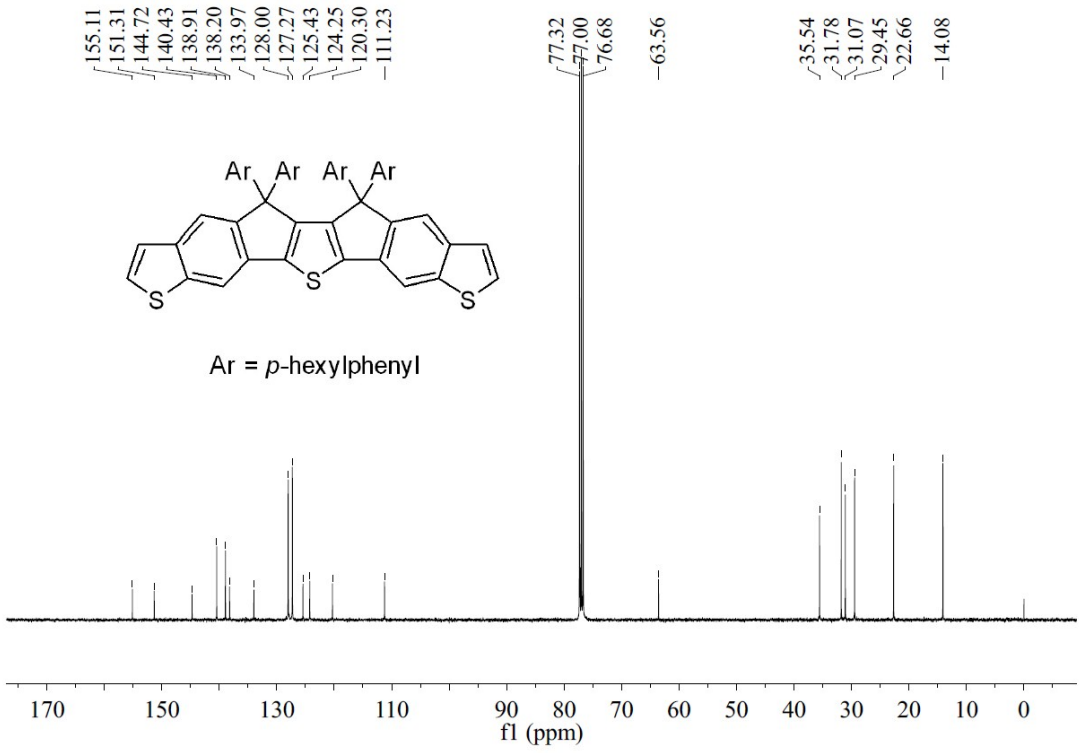
((3,7-Dichloro-10,10,11,11-tetrakis(4-hexylphenyl)-10,11-dihydrodiindeno[1,2-*b*:2',1'-*d*]thiophene-2,8-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (7a)



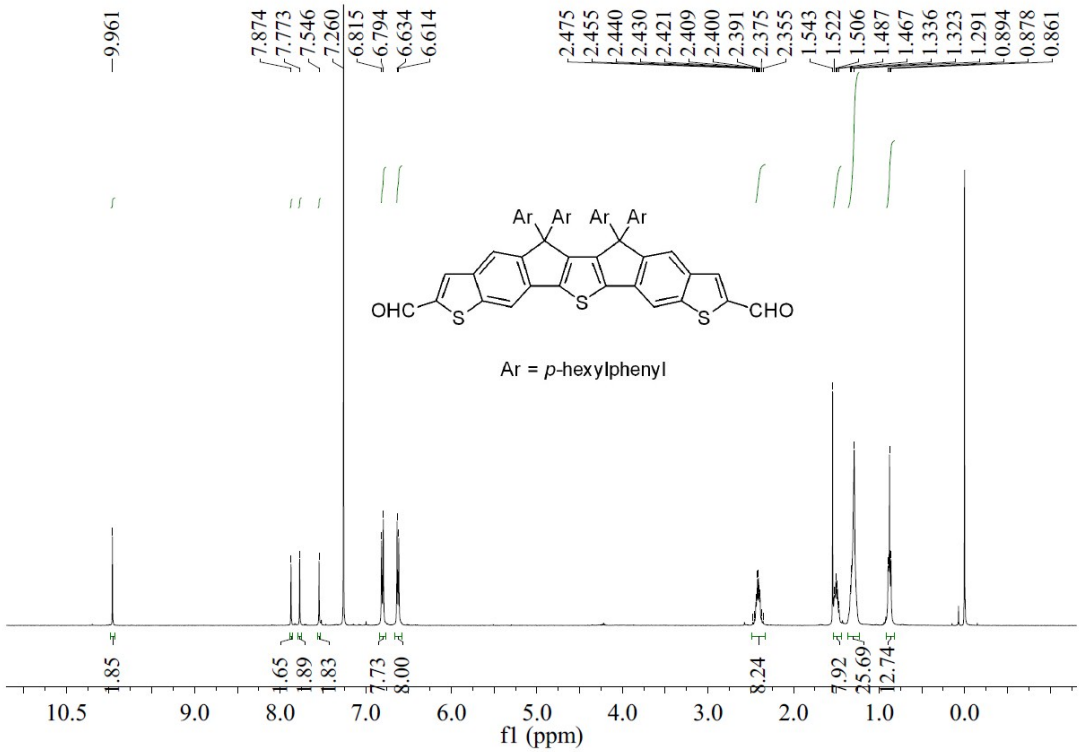


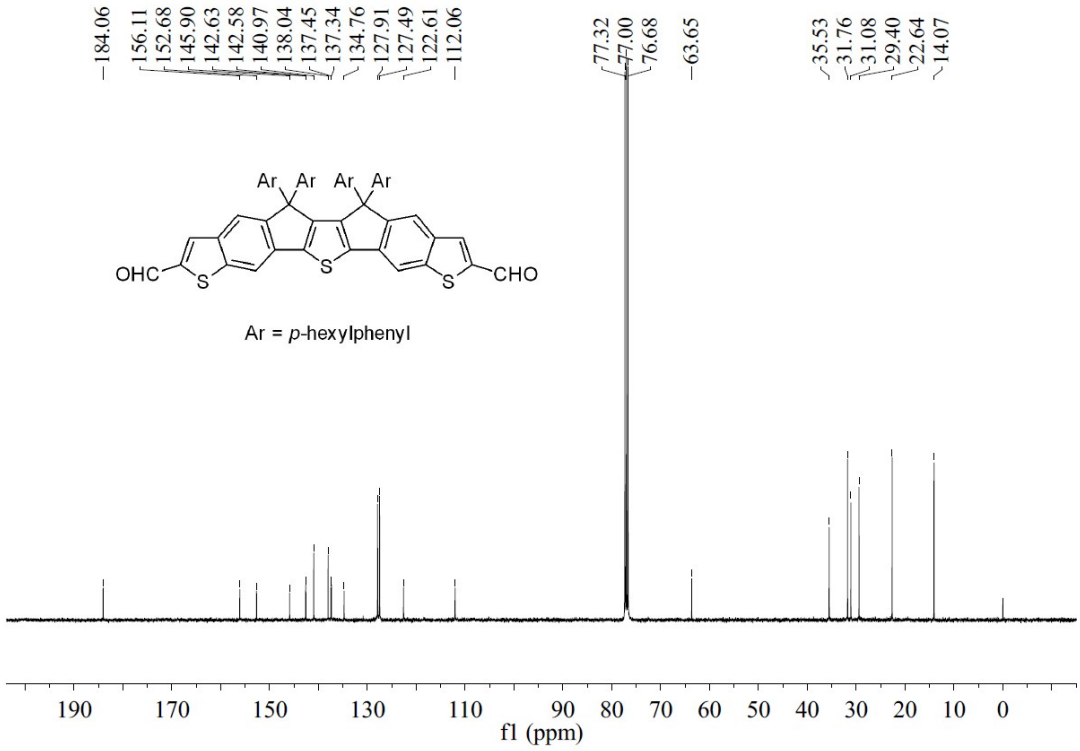
Compound 8a


7.859
7.445
7.284
7.270
7.260
7.113
7.099
6.829
6.808
6.605
6.584
2.465
2.446
2.430
2.421
2.411
2.400
2.390
2.382
2.365
2.346
1.540
1.520
1.504
1.485
1.465
1.353
1.335
1.323
1.292
0.896
0.880
0.863
Ar Ar Ar Ar
S S S
Ar = p-hexylphenyl
1.70
1.84
1.81
1.90
7.68
8.00
8.02
7.68
24.80
12.18
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

