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Supporting Information

Quinquethiophene-based fully nonfused electron acceptors towards efficient organic solar cells via side-chain engineering

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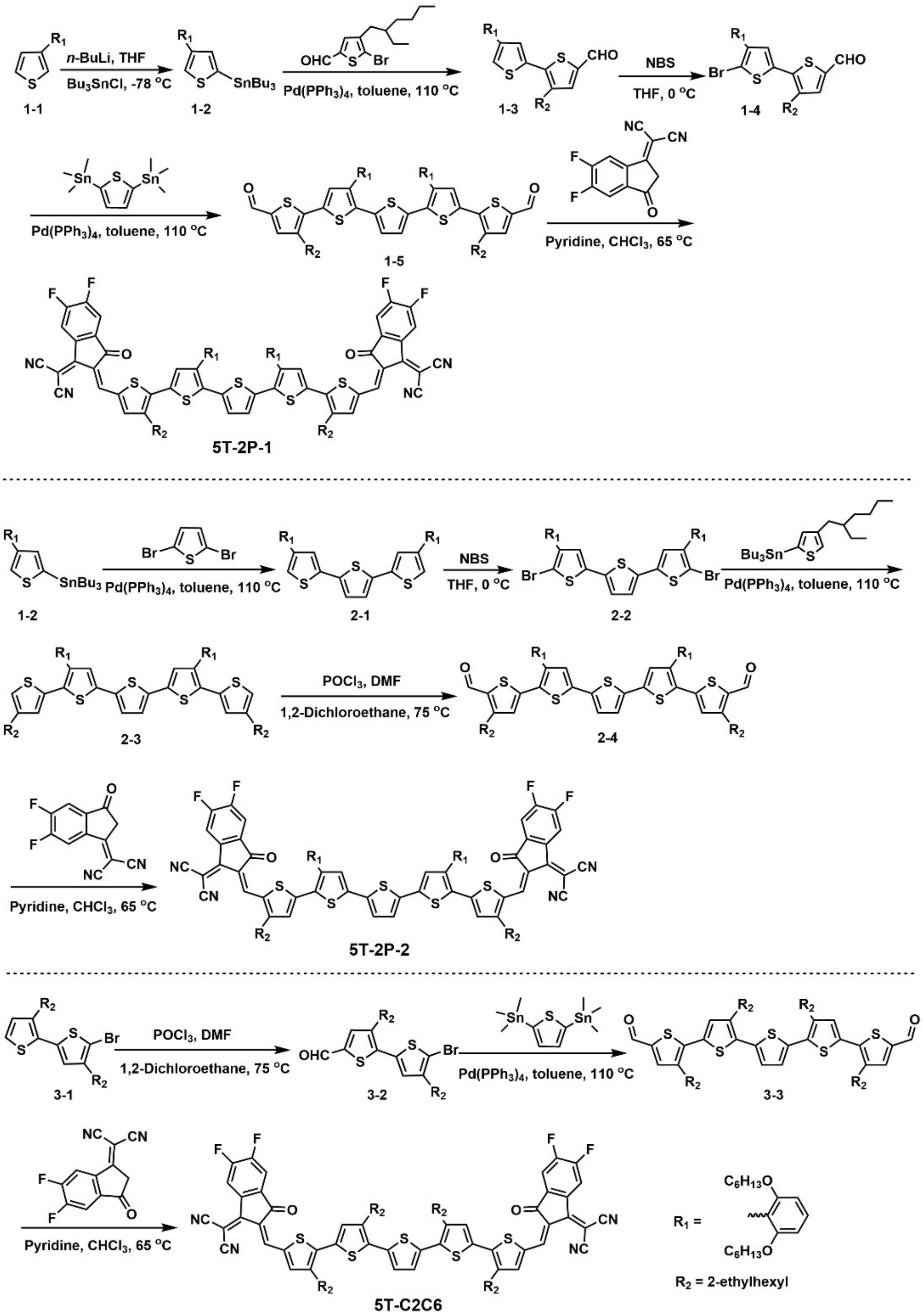
Materials and synthesis



Scheme S1 Synthetic routes of 5T-C2C6, 5T-2P-1 and 5T-2P-2.

All the used solvents and reagents were analytical grade and used without further purification. FNEAs were obtained following the synthetic routes as shown in Scheme 1. D18, and compound 1-1 and compound 7 were purchased from commercial sources. Compounds 1-1[1] and 3-1[2] were synthesized according to the reported literature.

(4-(2,6-bis(hexyloxy)phenyl)thiophen-2-yl)tributylstannane (Compound 1-2): To a solution of compound **1-1** (660 mg, 1.83 mmol) in dry tetrahydrofuran (20 mL) was added slowly *n*-butyllithium (2.5 M, 2.20 mmol in hexane, 0.88 mL) at -78 °C under nitrogen atmosphere and stirred for 2 h. Then tributyltin chloride (976 mg, 3.0

mmol) was added dropwise and stirred at -78 °C for 0.5 h and the mixture was gradually warmed to room temperature. After removal of solvent in vacuo, the mixture was then poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave the crude compound 1-2 as colorless oily liquid. Without any further purification, the product was used into the following reaction.

4'-(2,6-bis(hexyloxy)phenyl)-3-(2-ethylhexyl)-[2,2'-bithiophene]-5-carbaldehyde (Compound 1-3): Compound **1-2** (593 mg, 0.91 mmol), 5-bromo-4-(2-ethylhexyl)thiophene-2-carbaldehyde (303 mg, 0.91 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) were dissolved in anhydrous toluene (20 mL) and stirred at 110 °C for 12 h under nitrogen atmosphere. Then the reaction mixture was cooled to room temperature and poured into water (100 mL) and then extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The raw product was purified with chromatography column by using petroleum ether/dichloromethane (3:1, *v*/*v*) as eluent, which yielded compound **1-3** as yellow oily liquid (370 mg, 0.63 mmol, 70%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.62 (d, J = 1.2 Hz, 1H), 7.59 (d, J = 1.2 Hz, 1H), 7.58 (s, 1H), 7.21 (t, J = 8.3 Hz, 1H), 6.64 (d, J = 8.4 Hz, 2H), 3.97 (t, J = 6.5 Hz, 4H), 2.82 (d, J = 7.3 Hz, 2H), 1.77 – 1.72 (m, 5H), 1.42 – 1.36 (m, 7H), 1.31 – 1.27 (m, 12H), 0.91 – 0.86 (m, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.58, 157.34, 142.97, 139.82, 139.62, 139.04, 133.76, 131.96, 131.67, 128.73, 127.34, 113.97, 105.33, 68.84, 40.08, 33.49, 32.59, 31.55, 29.29, 28.76, 25.89, 25.68, 23.10, 22.63, 14.14, 14.02, 10.70.

5'-Bromo-4'-(2,6-bis(hexyloxy)phenyl)-3-(2-ethylhexyl)-[2,2'-bithiophene]-5-carbaldehyde (Compound 1-4): To a solution of compound 1-3 (326 mg, 0.56 mmol) in tetrahydrofuran (20 mL) was added by three times N-bromosuccinimide (109 mg, 0.61 mmol) slowly at 0 °C and the mixture was stirred at the same temperature for 3 h in the dark. After removal of solvent in vacuo, the mixture was then poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was purified with chromatography column by using petroleum ether/dichloromethane (5:1, *v*/*v*) as eluent to afford compound **1-4** as a yellow oily liquid (260 mg, 0.39 mmol, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.54 (s, 1H), 7.26 (t, J = 8.3 Hz, 1H), 7.08 (s, 1H), 6.59 (d, J = 8.4 Hz, 2H), 3.92 (t, J = 6.4 Hz, 4H), 2.73 (d, J = 7.3 Hz, 2H), 1.69 – 1.64 (m, 5H), 1.36 – 1.31 (m, 7H), 1.27 – 1.23 (m, 12H), 0.83 – 0.77 (m, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.58, 157.69, 141.55, 140.27, 139.57, 139.36, 136.19, 133.05, 131.29, 129.91, 114.25, 112.73, 104.98, 68.66, 40.10, 33.49, 32.60, 31.48, 29.18, 28.77, 25.69, 23.07, 22.62, 14.13, 14.03, 10.68.

3''',4'-bis(2,6-bis(hexyloxy)phenyl)-3,3''''-bis(2-ethylhexyl)-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde (Compound 1-5): Compound **1-4** (168 mg, 0.25 mmol), 2,5-bis(trimethylstannyl)thiophene (46.8 mg, 0.11 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) were dissolved in anhydrous toluene (20 mL) under nitrogen atmosphere. The mixture was stirred at 110 °C overnight. Then the reaction mixture was cooled to room temperature, removal of solvent in vacuo, poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated with reduced pressure. The mixture was purified with chromatography column by using petroleum ether/dichloromethane (1:1, *v*/*v*) as eluent to obtain compound **1-5** as an orange oily liquid (70 mg, 0.056 mmol, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.54 (s, 1H), 7.25 (d, J = 8.3 Hz, 1H), 7.06 (s, 1H), 6.89 (s, 1H), 6.49 (d, J = 8.4 Hz, 2H), 3.83 (dd, J = 15.0, 6.4 Hz, 2H), 3.65 (dd, J = 15.5, 6.4 Hz, 2H), 2.78 – 2.76 (m, 2H), 1.51 – 1.44 (m, 5H), 1.37 – 1.27 (m, 7H), 1.17 – 1.12 (m, 12H), 0.88 – 0.77 (m, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.52, 158.00, 142.43, 139.75, 139.59, 139.05, 136.55, 135.86, 132.71, 131.08, 130.66, 129.82, 124.64, 113.67, 105.42, 68.59, 39.89, 33.68, 32.63, 31.48, 29.11, 28.79, 25.72, 25.53, 23.08, 22.56, 14.12, 13.99, 10.67. MS (MALDI-TOF) m/z: calcd for $C_{74}H_{100}O_6S_5$ 1245.9; found, 1245.8.

2,2'-((2Z,2'Z)-((3''',4'-bis(2,6-bis(hexyloxy)phenyl)-3,3''''-bis(2-ethylhexyl)-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (5T-2P-1): A solution of compound 1-5 (30 mg, 0.023 mmol), 2F-IC (16mg, 0.069 mmol) in anhydrous chloroform (10 mL) was degassed and charged with nitrogen before and after the addition of pyridine (0.1 mL). Subsequently, the mixture was stirred at 65 °C overnight. Then the reaction mixture was cooled to room temperature and poured into methanol (100 mL). The crude product was purified with chromatography column by using petroleum ether/dichloromethane (1:2, *v*/*v*) as eluent to obtain 5T-2P-1 as a dark solid (25 mg, 0.015 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.53 (dd, J = 9.9, 6.5 Hz, 1H), 7.65 (dd, J = 12.9, 5.1 Hz, 2H), 7.34 (s, 1H), 7.29 (t, J = 8.4 Hz, 1H), 7.00 (s, 1H), 6.51 (d, J = 8.4 Hz, 2H), 3.85 (dd, J = 13.9, 6.5 Hz, 2H), 3.67 (dt, J = 8.9, 6.5 Hz, 2H), 2.80 (d, J = 7.3 Hz, 2H), 1.47 (d, J = 5.7 Hz, 4H), 1.37 – 1.29 (m, 8H), 1.14 (d, J = 9.8 Hz, 12H), 0.92 – 0.75 (m, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.88, 158.47, 157.91, 151.26, 149.62, 140.13, 138.13, 137.57, 137.10, 134.40, 133.81, 132.25, 130.93, 130.16, 125.45, 120.97, 115.00, 114.83, 114.41, 114.30, 113.06, 112.60, 112.45, 105.35, 99.99, 69.30, 68.55, 39.41, 33.67, 32.65, 31.45, 29.09, 28.74, 25.79, 25.53, 23.09, 22.56, 14.12, 13.98, 10.64. MS (MALDI-TOF) m/z: calcd for $C_{98}H_{104}F_4N_4O_6S_5$1668.6; found, 1668.1.

(4,4''-bis(2,6-bis(hexyloxy)phenyl)-2,2':5',2''-terthiophene (Compound 2-1): Compound **1-2** (570 mg, 0.88 mmol), 2,5-dibromothiophene (95 mg, 0.39 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) were dissolved in anhydrous toluene (20 mL) under nitrogen atmosphere. The mixture was stirred at 110 °C overnight. Then the reaction mixture was cooled to room temperature, removal of solvent in vacuo, poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated with reduced pressure. The mixture was purified with chromatography column by using petroleum ether/dichloromethane (9:1, *v*/*v*) as eluent to yield compound **2-1** (78 mg, 0.097 mmol, 25%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 1.1 Hz, 1H), 7.33 (d, J = 1.1 Hz, 1H), 7.19 (dd, J = 10.3, 6.3 Hz, 1H), 7.06 (s, 1H), 6.61 (d, J = 8.4 Hz, 2H), 3.95 (t, J = 6.4 Hz, 4H), 1.74 – 1.70 (m, 4H), 1.39 (dd, J = 14.3, 6.5 Hz, 5H), 1.27 (dd, J = 8.5, 4.7 Hz, 8H), 0.84 (t, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.43, 136.58, 134.16, 128.46, 127.63, 127.11, 124.22, 123.53, 114.61, 105.44, 68.88, 31.58, 29.29, 25.92, 22.65, 14.05.

