Supporting Information

Regiospecific *N*-Alkyl substitution Tuning the Molecular Packing of High-Performance Non-Fullerene Acceptors

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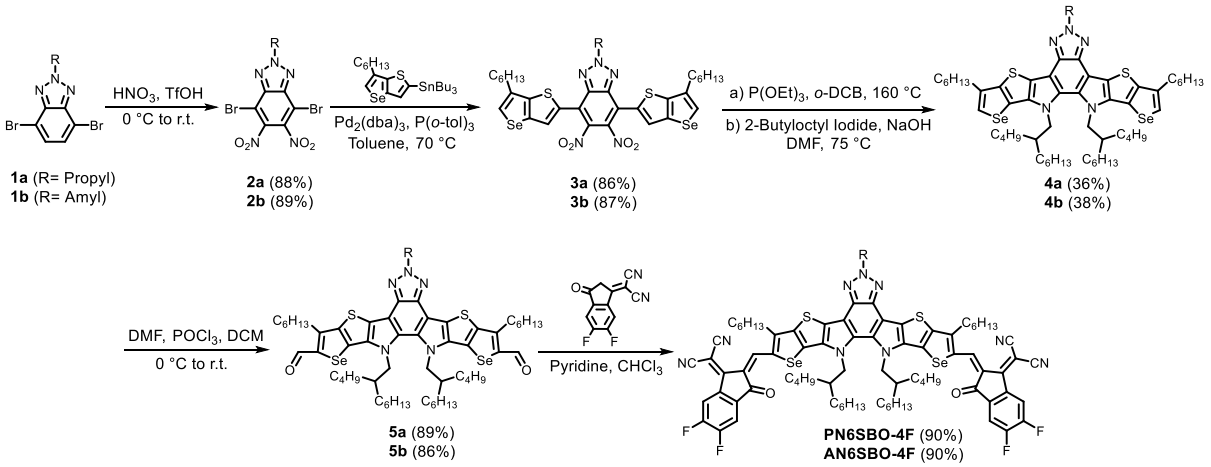
Materials: All chemicals and reagents were purchased from commercial resources and were used without further purification. Tributyl(6-hexylselenopheno[3,2-*b*]thiophen-2-yl)stannane and 2-(2-ethylhexyl)-4,7-bis(6-hexylselenopheno[3,2-*b*]thiophen-2-yl)-5,6-dinitro-2*H*-benzo[*d*][1,2,3]triazole were synthesized according to the route reported in our previous work.[1-3]

Measurements: The ^{1}H and ^{13}C NMR spectra were collected with a Bruker 300MHz AVANCE III HD and Bruker 400MHz AVANCE III spectrometer in $CDCl_3$. High-resolution mass spectroscopy was measured by a Q Exactive Focus Hybrid Quadrupole-Orbitrap Mass Spectrometer (QE Orbitrap MS, Thermo Fisher Scientific). UV-Vis absorption spectra were recorded by Ultra-Violet Visible Scanning Spectrophotometer (Shimadzu 1700). Cyclic voltammetry (CV) was probed on an Electrochemical Analyzer System (CH 1660C) in an anhydrous acetonitrile solution of tertra-*n*-butylammonium hexafluoro-phosphate (Bu4NPF6) (0.1 M) with a scan rate of 50 mV s^{-1}. A conventional three-electrode cell was used with a glassy carbon working electrode, a platinum wire counter-electrode, and an Ag/AgCl reference electrode. Besides, $FeCp_2/FeCp_2^+$ was used as an internal reference. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out at PLS-II 6A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength λ = 1.10994 Å) using a double crystal monochromator and focused both horizontally and vertically (450 (H) × 60 (V) μm2 in FWHM @ sample position) using K-B type mirrors. The GIWAXS sample stage was equipped with a 7-axis motorized stage for the fine alignment of the sample, and the incidence angle of X-ray beam was set to be 0.11º ~ 0.13º for the neat and blend films. GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165) and X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (Monoclinic, P21, a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å, β = 102.938°) and the sample-to-detector distance was ~231 mm. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident

at a grazing angle of 0.12°~0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. The crystal coherence length (CCL) was defined as CCL = 0.9 × (2π/FWHM) (Å), where FWHM is the full width at half maximum of the corresponding diffraction peak. Atomic force microscopy (AFM) images were investigated by an Environment Control AFM (Hitachi 5300E).

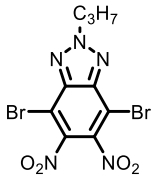
Materials Synthesis



Scheme S1 Synthesis routes of **PN6SBO-4F** and **AN6SBO-4F**.