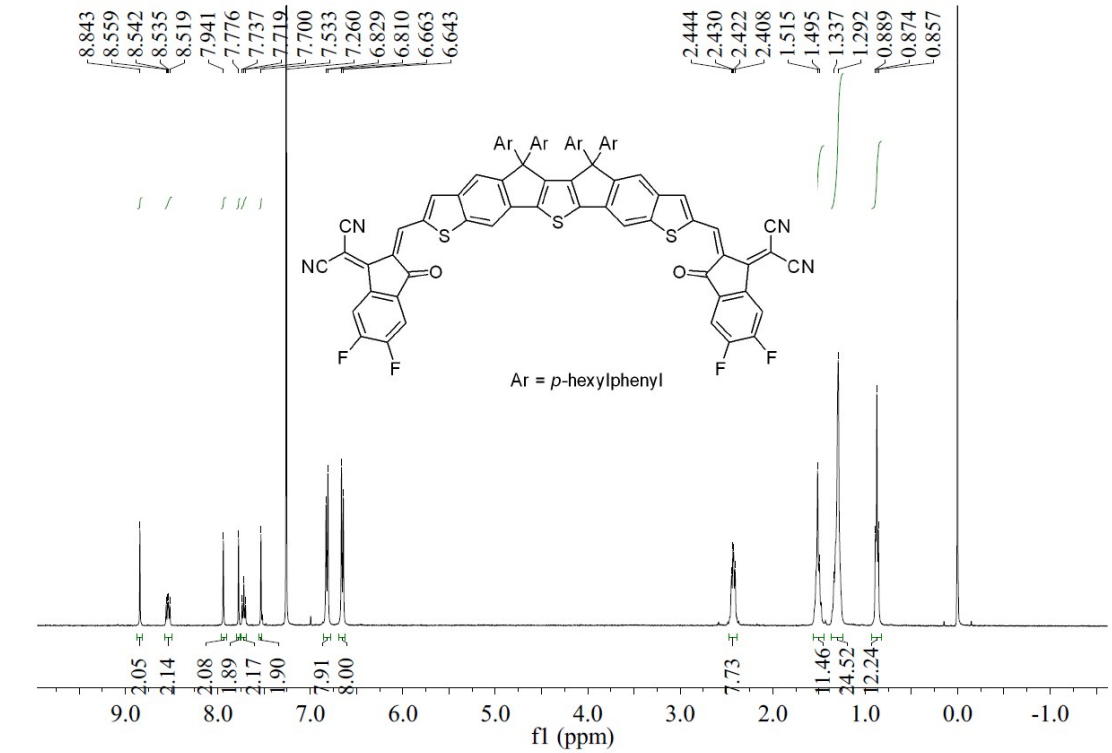

155.11
151.31
144.72
140.43
138.91
138.20
133.97
128.00
127.27
125.43
124.25
120.30
111.23
77.32
77.00
76.68
63.56
35.54
31.78
31.07
29.45
22.66
14.08
Ar Ar Ar Ar
S S S
Ar = p-hexylphenyl
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

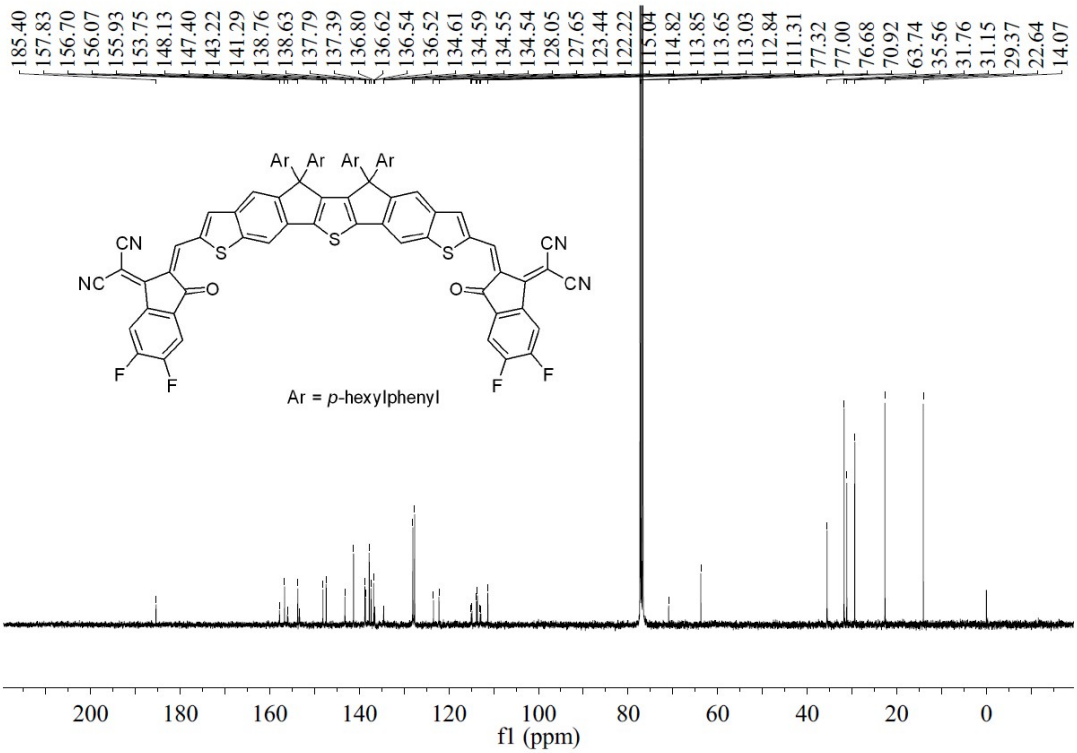
Compound 9a

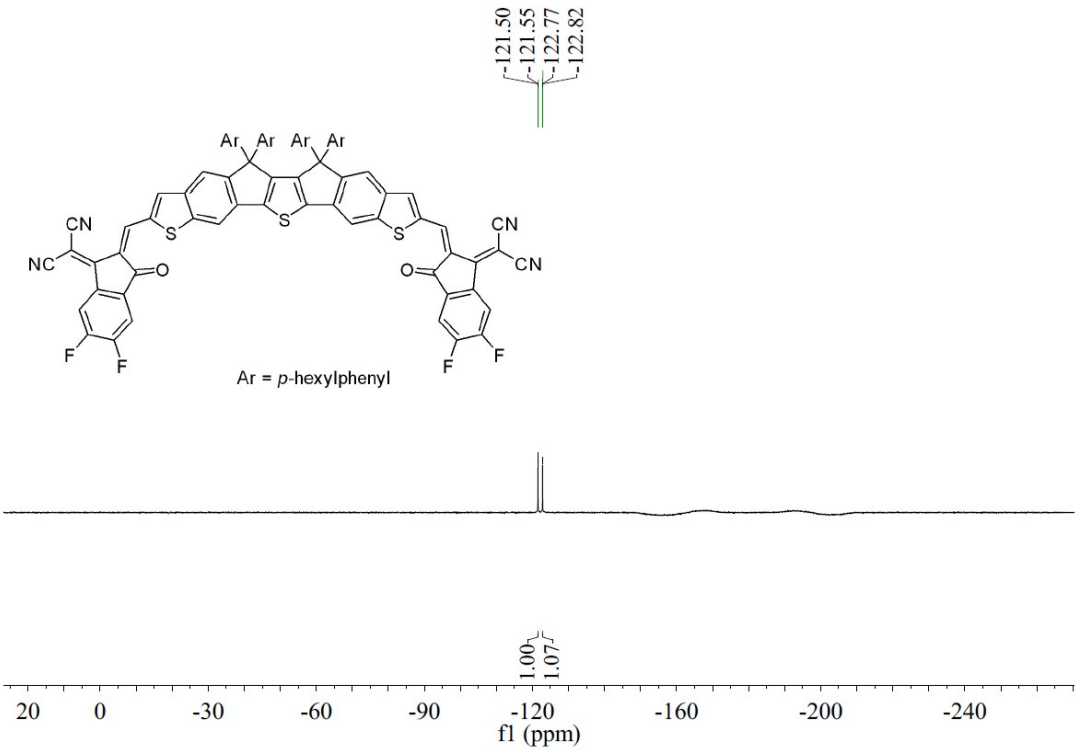

9.961
7.874
7.773
7.546
7.260
6.815
6.794
6.634
6.614
2.475
2.455
2.440
2.430
2.421
2.409
2.400
2.391
2.375
2.355
1.543
1.522
1.506
1.487
1.467
1.336
1.323
1.291
0.894
0.878
0.861
Ar Ar Ar Ar
OHC
CHO
S
Ar = p-hexylphenyl
1.85
1.65
1.89
1.83
7.73
8.00
8.24
7.92
25.69
12.74
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


