Supporting Information

Understanding the side-chain effects on A-D-A acceptors: in-plane and out-of-plane

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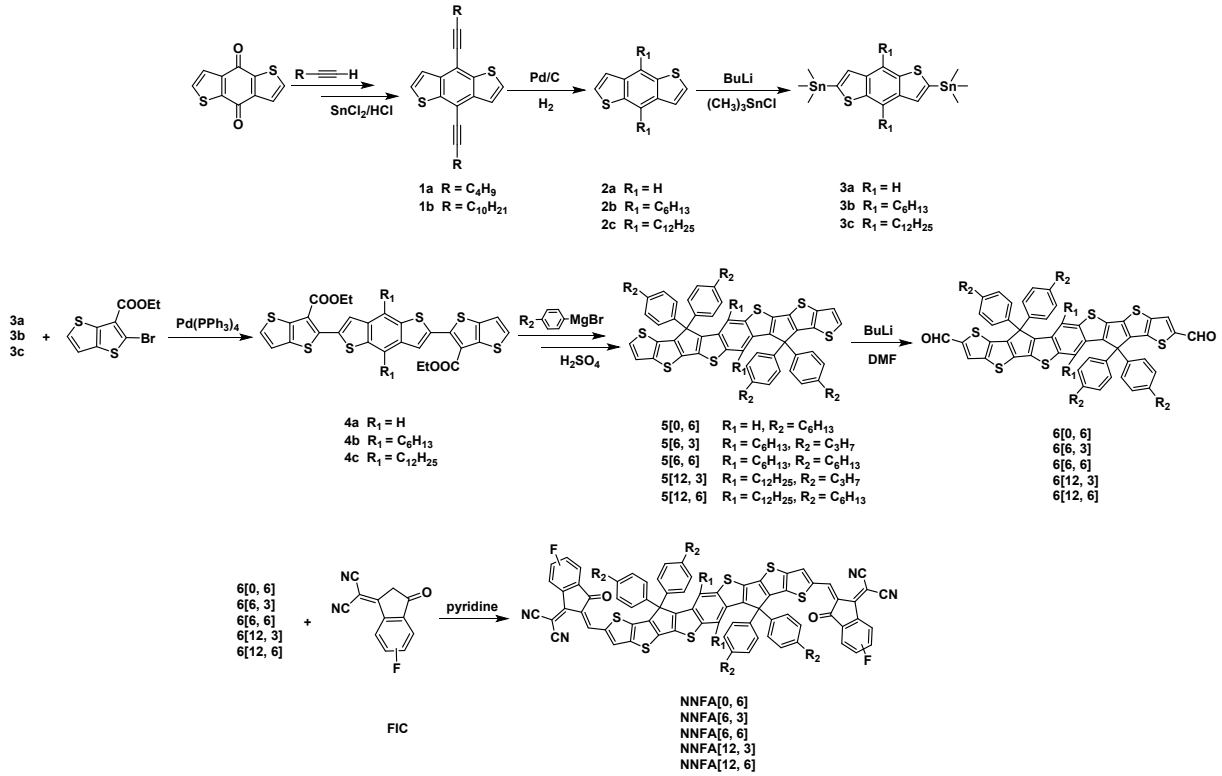
1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous ODCB/CH_3CN (9:1) solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). The nonfullerene acceptor was dissolved in the solution. A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag^+ electrode was used as the reference electrode. All potentials were corrected against Fc/Fc^+. AFM was performed on a Dimension 3100 microscope (Veeco) using tapping mode.

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co., SunaTech Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques. Compound **1b**,[1] compound **2c**,[1] ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate,[2] FIC[3] and FTAZ[4] were prepared according to literatures. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione and compound **2a** was purchased from SunaTech Co.



Scheme S1 Synthetic route for NNFA[n, m].

Compound 1a. To a solution of hexyne (3.28 g, 40 mmol) in THF (20 mL) was added isopropylmagnesium chloride (30.8 mL, 1.3 M in THF, 40 mmol) under argon at 0 °C. The reaction mixture was heated to 50 °C and stirred for 90 min. After cooling to room temperature, benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (2.2 g, 10 mmol) was added. The mixture was stirred at 50 °C for 1 h. Subsequently, a solution of $SnCl_2$ (20 g in 37 mL 10% aq HCl) was added. The mixture was stirred at 60 °C for 1 h and then poured into water followed by extraction with petroleum ether three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether as eluent to give **compound 1a** as a yellow solid (2.52 g, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.58 (d, *J* = 5.6 Hz, 2H), 7.50 (d, *J* = 5.6 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 4H), 1.70-1.77 (m, 4H), 1.57-1.66 (m, 4H), 1.02 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 140.18, 138.21, 127.55, 123.33, 112.18, 100.33, 30.86, 22.03, 19.63, 13.8.

Compound 2b. To a solution of compound 1a (3.5 g, 10 mmol) in THF (100 mL) was added 10% Pd/C (1.06 g, 1 mmol) under H_2 at room temperature. The mixture was stirred for 24 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether as eluent to give **compound 2b** as a white solid (2.04 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.47 (d, *J* = 5.5 Hz, 2H), 7.45 (d, *J* = 5.5 Hz, 2H), 3.16-3.20 (m, 4H), 1.76-1.84 (m, 4H), 1.45-1.49 (m, 4H), 1.30-1.36 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 137.31, 135.84, 128.96, 125.80, 121.82, 33.50, 31.71, 29.65, 29.62, 22.62, 14.11.

Compound 3a. To a solution of compound 2a (190 mg, 1 mmol) in dry THF (10 mL) was added *n*-BuLi (1.4 mL, 1.6 M in hexane, 2.2 mmol) at -78 °C under argon. After 1 h, the mixture was warmed to room temperature and stirred for 2 h. The mixture was cooled to -78 °C again and trimethyltin chloride (2.4 mL, 1 M in THF, 2.4 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred overnight. The reaction mixture was poured into water and extracted with petroleum ether three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was washed with methanol to give **compound 3a** as a white solid (300 mg, 58%). ^{1}H NMR ($CDCl_3$, 100 MHz, δ/ppm): 8.27 (s, 2H), 7.41 (s, 2H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$, 400 MHz, δ/ppm): 141.84, 141.35, 138.68, 131.09, 115.02, -8.33.

Compound 3b. To a solution of compound 2b (538 mg, 1.5 mmol) in dry THF (20 mL) was added *n*-BuLi (2.1 mL, 1.6 M in hexane, 3.4 mmol) at -78 °C under argon. After 1 h, the mixture was warmed to room temperature and stirred for 2 h. The mixture was cooled to -78 °C again and trimethyltin chloride (3.6 mL, 1 M in THF, 3.6 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred overnight. The reaction mixture was poured into water and extracted with petroleum ether three times. The combined organic layer was dried

over anhydrous Na_2SO_4. After removal of the solvent, the residue was washed with methanol to give **compound 3b** as a white solid (810 mg, 79%). ^{1}H NMR ($CDCl_3$, 100 MHz, δ/ppm): 7.50 (s, 2H), 3.19-3.23 (m, 4H), 1.80-1.84 (m, 4H), 1.46-1.50 (m, 4H), 1.33-1.39 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 6H), 0.45 (s, 18H). ^{13}C NMR ($CDCl_3$, 400 MHz, δ/ppm): 141.52, 140.05, 136.82, 129.76, 127.51, 33.56, 31.71, 29.68, 29.66, 22.66, 14.14, -8.31.

Compound 3c. To a solution of compound 2c (1.04 g, 2 mmol) in dry THF (50 mL) was added *n*-BuLi (2.8 mL, 1.6 M in hexane, 4.4 mmol) at -78 °C under argon. After 1 h, the mixture was warmed to room temperature and stirred for 2 h. The mixture was cooled to -78 °C again and trimethyltin chloride (4.8 mL, 1 M in THF, 4.8 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred overnight. The reaction mixture was poured into water and extracted with petroleum ether three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was washed with methanol to give **compound 3c** as a white solid (1.35 g, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.50 (s, 2H), 3.18-3.23 (m, 4H), 1.79-1.85 (m, 4H), 1.44-1.48 (m, 4H), 1.34-1.40 (m, 4H), 1.25-1.30 (m, 28H), 0.89 (t, *J* = 6.7 Hz, 6H), 0.46 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 141.52, 140.05, 136.82, 129.77, 127.51, 33.56, 31.93, 29.99, 29.73, 29.70, 29.67, 29.63, 29.51, 29.37, 22.70, 14.13, -8.31.

Compound 4a. To a solution of compound 3a (208 mg, 0.4 mmol) and ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate (256 mg, 0.88 mmol) in toluene was added $Pd(PPh_3)_4$ (47 mg, 0.04 mmol) under argon. The mixture was heated to reflux and stirred overnight. The mixture was poured into MeOH. The precipitate was collected and dried under vacuum to give **compound 4a** as a yellow solid (176 mg, 72%). NMR data were not acquired due to the extremely low solubility of compound 4a.

Compound 4b. To a solution of compound 3b (411 mg, 0.6 mmol) and ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate (385 mg, 1.32 mmol) in toluene was added $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) under N_2. The mixture was heated to reflux and stirred overnight. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (2:1) as eluent to give **compound 4b** as a orange solid (420 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.94 (s, 2H), 7.50 (d, *J* = 4.6 Hz, 2H), 7.28 (d, *J* = 4.6 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 4H), 3.17-3.21 (m, 4H), 1.82-1.88 (m, 4H), 1.46-1.52 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 6H), 1.31-1.37 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.94, 145.14, 141.28, 138.51, 136.62, 136.43, 134.23, 129.45, 129.41, 127.70, 121.40, 118.76, 61.27, 33.40, 31.70, 29.71, 29.65, 29.59, 14.24, 14.11.

Compound 4c. To a solution of compound 3c (639 mg, 0.75 mmol) and ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate (480 mg, 1.65 mmol) in toluene was added $Pd(PPh_3)_4$ (87 mg, 0.075 mmol) under N_2. The mixture was heated to reflux

and stirred overnight. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (2:1) as eluent to give **compound 4c** as a orange solid (420 mg, 59%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.94 (s, 2H), 7.50 (d, *J* = 5.3 Hz, 2H), 7.27 (d, *J* = 5.3 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 4H), 3.16-3.20 (m, 4H), 1.84-1.87 (m, 4H), 1.47-1.51 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 6H), 1.20-1.26 (m, 32H), 0.86 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.93, 145.15, 141.28, 138.51, 136.63, 136.42, 134.22, 129.44, 129.41, 124.71, 121.39, 118.74, 61.28, 33.38, 31.90, 29.98, 29.73, 29.69, 29.64, 29.59, 19.53, 29.34, 22.67, 14.25, 14.10.

Compound 5[0, 6]. To a suspension of compound 4a (122 mg, 0.2 mmol) in dry THF (5 mL) was added (4-hexylphenyl)magnesium bromide (2.7 mL, 0.6 M in THF, 1.6 mmol) at room temperature under argon. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was dissolved in a mixed solvent of toluene (2 mL), CH_3COOH (2 mL) and concentrated sulfuric acid (0.1 mL). The mixture was stirred at room temperature for 0.5 h and was poured into MeOH. The precipitate was collected and purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to give **compound 5[0, 6]** as a yellow solid (120 mg, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.99 (s, 2H), 7.30 (d, *J* = 5.0 Hz, 4H), 7.21 (d, *J* = 8.2 Hz, 8H), 7.07 (d, *J* = 8.2 Hz, 8H), 2.51-2.55 (m, 8H), 1.51-1.59 (m, 8H), 1.27-1.33 (m, 24H), 0.85 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 150.97, 148.42, 142.03, 141.55, 141.43, 138.52, 137.94, 137.67, 133.55, 130.70, 128.64, 128.13, 126.11, 120.26, 116.00, 62.85, 35.57, 31.66, 31.18, 29.16, 22.56, 14.06.

Compound 5[6, 3]. To a solution of compound 4b (156 mg, 0.2 mmol) in dry THF (5 mL) was added (4-propylphenyl)magnesium bromide (2.7 mL, 0.6 M in THF, 1.6 mmol) at room temperature under argon. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was dissolved in a mixed solvent of toluene (2 mL), CH_3COOH (2 mL) and concentrated sulfuric acid (0.1 mL). The mixture was stirred at room temperature for 0.5 h and was poured into MeOH. The precipitate was collected and purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to give **compound 5[6, 3]** as a yellow solid (156 mg, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.40 (d, *J* = 8.2 Hz, 8H), 7.22 (d, *J* = 5.1 Hz, 2H), 7.19 (d, *J* = 5.1 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 8H), 2.77-2.81 (m, 4H), 2.51-2.55 (m, 8H), 1.54-1.61 (m, 8H), 1.20-1.23 (m, 4H), 0.98-1.02 (m, 4H), 0.86-0.93 (m, 26H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 154.00, 150.50, 142.83, 141.51, 141.41, 139.44, 136.75, 135.21, 133.35, 131.36, 129.83, 128.60, 128.38, 125.47, 120.19, 63.85 , 37.57, 34.72, 31.63, 30.39, 28.88,24.16, 22.91, 14.20, 13.94.

Compound 5[6, 6]. To a solution of compound 4b (156 mg, 0.2 mmol) in dry THF (5 mL) was added (4-hexylphenyl)magnesium bromide (2.7 mL, 0.6 M in THF, 1.6 mmol) at room temperature under argon. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was dissolved in a mixed solvent of toluene (2 mL), CH_3COOH (2 mL) and concentrated sulfuric acid (0.1 mL). The mixture was stirred at room temperature for 0.5 h and was poured into MeOH. The precipitate was collected and purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to give **compound 5[6, 6]** as a yellow solid (172 mg, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.40 (d, J = 7.9 Hz, 8H), 7.22 (d, J = 5.0 Hz, 2H), 7.19 (d, J = 5.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 8H), 2.77-2.81 (m, 4H), 2.52-2.56 (m, 8H), 1.54-1.58 (m, 12H), 1.27 (br, 28H), 0.94-1.02 (m, 8H), 0.82-0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 154.01, 150.52, 142.84, 141.69, 141.51, 139.43, 136.76, 135.15, 133.36, 131.36, 129.83, 128.61, 128.31, 125.45, 120.19, 63.84, 35.50, 34.73, 31.69, 31.63, 31.07, 30.39, 29.10, 28.87, 22.91, 22.57, 14.21, 14.07.

Compound 5[12, 3]. To a solution of compound 4c (190 mg, 0.2 mmol) in dry THF (5 mL) was added (4-propylphenyl)magnesium bromide (2.7 mL, 0.6 M in THF, 1.6 mmol) at room temperature under argon. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was dissolved in a mixed solvent of toluene (2 mL), CH_3COOH (2 mL) and concentrated sulfuric acid (0.1 mL). The mixture was stirred at room temperature for 0.5 h and was poured into MeOH. The precipitate was collected and purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to give **compound 5[12, 3]** as a yellow solid (159 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.40 (d, J = 8.3 Hz, 8H), 7.22 (d, J = 5.2 Hz, 2H), 7.19 (d, J = 5.2 Hz, 2H), 7.07 (d, J = 8.2 Hz, 8H), 2.77-2.81 (m, 4H), 2.51-2.55 (m, 8H), 1.57-1.63 (m, 8H), 1.29 (br, 32H), 1.00-1.02 (m, 4H), 0.87-0.93 (m, 22H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 153.99, 150.51, 142.82, 141.50, 141.41, 139.43, 136.77, 135.21, 133.36, 131.35, 129.83, 128.60, 128.37, 125.46, 120.19, 63.85, 37.58, 34.71, 31.95, 30.70, 29.90, 29.83, 29.77, 29.73, 29.46, 29.39, 28.88, 24.18, 22.72, 14.14, 13.94.

Compound 5[12, 6]. To a solution of compound 4c (190 mg, 0.2 mmol) in dry THF (5 mL) was added (4-hexylphenyl)magnesium bromide (2.7 mL, 0.6 M in THF, 1.6 mmol) at room temperature under argon. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into ice water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was dissolved in a mixed solvent of toluene (2 mL), CH_3COOH (2 mL) and concentrated sulfuric acid (0.1 mL). The mixture was stirred at room temperature for 0.5 h and was poured

into MeOH. The precipitate was collected and purified via column chromatography (silica gel) by using CH_2Cl_2 as eluent to give **compound 5[12, 6]** as a yellow solid (191 mg, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.41 (d, *J* = 8.2 Hz, 8H), 7.21 (d, *J* = 5.2 Hz, 2H), 7.18 (d, *J* = 5.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 8H), 2.71-2.81 (m, 4H), 2.53-2.55 (m, 8H), 1.53-1.59 (m, 4H), 1.29 (br, 64H), 0.98-1.05 (m, 4H), 0.85-0.89 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 153.99, 150.52, 142.83, 141.68, 141.49, 139.42, 136.77, 135.15, 133.36, 131.35, 129.82, 128.60, 128.30, 125.44, 120.19, 63.84 , 35.52, 34.73, 31.97, 31.70, 31.09, 30.70, 29.94, 29.87, 29.82, 29.76, 29.48, 29.41, 29.12, 28.89, 22.72, 22.50, 14.14, 14.08.

Compound 6[0, 6]. To a solution of compound 5[0, 6] (91 mg, 0.08 mmol) in dry THF (10 mL) was added *n*-BuLi (0.15 mL, 1.6 M, 0.24 mmol) at -78 °C under argon. The resulting mixture was warmed to -50 °C and stirred for 2 h. To the mixture was added N,N-dimethylformamide (65 μL, 0.8 mmol). The resulting mixture was stirred for 1 h and was then quenched by water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 6[0, 6]** as an orange solid (79 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.88 (s, 2H), 8.05 (s, 2H), 7.94 (s, 2H), 7.17 (d, *J* = 8.2 Hz, 8H), 7.08 (d, *J* = 8.2 Hz, 8H), 2.51-2.55 (m, 8H), 1.53-1.59 (m, 8H), 1.23-1.30 (m, 24H), 0.85 (t, *J* = 6.7 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.72, 151.41, 150.98, 145.17, 143.66, 142.57, 142.29, 141.20, 139.60, 137.81, 136.61, 130.97, 129.78, 128.91, 127.93, 116.87, 63.00, 35.55, 31.64, 31.17, 29.12, 22.54, 14.05.

Compound 6[6, 3]. To a solution of compound 5[6, 3] (91 mg, 0.08 mmol) in dry THF (10 mL) was added *n*-BuLi (0.15 mL, 1.6 M, 0.24 mmol) at -78 °C under argon. The resulting mixture was warmed to -50 °C and stirred for 1.5 h. To the mixture was added N,N-dimethylformamide (65 μL, 0.8 mmol). The resulting mixture was stirred for 1 h and was then quenched by water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 6[6, 3]** as an orange solid (78 mg, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.83 (s, 2H), 7.85 (s, 2H), 7.38 (d, *J* = 7.7 Hz, 8H), 7.09 (d, *J* = 7.7 Hz, 8H), 2.79-2.82 (m, 4H), 2.54 (t, *J* = 7.6 Hz, 8H), 1.57-1.63 (m, 8H), 1.20-1.24 (m, 4H), 0.86-1.01 (m, 30H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.75, 153.90, 153.37, 143.66, 143.60, 143.08, 142.02, 141.35, 139.54, 139.26, 134.13, 131.63, 130.85, 129.73, 128.65, 128.41, 63.99, 37.54, 34.71, 31.60, 30.33, 28.88, 24.13, 22.85, 14.18, 13.93.

Compound 6[6, 6]. To a solution of compound 5[6, 6] (104 mg, 0.08 mmol) in dry THF (10 mL) was added *n*-BuLi (0.15 mL, 1.6 M, 0.24 mmol) at -78 °C under argon. The resulting mixture was warmed to -50 °C and stirred for 1.5 h. To the mixture was added N,N-dimethylformamide (65 μL, 0.8 mmol). The resulting mixture was stirred

for 1 h and was then quenched by water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 6[6, 6]** as an orange solid (80 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.83 (s, 2H), 7.86 (s, 2H), 7.38 (d, *J* = 8.2 Hz, 8H), 7.09 (d, *J* = 8.2 Hz, 8H), 2.78-2.82 (m, 4H), 2.53-2.57 (m, 8H), 1.54-1.58 (m, 12H), 1.28 (br, 28H), 0.98-1.02 (m, 8H), 0.84-0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.70, 153.89, 153.36, 143.65, 143.57, 143.06, 142.28, 141.33, 139.53, 139.24, 134.06, 131.61, 130.83, 129.69, 128.57, 128.40, 63.97, 35.49, 34.72, 31.66, 31.61, 31.05, 30.33, 29.10, 28.88, 22.86, 22.55, 14.19, 14.05.

Compound 6[12, 3]. To a solution of compound 5[12, 3] (104 mg, 0.08 mmol) in dry THF (10 mL) was added *n*-BuLi (0.15 mL, 1.6 M, 0.24 mmol) at -78 °C under argon. The resulting mixture was warmed to -50 °C and stirred for 1.5 h. To the mixture was added N,N-dimethylformamide (65 μL, 0.8 mmol). The resulting mixture was stirred for 1 h and was then quenched by water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 6[12, 3]** as an orange solid (98 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.83 (s, 2H), 7.85 (s, 2H), 7.38 (d, *J* = 8.3 Hz, 8H), 7.09 (d, *J* = 8.3 Hz, 8H), 2.78-2.82 (m, 4H), 2.52-2.56 (m, 8H), 1.59-1.63 (m, 8H), 1.29 (br, 32H), 0.98-1.06 (m, 4H), 0.87-0.93 (m, 22H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.74, 153.89, 153.36, 143.65, 143.61, 143.07, 142.01, 141.34, 139.54, 139.25, 134.13, 131.62, 130.84, 129.72, 128.64, 128.40, 63.99, 37.55, 34.71, 31.94, 30.64, 29.85, 29.81, 29.76, 29.72, 29.44, 29.39, 28.88, 24.15, 22.71, 14.14, 13.94.