4,4''-bis(2,6-bis(hexyloxy)phenyl)-5,5''-dibromo-2,2':5',2''-terthiophene (Compound 2-2): To a solution of compound **2-1** (78 mg, 0.097 mmol) in tetrahydrofuran (20 mL) was added by three times N-bromosuccinimide (36 mg, 0.2 mmol) slowly at 0 °C and the mixture was stirred at the same temperature for 3 h in the dark. After removal of solvent in vacuo, the mixture was then poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous MgSO4. After concentrate the organic layer by vacuum evaporation, the raw product was purified with chromatography column by using petroleum ether/dichloromethane (7:1) as eluent, and compound **2-2** was obtained as yellow oily liquid(70 mg, 0.073 mmol, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.3 Hz, 1H), 6.99 (s, 1H), 6.94 (s, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 3.95 (t, *J* = 6.4 Hz, 3H), 1.77 – 1.68 (m, 3H), 1.39 (m, 4H), 1.27 (m, 8H), 0.84 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.69, 135.03, 134.84, 134.19, 128.62, 126.03, 122.80, 112.27, 109.87, 104.08, 67.73, 30.44, 28.11, 24.65, 21.57, 12.96.

3',4'''-bis(2,6-bis(hexyloxy)phenyl)-4,4''''-bis(2-ethylhexyl)-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (Compound 2-3): Compound **2-2** (70 mg, 0.073 mmol), tributyl(4-(2-ethylhexyl)thiophen-2-yl)stannane (73 mg, 0.15 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) were dissolved in anhydrous toluene (20 mL) under nitrogen atmosphere. The mixture was stirred at 110 °C overnight.. Then the reaction mixture was cooled to room temperature, removal of solvent in vacuo, poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated with reduced pressure. The mixture was purified with chromatography column by using petroleum ether/dichloromethane (5:1, *v*/*v*) as eluent to obtain compound **2-3** as a yellow oily liquid (42 mg, 0.035mmol, 24%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 8.3 Hz, 1H), 7.08 (s, 1H), 7.02 (s, 1H), 6.80 (s, 1H), 6.62 (d, J = 2.8 Hz, 2H), 6.60 (s, 1H), 3.91 (dt, J = 9.0, 6.4 Hz, 2H), 3.80 (dd, J = 8.9, 1.5 Hz, 2H), 2.44 (t, J = 6.4 Hz, 2H), 1.57 – 1.52 (m, 4H), 1.31 (s, 2H), 1.28 (s, 6H), 1.25 – 1.18 (m, 13H), 0.91 (t, J = 6.6 Hz, 3H), 0.88 – 0.8 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.31, 141.38, 136.68, 136.18, 132.92, 132.84, 130.89, 129.51, 128.35, 125.90, 123.59, 120.30, 114.61, 105.44, 68.74, 40.20, 34.33, 32.48, 31.50, 29.10, 28.92, 25.56, 25.52, 23.08, 22.60, 14.20, 14.02, 10.85.

3',4'''-bis(2,6-bis(hexyloxy)phenyl)-4,4''''-bis(2-ethylhexyl)-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde (Compound 2-4): Compound **2-3** (42 mg, 0.035mmol) was dissolved in 1,2-dichloroethane (20 mL) under nitrogen atmosphere, and then the fresh Vilsmeier reagent (1 mL $POCl_3$ in 1 mL DMF) was added dropwise at 0 °C. The mixture was heated to 80 °C and stirred for 8 h. The reaction was quenched with saturated $NaHCO_3$ solution and allowed to stir at room temperature for 24 h. Removal of solvent in vacuo, poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated with reduced pressure. The mixture was purified with chromatography column by using petroleum ether/dichloromethane (2:1, *v*/*v*) as eluent to obtain compound **2-4** as an orange-red oily liquid (30 mg, 0.024 mmol, 69%). ^1H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.31 (t, *J* = 8.4 Hz, 1H), 7.14 (s, 1H), 7.05 (s, 1H), 6.83 (s, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 3.90 (dt, *J* = 8.9, 6.3 Hz, 2H), 3.84 – 3.79 (m, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 1.53 – 1.50 (m, 4H), 1.29 – 1.25 (m, 8H), 1.16 (dd, *J* = 9.7, 4.6 Hz, 11H), 0.87 (dd, *J* = 15.4, 8.0 Hz, 8H), 0.77 (d, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.65, 157.84, 152.07, 145.98, 136.33, 136.31, 135.37, 134.75, 131.35, 130.44, 129.00, 127.49, 124.58, 113.23, 105.44, 68.60, 41.38, 32.51, 32.47, 31.40, 29.01, 28.78, 25.55, 25.53, 22.98, 22.57, 14.13, 13.96, 10.75. MS (MALDI-TOF) m/z: calcd for $C_{74}H_{100}O_6S_5$ 1245.9; found, 1245.6.

2,2'-((2Z,2'Z)-((3',4'''-bis(2,6-bis(hexyloxy)phenyl)-4,4''''-bis(2-ethylhexyl)-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (5T-2P-2): 5T-2P-2 (23 mg, 0.014 mmol, 60%) was obtained as a dark red solid from compound **2-4** (30 mg, 0.023 mmol) and 2F-IC (16mg, 0.069 mmol) following the procedure for the synthesis of 5T-2P-1. ^1H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.51 (dd, J = 10.0, 6.5 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 8.4 Hz, 1H), 7.24 (s, 1H), 7.17 (s, 1H), 6.83 (s, 1H), 6.67 (d, J = 8.5 Hz, 2H), 3.95 – 3.92 (m, 2H), 3.88 (dd, J = 6.2, 2.8 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 1.54 (d, J = 6.8 Hz, 4H), 1.27 – 1.15 (m, 21H), 0.88 (s, 3H), 0.81 (s, 3H), 0.75 (d, J = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.42, 161.48, 159.62, 157.70, 153.17, 138.82, 137.38, 136.80, 136.38, 134.68, 133.22, 132.03, 131.49, 130.57, 129.78, 127.81, 125.53, 124.46, 119.78, 115.18, 114.81, 114.68, 113.23, 112.46, 112.40, 105.34, 68.64, 41.58, 34.15, 32.14, 31.41, 29.03, 28.64, 25.60, 25.22, 22.96, 22.57, 14.14, 13.98, 10.68. MS (MALDI-TOF) m/z: calcd for $C_{98}H_{104}F_4N_4O_6S_5$ 1668.65; found, 1668.18.

5'-bromo-3,4'-bis(2-ethylhexyl)-[2,2'-bithiophene]-5-carbaldehyde (Compound 3-2): Adding DMF and dichloroethane in a reactor reacting at 0°C for 0.5 h to obtain Vilsmeier-Haack reagent. Compound **3-1** (468 mg, 1.0 mmol) and 1,2-dichloroethane (20 mL) was dissolved in Vilsmeier-Haack reagent. The mixture was stirred at 75 °C for 8 h. Then the reaction mixture was cooled to room temperature, removal of solvent in vacuo, poured into water (100 mL) and extracted with dichloromethane (100 mL × 3). The combined organic layer was dried over anhydrous MgSO4. After concentrate the organic layer by vacuum evaporation, the raw product was purified with chromatography column by using petroleum ether/dichloromethane (3:1, *v*/*v*) as eluent, and compound **3-2** was obtained as yellow oily liquid(313 mg, 0.63 mmol, 63%). ^1H NMR (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.54 (s, 1H), 6.92 (s, 1H), 2.68 (d, *J* = 7.3 Hz, 2H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.63 (dt, *J* = 12.1, 5.9 Hz, 2H), 1.34 (dd, *J* = 13.6, 7.4 Hz, 5H), 1.31 – 1.28 (m, 7H), 1.25 (d, *J* = 6.5 Hz, 6H), 0.91 – 0.83 (m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.53, 142.13, 140.86, 140.55, 139.90, 139.29, 134.17, 129.08, 111.77, 40.10, 39.96, 33.72, 33.42, 32.49, 32.45, 28.80, 28.65, 25.72, 25.64, 23.05, 23.04, 14.14, 14.10, 10.84, 10.66. MS (MALDI-TOF) m/z: calcd for $C_{25}H_{37}BrOS_2$ 497.6; found, 498.5.

3,3''',3'''',4'-tetrakis(2-ethylhexyl)-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-dicarbaldehyde (Compound 3-3): Compound **3-3** (60 mg, 0.065 mmol, 73%) was obtained as an orange solid from compound **3-2** (100 mg, 0.2 mmol), 2,5-bis(trimethylstannyl)thiophene (38 mg, 0.09 mmol) and Pd $(PPh_3)_4$ (20 mg, 0.017 mmol) following the procedure for the synthesis of **1-5**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.56 (s, 1H), 7.13 (s, 1H), 7.10 (s, 1H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.74 (d, *J* = 7.4 Hz, 2H), 1.73 – 1.66 (m, 2H), 1.37 – 1.33 (m, 4H), 1.28 (dd, *J* = 13.0, 5.9 Hz, 12H), 0.87 (dt, *J* = 7.3, 3.5 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.57, 141.48, 140.21, 139.70, 139.67, 139.65, 135.81, 132.99, 132.83, 131.19, 126.83, 40.26, 40.07, 33.63, 33.60, 32.56, 32.53, 28.72, 28.71, 25.81, 25.71, 23.08, 23.08, 14.14, 14.14, 10.78, 10.71. MS (MALDI-TOF) m/z: calcd for $C_{54}H_{76}O_2S_5$ 917.5; found, 917.6.

2,2'-((2Z,2'Z)-((3,3''',3'''',4'-tetrakis(2-ethylhexyl)-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (5T-C2C6): 5T-C2C6 (58 mg, 0.043 mmol, 59%) was obtained as a dark red solid from compound **3-3** (63 mg, 0.073 mmol) and 2F-IC (50 mg, 0.219 mmol) following the procedure for the synthesis of **5T-2P-1**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.53 (dd, *J* = 9.7, 6.4 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.64 (s, 1H), 7.34 (s, 1H), 7.21 (s, 1H), 2.80 (t, *J* = 7.4 Hz, 4H), 1.74 (d, *J* = 5.5 Hz, 2H), 1.57 (s, 2H), 1.43 – 1.35 (m, 6H), 1.29 (d, *J* = 4.2 Hz, 12H), 0.95 – 0.86 (m, 12H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.53 (dd, J = 9.9, 6.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.64 (s, 1H), 7.34 (s, 1H), 7.21 (s, 1H), 2.80 (t, J = 7.4 Hz, 4H), 1.81 – 1.71 (m, 2H), 1.41 – 1.37 (m, 4H), 1.29 (s, 10H), 0.94 – 0.86 (m, 13H). ^{13}C NMR (126 MHz, CDCl3) δ 185.92, 158.47, 158.16, 149.71, 148.01, 141.54, 140.70, 140.16, 138.42, 137.52, 134.03, 132.84, 131.32, 130.65, 127.12, 120.34, 114.43, 114.32, 114.04, 112.62, 109.37, 105.40, 68.53, 53.44, 39.37, 33.70, 32.69, 31.44, 29.71, 29.07, 28.76, 25.79, 25.54, 23.08, 22.58, 14.11, 13.96, 10.63. MS (MALDI-TOF) m/z: calcd for $C_{78}H_{80}F_4N_4O_2S_5$ 1341.8; found, 1341.6.

Material Characterizations

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AVANCE 500 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were referenced to tetramethylsilane (0 ppm) for $CDCl_3$. Mass spectra analyses were measured on a Bruker Autoflex maX MALDI-TOF mass spectrometry.

Thermal gravimetric analyses (TGA) were performed on TA Q500 instrument under nitrogen gas flow with a 10 ^{o}C min^{-1} heating rate from 40 to 600 ^{o}C. Film UV-visible absorption spectra were obtained with double-beam Hitachi UH5300 spectrophotometer. The films were cast from the solutions of the acceptors with a concentration of 10 mg/mL in chloroform. UV-Vis absorption spectra were collected from the solution of two small molecules with the concentration of 1.0×10^{-5} M in chloroform and a cuvette with a stopper (Sigma Z600628) was used to avoid volatilization during the measurement. The films were spin-coated from the chloroform solution (15 mg mL^{-1}) on a quartz substrate at 2000 rpm for 30 s. The transmission electron microscopy (TEM) investigation was performed on Tecnai G2 F20 (FEI).