184.06
156.11
152.68
145.90
142.63
142.58
140.97
138.04
137.45
137.34
134.76
127.91
127.49
122.61
112.06
77.32
77.00
76.68
63.65
35.53
31.76
31.08
29.40
22.64
14.07
Ar Ar Ar Ar
OHC
CHO
S
Ar = p-hexylphenyl
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

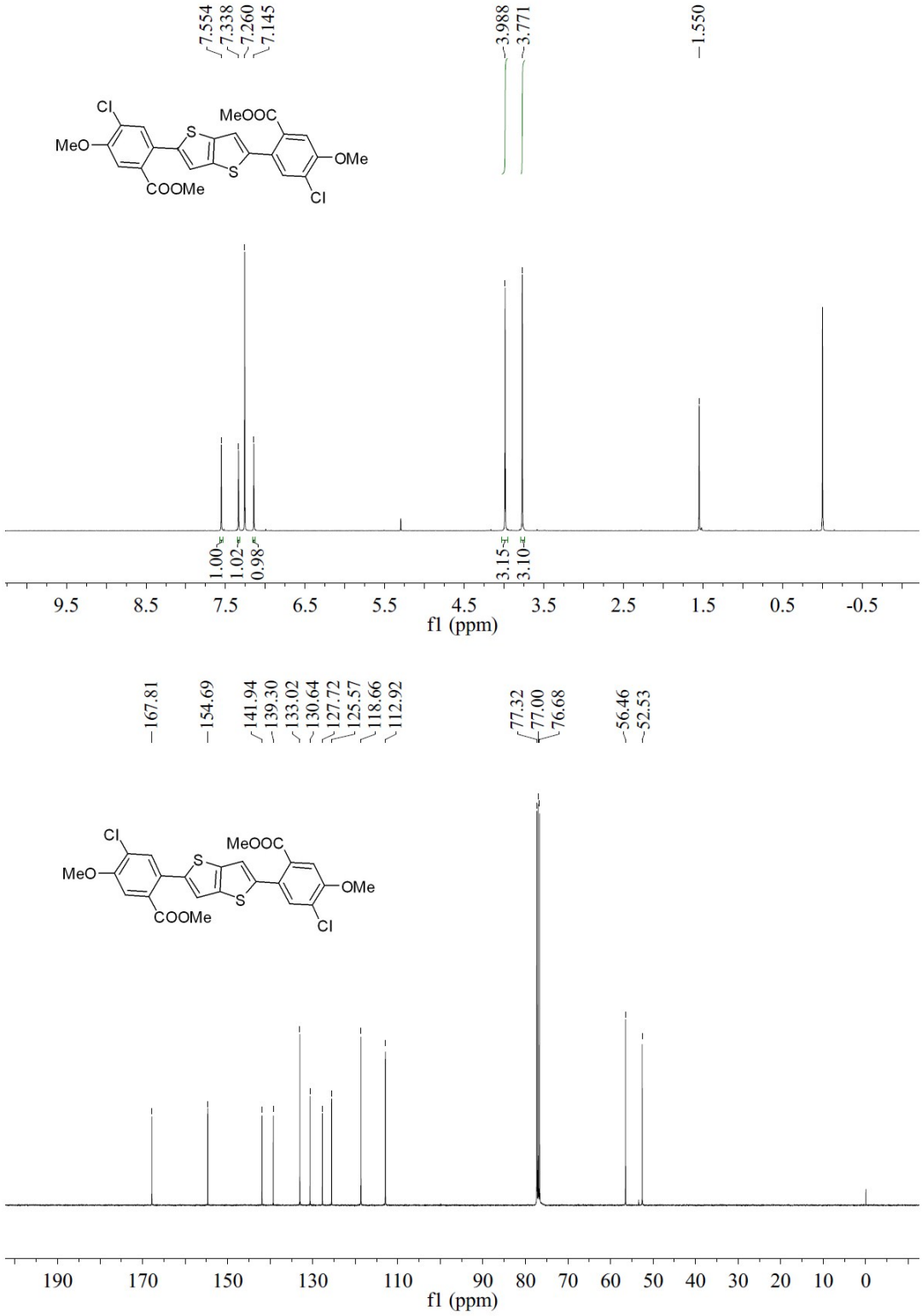
FTBT


8.843
8.559
8.542
8.535
8.519
7.941
7.776
7.737
7.719
7.700
7.533
7.260
6.829
6.810
6.663
6.643
2.444
2.430
2.422
2.408
1.515
1.495
1.337
1.292
0.889
0.874
0.857
Ar Ar Ar Ar
CN
NC
S
S
S
CN
CN
O
O
F
F
F
F
Ar = p-hexylphenyl
2.05
2.14
2.08
1.89
2.17
1.90
7.91
8.00
7.73
11.46
24.52
12.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


185.40
157.83
156.70
156.07
155.93
153.75
148.13
147.40
143.22
141.29
138.76
138.63
137.79
137.39
136.80
136.62
136.54
136.52
134.61
134.59
134.55
134.54
128.05
127.65
123.44
122.22
115.04
114.82
113.85
113.65
113.03
112.84
111.31
77.32
77.00
76.68
70.92
63.74
35.56
31.76
31.15
29.37
22.64
14.07
Ar Ar Ar Ar
CN
NC
S
S
S
CN
CN
O
O
F
F
F
F
Ar = p-hexylphenyl
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

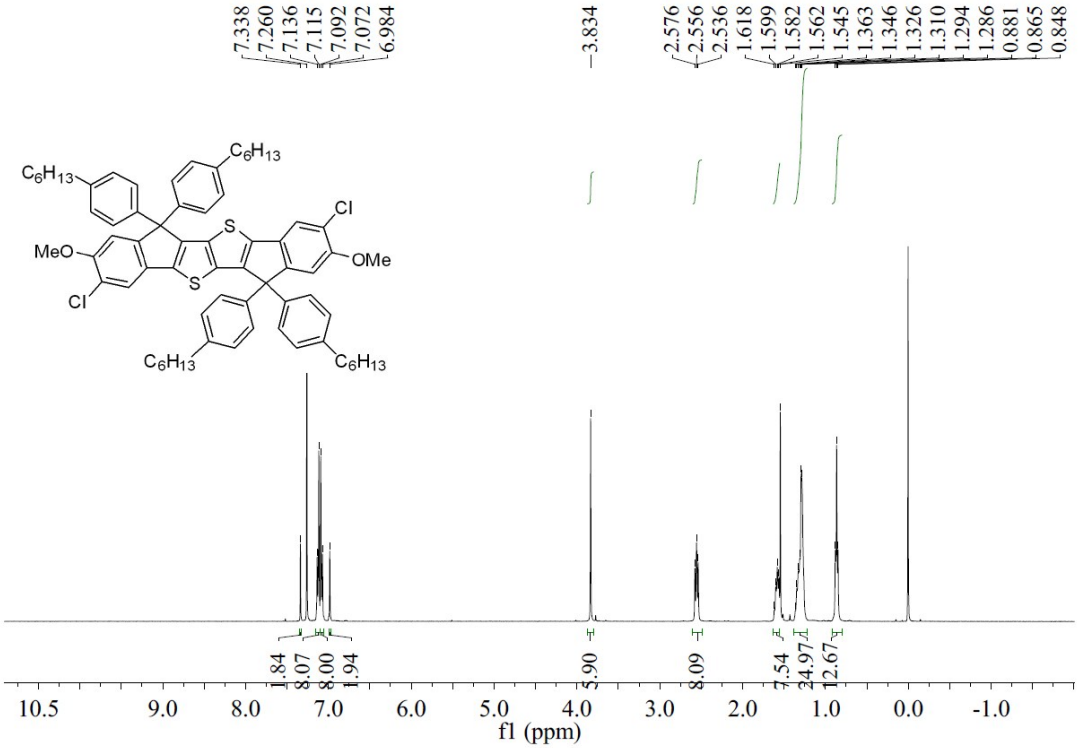

-121.50
-121.55
-122.77
-122.82
Ar Ar Ar Ar
CN
NC
S
S
S
CN
CN
O
O
F
F
F
F
Ar = p-hexylphenyl
1.00
1.07
20
0
-30
-60
-90
-120
-160
-200
-240
f1 (ppm)