Compound 6[12, 6]. To a solution of compound 5[12, 6] (118 mg, 0.08 mmol) in dry THF (10 mL) was added *n*-BuLi (0.15 mL, 1.6 M, 0.24 mmol) at -78 °C under argon. The resulting mixture was warmed to -50 °C and stirred for 1.5 h. To the mixture was added N,N-dimethylformamide (65 μL, 0.8 mmol). The resulting mixture was stirred for 1 h and was then quenched by water followed by extraction with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH_2Cl_2:petroleum ether (1:2) as eluent to give **compound 6[12, 6]** as an orange solid (104 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.84 (s, 2H), 7.86 (s, 2H), 7.38 (d, *J* = 8.2 Hz, 8H), 7.09 (d, *J* = 8.2 Hz, 8H), 2.78-2.82 (m, 4H), 2.53-2.57 (m, 8H), 1.52-1.58 (m, 10H), 1.28 (br, 62H), 0.99-1.03 (m, 4H), 0.84-0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.71, 153.89, 153.37, 143.65, 143.59, 143.06, 142.28, 141.33, 139.53, 139.24, 134.06, 131.61, 130.84, 129.69, 128.57, 128.41, 63.98, 35.50, 34.72, 31.96, 31.67, 31.06, 30.65, 29.89, 29.85, 29.80, 29.74, 29.46, 29.40, 29.12, 28.89, 22.71, 22.57, 14.14, 14.06.

NNFA[0, 6]. To a solution of compound 6[0, 6] (60 mg, 0.05 mmol) in $CHCl_3$ (10 mL) was added FIC (53 mg, 0.25 mmol) and pyridine (0.2 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as eluent to give **NNFA[0, 6]** as a black solid (73 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.82-8.84 (m, 2H), 8.66-8.69 (m, 1H), 8.32-8.34 (m, 1H), 8.13-8.15 (m, 1H), 8.07-8.09 (m, 3H), 7.90-7.96 (m, 1H), 7.55-7.70 (m, 1H), 7.40-7.44 (m, 2H), 7.23-7.25 (m, 8H), 7.13-7.15 (m, 8H), 2.53-2.57 (m, 8H), 1.53-1.61 (m, 8H), 1.25-1.31 (m, 24H), 0.82-0.85 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 186.73, 165.36, 159.03, 153.66, 151.66, 149.36, 146.78, 143.23, 143.01, 142.87, 138.89, 138.85, 138.45, 138.25, 138.14, 137.41, 136.27, 135.82, 131.27, 129.10, 128.04, 127.82, 122.02, 121.85, 117.40, 114.70, 114.45, 69.69, 68.73, 63.16, 35.58, 31.65, 31.19, 29.16, 22.55, 14.05. MALDI-TOF MS (m/z): 1575.6 (M^+).

NNFA[6, 3]. To a solution of compound 6[6, 3] (60 mg, 0.05 mmol) in $CHCl_3$ (10 mL) was added FIC (53 mg, 0.25 mmol) and pyridine (0.2 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as eluent to give **NNFA[6, 3]** as a black solid (71 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.77 (s, 2H), 8.67-8.70 (m, 1H), 8.34-8.36 (m, 2H), 8.17-8.20 (m, 2H), 7.92-7.95 (m, 1H), 7.57-7.59 (m, 1H), 7.44 (d, J = 8.1 Hz, 8H), 7.37-7.40 (m, 1H), 7.15 (d, J = 8.2 Hz, 8H), 2.80-2.84 (m, 4H), 2.53-2.57 (m, 8H), 1.60-1.64 (m, 8H), 1.22-1.25 (m, 4H), 0.88-1.00 (m, 30H). ^{13}C NMR data were not acquired due to the extremely low solubility of compound NNFA[6, 3]. MALDI-TOF MS (m/z): 1575.6 (M^+).

NNFA[6, 6]. To a solution of compound 6[6, 6] (68 mg, 0.05 mmol) in $CHCl_3$ (10 mL) was added FIC (53 mg, 0.25 mmol) and pyridine (0.2 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as eluent to give **NNFA[6, 6]** as a black solid (77 mg, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.77 (d, J = 3.9 Hz, 2H), 8.66-8.69 (m, 1H), 8.33-8.35 (m, 1H), 8.12-8.17 (m, 2H), 7.92-7.95 (m, 1H), 7.57-7.59 (m, 1H), 7.44 (d, J = 8.2 Hz, 8H), 7.37-7.41 (m, 2H), 7.15 (d, J = 8.2 Hz, 8H), 2.82-2.84 (m, 4H), 2.55-2.58 (m, 8H), 1.56-1.58 (m, 8H), 1.24-1.26 (m, 32H), 0.98-1.04 (m, 8H), 0.90(t, J = 7.3Hz, 6H), 0.80-0.84 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 186.61, 165.33, 155.60, 154.54, 147.84, 144.42, 143.60, 142.51, 139.88, 138.35, 138.10, 137.99, 137.09, 133.67, 132.97, 131.93, 131.53, 128.79, 128.46, 121.81, 114.77, 114.53, 114.37, 76.68, 69.42, 35.49, 34.76, 31.66, 31.60, 31.01, 30.32, 29.08, 28.89, 22.86, 22.54, 14.20, 14.04. MALDI-TOF MS (m/z): 1744.8 ($M + H^+$).

NNFA[12, 3]. To a solution of compound 6[12, 3] (68 mg, 0.05 mmol) in $CHCl_3$ (10 mL) was added FIC (53 mg, 0.25 mmol) and pyridine (0.2 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as

eluent to give **NNFA[12, 3]** as a black solid (75 mg, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.77 (d, *J* = 4.1 Hz, 2H), 8.65-8.69 (m, 1H), 8.31-8.34 (m, 1H), 8.14 (d, *J* = 19.3 Hz, 2H), 7.92-7.95 (m, 1H), 7.57-7.59 (m, 1H), 7.44 (d, *J* = 8.2 Hz, 8H), 7.39-7.41 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 8H), 2.82-2.84 (m, 4H), 2.53-2.57 (m, 8H), 1.58-1.64 (m, 8H), 1.29 (br, 32H), 1.00-1.04 (m, 8H), 0.88-0.93 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 186.62, 165.33, 158.85, 155.57, 154.50, 147.83, 146.67, 144.41, 143.60, 142.24, 139.88, 138.34, 137.97, 137.03, 135.84, 133.74, 133.01, 131.93, 128.84, 128.46, 125.70, 121.87, 114.53, 114.38, 112.51, 69.43, 68.49, 64.21, 37.57, 31.95, 30.62, 29.85, 29.83, 29.77, 29.73, 29.43, 29.40, 24.14, 22.72, 14.15, 13.95. MALDI-TOF MS (m/z): 1743.9 (M^+).

NNFA[12, 6]. To a solution of compound 6[12, 6] (76 mg, 0.05 mmol) in $CHCl_3$ (10 mL) was added FIC (53 mg, 0.25 mmol) and pyridine (0.2 mL) at room temperature. The mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using $CHCl_3$ as eluent to give **NNFA[12, 6]** as a black solid (81 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.77 (d, *J* = 4.0 Hz, 2H), 8.66-8.69 (m, 1H), 8.33-8.35 (m, 1H), 8.12-8.17 (m, 2H), 7.93-7.95 (m, 1H), 7.57-7.59 (m, 1H), 7.43 (d, *J* = 8.2 Hz, 8H), 7.37-7.41 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 8H), 2.82-2.84 (m, 4H), 2.55-2.58 (m, 8H), 1.56-1.58 (m, 8H), 1.24-1.30 (m, 56H), 0.96-1.04 (m, 8H), 0.81-0.91 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 186.63, 155.58, 154.55, 144.41, 143.61, 142.48, 139.87, 138.36, 133.68, 131.93, 131.52, 128.77, 128.45, 114.39, 114.33, 76.68, 69.43, 64.20, 31.96, 31.68, 31.02, 29.75, 29.41, 29.10, 22.72, 22.56, 14.15, 14.05. MALDI-TOF MS (m/z): 1913.2 ($M + H^+$).