GIWAXS measurement was performed at MetalJet-D2, Excillum on the wavelength of 0.134144 nm with Xeuss 2.0. All simples were deposited on the silicon and were irradiated at a fixed X-ray incident angle of 0.2° with an exposure time of 1800 s.

Cyclic voltammetry (CV) analyses were conducted with the films on the glassy carbon working electrode in dry methanol solution via a LK2005A electrochemical workstation. All CV measurements were carried out at room temperature with a standard three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 M) in methanol was used as the supporting electrolyte, and the scan rate was 100 mV s^{-1}. The HOMO energy levels were determined by $E_{\mathrm{HOMO}} = -(E_{\mathrm{re}} - E_{\mathrm{ferrocene}} + 4.8)$ eV, while the LUMO energy levels were determined by $E_{\mathrm{LUMO}} = -(E_{\mathrm{ox}} - E_{\mathrm{ferrocene}} + 4.8)$ eV.

Device fabrication and measurements.

The ITO-coated glass substrates were cleaned via detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by nitrogen. The ITO glasses were then treated with oxygen plasma for 60 s, 30 nm thick PEDOT:PSS (Clevios P AI4083) was spin-coated on the ITO substrates. After baking at 150 °C for 15 min, the substrates were transferred into a nitrogen-filled glovebox. Subsequently, the D18:NFEAs (1:1.6, w/w, D = 4 mg/mL) active layer dissolved in chloroform was spin-coated to form a film of 120 nm. The solution of PNDIT-F3N was spin-coated on the top of active layers. The top electrode was then formed by evaporation of 100 nm Ag through a shadow mask to define the active area (4 mm^2) of the device.

The current density-voltage (J-V) curves were recorded at 100 $mW\cdot cm^{-2}$ using an SS-X50 solar simulator (Enli Tech) with a standard Si solar cell as a calibration standard. The external quantum efficiency (EQE) was measured by QE-R solar cell spectral response measurement system (Enli Technology Co., Ltd., Taiwan). Photocurrent density-effective voltage (J_{ph}-V_{eff}) curves and photo-induced charge-carrier extraction in linearly increasing voltage (photo-CELIV) were measured via the all-in-one characterization platform Paios (Fluxim AG, Switzerland).

Contact angle measurement.

The contact angles were measured by a contact angle meter (SL200KS). The droplets of water and ethylene glycol (EG) were dripped on the neat films.

The surface tension (γ) is estimated by the Harmonic mean equations:

$$(1 + cos\theta_{water})\gamma_{water} = 2\sqrt{\gamma_{water}^{d}\gamma^{d}} + 2\sqrt{\gamma_{water}^{p}\gamma^{p}}$$

$$(1 + cos\theta_{EG})\gamma_{EG} = 2\sqrt{\gamma_{EG}^{d}\gamma^{d}} + 2\sqrt{\gamma_{EG}^{p}\gamma^{p}}$$

$$\gamma^{total} = \gamma^{d} + \gamma^{p}$$

The interfacial tension between two different materials can be calculated by the following equation:

$$\gamma_{A-B} = \gamma_A + \gamma_B - 4\left(\frac{\gamma_A^d \gamma_B^d}{\gamma_A^d + \gamma_B^d} + \frac{\gamma_A^p \gamma_B^p}{\gamma_A^p + \gamma_B^p}\right)$$

where θ is the droplet contact angle on the neat film; $\gamma_{A\text{-}B}$ represents the interface tension between A and B, γA and γB are the surface tensions of pure films, respectively. The $\gamma^d{}_A$ and $\gamma^p{}_A$ are the dispersion and polar forces of A, and the $\gamma^d{}_B$ and $\gamma^p{}_B$ are the dispersion and polar forces of B.

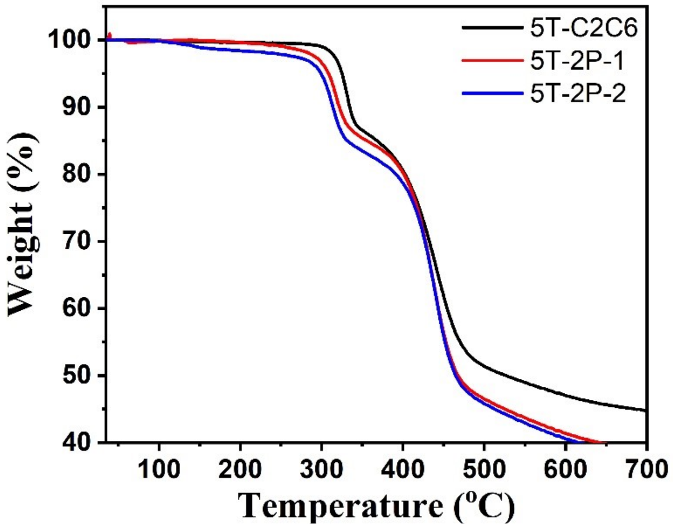


Fig. S1 TGA curves of FNEAs recorded under N_2 atmosphere at a heating rate of 10 °C min^{-1}.

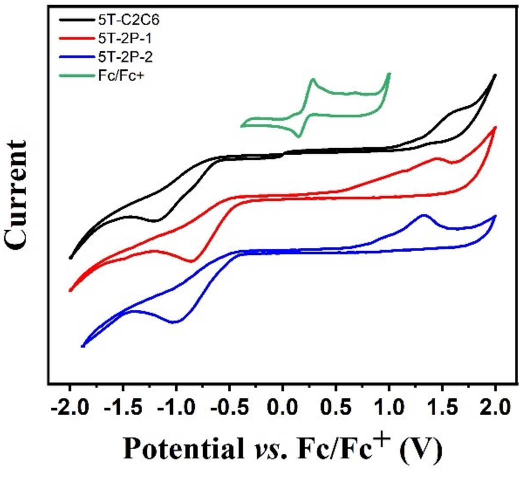


Fig. S2 Cyclic voltammogram curves of FNEAs in methanol with 0.1 mol L^{-1} Bu_4NPF_6 with a scan rate of 100 mV s^{-1}.

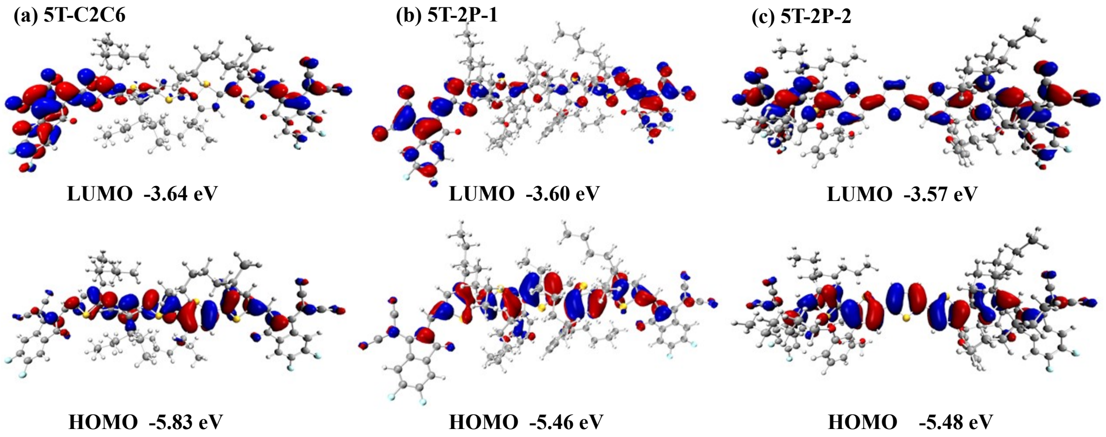


Fig. S3 The calculated electron density distributions of HOMO and LUMO orbitals of the simplified FNEAs.

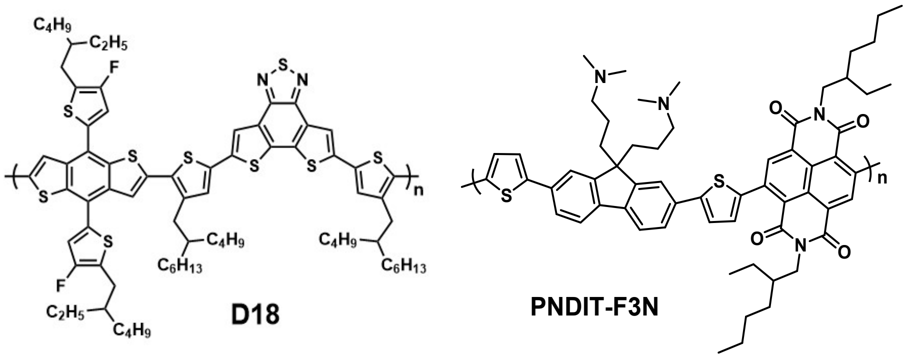


Fig. S4 Chemical structures of D18 and PNDIT-F3N.

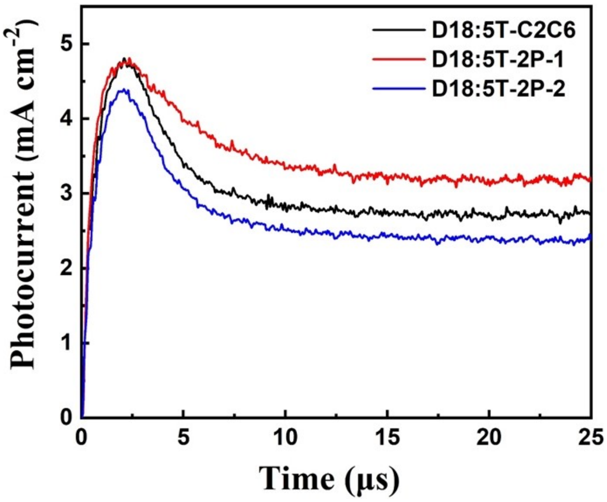


Fig. S5 Photo-CELIV curves of FNEAs based devices.

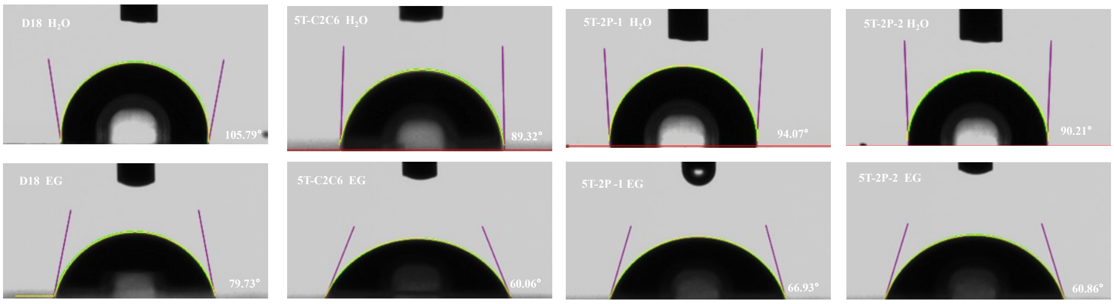


Fig. S6 Contact angle images for water and ethylene glycol on D18 and FNEAs.

Table S1. Photovoltaic parameters of the as-cast OSCs based on nonfused acceptors under standard AM 1.5G illumination, 100 mW cm^{-2}.

Acceptor	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
5T-C2C6	0.937	49.86	9.69	4.53 (4.32)
5T-2P-1	0.862	52.12	12.51	5.62 (5.31)
5T-2P-2	0.962	46.38	8.12	3.62 (3.45)

Table S2. Parameters of the blend films based on different FNEAs from GIWAXS data.

	Lamellar stacking				**π-π stacking**			
	q (Å^{-1})	d-spacing (Å)	FWHM (Å^{-1})	CCL (Å)	q (Å^{-1})	d-spacing (Å)	FWHM (Å^{-1})	CCL (Å)
D18:5T-C2C6	0.37	16.98	0.058	97.5	1.77	3.55	0.18	32.1
D18:5T-2P-1	0.31	20.26	0.061	92.7	1.68	3.74	0.31	17.1
D18:5T-2P-2	0.31	20.26	0.063	89.7	1.68	3.74	0.36	15.6

[a]Full width at half-maximum (FWHM) of the diffraction peak. [b]Crystal Coherent length (CCL) estimated from the Scherrer equation (CCL = 2π x 0.9/FWHM) for the π-π stacking of the face-on crystallite.

Table S3. Statistical data of surface tension and interaction parameter.