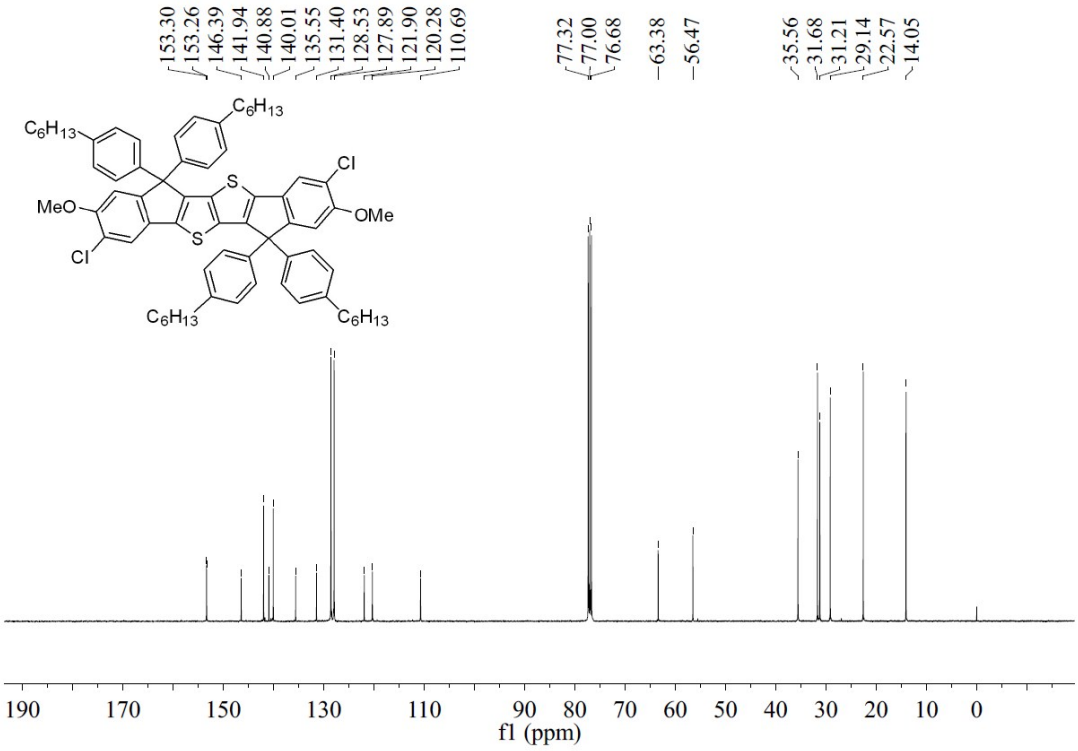
Dimethyl 6,6'-(thieno[3,2-*b*]thiophene-2,5-diyl)bis(4-chloro-3-methoxybenzoate) (3b)



3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-2,8-dimethoxy-6,12-dihydroindeno[1,2-

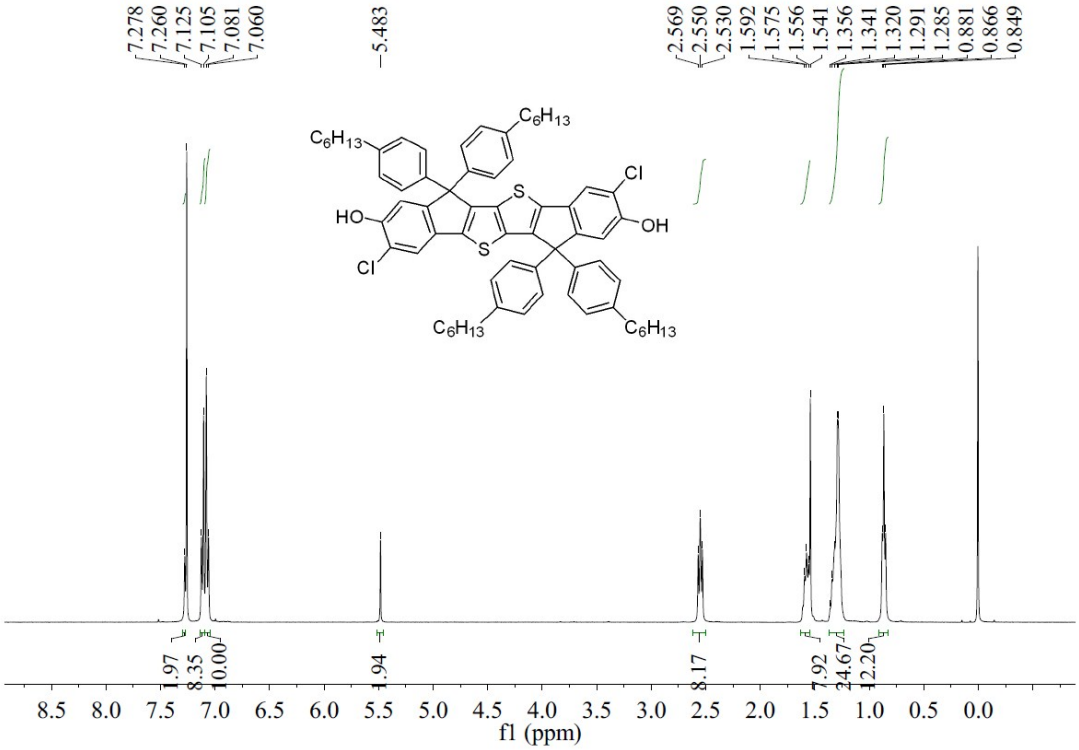
***b*]indeno[2',1':4,5]thieno[2,3-*d*]thiophene (4b)**