3. NMR

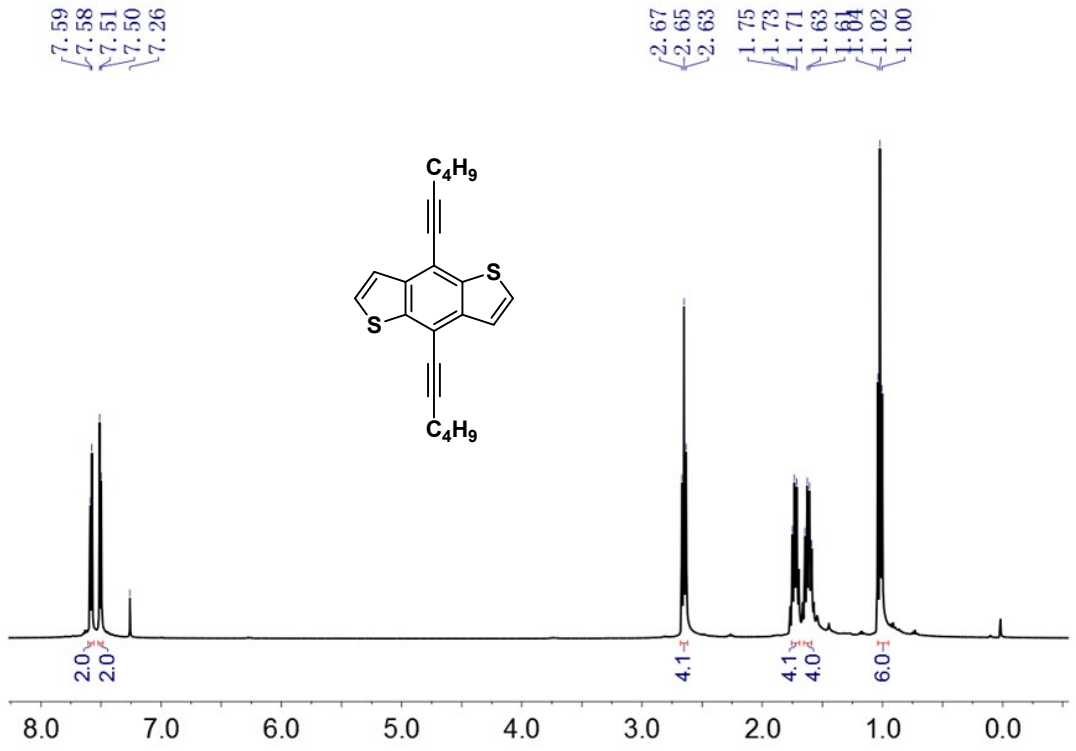


Fig. S1 ^{1}H NMR spectrum of **compound 1a.**

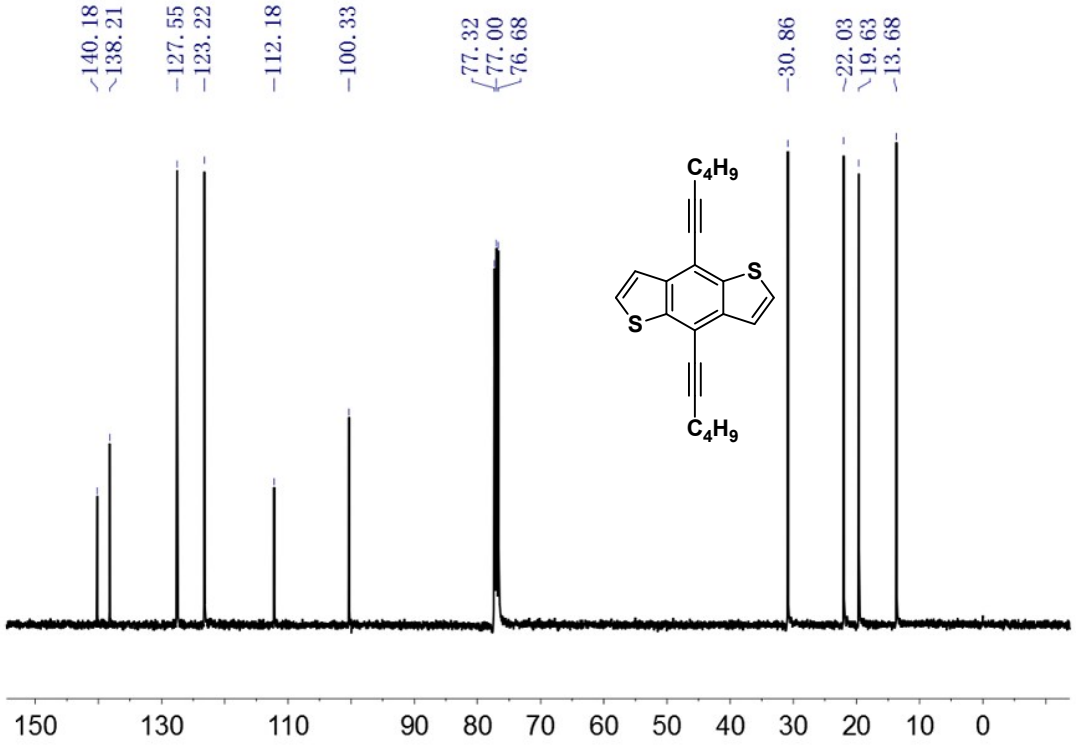


Fig. S2 ^{13}C NMR spectrum of **compound 1a.**

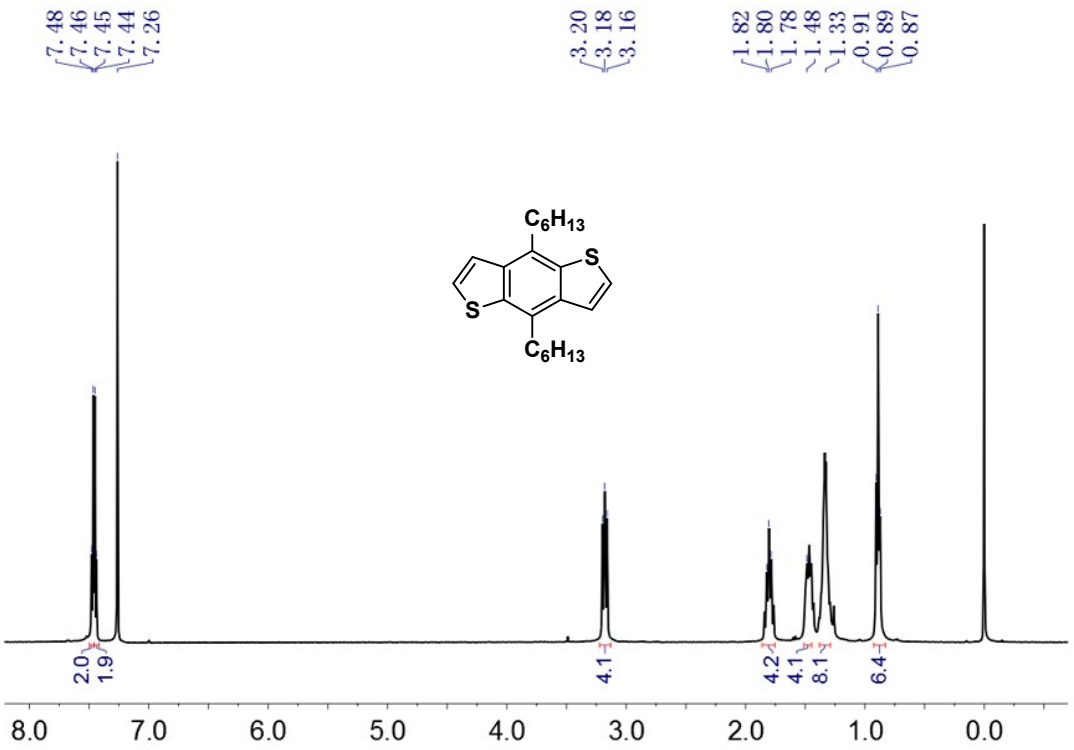


Fig. S3 ^{1}H NMR spectrum of **compound 2b.**

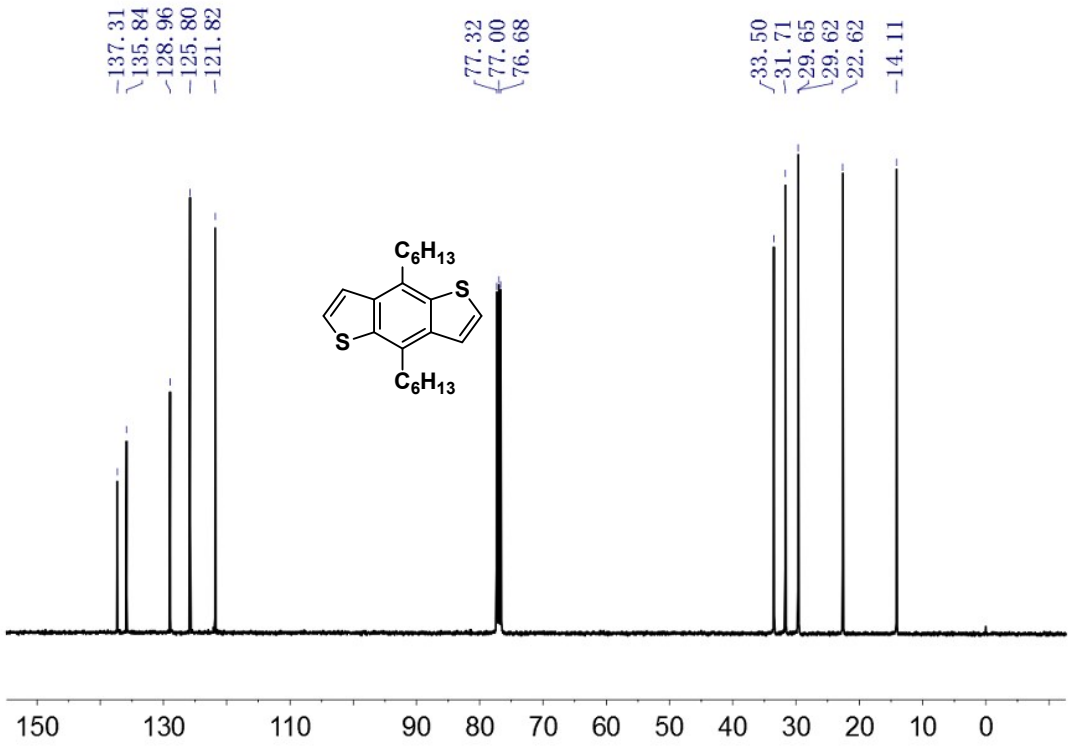


Fig. S4 ^{13}C NMR spectrum of **compound 2b.**

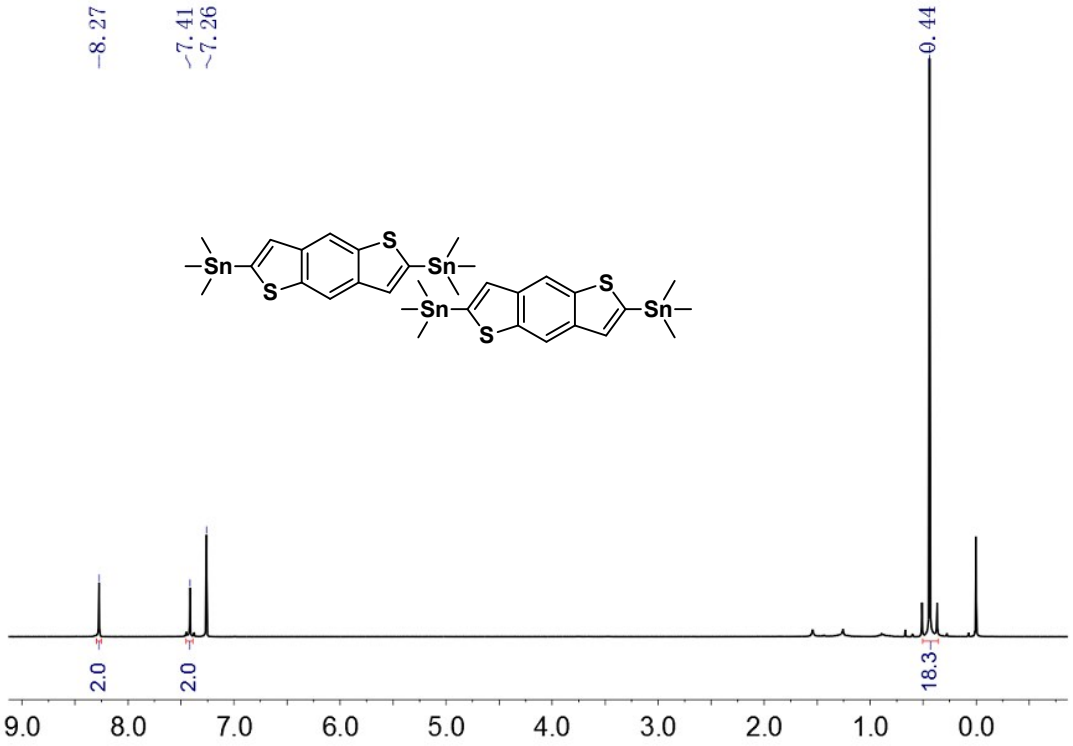


Fig. S5 ^{1}H NMR spectrum of **compound 3a.**

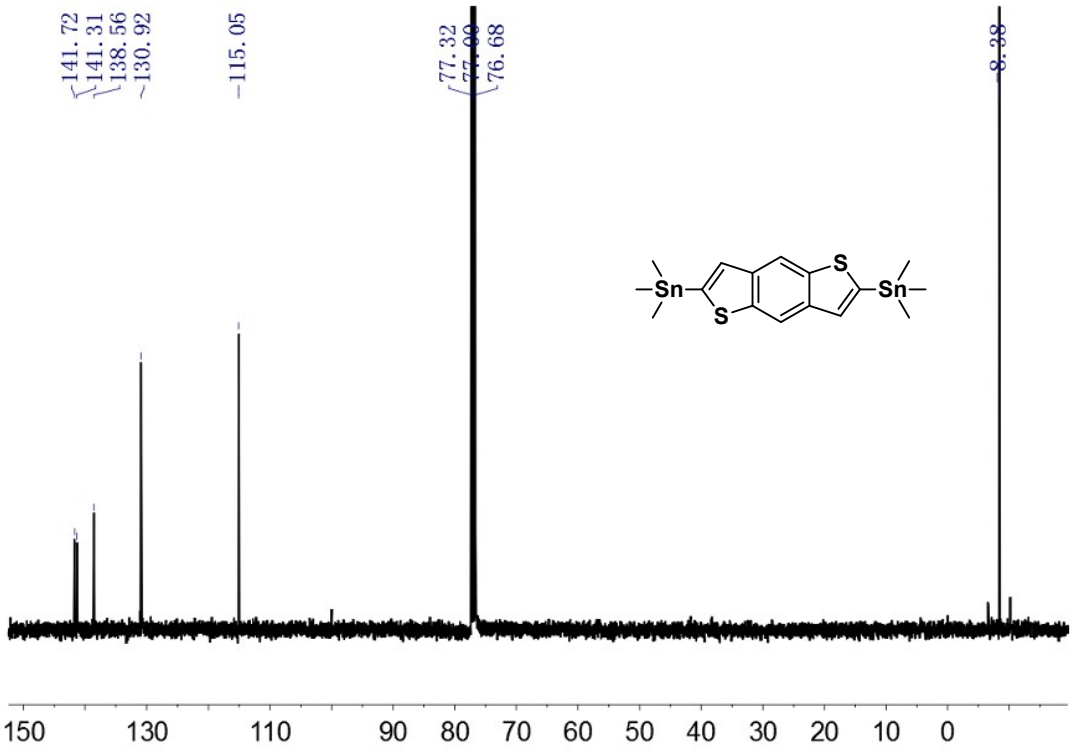


Fig. S6 ^{13}C NMR spectrum of **compound 3a.**

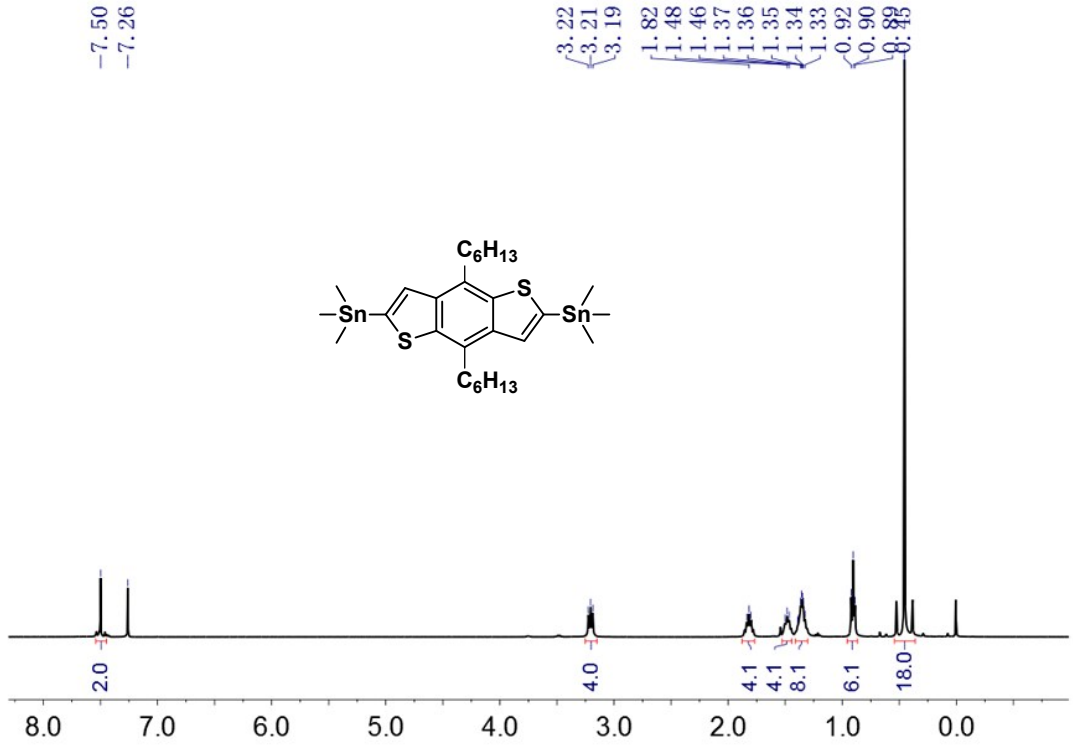


Fig. S7 ^{1}H NMR spectrum of **compound 3b.**

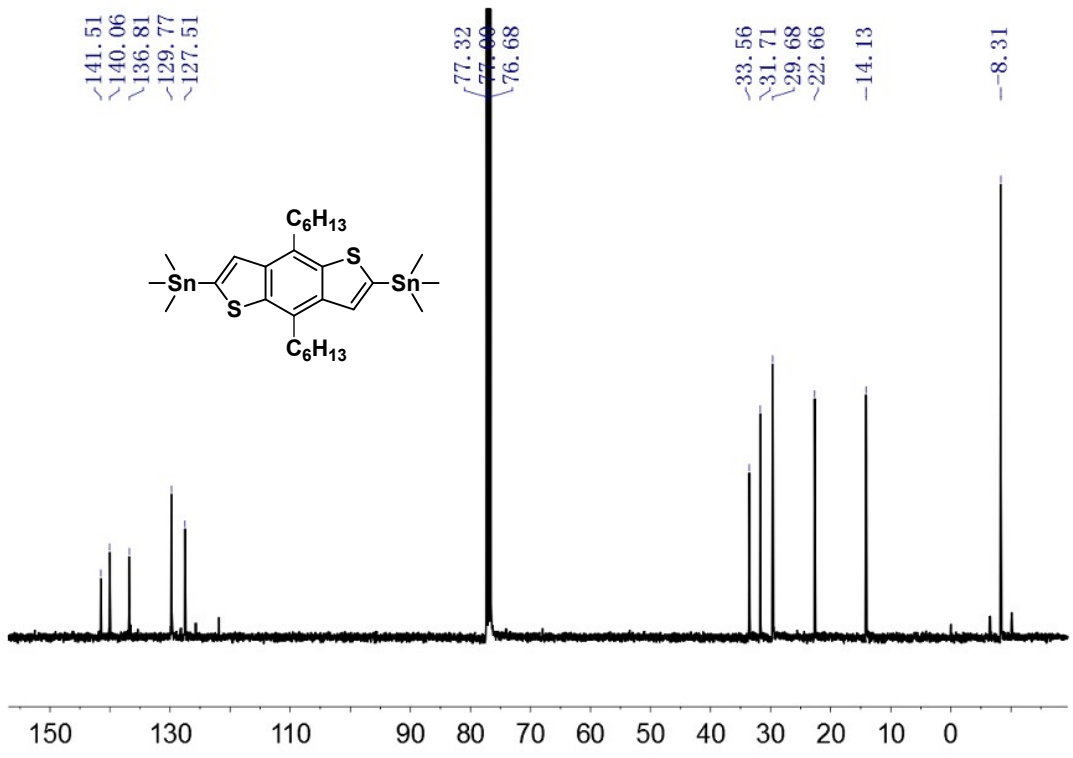


Fig. S8 ^{13}C NMR spectrum of **compound 3b.**

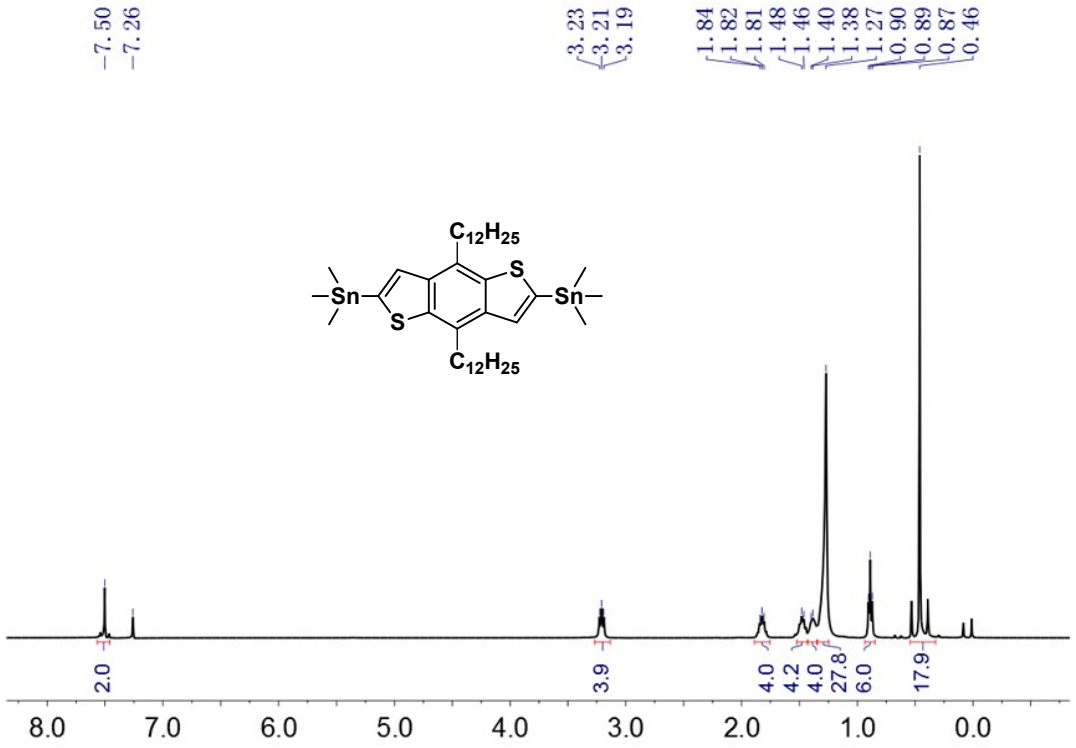


Fig. S9 ^{1}H NMR spectrum of **compound 3c.**

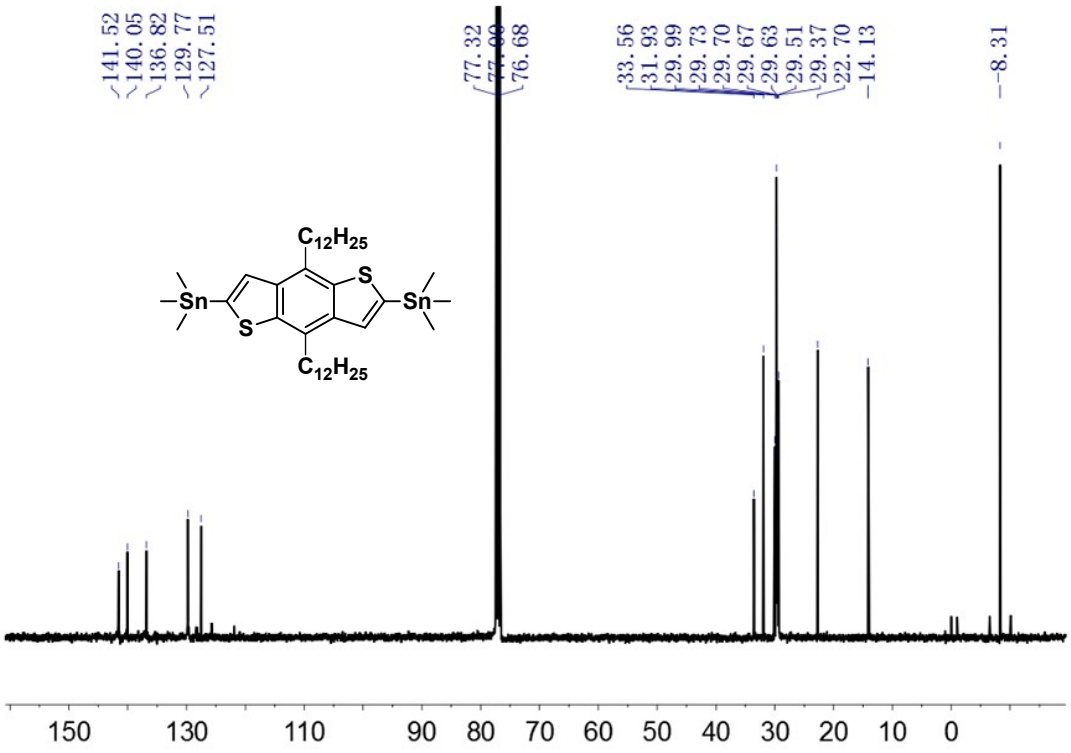


Fig. S10 ^{13}C NMR spectrum of **compound 3c.**

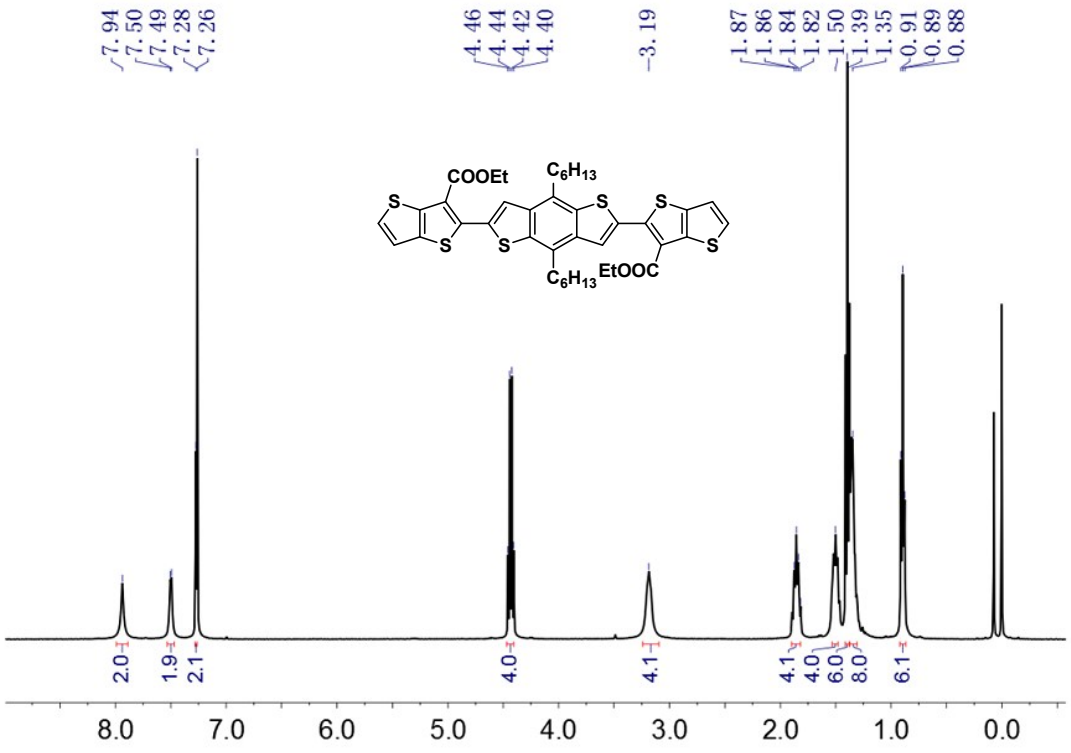


Fig. S11 ^{1}H NMR spectrum of **compound 4b.**

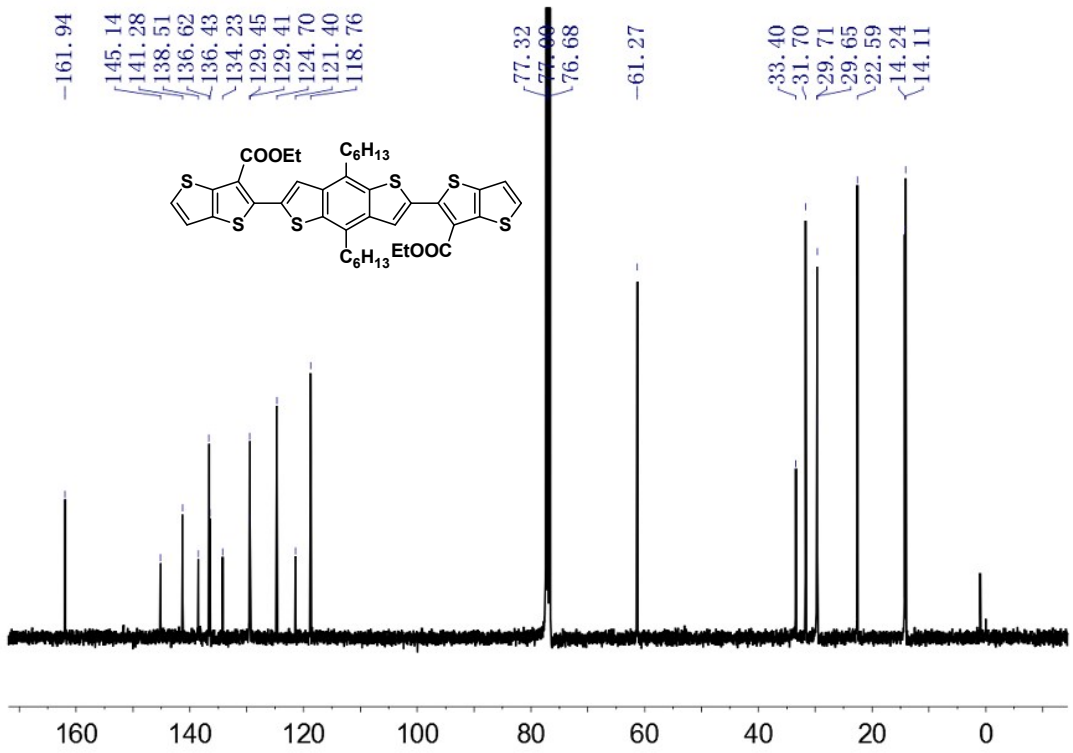


Fig. S12 ^{13}C NMR spectrum of **compound 4b.**