Materials	CA Water [deg]	CA EG [deg]	γ^{d} [mN/m]	γ^{p} [mN/m]	γ^{total} [mN/m]	$\gamma_{D18\text{-}A}$ [mN/m]
D18	105.79	79.73	22.8	0.346	23.146	--
5T-C2C6	89.32	60.06	27.522	2.985	30.507	3.365
5T-2P-1	94.07	66.93	25.346	2.084	27.430	1.378
5T-2P-2	90.21	60.86	28.566	2.509	31.075	2.286

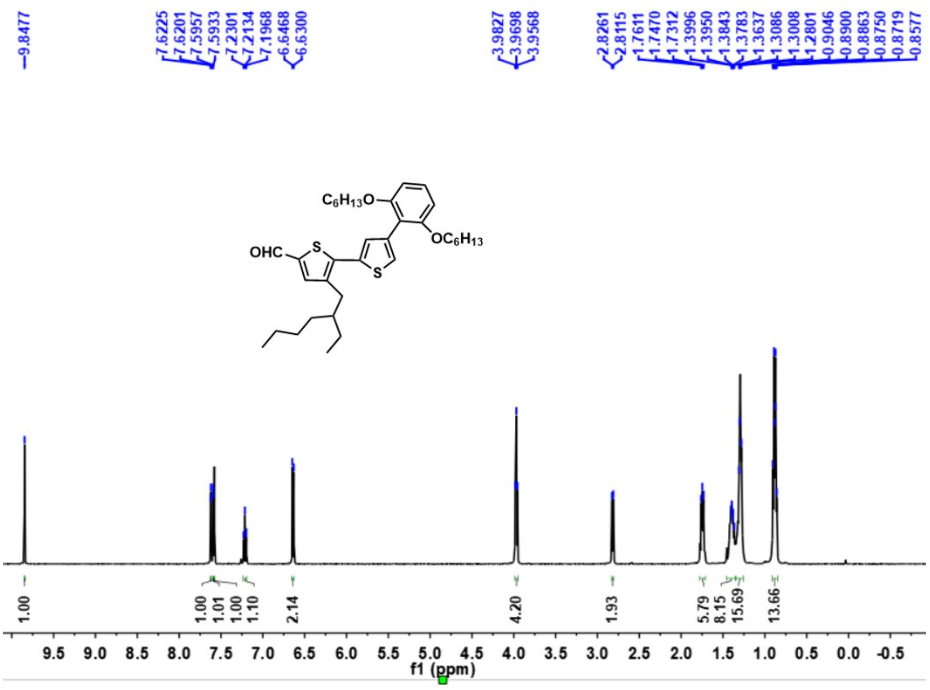


Fig. S7 ^{1}H NMR spectrum of compound 1-3 in $CDCl_3$

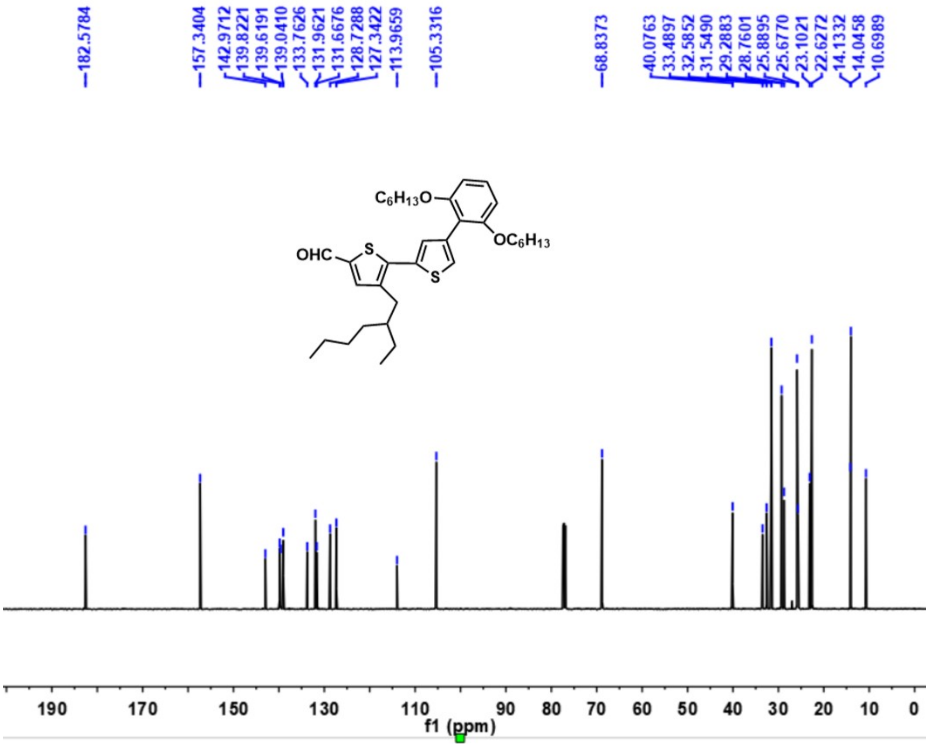
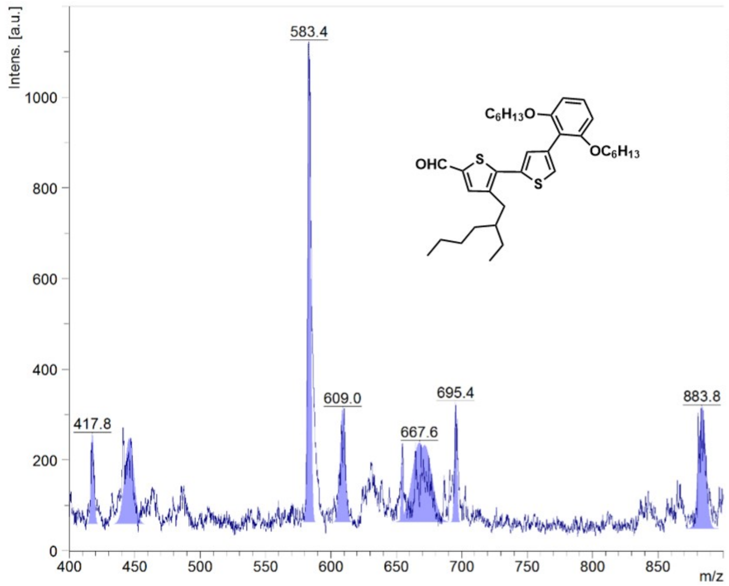


Fig. S8 ^{13}C NMR spectrum of compound 1-3 in $CDCl_3$



m/z	S/N	Res.	Intens.
285.0	4	151	269
379.2	8	170	461
417.8	4	155	257
445.9	4	54.4	248
583.4	24	199	1092
609.0	6	127	314
654.3	4	428	237
667.6	4	50.9	239
671.5	4	51.1	233
695.4	6	284	326
883.8	8	135	318
908.8	4	204	205

Fig. S9 MALDI-TOF spectrum of compound 1-3 in $CDCl_3$

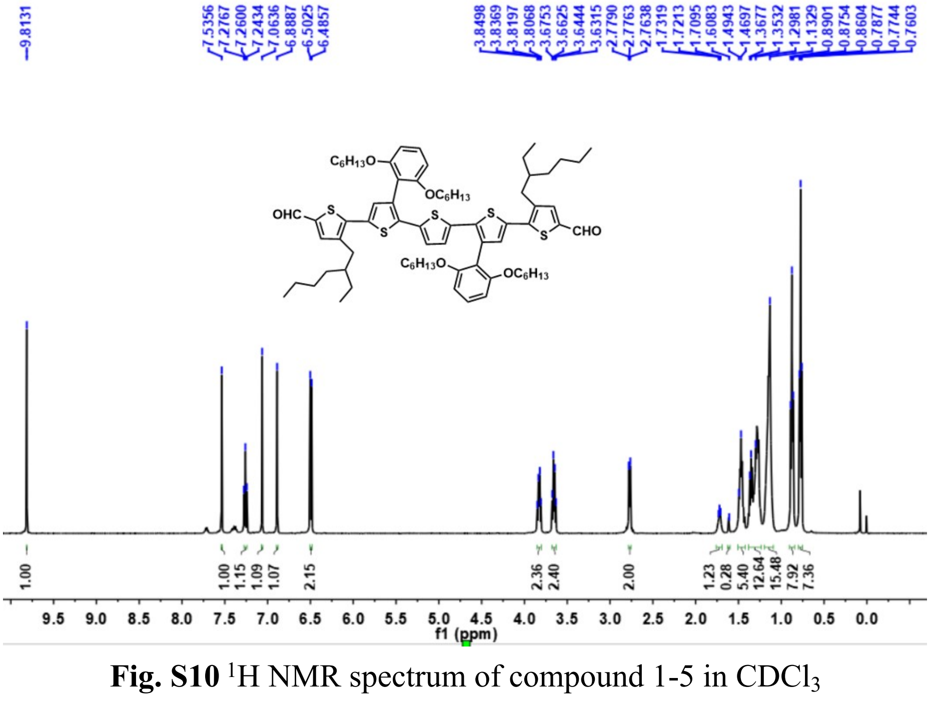


Fig. S10 ^1H NMR spectrum of compound 1-5 in $CDCl_3$

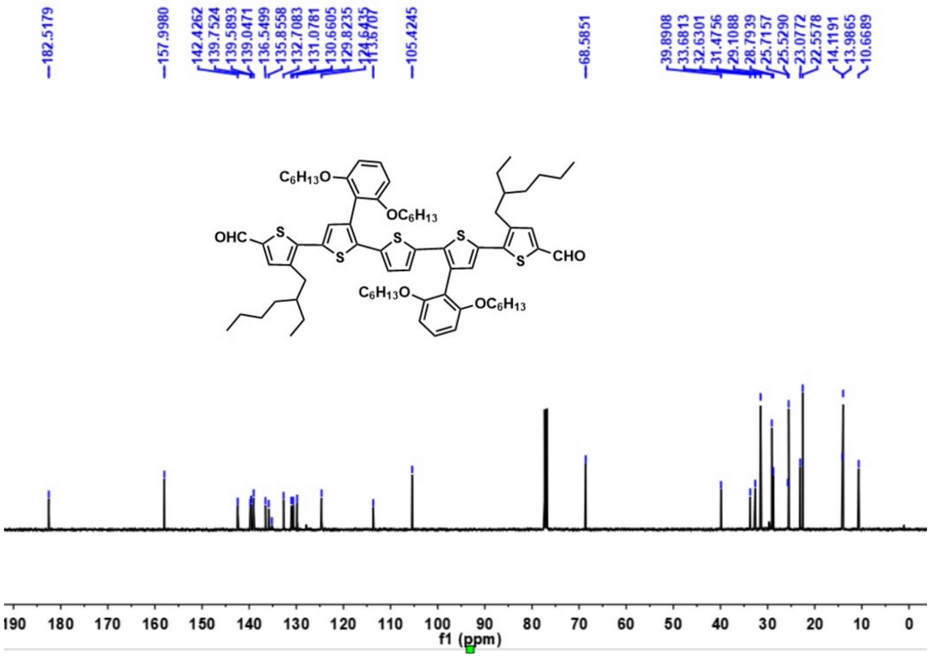
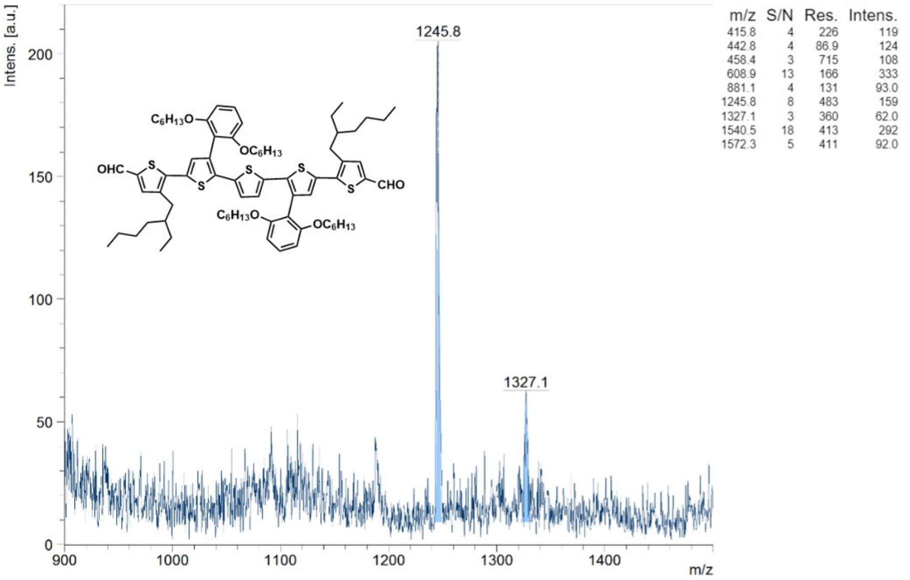


Fig. S11 ^{13}C NMR spectrum of compound 1-5 in $CDCl_3$



m/z	S/N	Res.	Intens.
415.8	4	226	119
442.8	4	86.9	124
458.4	3	715	108
608.9	13	166	333
881.1	4	131	93.0
1245.8	8	483	159
1327.1	3	360	62.0
1540.5	18	413	292
1572.3	5	411	92.0