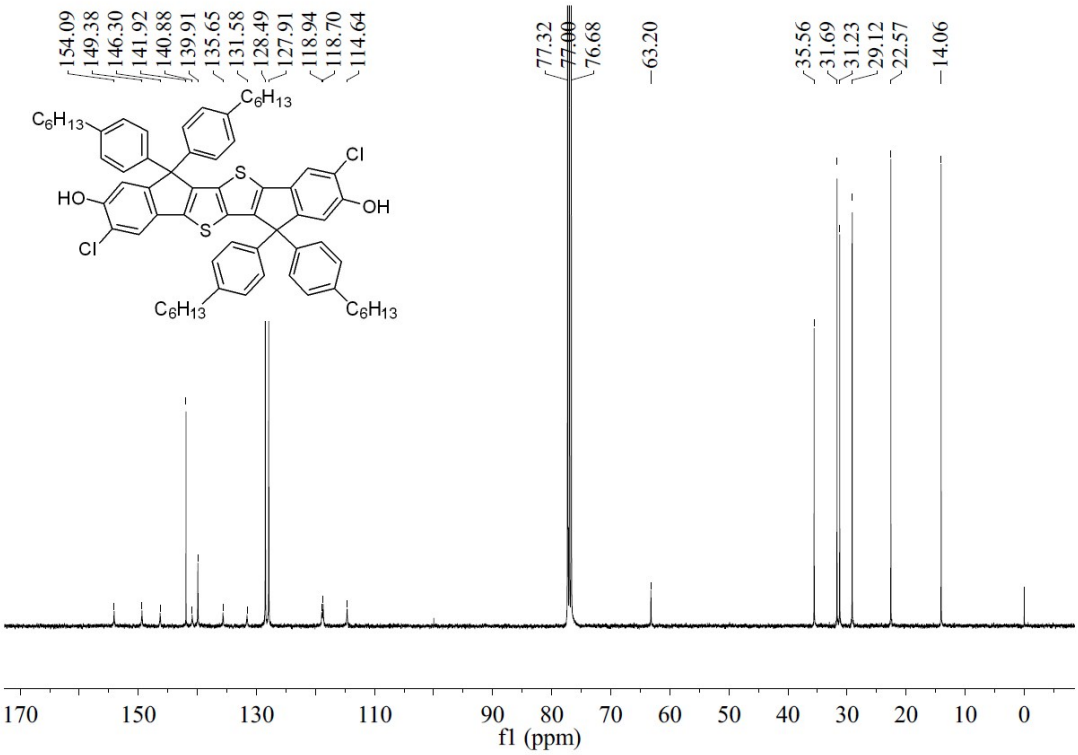




3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydroindeno[1,2-

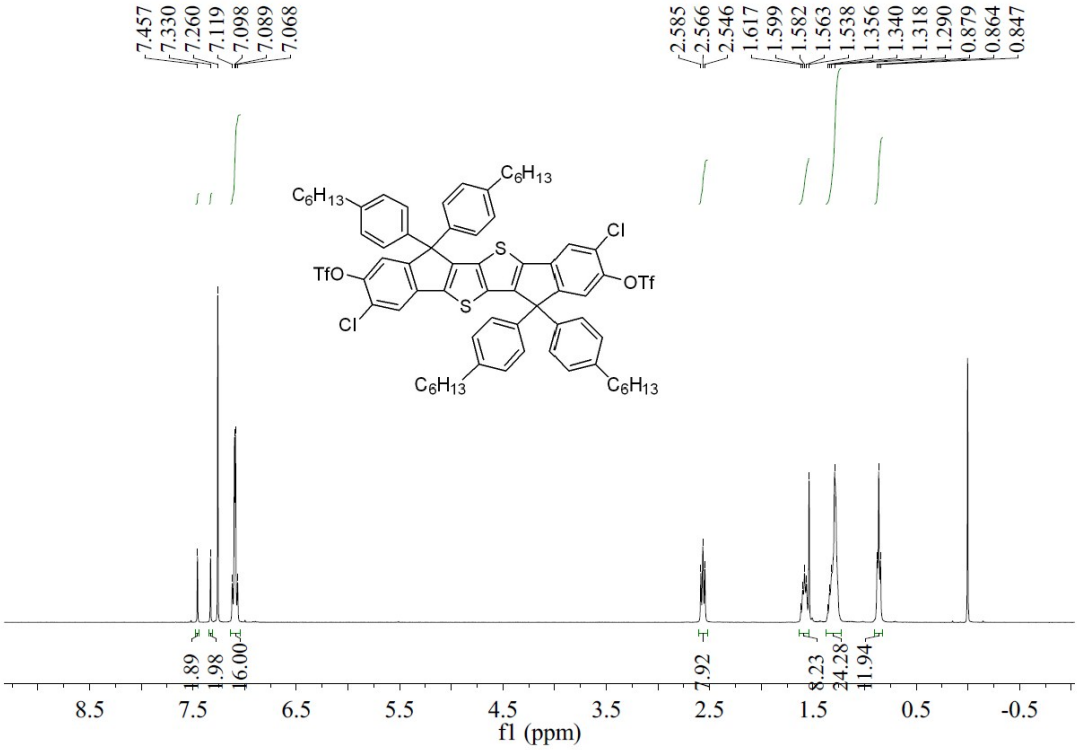
***b*]indeno[2',1':4,5]thieno[2,3-*d*]thiophene-2,8-diol (5b)**

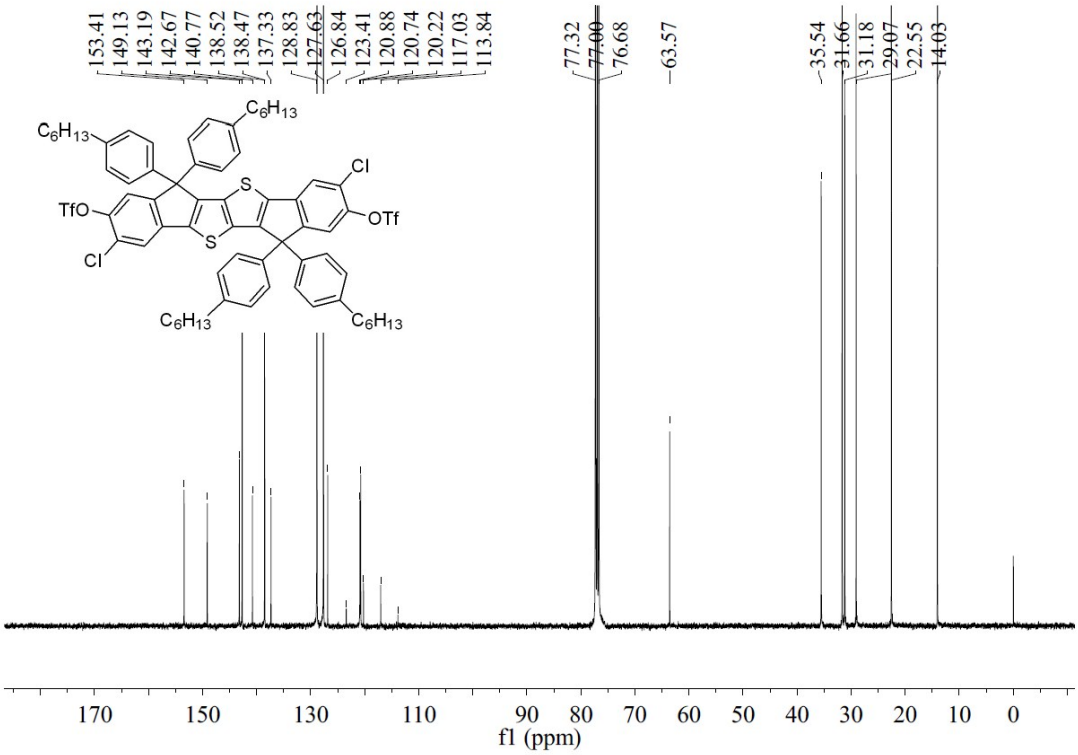




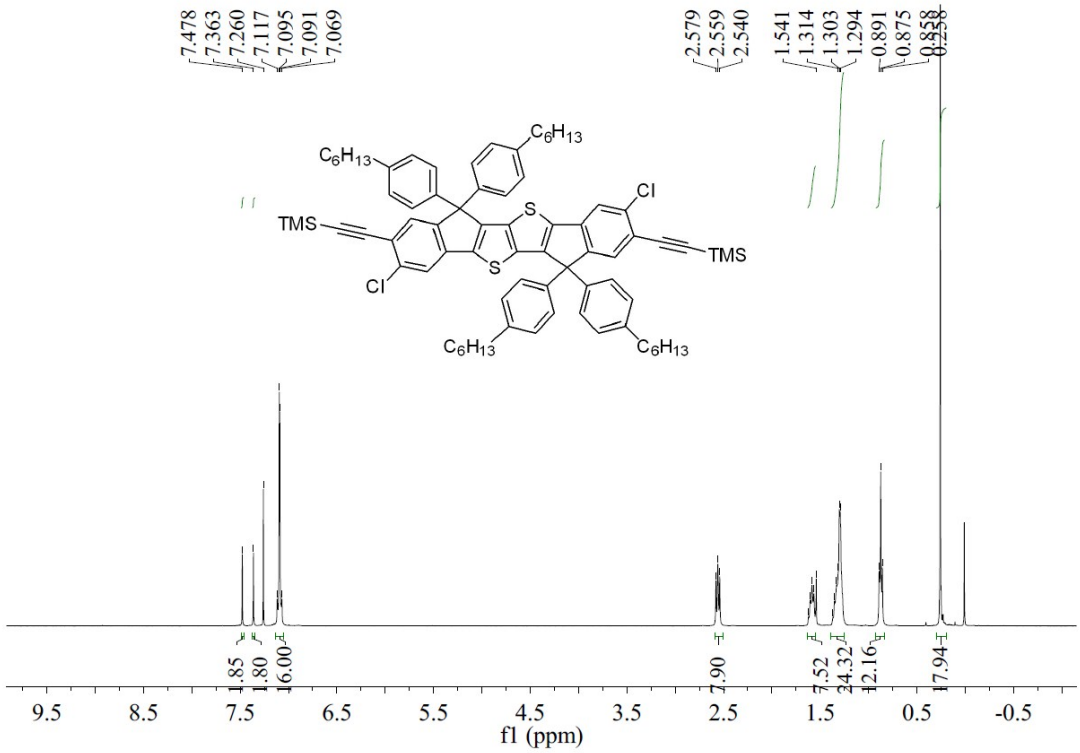
3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydroindeno[1,2-