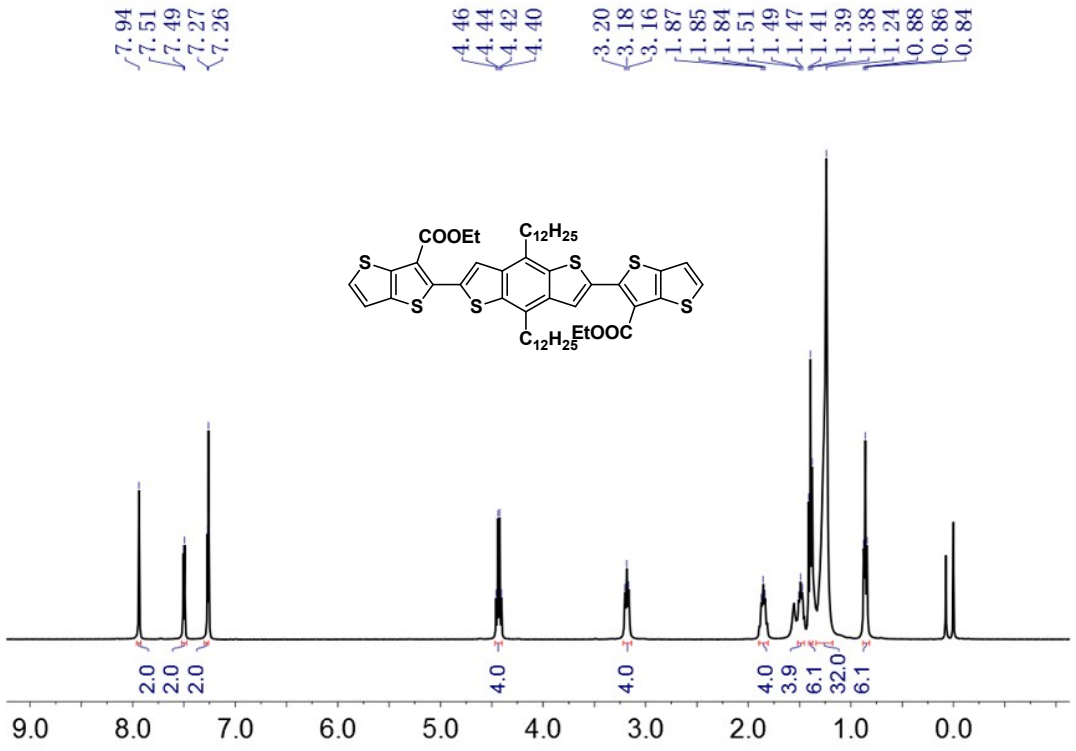


Fig. S13 ^{1}H NMR spectrum of **compound 4c.**

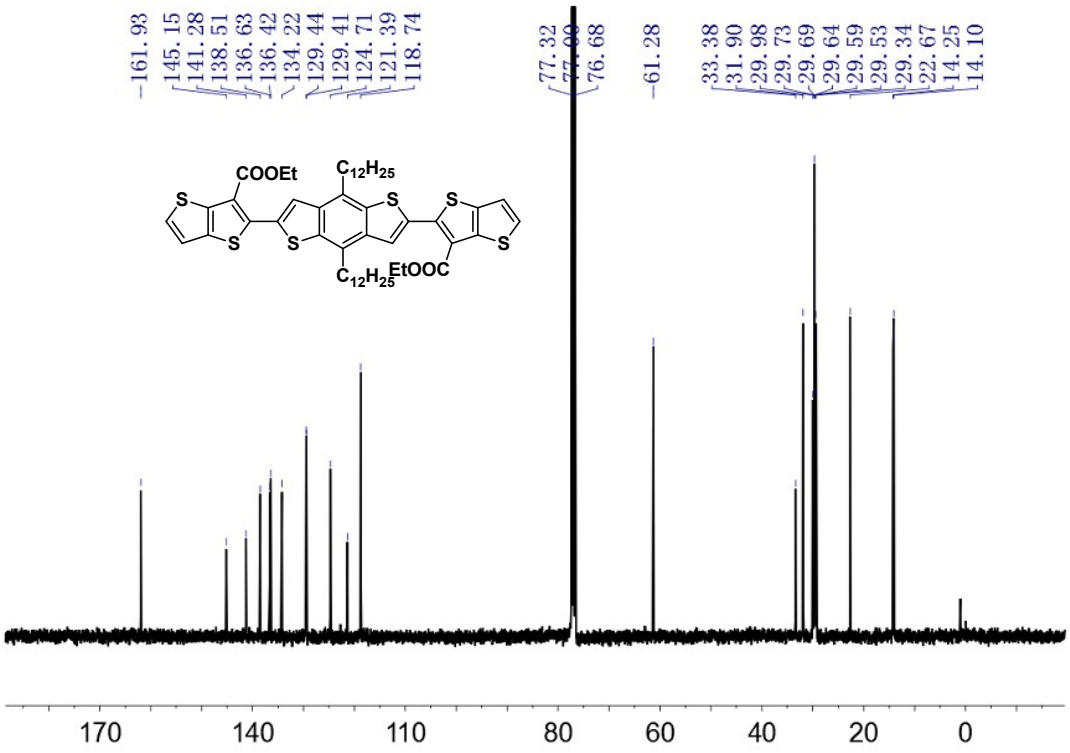


Fig. S14 ^{13}C NMR spectrum of **compound 4c.**

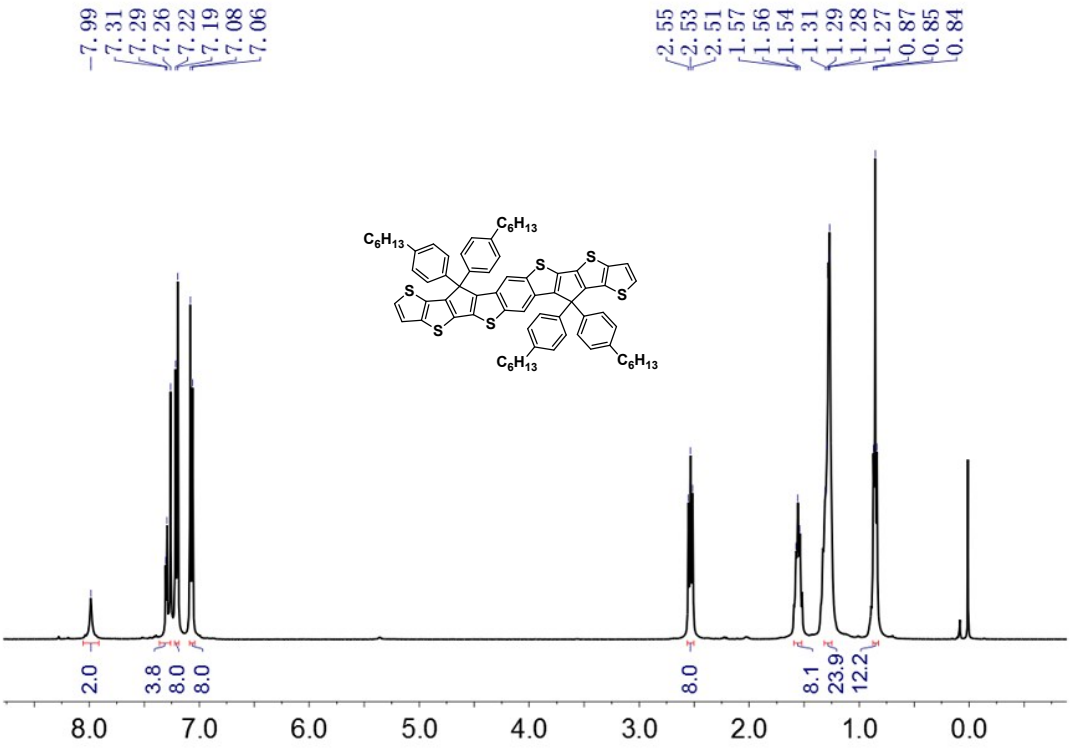


Fig. S15 ^{1}H NMR spectrum of **compound 5[0, 6].**

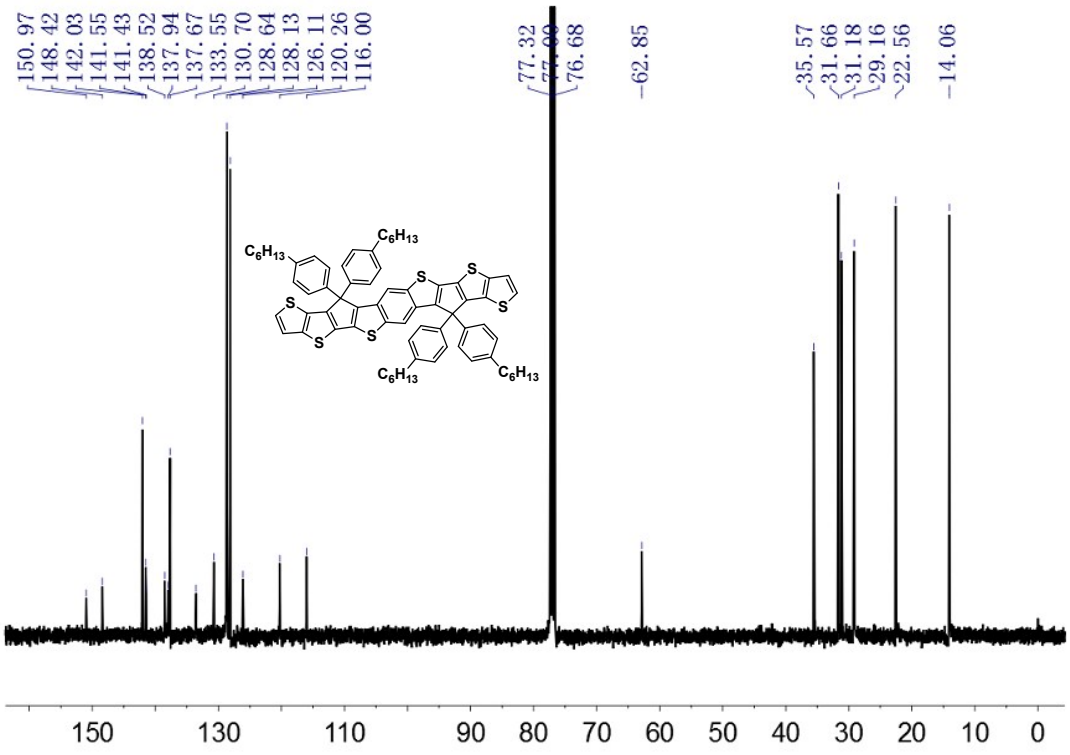


Fig. S16 ^{13}C NMR spectrum of **compound 5[0, 6].**

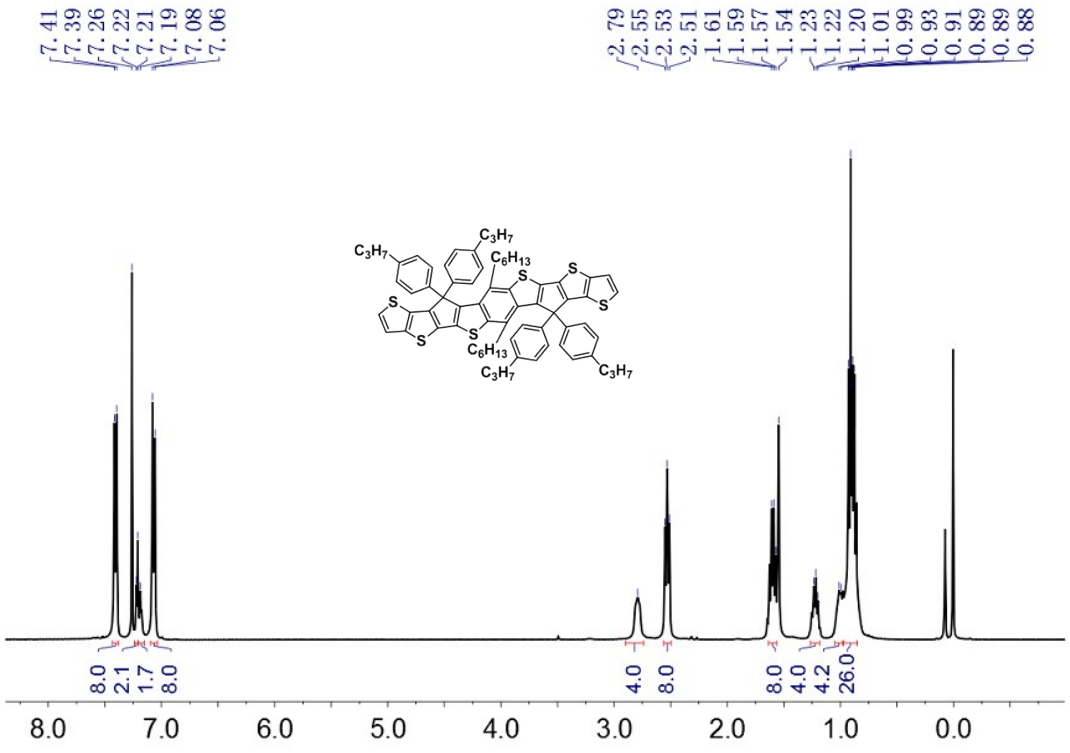


Fig. S17 ^{1}H NMR spectrum of **compound 5[6, 3].**

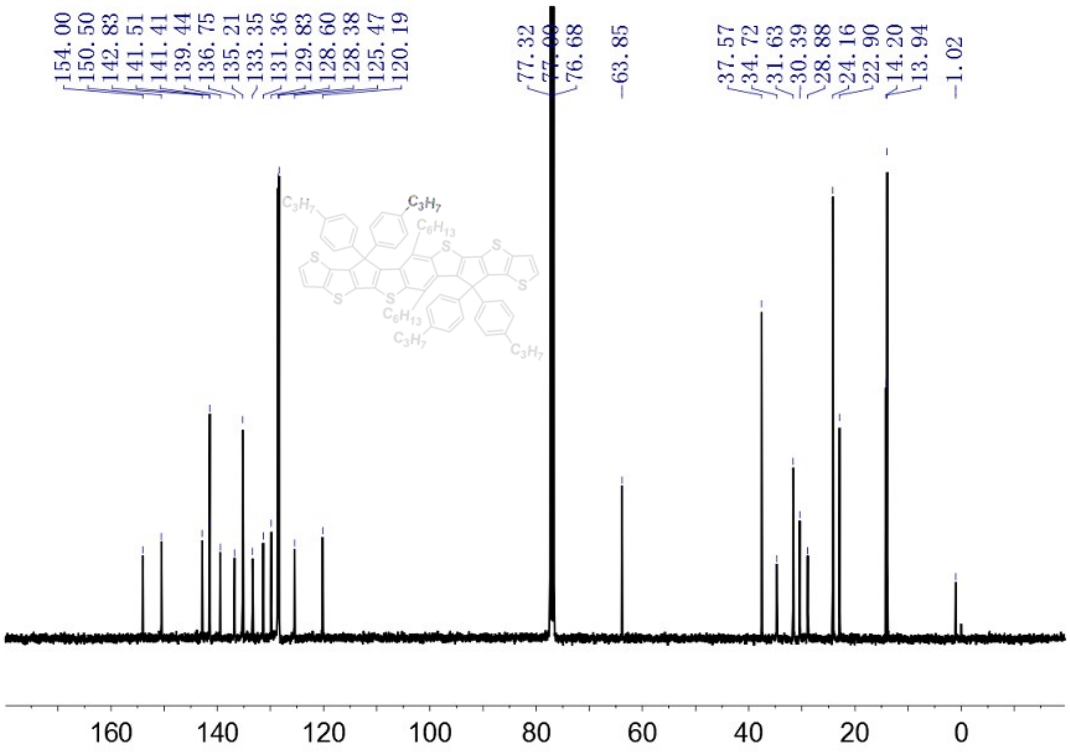


Fig. S18 ^{13}C NMR spectrum of **compound 5[6, 3].**

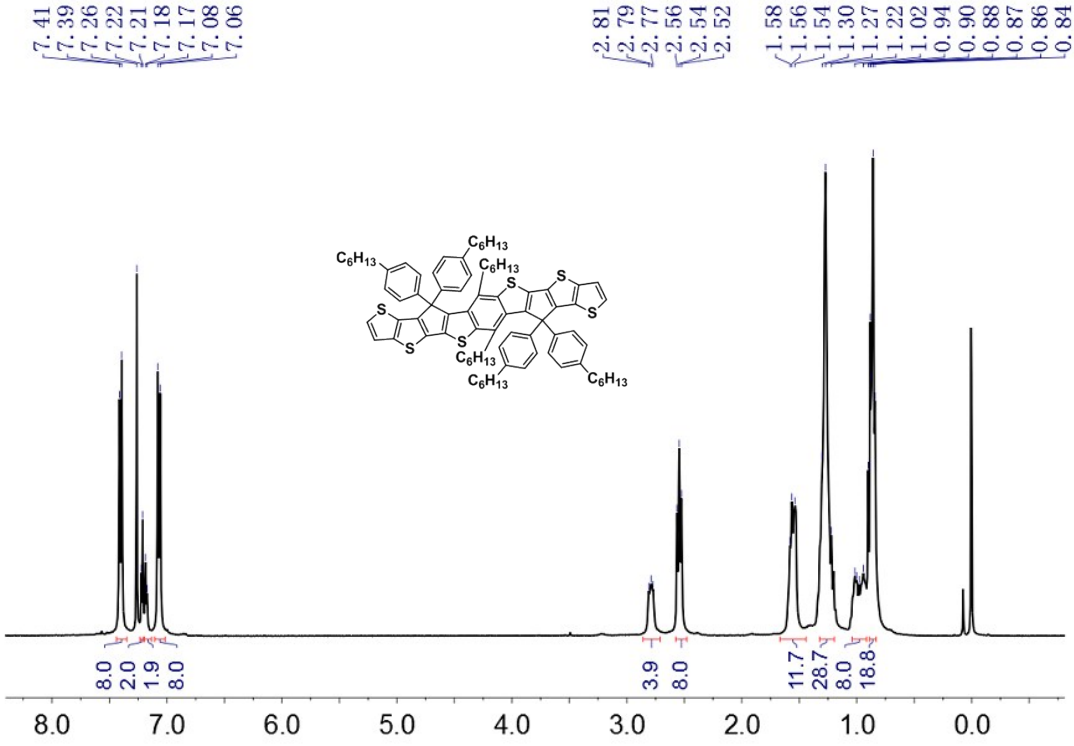


Fig. S19 [1]H NMR spectrum of **compound 5[6, 6].**

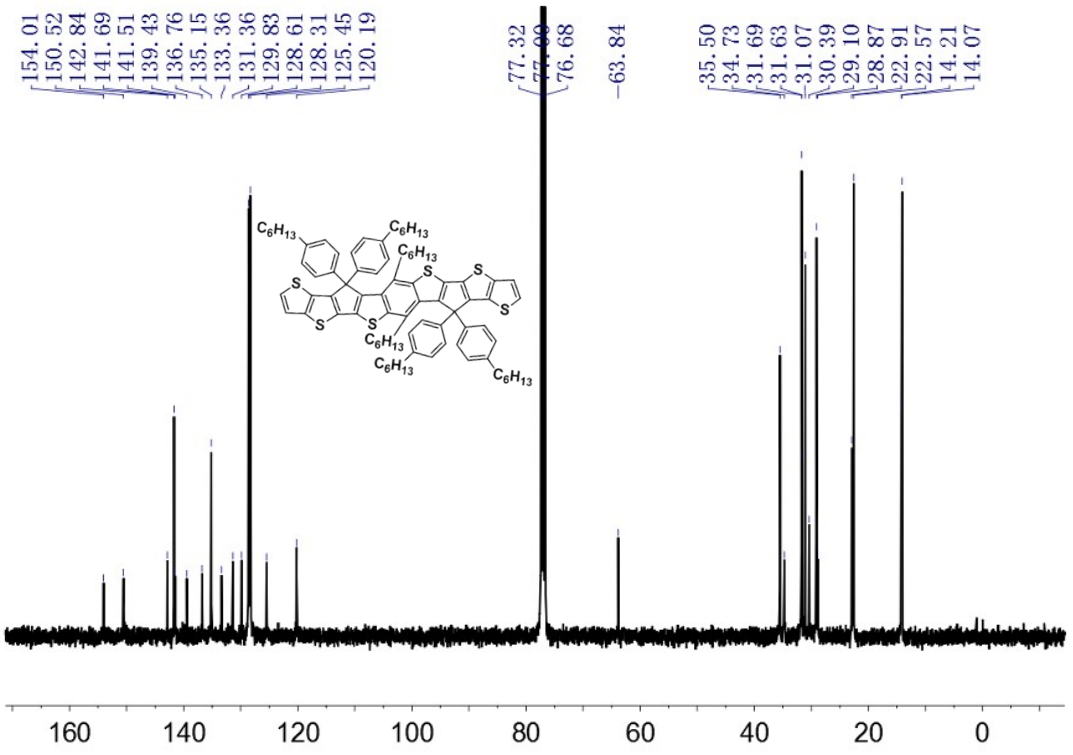


Fig. S20 [13]C NMR spectrum of **compound 5[6, 6].**

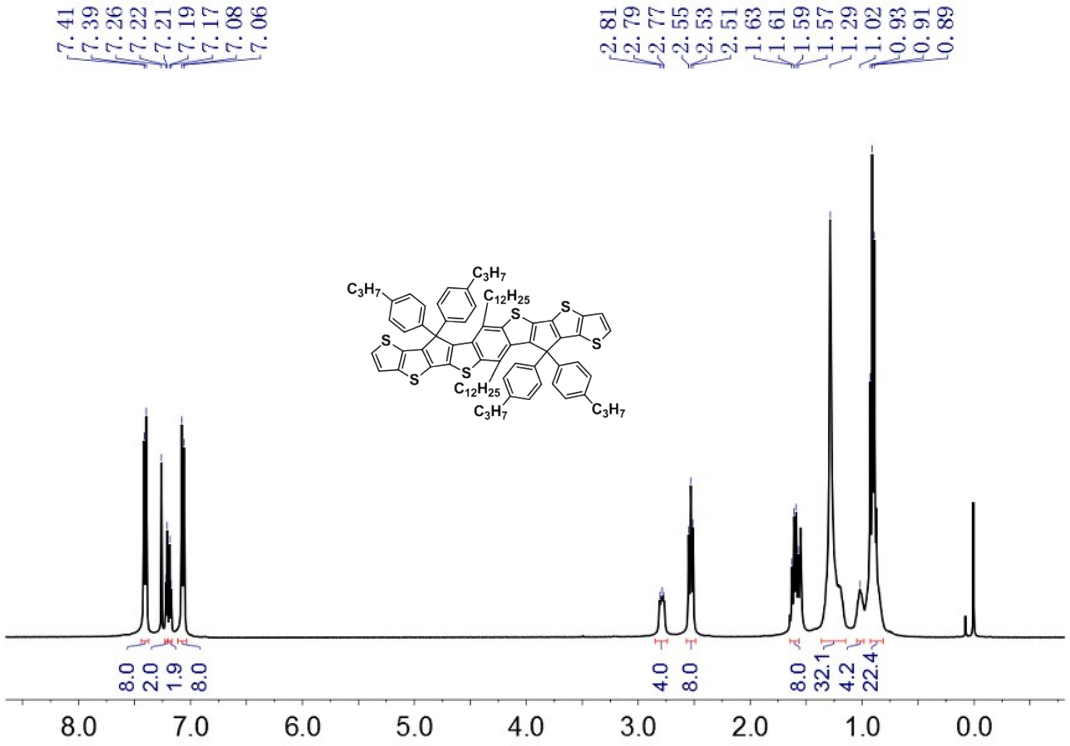


Fig. S21 [1]H NMR spectrum of **compound 5[12, 3].**

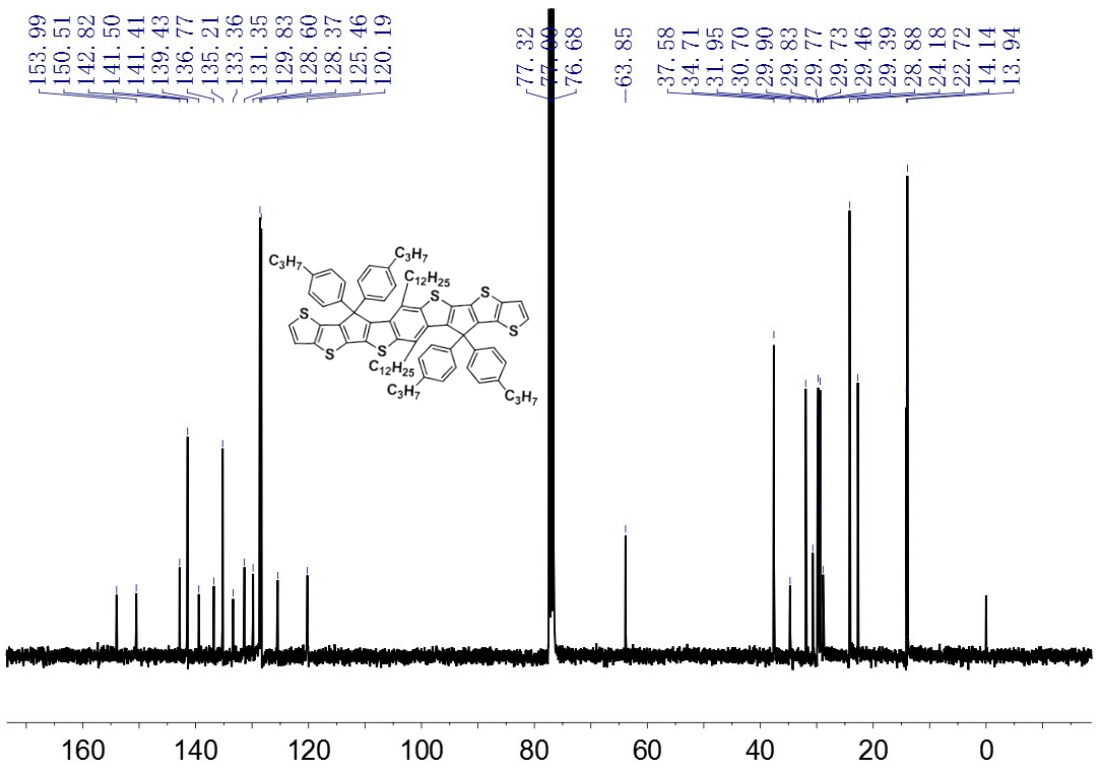


Fig. S22 [13]C NMR spectrum of **compound 5[12, 3].**

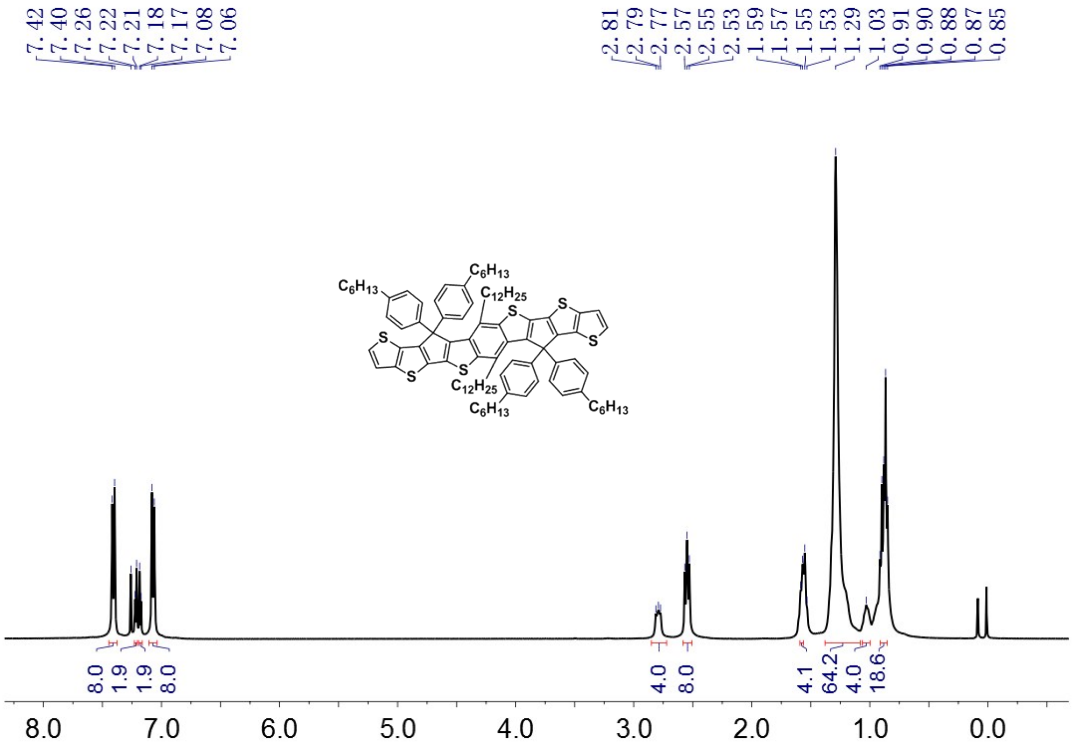


Fig. S23 [1]H NMR spectrum of **compound 5[12, 6].**

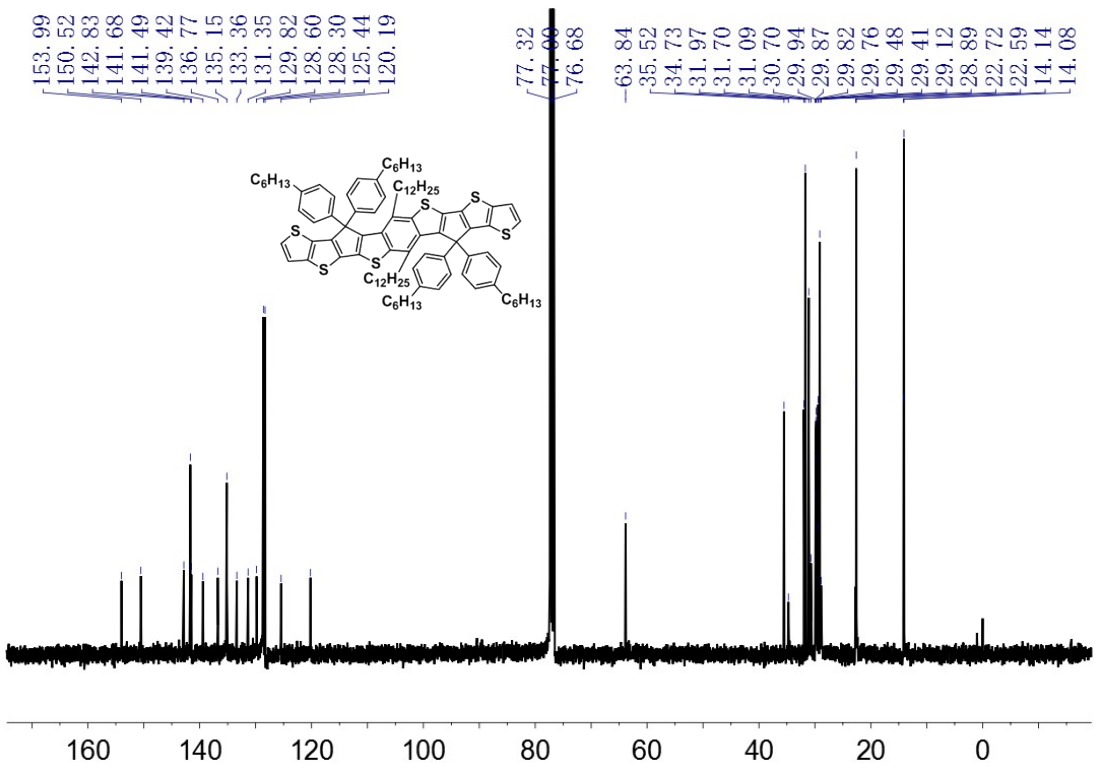