Fig. S12 MALDI-TOF spectrum of compound 1-5

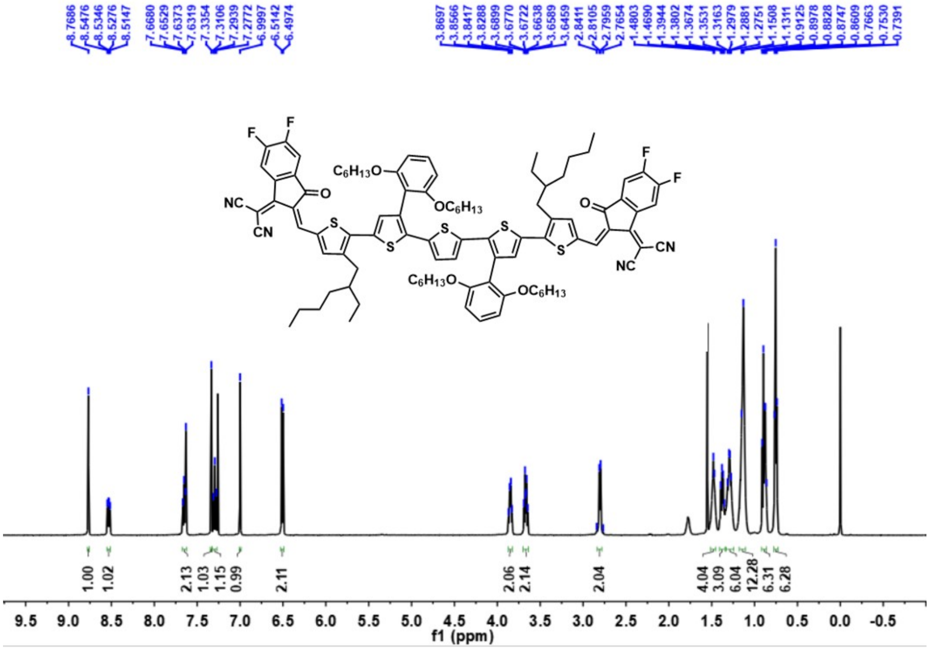


Fig. S13 ^{1}H NMR spectrum of compound 5T-2P-1 in $CDCl_3$

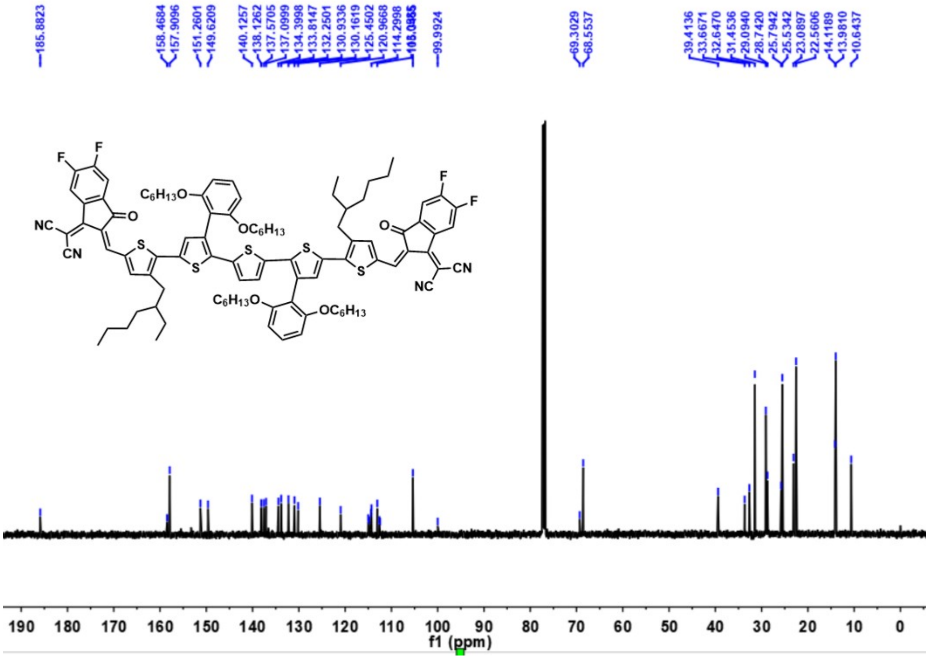
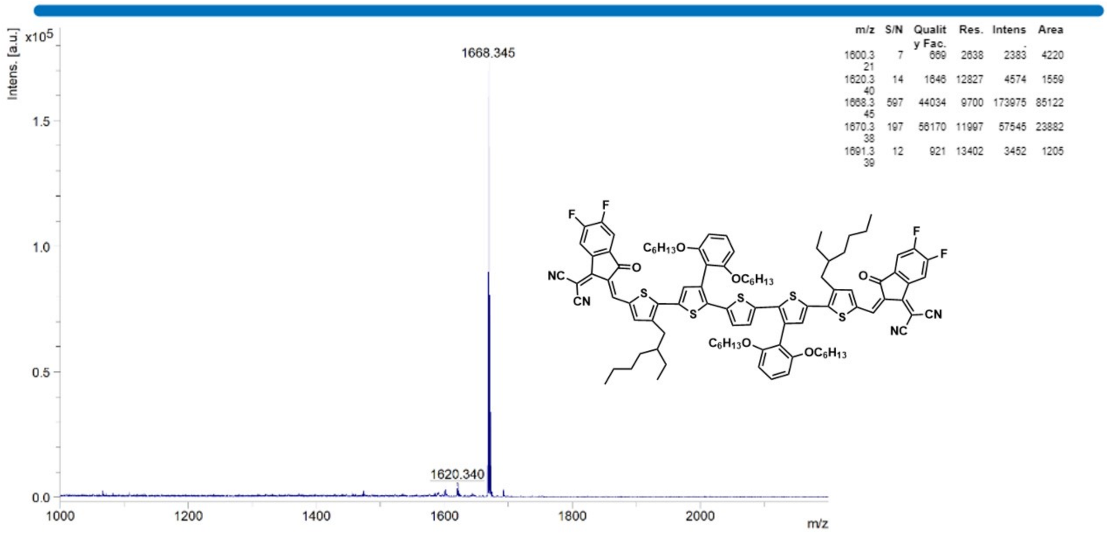


Fig. S14 ^{13}C NMR spectrum of compound 5T-2P-1 in $CDCl_3$



m/z	S/N	Quality Fac.	Res.	Intens.	Area
1600.321	7	669	2638	2383	4220
1620.340	14	1646	12827	4574	1559
1668.345	597	44034	9700	173975	85122
1670.338	197	56170	11997	57545	23882
1691.339	12	921	13402	3452	1205