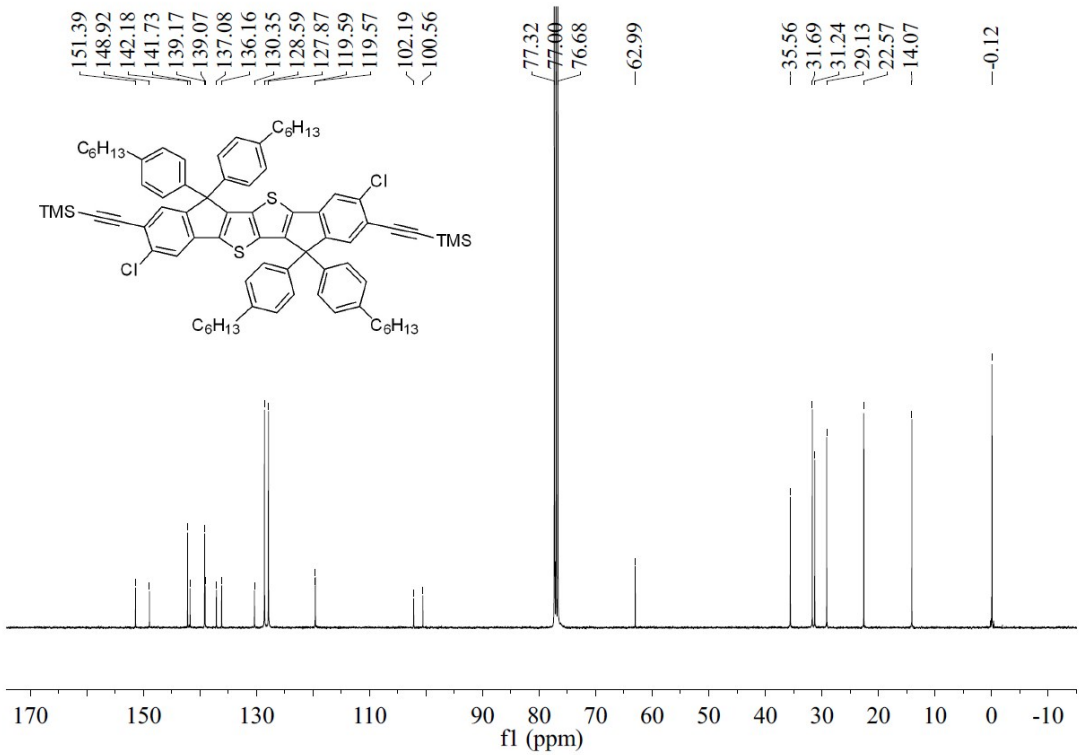
***b*]indeno[2',1':4,5]thieno[2,3-*d*]thiophene-2,8-diyl bis(trifluoromethanesulfonate) (6b)**



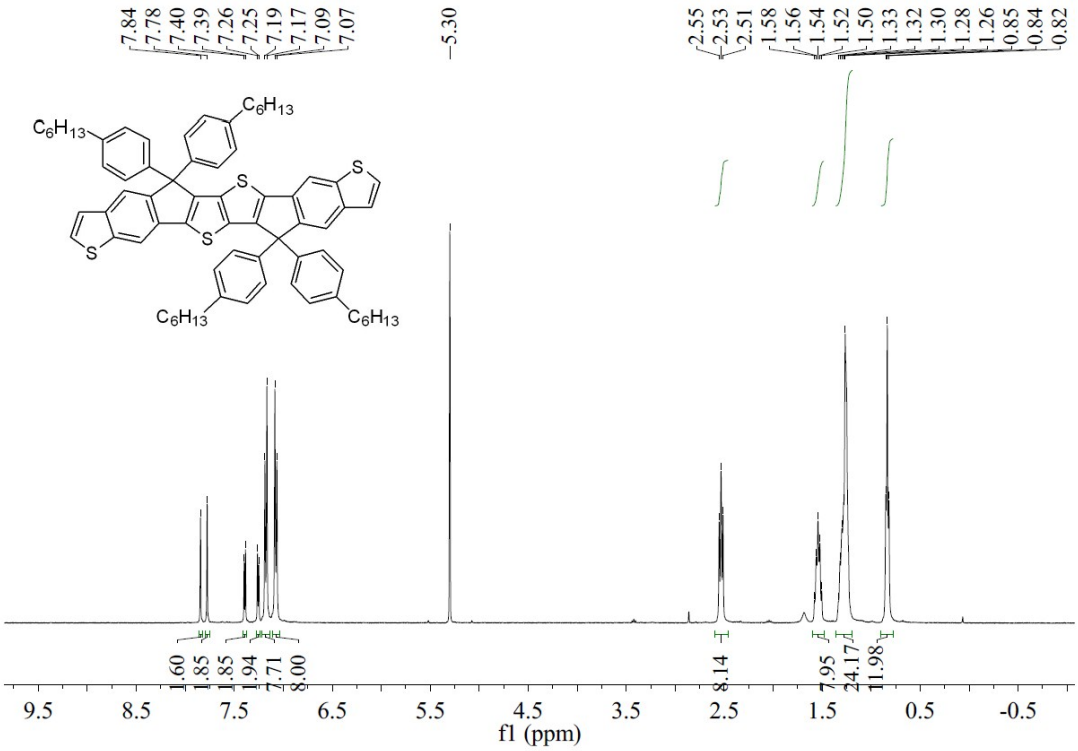


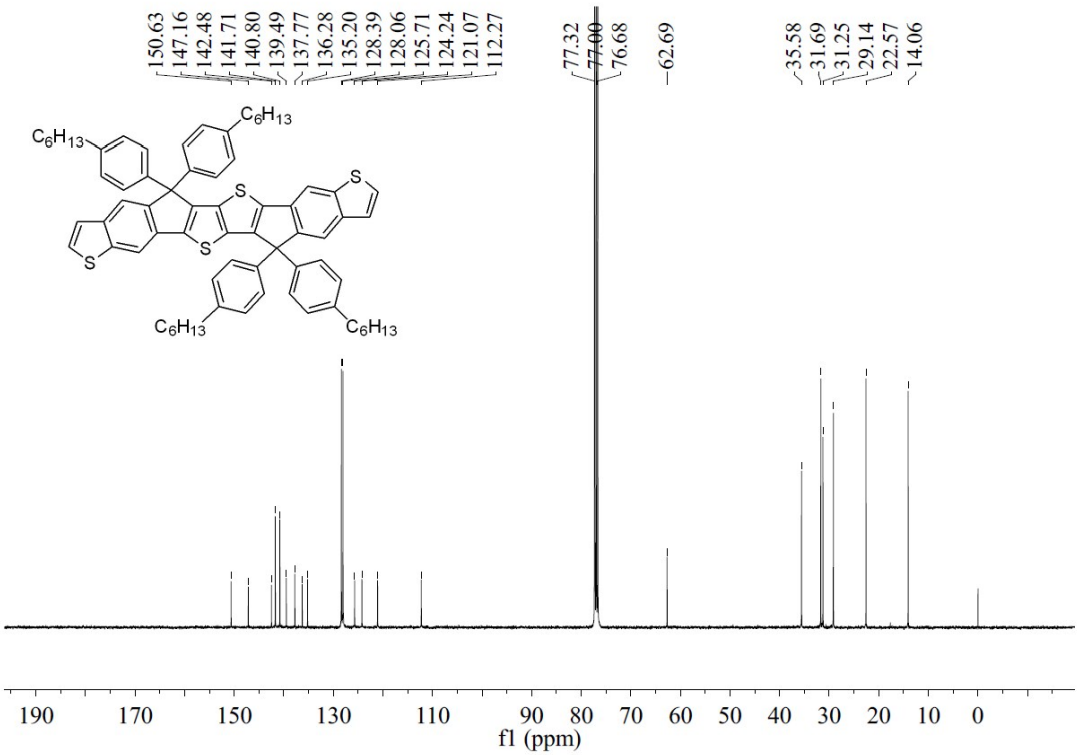
((3,9-Dichloro-6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydroindeno[1,2-*b*]indeno[2',1':4,5]thieno[2,3-*d*]thiophene-2,8-diyl)bis(ethyne-2,1-diyl))bis(trimethylsilane) (7b)