Fig. S24 [13]C NMR spectrum of **compound 5[12, 6].**

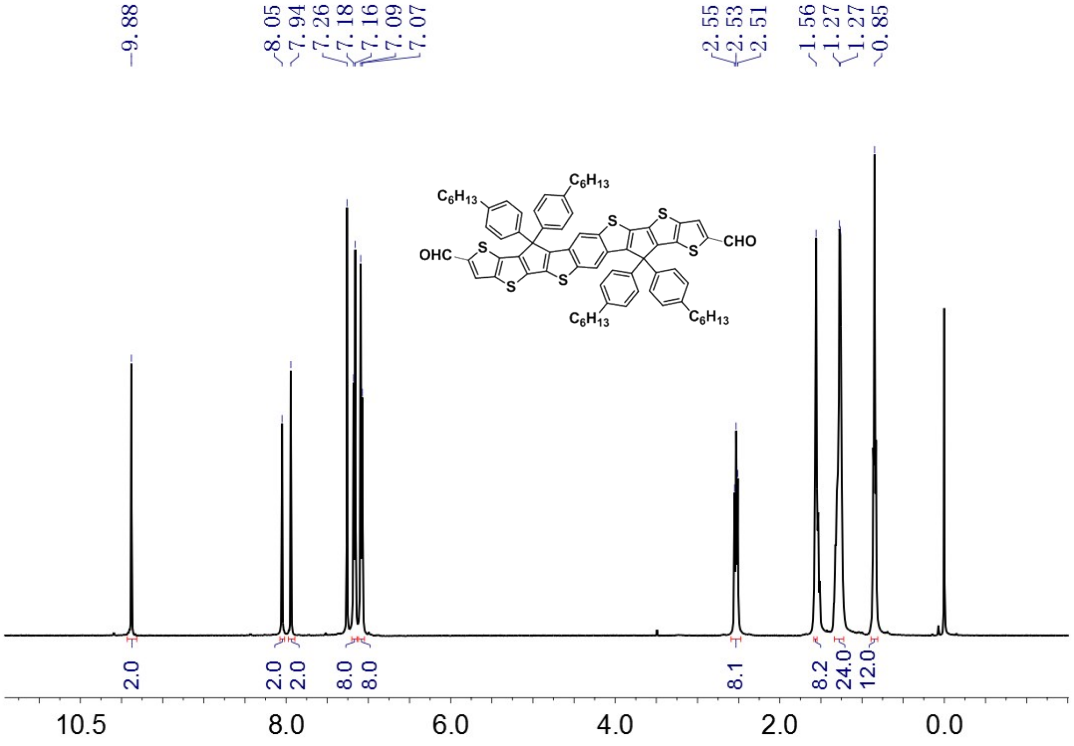


Fig. S25 [1]H NMR spectrum of **compound 6[0, 6].**

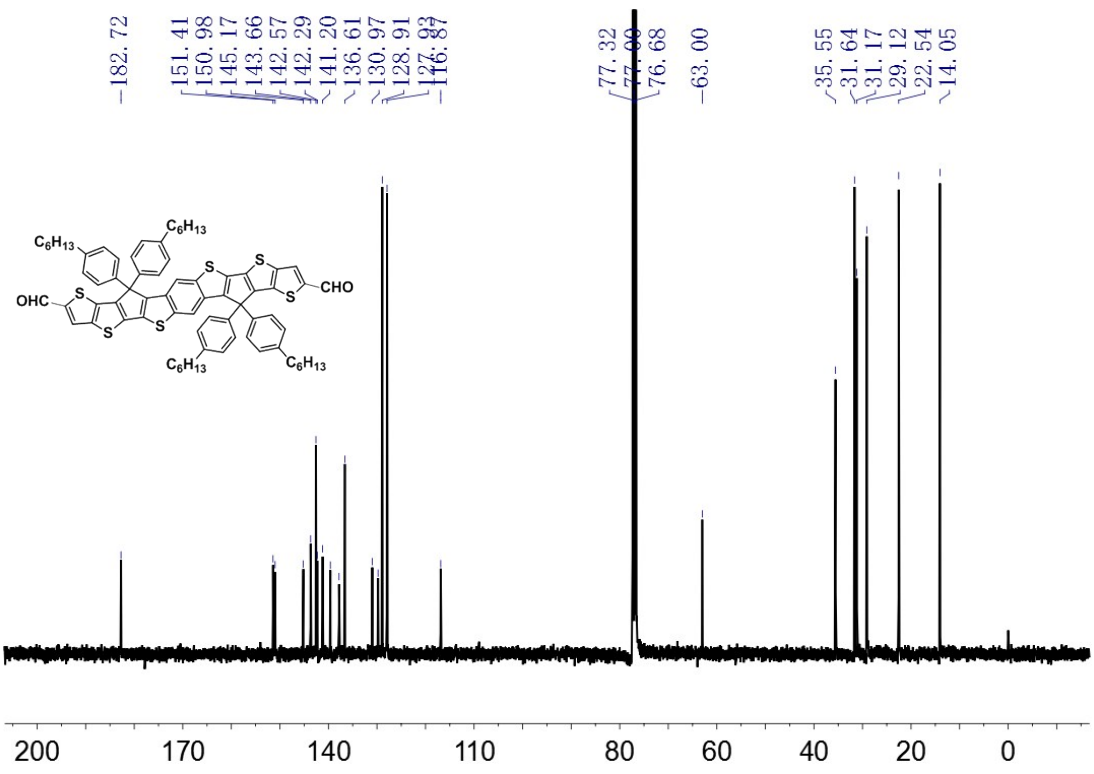


Fig. S26 [13]C NMR spectrum of **compound 6[0, 6].**

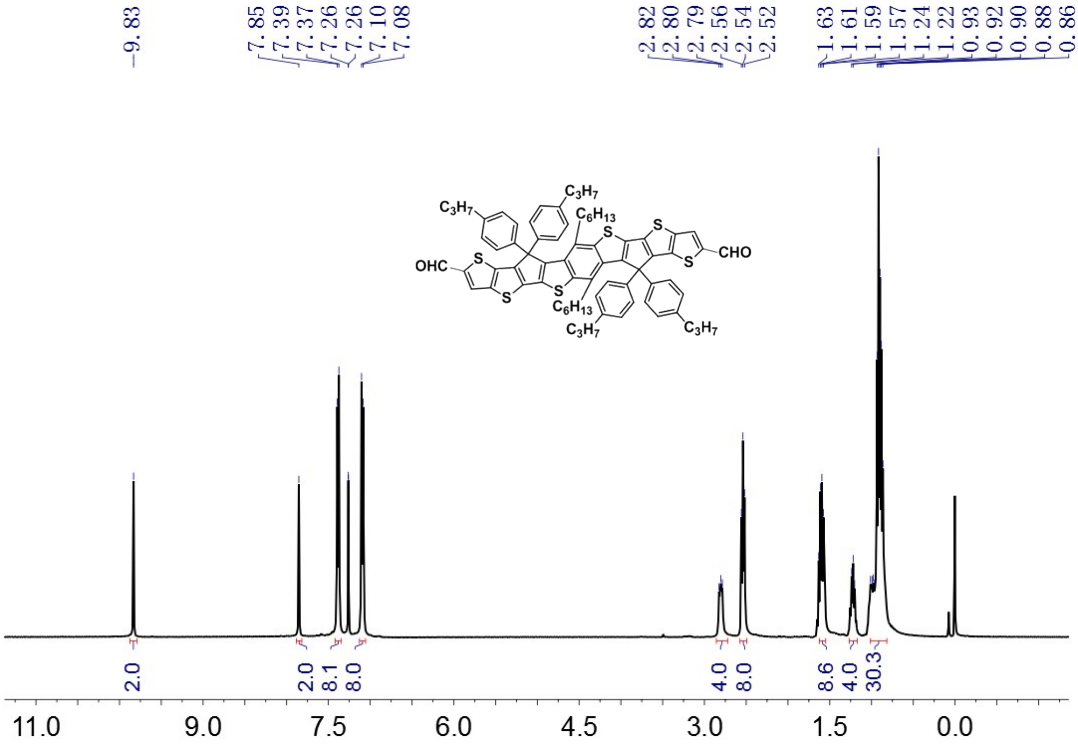


Fig. S27 ^{1}H NMR spectrum of **compound 6[6, 3].**

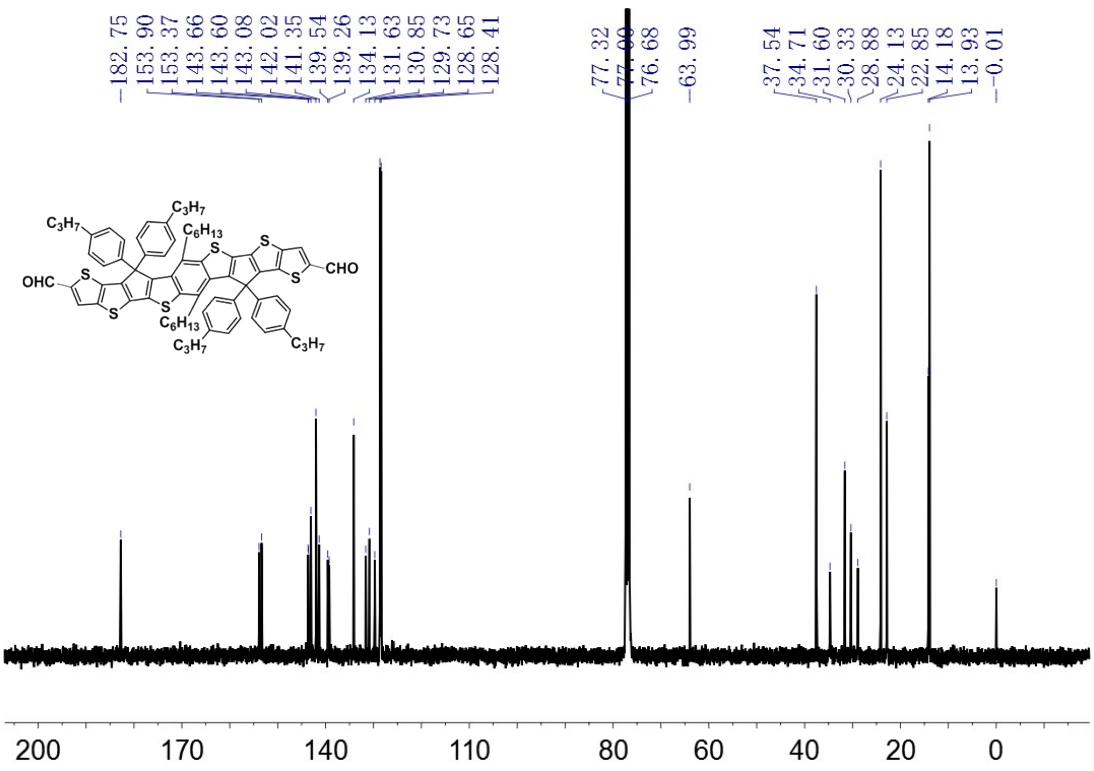


Fig. S28 ^{13}C NMR spectrum of **compound 6[6, 3].**

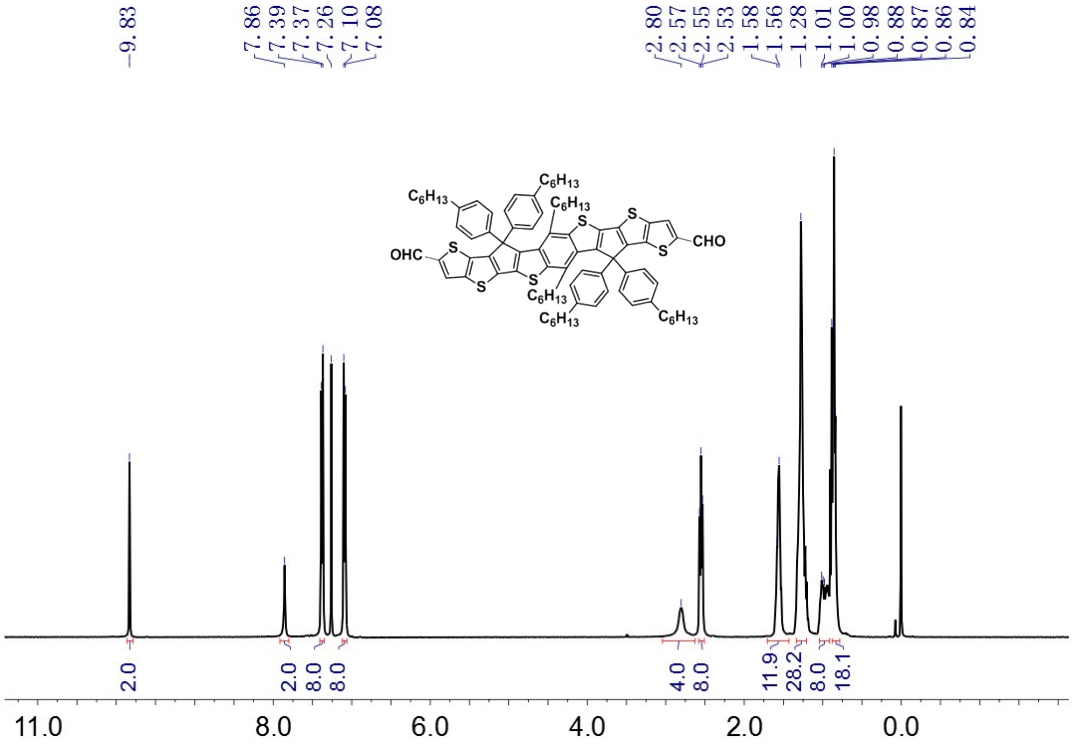


Fig. S29 ^{1}H NMR spectrum of **compound 6[6, 6].**

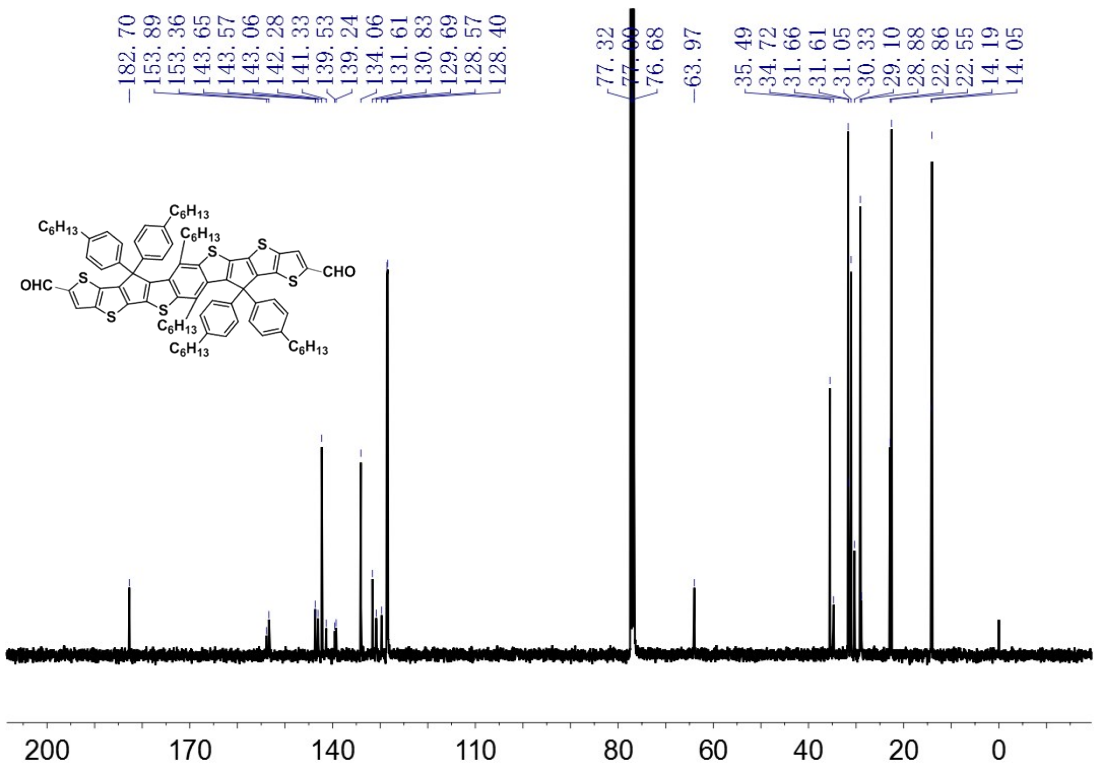


Fig. S30 ^{13}C NMR spectrum of **compound 6[6, 6].**

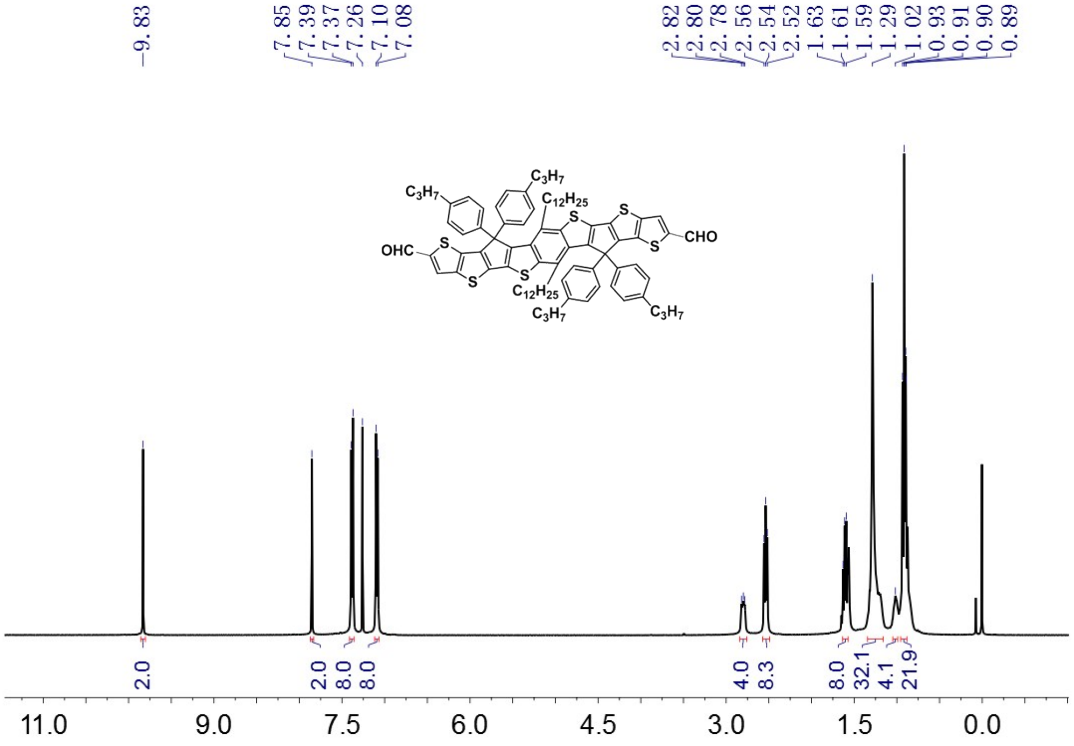


Fig. S31 ^{1}H NMR spectrum of **compound 6[12, 3].**

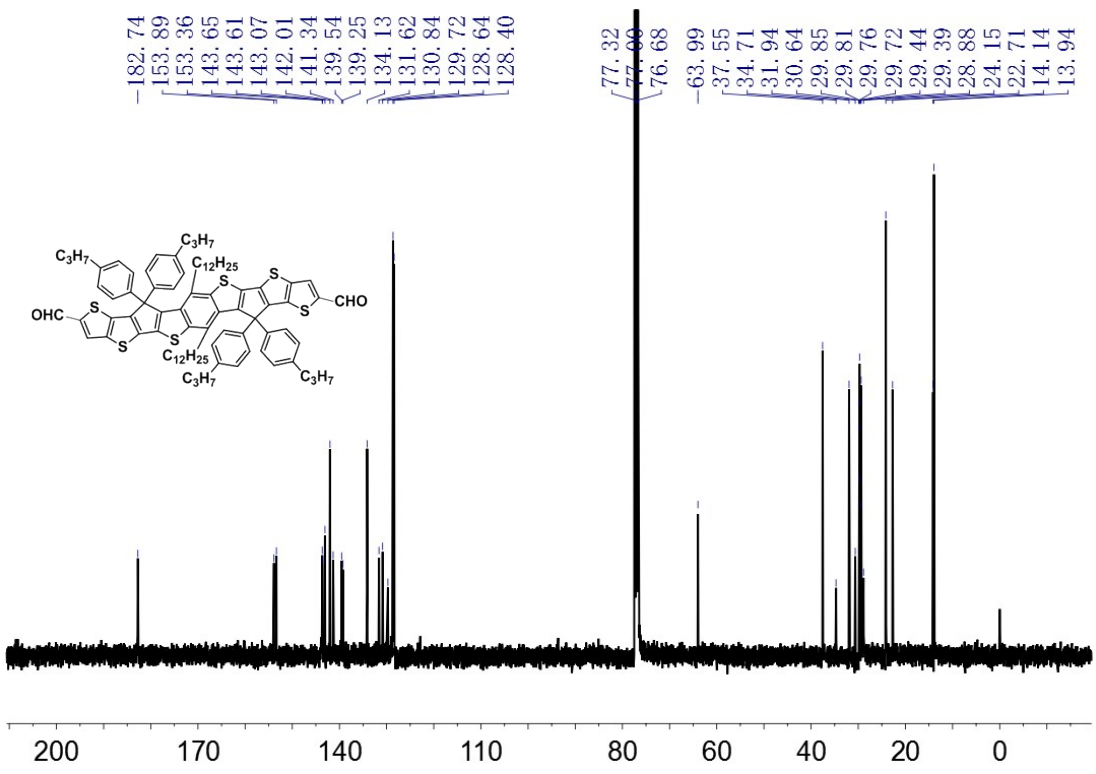


Fig. S32 ^{13}C NMR spectrum of **compound 6[12, 3].**

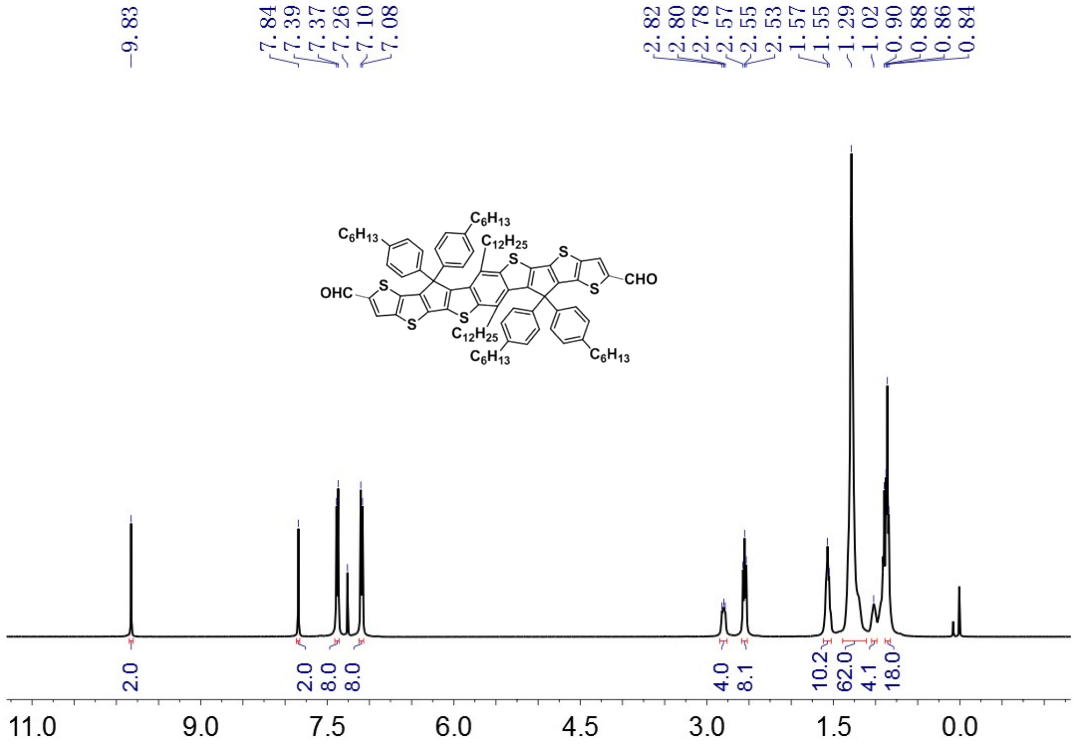


Fig. S33 [1]H NMR spectrum of **compound 6[12, 6].**

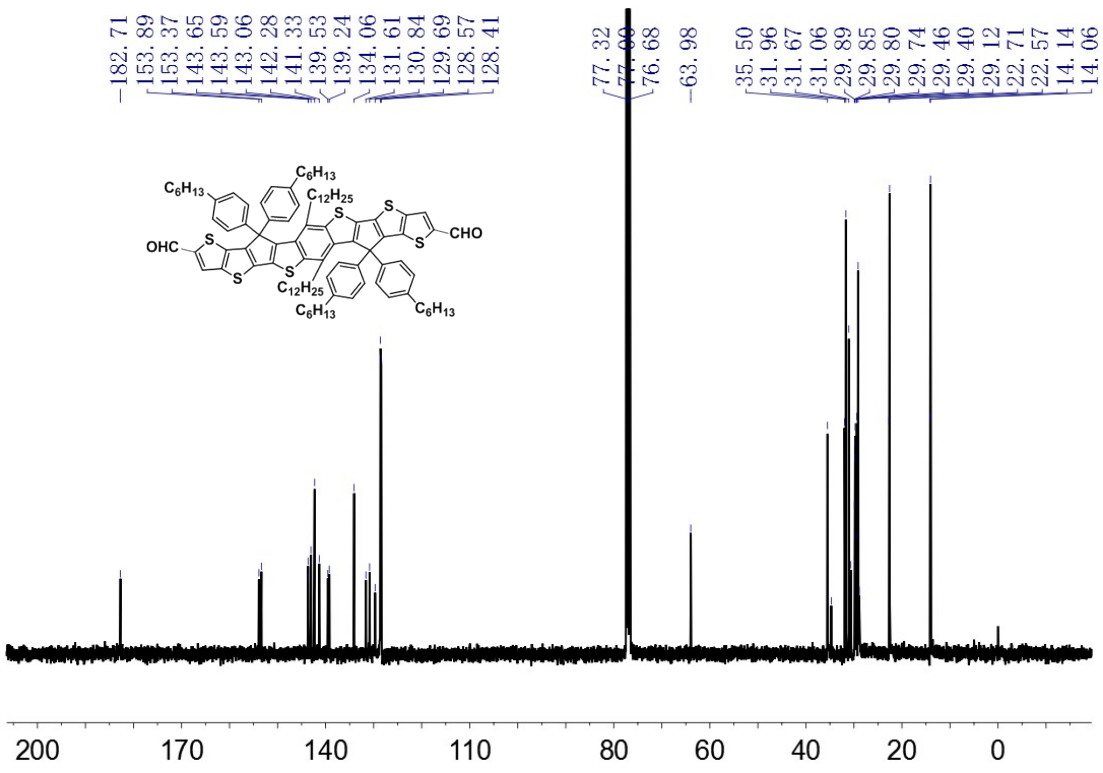


Fig. S34 [13]C NMR spectrum of **compound 6[12, 6].**

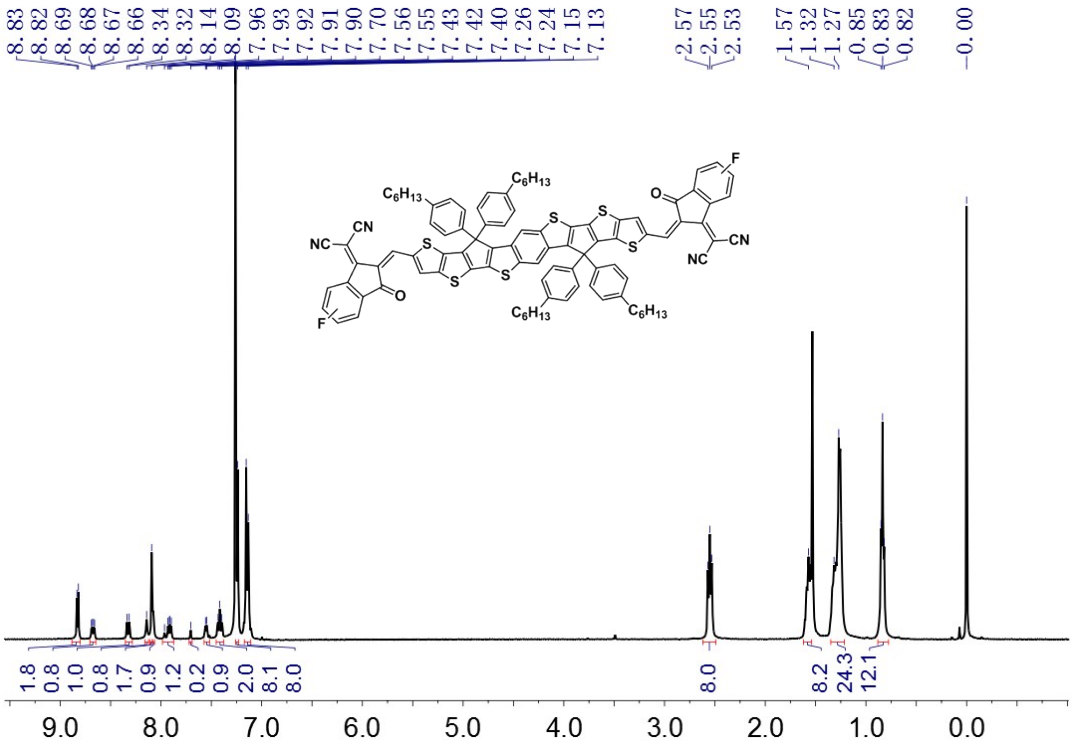