Fig. S15 MALDI-TOF spectrum of compound 5T-2P-1

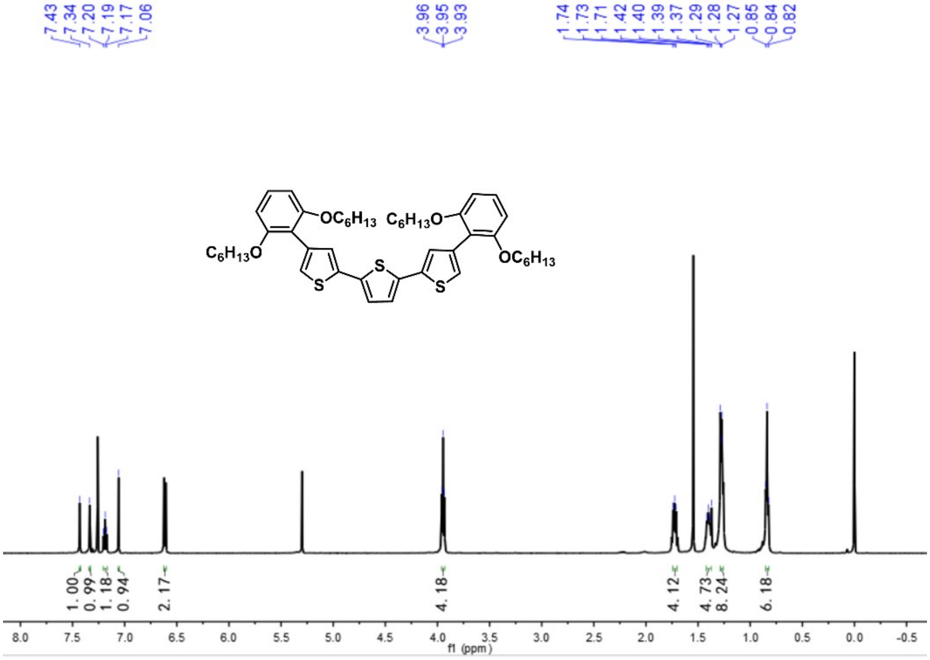


Fig. S16 ^{1}H NMR spectrum of compound 2-1 in $CDCl_3$

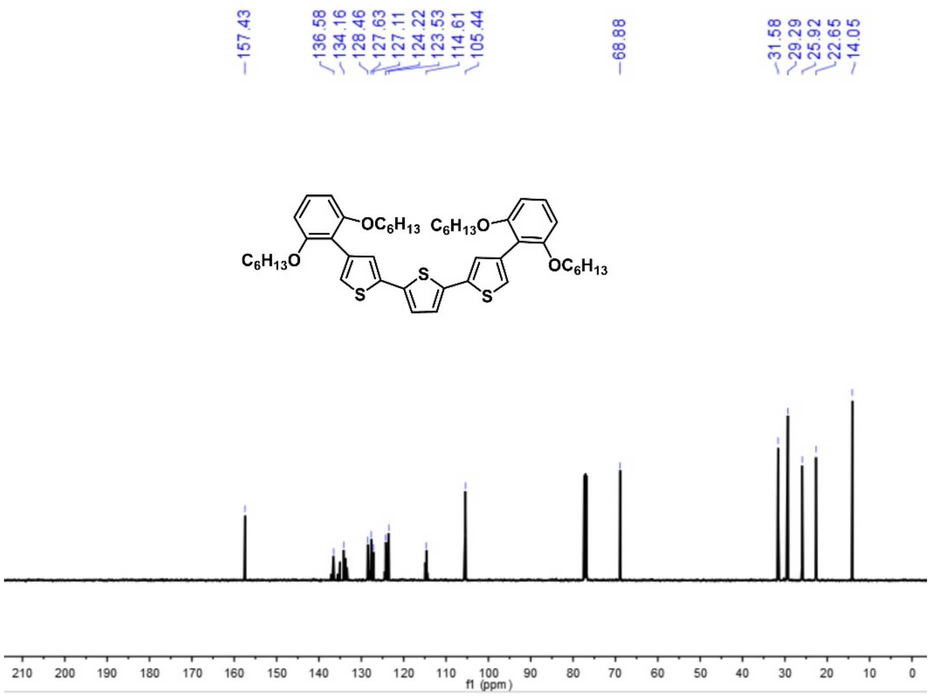


Fig. S17 ^{13}C NMR spectrum of compound 2-1 in $CDCl_3$

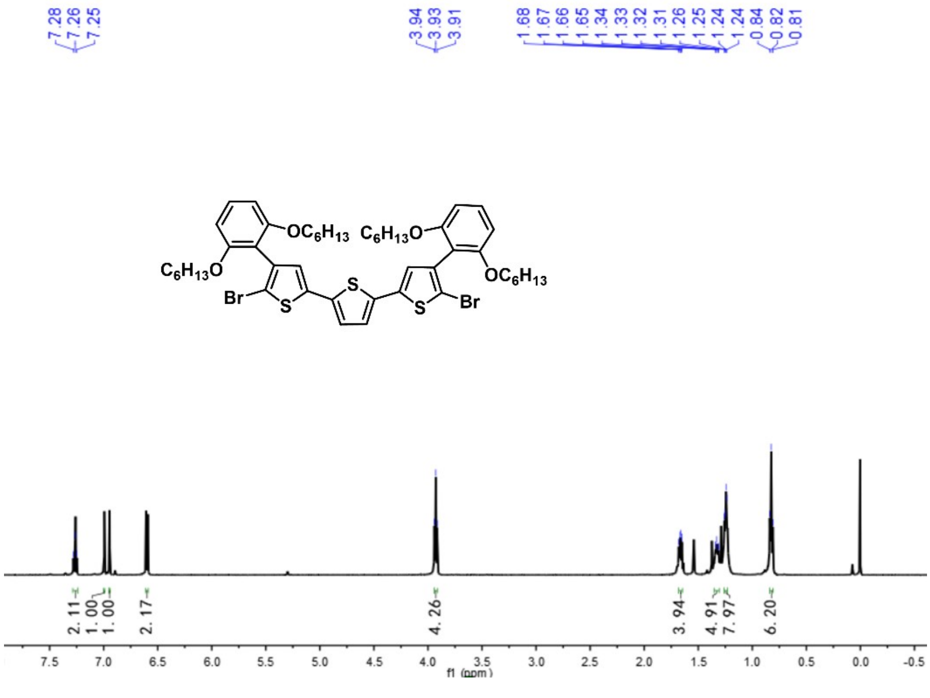


Fig. S18 ^{1}H NMR spectrum of compound 2-2 in $CDCl_3$

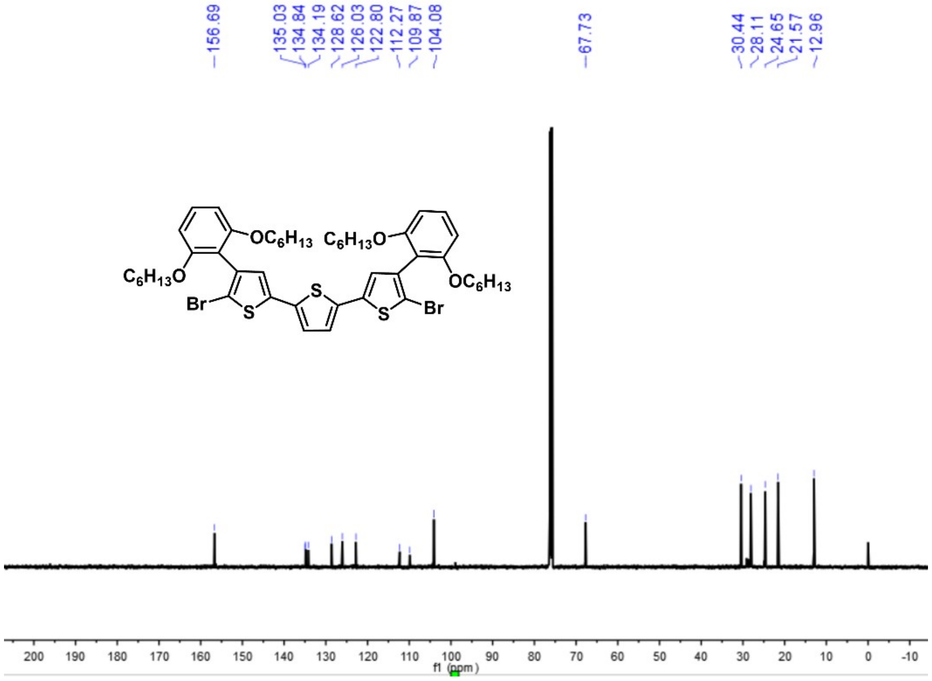


Fig. S19 ^{13}C NMR spectrum of compound 2-2 in CDCl$_3$

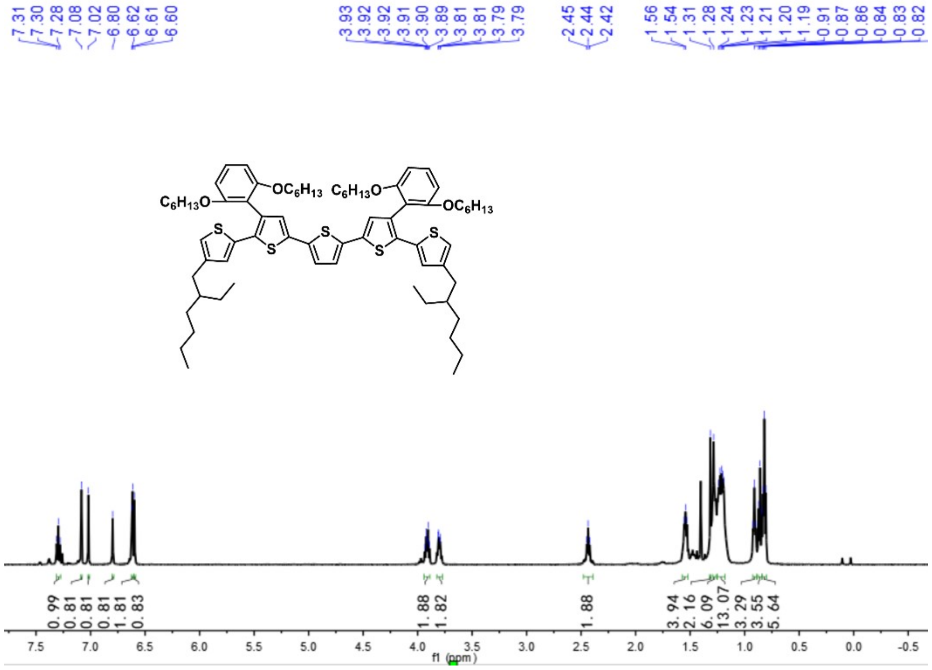


Fig. S20 ^{1}H NMR spectrum of compound 2-3 in CDCl$_3$

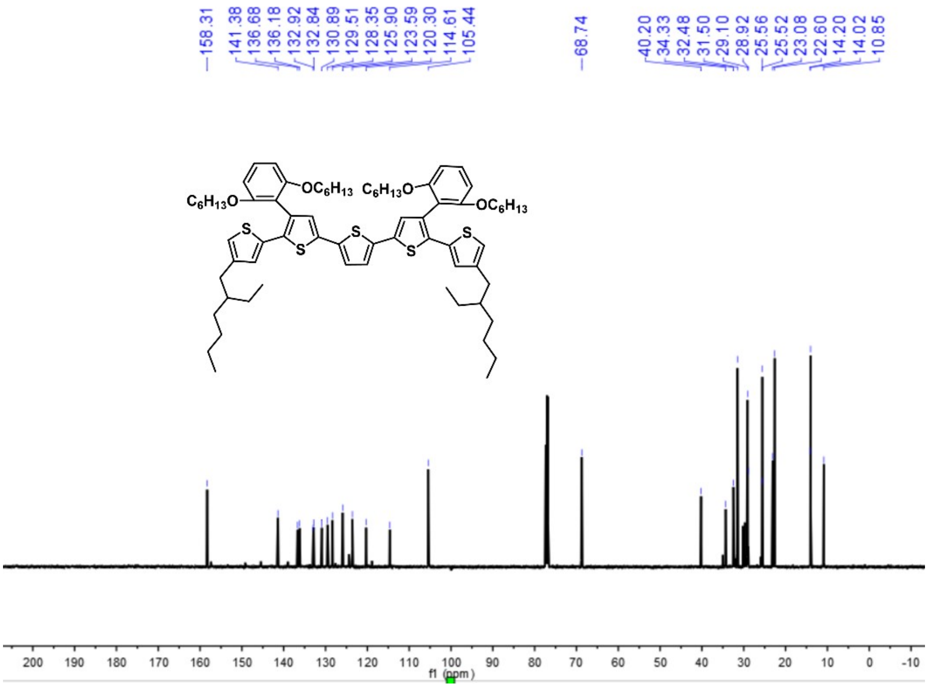


Fig. S21 ^{13}C NMR spectrum of compound 2-3 in $CDCl_3$

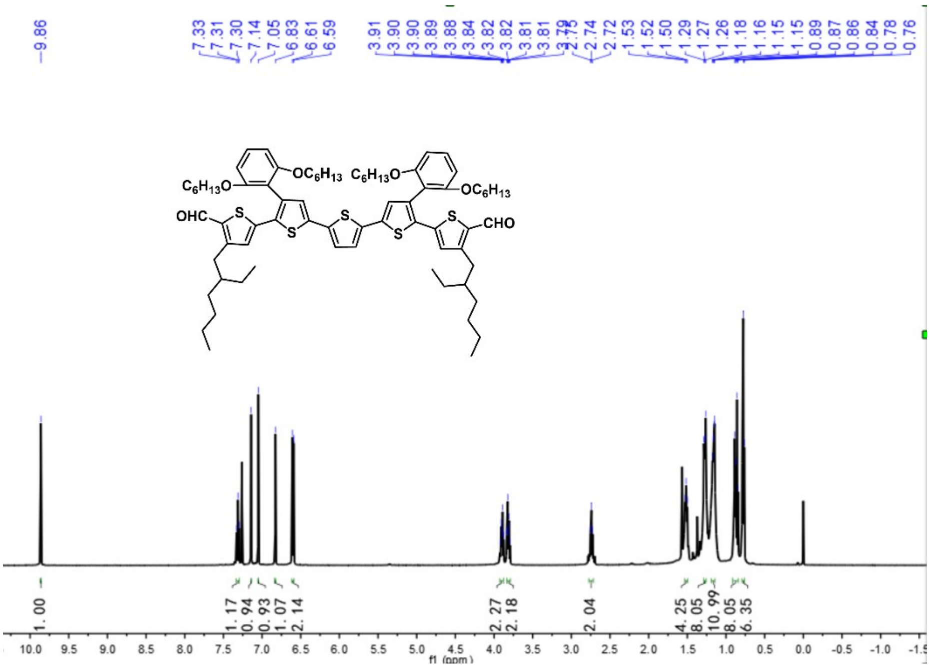


Fig. S22 ^{1}H NMR spectrum of compound 2-4 in $CDCl_3$

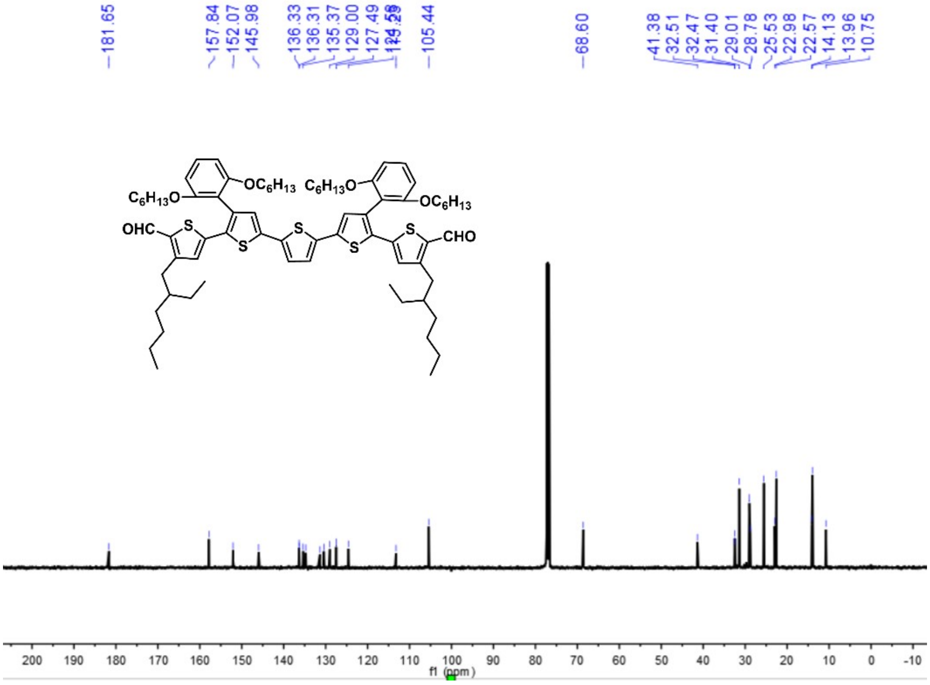


Fig. S23 ^{13}C NMR spectrum of compound 2-4 in $CDCl_3$

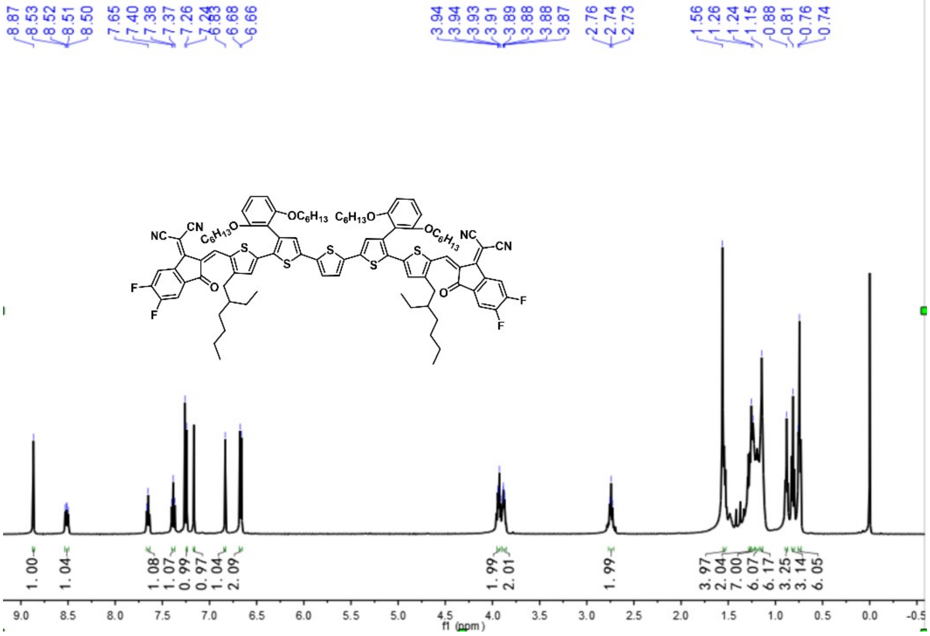