7.478
7.363
7.260
7.117
7.095
7.091
7.069
2.579
2.559
2.540
1.541
1.314
1.303
1.294
0.891
0.875
0.858
0.256
C6H13
C6H13
TMS
Cl
S
S
Cl
TMS
C6H13
C6H13
1.85
1.80
16.00
7.90
7.52
24.32
12.16
17.94
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

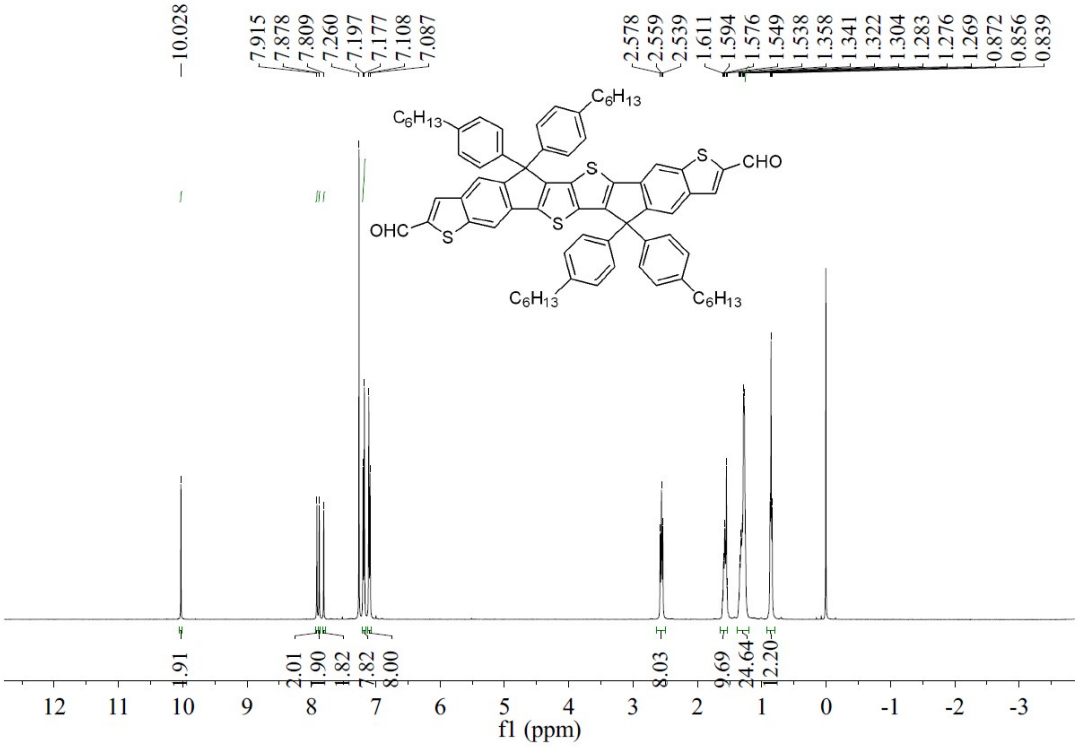

151.39
148.92
142.18
141.73
139.17
139.07
137.08
136.16
130.35
128.59
127.87
119.59
119.57
102.19
100.56
77.32
77.00
76.68
62.99
35.56
31.69
31.24
29.13
22.57
14.07
0.12
C6H13
C6H13
TMS
Cl
S
S
Cl
TMS
C6H13
C6H13
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

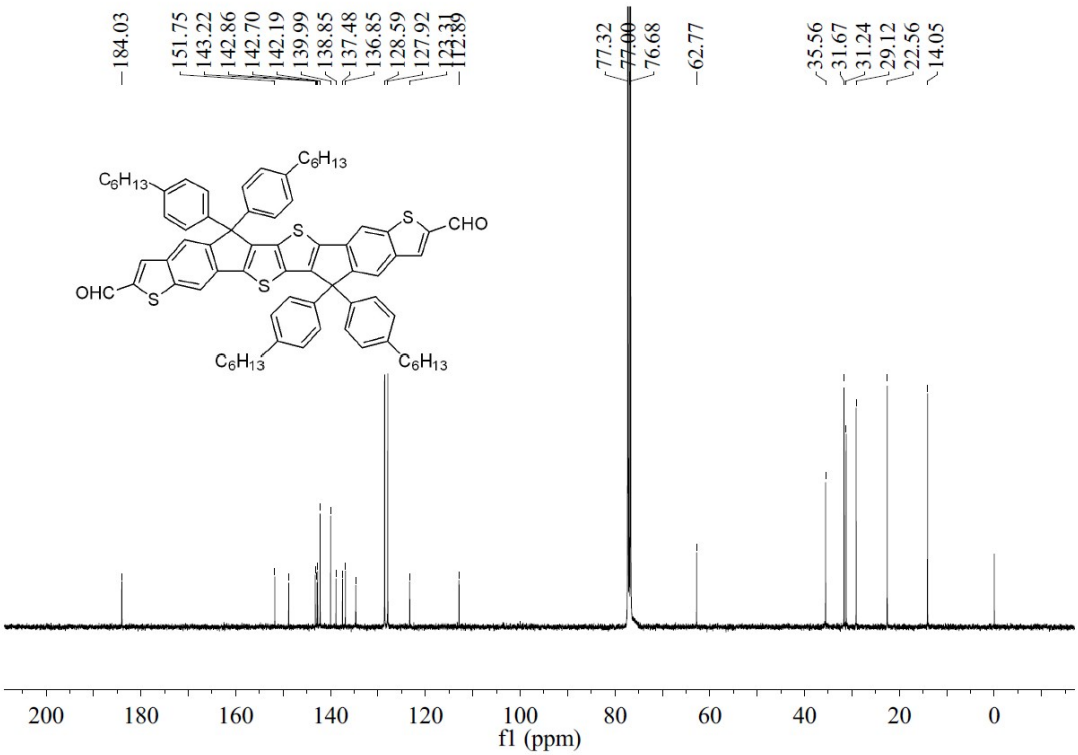
Compound 8b


7.84
7.78
7.40
7.39
7.26
7.25
7.19
7.17
7.09
7.07
5.30
2.55
2.53
2.51
1.58
1.56
1.54
1.52
1.50
1.33
1.32
1.30
1.28
1.26
0.85
0.84
0.82
C6H13
C6H13
C6H13
C6H13
S
1.60
1.85
1.85
1.94
7.71
8.00
8.14
7.95
24.17
11.98
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

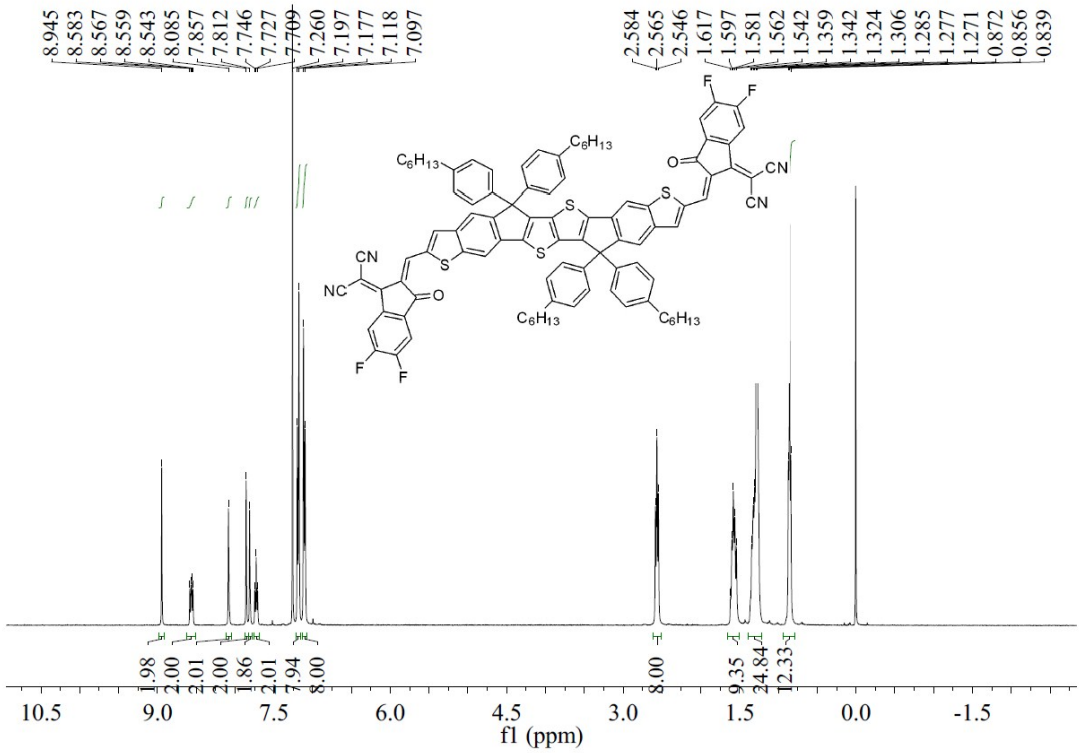

150.63
147.16
142.48
141.71
140.80
139.49
137.77
136.28
135.20
128.39
128.06
125.71
124.24
121.07
112.27
77.32
77.00
76.68
62.69
35.58
31.69
31.25
29.14
22.57
14.06
C6H13
C6H13
C6H13
C6H13
S
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