Fig. S35 [1]H NMR spectrum of **compound NNFA[0, 6].**

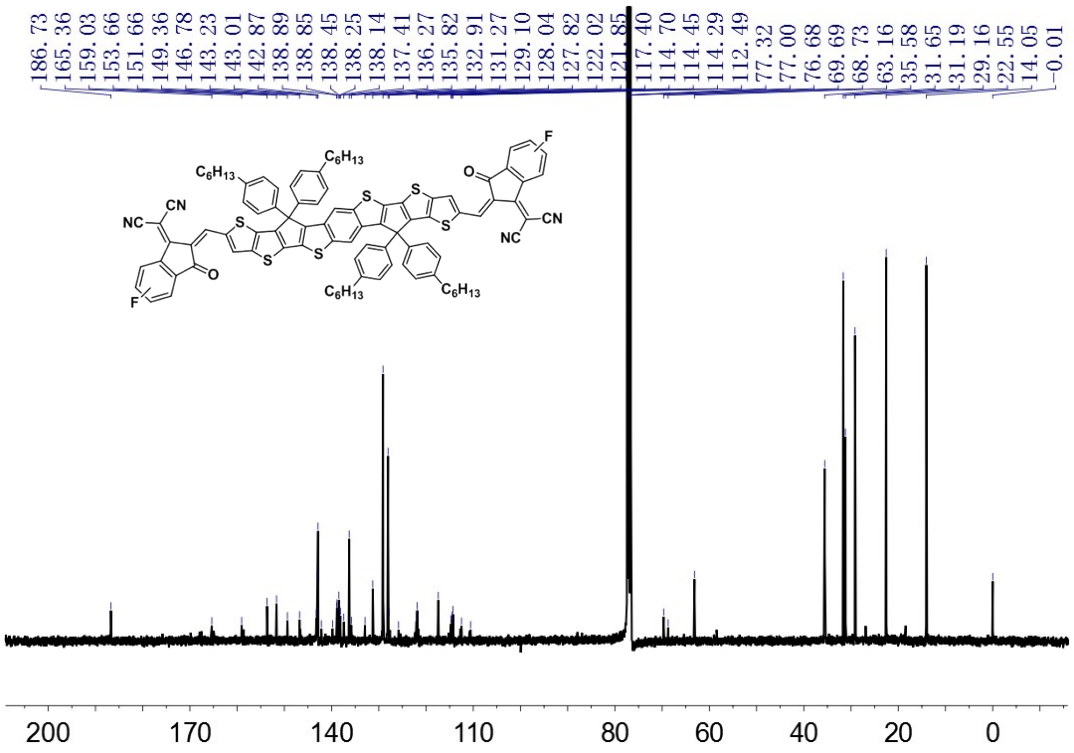


Fig. S36 [13]C NMR spectrum of **compound NNFA[0, 6].**

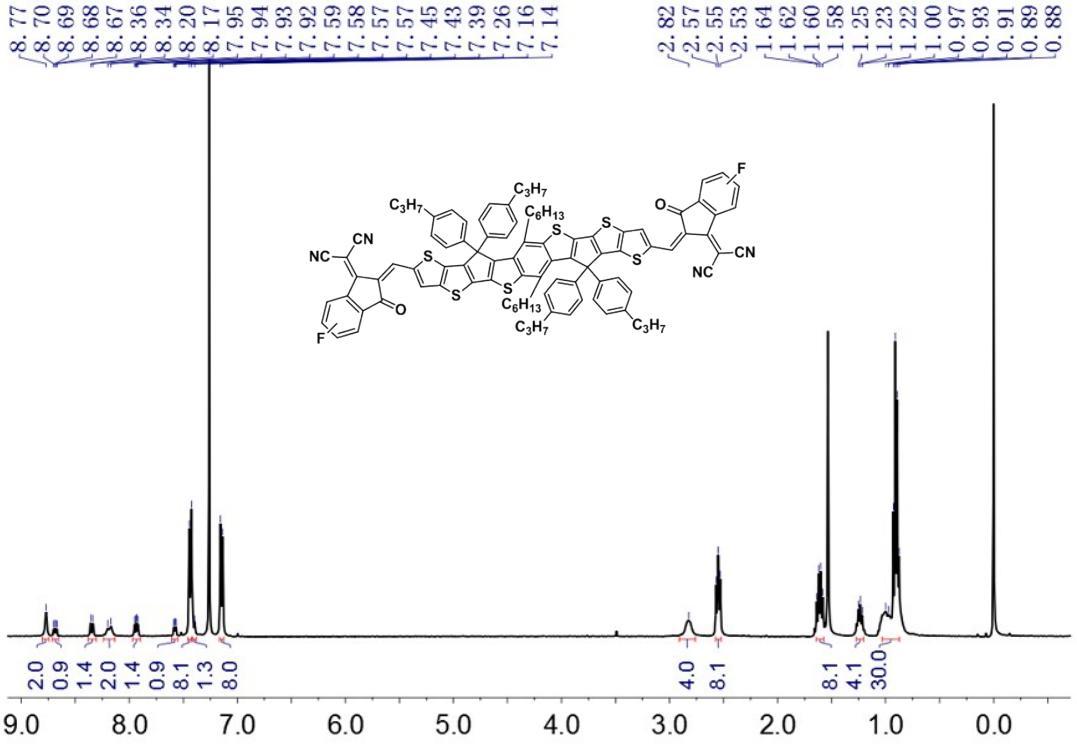


Fig. S37 ^{1}H NMR spectrum of **compound NNFA[6, 3].**

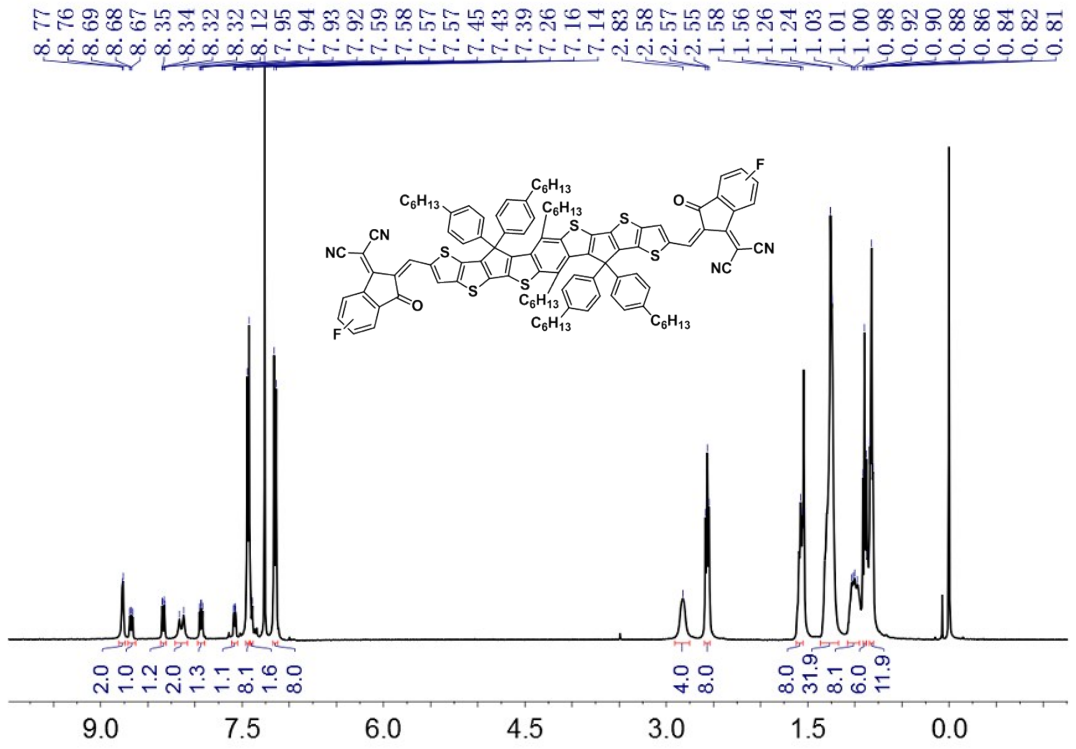


Fig. S38 ^{1}H NMR spectrum of **compound NNFA[6, 6].**

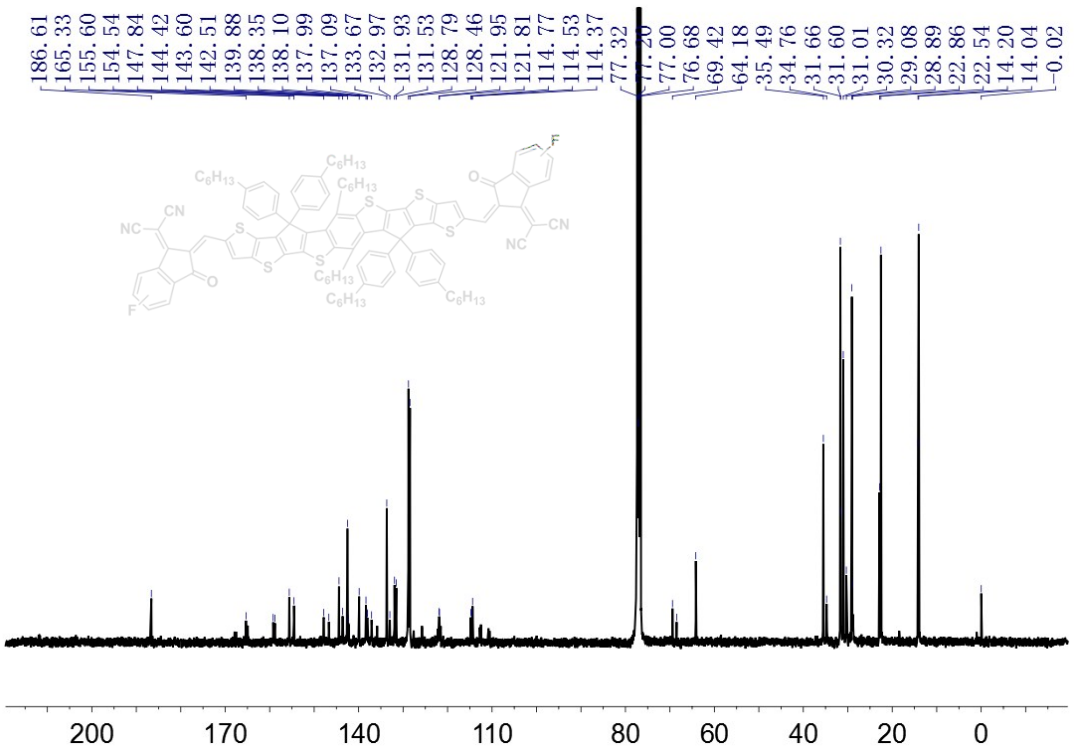


Fig. S39 ^{13}C NMR spectrum of **compound NNFA[6, 6].**

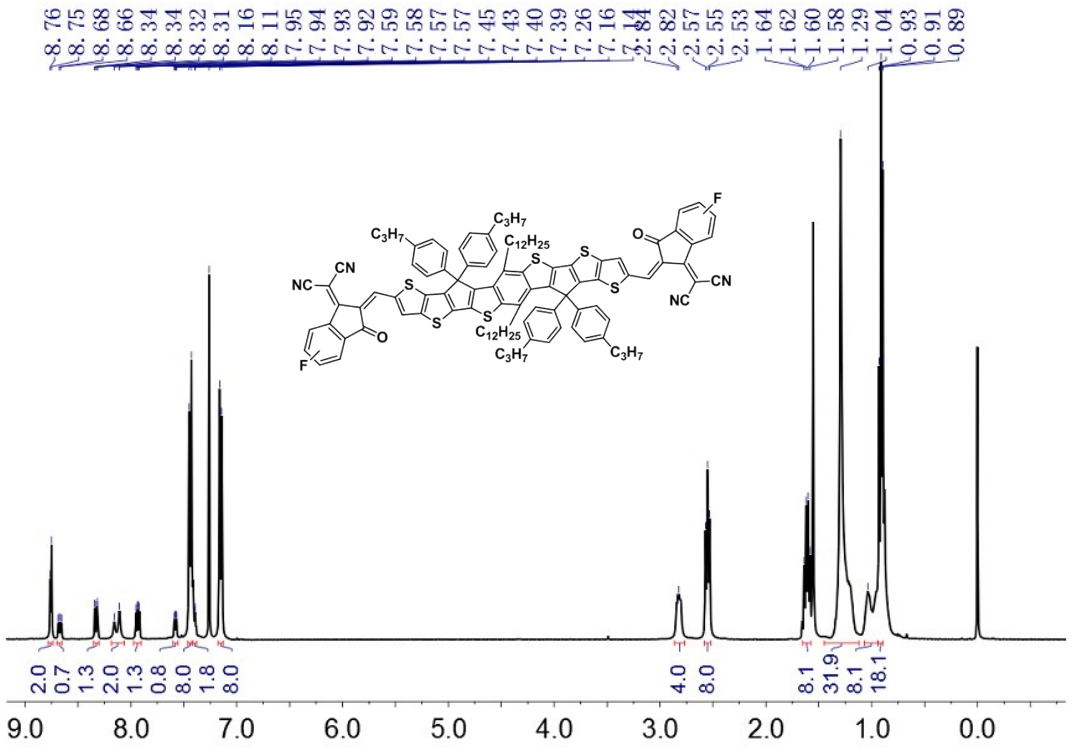


Fig. S40 ^{1}H NMR spectrum of **compound NNFA[12, 3].**

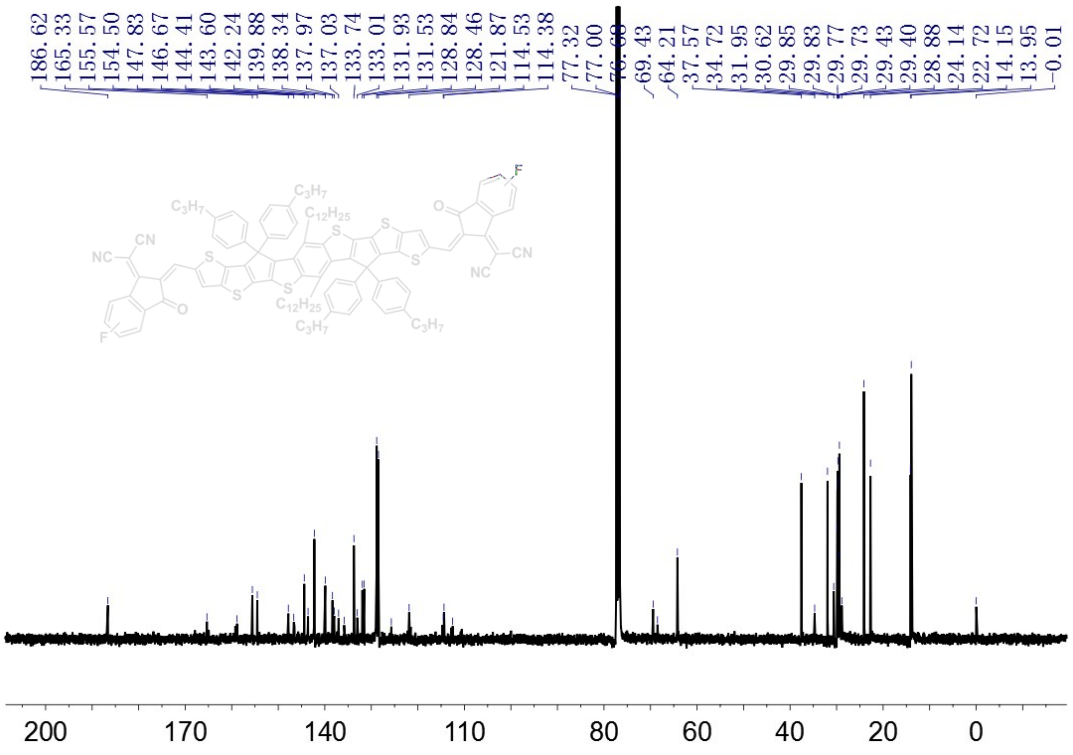


Fig. S41 ^{13}C NMR spectrum of **compound NNFA[12, 3].**

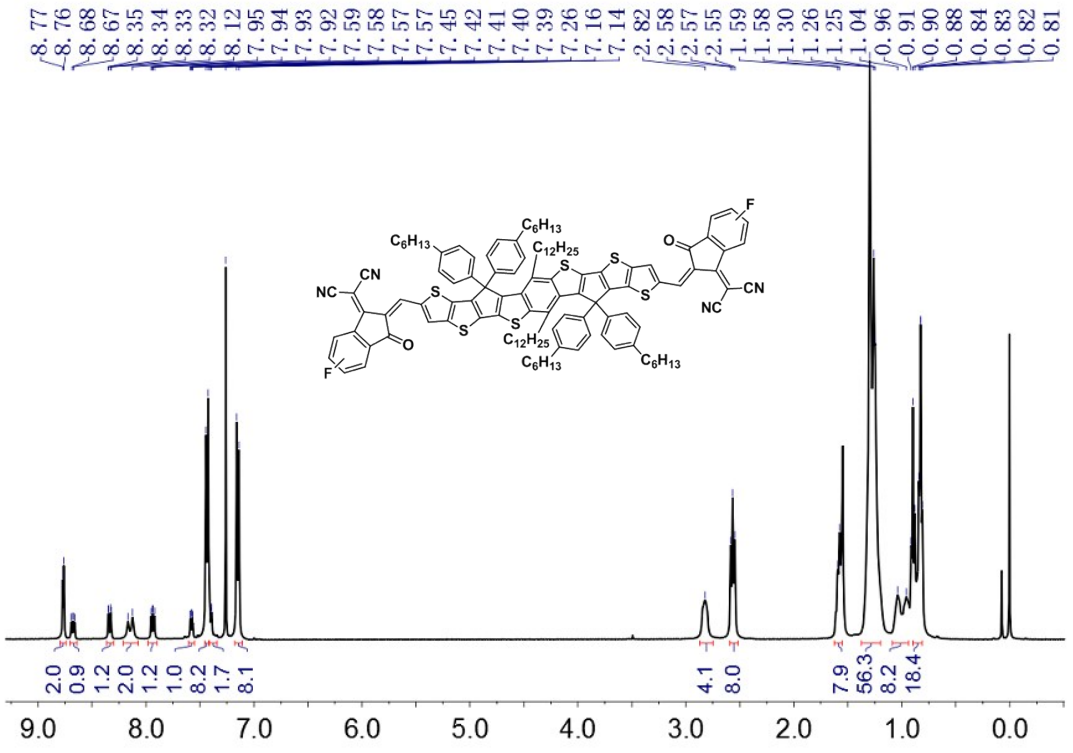


Fig. S42 ^{1}H NMR spectrum of **compound NNFA[12, 6].**

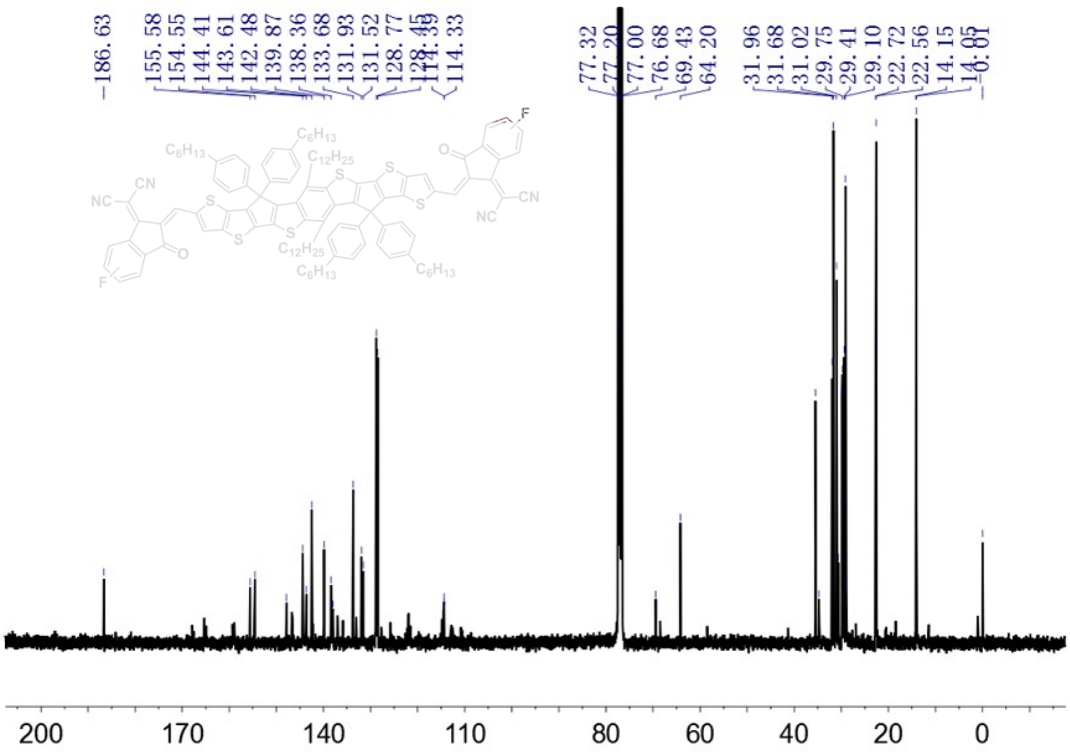


Fig. S43 ^{13}C NMR spectrum of **compound NNFA[12, 6].**

4. Solubility measurements

The solubility of materials was measured according to literature.[5] The experimental procedure for NNFA[0, 6] is given for illustration. NNFA[0, 6] chloroform solutions with different concentrations (1 μg/mL, 2 μg/mL, 4 μg/mL and 8 