Fig. S24 ^{1}H NMR spectrum of compound 5T-2P-2 in $CDCl_3$

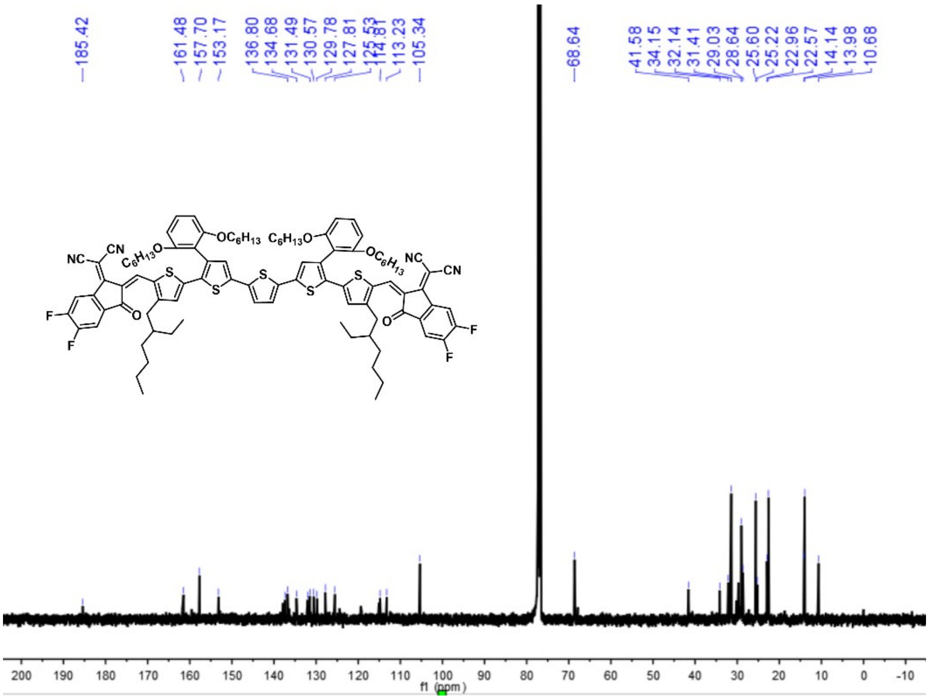
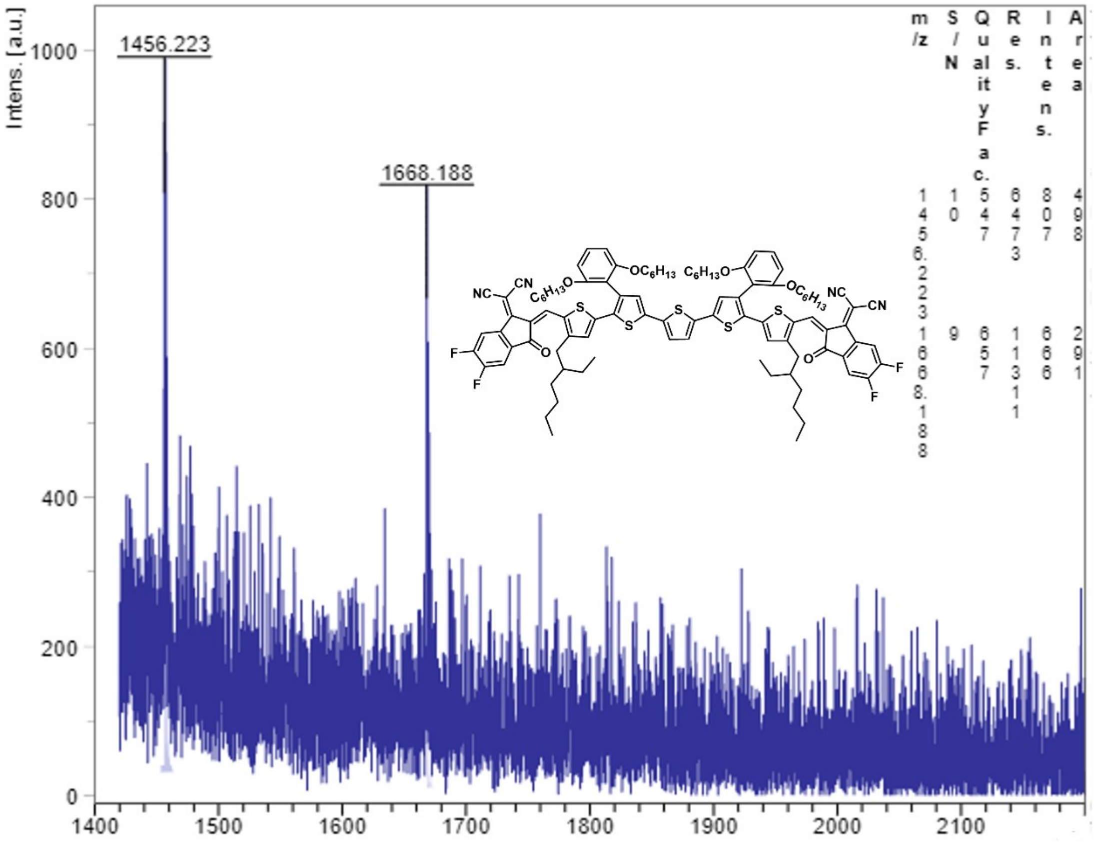


Fig. S25 ^{13}C NMR spectrum of compound 5T-2P-2 in $CDCl_3$



m/z	S/N	Quality Fac.	Res.	Intens.	Area
1456.223	10	547	6473	807	498
1668.188	9	657	11311	686	291

Fig. S26 MALDI-TOF spectrum of compound 5T-2P-2

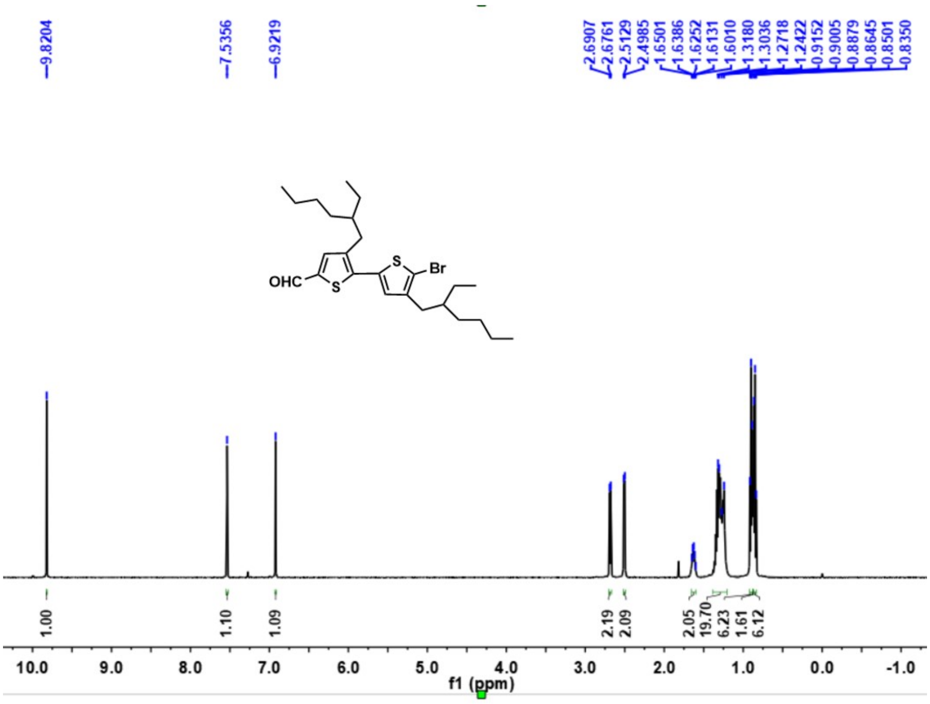


Fig. S27 ^{1}H NMR spectrum of compound 3-2 in $CDCl_3$

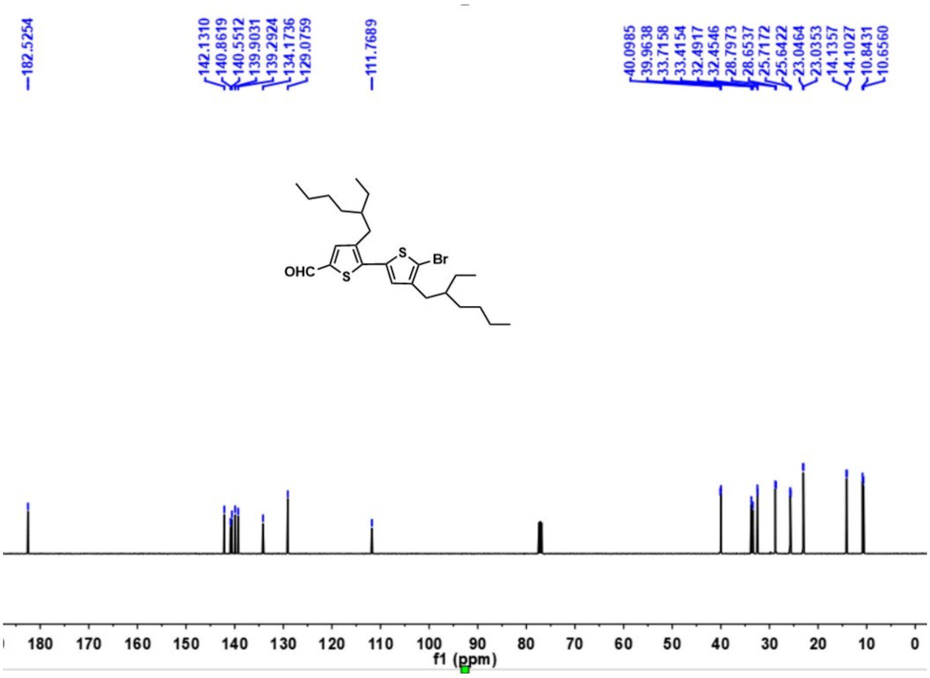
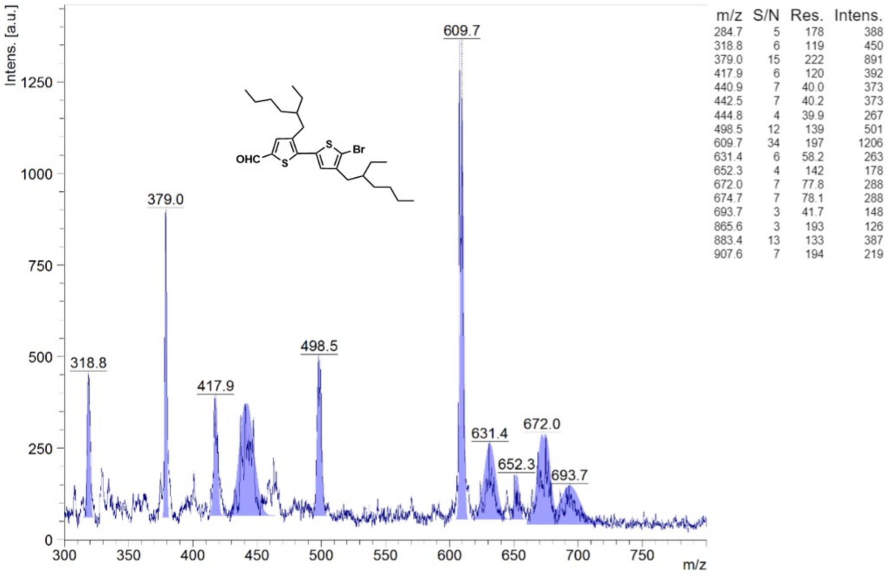


Fig. S28 ^{13}C NMR spectrum of compound 3-2 in $CDCl_3$



m/z	S/N	Res.	Intens.
284.7	5	178	388
318.8	6	119	450
379.0	15	222	891
417.9	6	120	392
440.9	7	40.0	373
442.5	7	40.2	373
444.8	4	39.9	267
498.5	12	139	501
609.7	34	197	1206
631.4	6	58.2	263
652.3	4	142	178
672.0	7	77.8	288
674.7	7	78.1	288
693.7	3	41.7	148
865.6	3	193	126
883.4	13	133	387
907.6	7	194	219