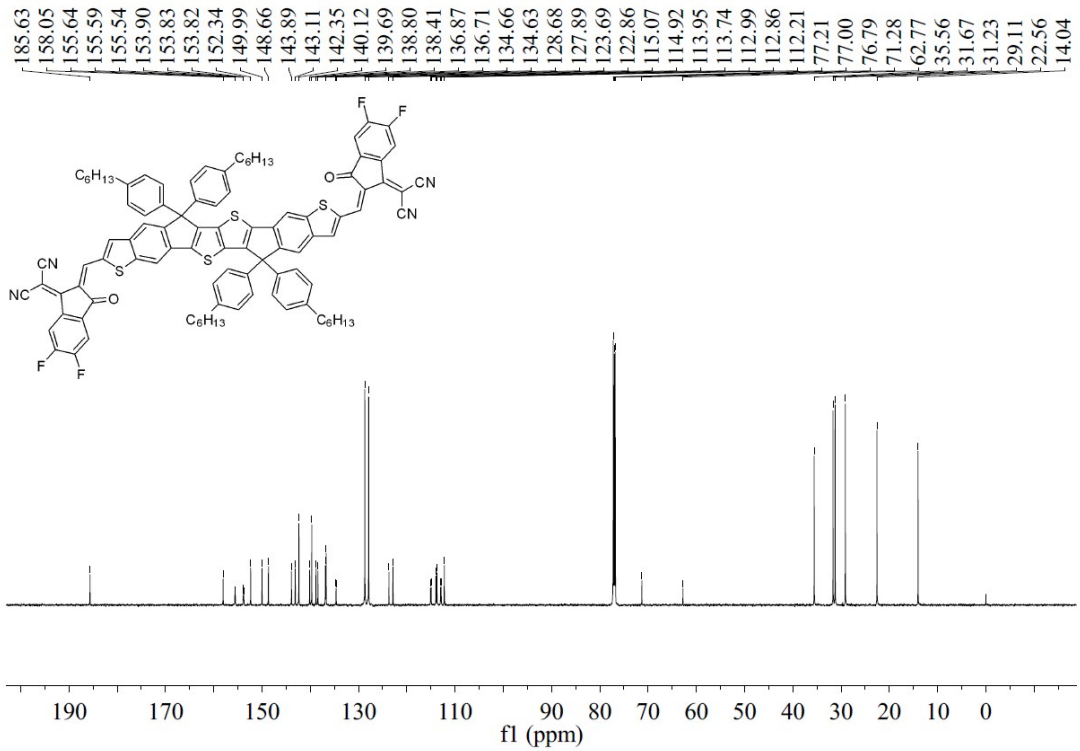
Compound 9b

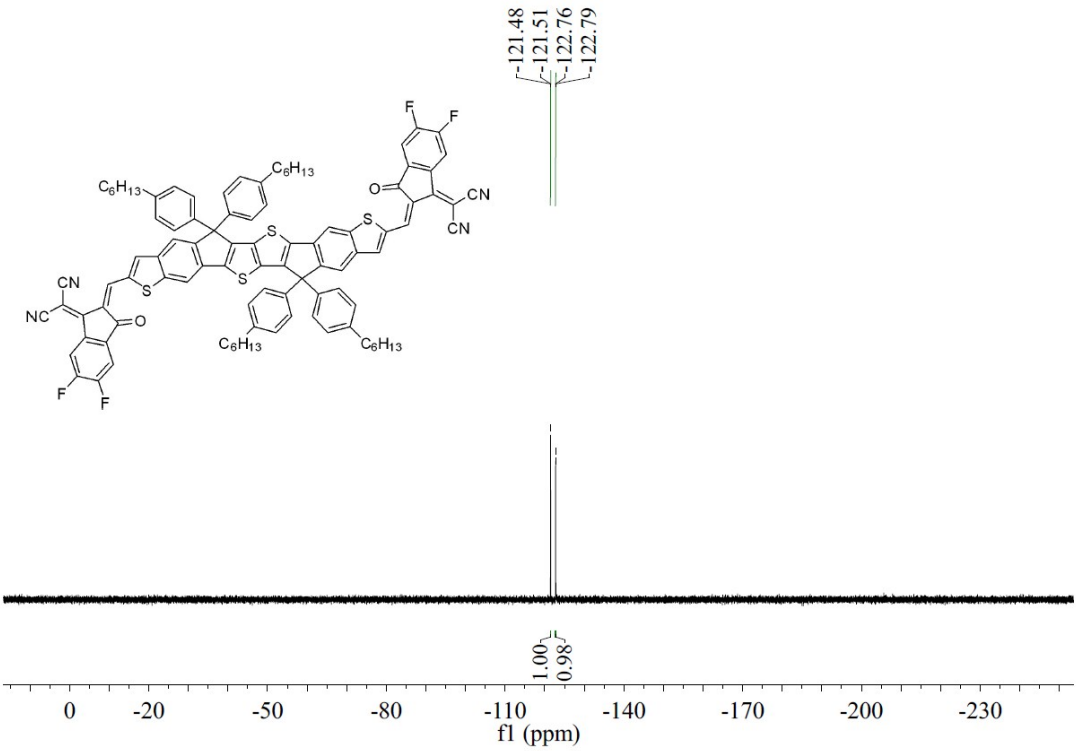

10.028
7.915
7.878
7.809
7.260
7.197
7.177
7.108
7.087
2.578
2.559
2.539
1.611
1.594
1.576
1.549
1.538
1.358
1.341
1.322
1.304
1.283
1.276
1.269
0.872
0.856
0.839
C6H13
CHO
OHC
S
1.91
2.01
1.90
1.82
7.82
8.00
8.03
9.69
24.64
12.20
fl (ppm)


184.03
151.75
143.22
142.86
142.70
142.19
139.99
138.85
137.48
136.85
128.59
127.92
123.31
112.89
77.32
77.00
76.68
62.77
35.56
31.67
31.24
29.12
22.56
14.05
C6H13
CHO
OHC
S
fl (ppm)

FTTBT


8.945
8.583
8.567
8.559
8.543
8.085
7.857
7.812
7.746
7.727
7.709
7.260
7.197
7.177
7.118
7.097
2.584
2.565
2.546
1.617
1.597
1.581
1.562
1.542
1.359
1.342
1.324
1.306
1.285
1.277
1.271
0.872
0.856
0.839
1.98
2.00
2.01
2.00
1.86
2.01
7.94
8.00
8.00
9.35
24.84
12.33
10.5
9.0
7.5
6.0
4.5
3.0
1.5
0.0
-1.5
f1 (ppm)


185.63
158.05
155.64
155.59
155.54
153.90
153.83
153.82
152.34
149.99
148.66
143.89
143.11
142.35
140.12
139.69
138.80
138.41
136.87
136.71
134.66
134.63
128.68
127.89
123.69
122.86
115.07
114.92
113.95
113.74
112.99
112.86
112.21
77.21
77.00
76.79
71.28
62.77
35.56
31.67
31.23
29.11
22.56
14.04
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



References

1. M. Zhang; X. Guo; W. Ma; H. Ade; J. Hou. *Adv. Mater.* 2015, **27**, 4655.
2. N. M. Kirby; S. T. Mudie; A. M. Hawley; D. J. Cookson; H. D. T. Mertens; N. Cowieson; V. Samardzic-Boban. *J. Appl. Crystallogr.* 2013, **46**, 1670.
3. J. Ilavsky. *J. Appl. Crystallogr.* 2012, **45**, 324.