μg/mL) were prepared. The absorption spectra of the solutions were measured (**Fig. S44a**). A linear correlation between the concentration and the absorbance (@730nm) was found, agreeing well with Beer-Lambert law (**Fig. S44b**). Then, a saturated solution of NNFA[0, 6] in chloroform was prepared. The solution was diluted 20000 times. The absorption spectrum of the diluted solution was measured. With the aid of Figure S44b, the concentration of the diluted solution was found to be 3.7 μg/mL. Finally, the solubility of NNFA[0, 6] was calculated to be 74 mg/mL (3.7×20000 μg/mL). The solubility for other NNFAs were measured similarly.

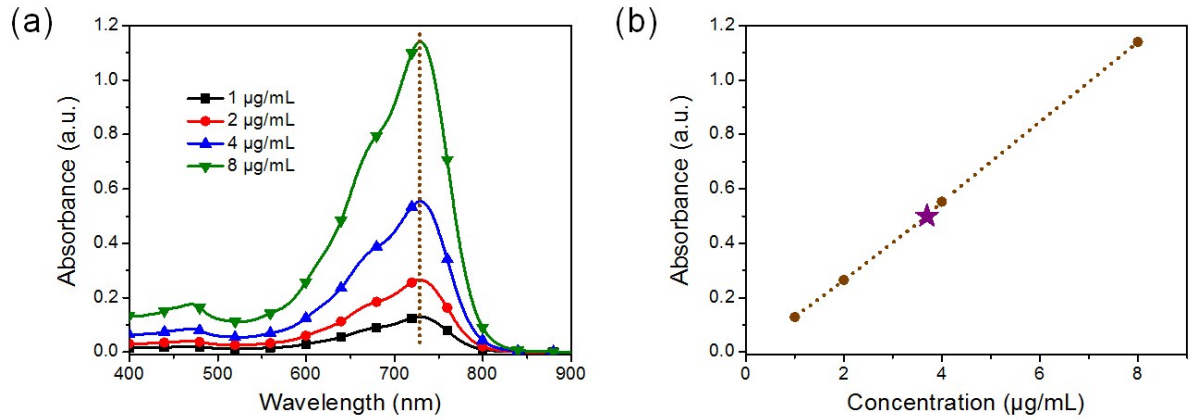


Fig. S44 (a) Absorption spectra for NNFA[0, 6] solution with different concentrations; (b) the absorbance-concentration plot.

Table S1 The solubility of acceptors in $CHCl_3$ at room temperature.

Acceptor	NNFA[0, 6]	NNFA[6, 3]	NNFA[6, 6]	NNFA[12, 3]	NNFA[12, 6]
Solubility (mg/mL)	74	23	117	96	226

5. UV-Vis

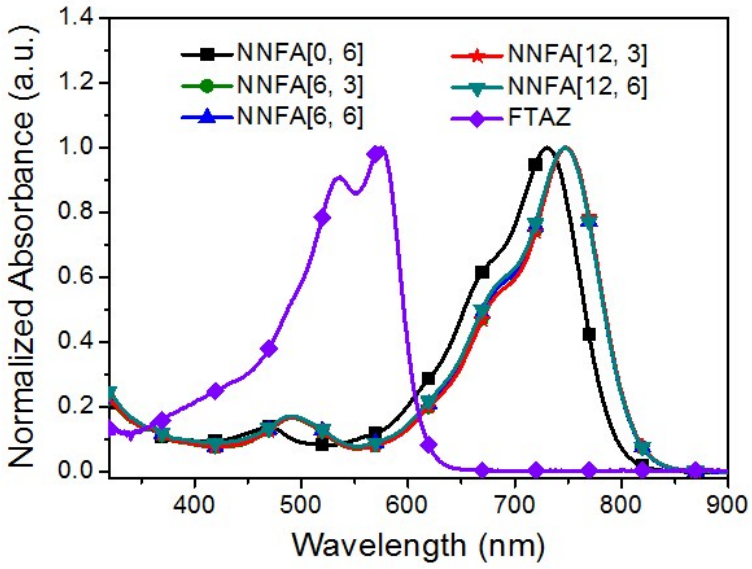


Fig. S45 Absorption spectra for NNFA[n, m] and FTAZ in $CHCl_3$.