Fig. S29 MALDI-TOF spectrum of compound 3-2

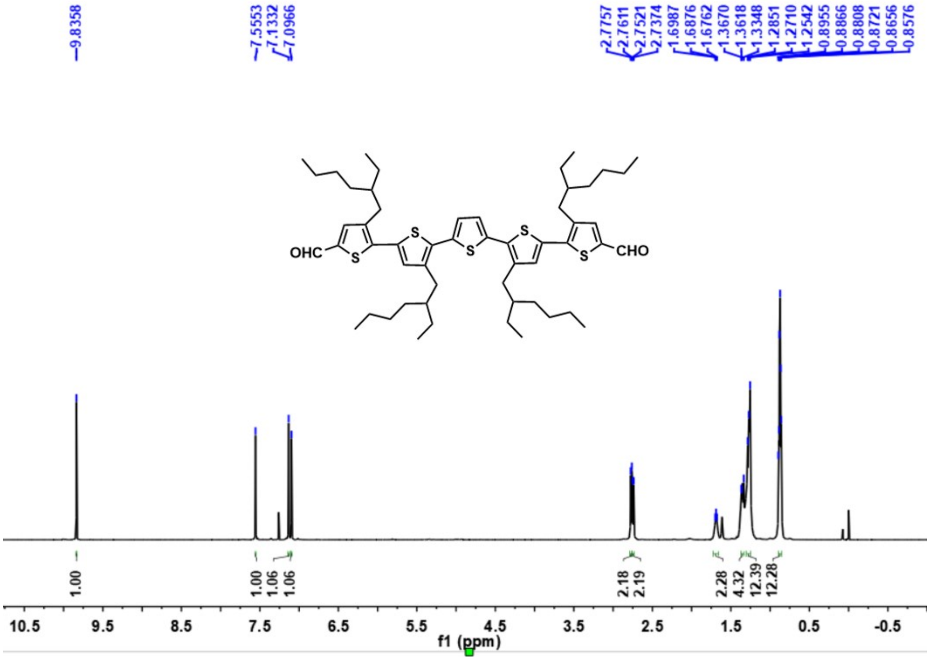


Fig. S30 ^{1}H NMR spectrum of compound 3-3 in $CDCl_3$

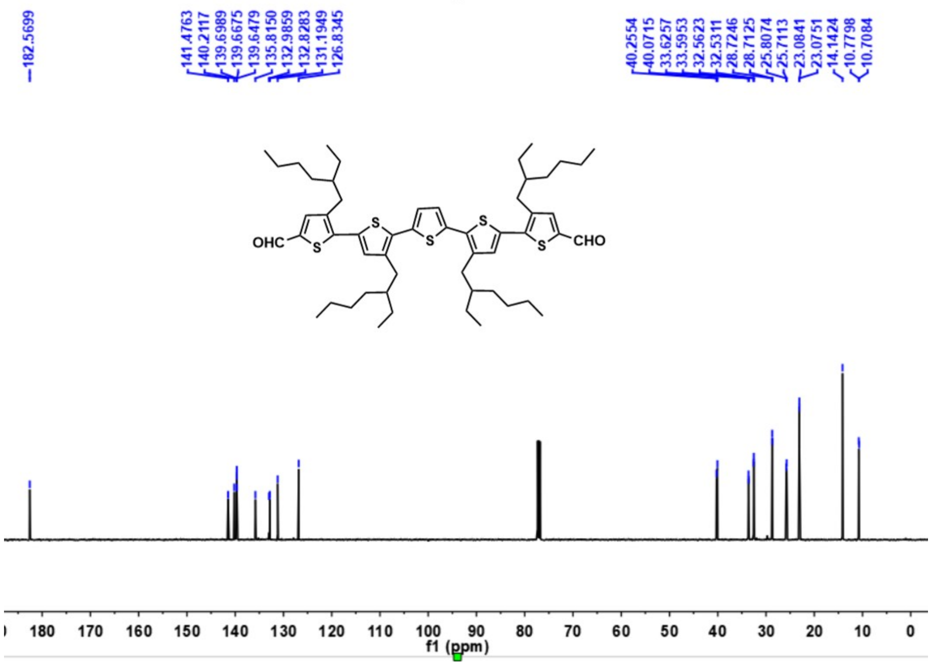
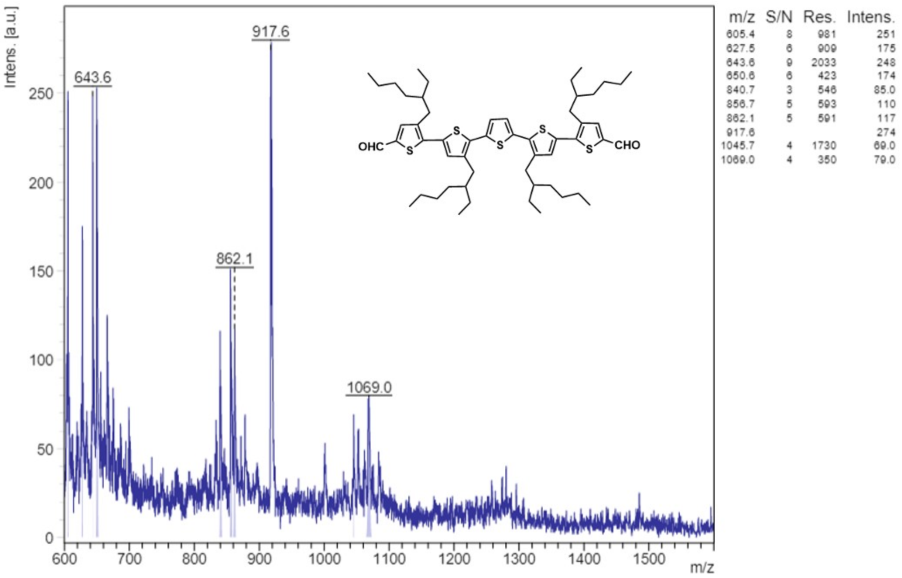


Fig. S31 ^{13}C NMR spectrum of compound 3-3 in $CDCl_3$



m/z	S/N	Res.	Intens.
605.4	8	981	251
627.5	6	909	175
643.6	9	2033	248
650.6	6	423	174
840.7	3	546	85.0
856.7	5	593	110
862.1	5	591	117
917.6			274
1045.7	4	1730	69.0
1069.0	4	350	79.0

Fig. S32 MALDI-TOF spectrum of compound 3-3

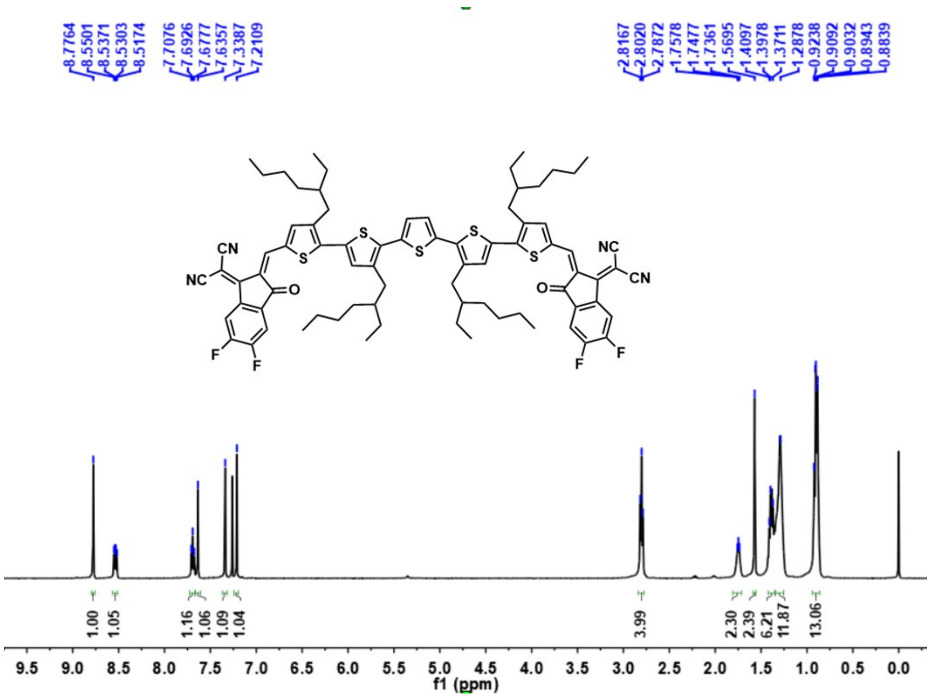


Fig. S33 ^{1}H NMR spectrum of compound 5T-C2C6 in $CDCl_3$

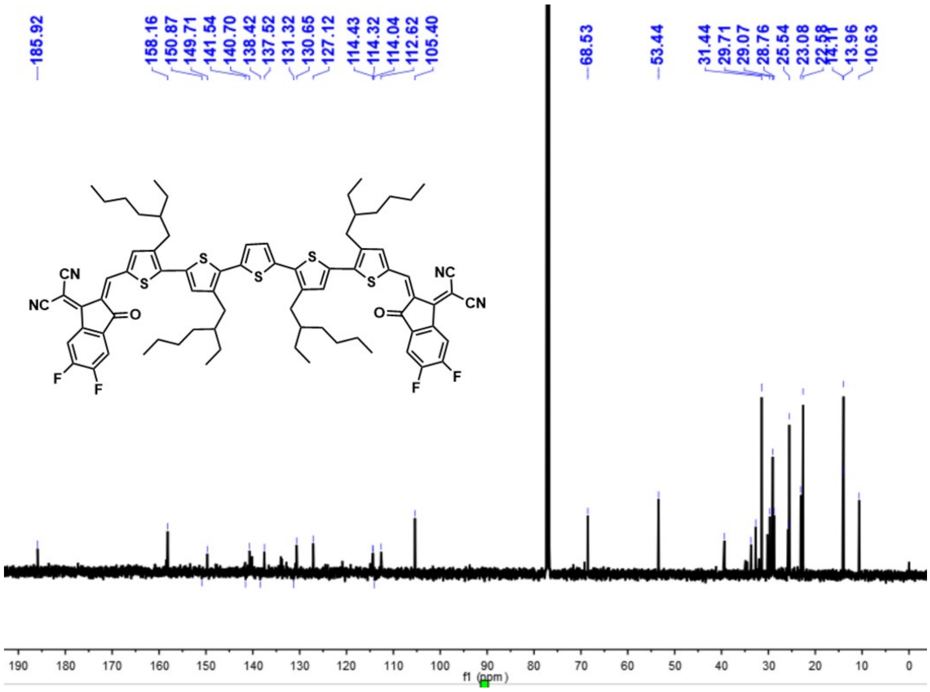
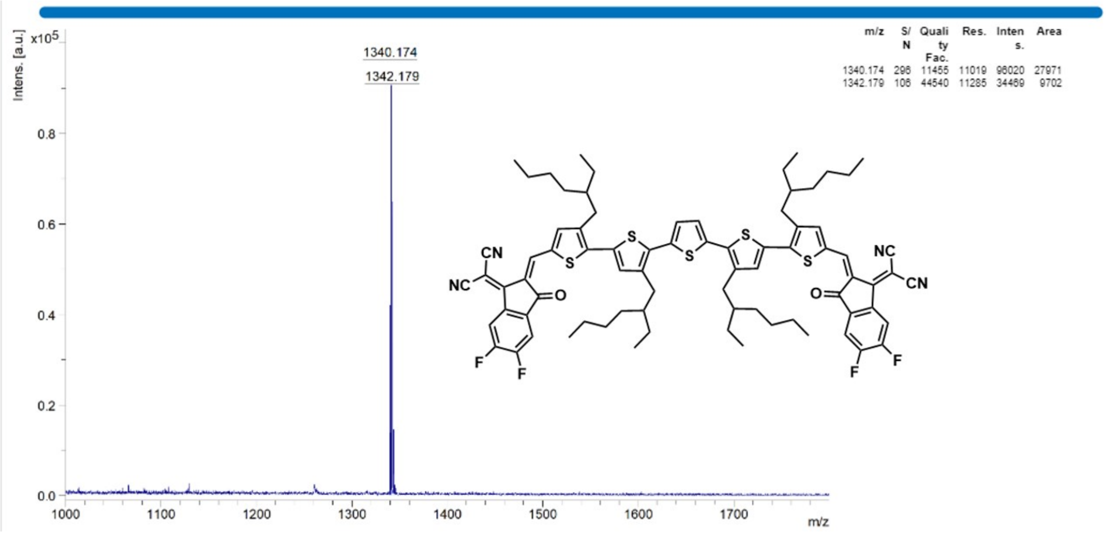


Fig. S34 ^{13}C NMR spectrum of compound 5T-C2C6 in $CDCl_3$



m/z	S/N	Quality Fac.	Res.	Intens.	Area
1340.174	296	11455	11019	96020	27971
1342.179	106	44540	11285	34469	9702

Fig. S35 MALDI-TOF spectrum of compound5T-C2C6

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[2] Lin X. Chen S X, Luping Yu. Dynamics of Photoinduced Electron Transfer in a Molecular Donor-Acceptor Quartet [J]. The Journal of Physical Chemistry B, 2006, 110: 11730-11738.