6. CV

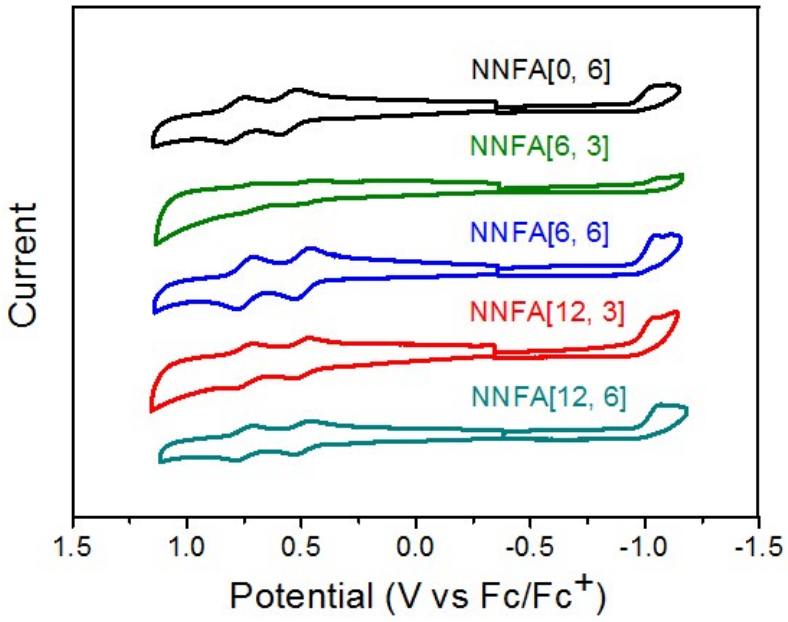


Fig. S46 Cyclic voltammograms for NNFA[n, m].

7. XRD

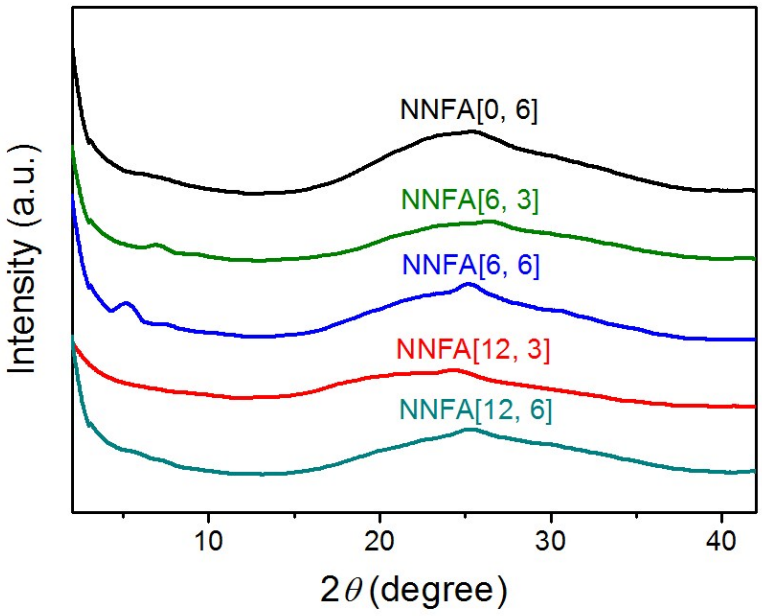


Fig. S47 XRD profiles for NNFA[n, m] films.

8. Device fabrication and measurements

Inverted solar cells

The ZnO precursor solution was prepared according to literature.[6] It was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C in air for 30 min. ZnO film thickness is ~30 nm. A FTAZ:NNFA[n, m] blend in chloroform (CF) was spin-coated onto ZnO layer. MoO_3 (~6 nm) and Ag (~80 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/FTAZ:NNFA[n, m]/MoO_3/Al. A 30 nm thick PEDOT:PSS layer was made by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT substrates were dried at 150 °C for 10 min. A FTAZ:NNFA[n, m] blend in CF was spin-coated onto PEDOT layer. Finally, MoO_3 (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is Al/FTAZ:NNFA[n, m]/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. A FTAZ:NNFA[n, m] blend in CF was spin-coated onto Al. Ca (~5 nm) and Al (~100 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

9. Optimization of device performance

Table S2 Optimization of D/A ratio for FTAZ:NNFA[0, 6] inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.84	19.31	52.5	8.51 (8.27)[b]
1:1.2	0.84	19.49	55.5	9.09 (8.72)
1:1.4	0.84	19.83	57.0	9.52 (9.42)
1:1.6	0.85	19.65	53.0	8.83 (8.57)

[a]Blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of the active layer thickness for FTAZ:NNFA[0, 6] inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
89	0.85	18.67	52.1	8.26 (8.23)[b]
80	0.84	19.83	57.0	9.52 (9.42)
68	0.84	19.49	55.8	9.14 (8.94)
60	0.85	18.83	52.6	8.44 (8.35)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of DIO content for FTAZ:NNFA[0, 6] inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.84	19.83	57.0	9.52 (9.42)[b]
0.25	0.84	19.59	55.6	9.16 (8.91)
0.5	0.82	19.39	55.9	8.90 (8.74)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of D/A ratio for FTAZ:NNFA[6, 3] inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.86	11.63	50.0	5.05 (4.89)[b]
1:1.2	0.87	13.10	52.9	6.03 (5.71)
1:1.4	0.87	14.72	59.1	7.56 (7.25)
1:1.6	0.87	13.16	55.7	6.39 (6.06)

[a]Blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of the active layer thickness for FTAZ:NNFA[6, 3] inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
87	0.87	13.10	52.9	6.03 (5.81)[b]
80	0.87	14.72	59.1	7.56 (7.25)
71	0.87	13.72	56.8	6.77 (6.49)
68	0.87	12.96	52.5	5.92 (5.60)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of DIO content for FTAZ:NNFA[6, 3] inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.87	14.72	59.1	7.56 (7.25)[b]
0.25	0.87	14.16	58.0	7.19 (7.00)
0.5	0.84	13.31	53.8	6.02 (5.89)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of D/A ratio for FTAZ:NNFA[6, 6] inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.86	19.40	55.3	9.23 (9.04)[b]
1:1.2	0.86	19.55	58.9	9.95 (9.69)
1:1.4	0.87	19.86	61.3	10.56 (10.32)
1:1.6	0.85	19.16	54.8	8.89 (8.56)

[a]Blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S9 Optimization of the active layer thickness for FTAZ:NNFA[6, 6] inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
95	0.86	19.26	57.6	9.60 (9.31)[b]
83	0.87	19.86	61.3	10.56 (10.32)
74	0.86	19.17	57.4	9.51 (9.27)
69	0.86	18.26	58.1	9.14 (8.89)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S10 Optimization of DIO content for FTAZ:NNFA[6, 6] inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.87	19.86	61.3	10.56 (10.32)[b]
0.25	0.84	19.16	60.7	9.79 (9.58)
0.5	0.82	18.02	60.6	8.93 (8.72)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S11 Optimization of D/A ratio for FTAZ:NNFA[12, 3] inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.86	18.77	57.2	9.19 (9.00)[b]
1:1.2	0.86	18.93	61.4	10.01 (9.83)
1:1.4	0.86	19.33	64.7	10.81 (10.58)
1:1.6	0.87	18.42	64.7	10.38 (10.15)

[a]Blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S12 Optimization of the active layer thickness for FTAZ:NNFA[12, 3] inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
98	0.87	18.47	63.7	10.22 (10.03)[b]
82	0.86	19.33	64.7	10.81 (10.58)
74	0.86	19.28	61.4	10.21 (9.98)
70	0.87	18.61	61.5	9.91 (9.67)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S13 Optimization of DIO content for FTAZ:NNFA[12, 3] inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.86	19.33	64.7	10.81 (10.58)[b]
0.25	0.85	18.98	61.8	10.02 (9.87)
0.5	0.84	18.45	61.2	9.47 (9.26)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S14 Optimization of D/A ratio for FTAZ:NNFA[12, 6] inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.86	18.15	53.4	8.33 (8.19)[b]
1:1.2	0.87	18.64	55.1	8.90 (8.60)
1:1.4	0.86	18.85	58.7	9.54 (9.31)
1:1.6	0.85	18.66	56.5	9.01 (8.89)

[a]Blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S15 Optimization of the active layer thickness for FTAZ:NNFA[12, 6] inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
95	0.85	18.67	52.1	8.26 (8.13)[b]
81	0.86	18.85	58.7	9.54 (9.31)
70	0.86	18.40	58.3	9.21 (8.99)
65	0.86	17.92	54.8	8.45 (8.20)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF .
[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S16 Optimization of DIO content for FTAZ:NNFA[12, 6] inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.86	18.85	58.7	9.54 (9.31)[b]
0.25	0.85	18.43	53.5	8.39 (8.15)
0.5	0.84	18.35	53.4	8.26 (8.07)

[a]D/A ratio: 1:1.4 (w/w); blend solution: 10 mg/mL in CF; spin-coating: 4000 rpm for 30 s.
[b]Data in parentheses stand for the average PCEs for 10 cells.

10. SCLC

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

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

where J is the current density, μ is the zero-field mobility of holes (μ_h) or electrons (μ_e), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, ($V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference). Here, $V_{bi} = 0.1$ V for hole-only devices, $V_{bi} = 0$ V for electron-only devices.[7] The mobility was calculated from the slope of $J^{1/2}$-V plots.

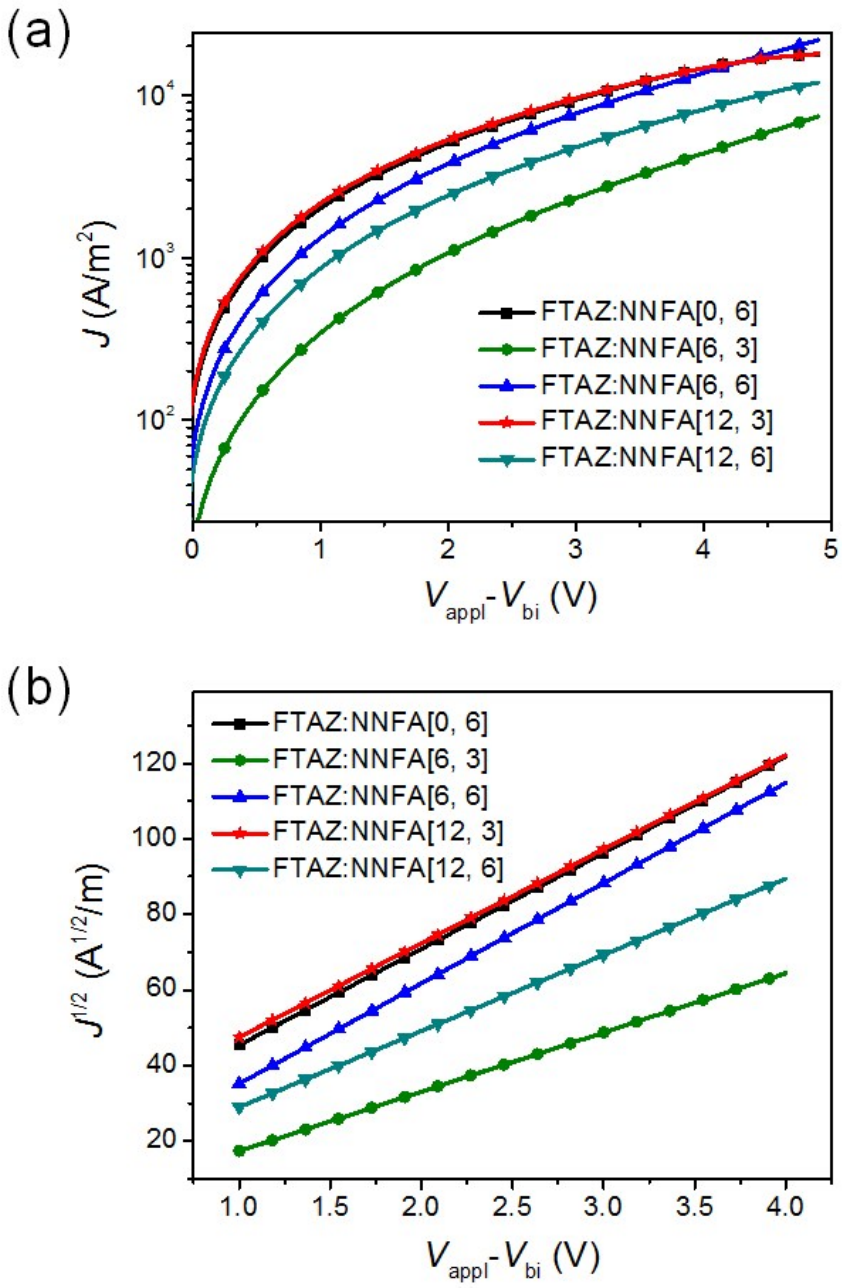


Fig. S48 *J-V* curves (a) and corresponding $J^{1/2}$-*V* plots (b) for the hole-only devices (in dark). The thicknesses for FTAZ:NNFA[0, 6], FTAZ:NNFA[6, 3], FTAZ:NNFA[6, 6], FTAZ:NNFA[12, 3] and FTAZ:NNFA[12, 6] blend films are 70 nm, 72 nm, 76 nm, 80 nm and 75 nm, respectively.

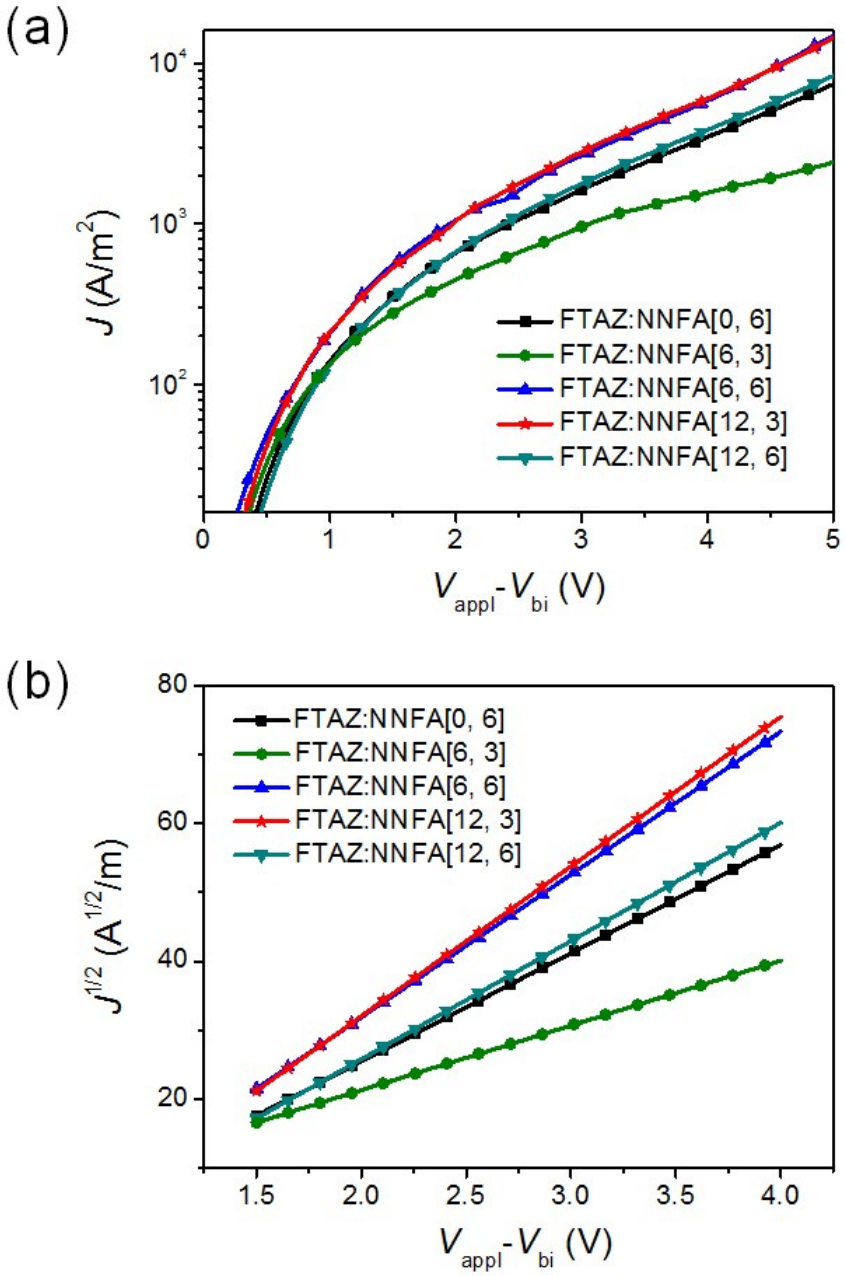


Fig. S49 *J*-*V* curves (a) and corresponding $J^{1/2}$-*V* plots (b) for the electron-only devices (in dark). The thicknesses for FTAZ:NNFA[0, 6], FTAZ:NNFA[6, 3], FTAZ:NNFA[6, 6], FTAZ:NNFA[12, 3] and FTAZ:NNFA[12, 6] blend films are 73 nm, 76 nm, 72 nm, 79 nm and 74 nm, respectively.

Table S17 Hole and electron mobilities for FTAZ:NNFA[n, m] blend films.

FTAZ:NNFA[n, m]	μ_h [$cm^2\ V^{-1}\ s^{-1}$]	μ_e [$cm^2\ V^{-1}\ s^{-1}$]	μ_h/μ_e
FTAZ:NNFA[0, 6]	2.30×10^{-4}	3.90×10^{-5}	5.90
FTAZ:NNFA[6, 3]	5.20×10^{-5}	7.16×10^{-6}	7.26
FTAZ:NNFA[6, 6]	2.41×10^{-4}	4.90×10^{-5}	4.92
FTAZ:NNFA[12, 3]	2.12×10^{-4}	5.72×10^{-5}	3.71
FTAZ:NNFA[12, 6]	1.68×10^{-4}	2.81×10^{-5}	5.98

11. AFM

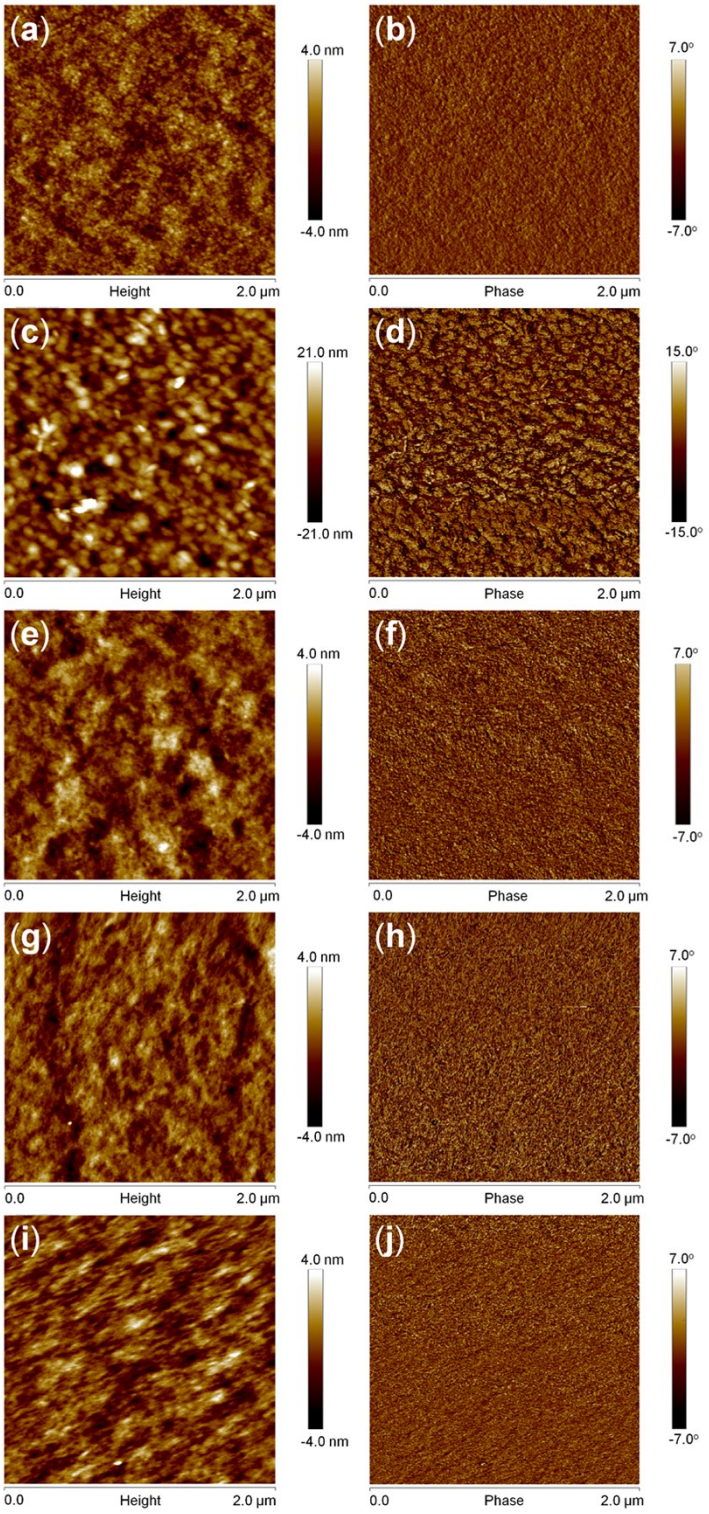


Fig. S50 AFM height (left) and phase (right) images for the blend films. (a) and (b), FTAZ:NNFA[0, 6] film (R_{rms} = 0.95 nm); (c) and (d), FTAZ:NNFA[6, 3] film (R_{rms} = 6.09 nm); (e) and (f) FTAZ:NNFA[6, 6] film (R_{rms} = 1.01 nm); (g) and (h), FTAZ:NNFA[12, 3] film (R_{rms} = 0.89 nm); (i) and (j), FTAZ:NNFA[12, 6] film (R_{rms} = 0.97 nm). R_{rms}: root-mean-square roughness.

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