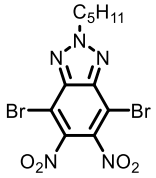
General procedure for the synthesis of 2a and 2b

Trifluoromethanesulfonic acid (11.0 mL, 125 mmol) was added into in a flask (50 mL) and 65% HNO_3 (4.50 mL, 100 mmol) was added dropwise to make a solution. Then the mixture was stirred at 0 °C for 0.5 h. Compound 1a or 1b (5.00 mmol) was added slowly to the solution and the reaction mixture was stirred at room temperature overnight. Then the mixture was poured into ice water (50 mL), the organic layer was extracted by dichloromethane (3×50 mL) and dried over with $MgSO_4$. The solvent was evaporated under reduced pressure to get the crude product, which was further purified by silica gel column chromatography with hexane/dichloromethane (2:1) as the eluent to afford pale-yellow solids **2a** or **2b**.



2a

Synthesis of 4,7-dibromo-5,6-dinitro-2-propyl-2*H*-benzo[*d*][1,2,3]triazole (2a): Yield: 1.80 g, 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.84 (t, *J* = 7.2 Hz, 2H), 2.29-2.17 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.93, 107.27, 99.96, 77.46, 77.03, 76.61, 60.21, 23.54, 10.98.

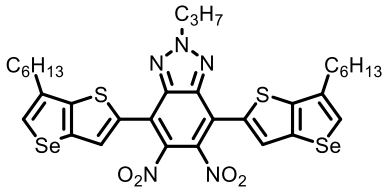


2b

Synthesis of 4,7-dibromo-5,6-dinitro-2-pentyl-2*H*-benzo[d][1,2,3]triazole (2b): Yield: 1.94 g, 89%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.84 (t, *J* = 7.2 Hz, 2H), 2.24-2.14 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.92, 136.62, 107.24, 77.45, 77.03, 76.61, 58.74, 29.70, 28.46, 21.99, 13.78.

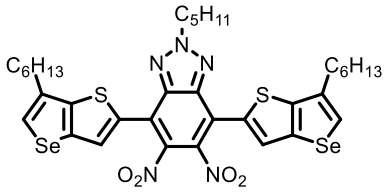
General procedure for the synthesis of 3a and 3b

A mixture of compound **2a** or **2b** (3.00 mmol), tributyl(6-hexylselenopheno[3,2-*b*]thiophen-2-yl)stannane (3.53 g, 6.30 mmol), $Pd_2(dba)_3$ (31.1 mg, 0.03 mmol), P(*o*-tol)$_3$ (73.0 mg, 0.24 mmol) were added and dissolved in toluene (20 mL) in a flask (100 mL). The reaction mixture was stirred overnight under the protection of nitrogen at 70 °C. After the mixture was allowed to cool to the room temperature, the solution was filtered, solvent was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography with hexane/dichloromethane (5:1) as the eluent to afford orange solids **3a** or **3b**.



3a

Synthesis of 4,7-bis(6-hexylselenopheno[3,2-b]thiophen-2-yl)-5,6-dinitro-2-propyl-2*H*-benzo[*d*][1,2,3]triazole (3a): Yield: 2.04 g, 86%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 1.2 Hz, 2H), 7.68 (s, 2H), 4.82 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 4H), 2.25-2.18 (m, 2H), 1.85-1.74 (m, 4H), 1.47-1.31 (m, 12H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.74, 141.63, 139.63, 137.71, 136.99, 129.64, 127.25, 126.59, 119.41, 77.45, 77.03, 76.61, 59.56, 31.56, 31.35, 29.01, 28.29, 23.52, 22.57, 14.09, 11.03.



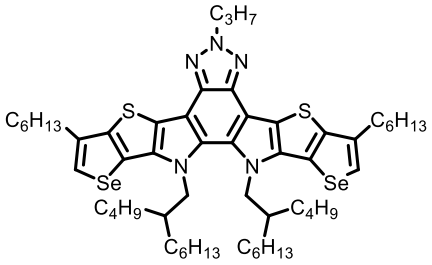
3b

Synthesis of 4,7-bis(6-hexylselenopheno[3,2-b]thiophen-2-yl)-5,6-dinitro-2-pentyl-2*H*-benzo[*d*][1,2,3]triazole (3b): Yield: 2.13 g, 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 1.4 Hz, 2H), 7.68 (s, 2H), 4.85 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 4H), 2.21-2.14 (m, 2H), 1.83-1.75 (m, 4H), 1.45-1.33 (m, 16H), 0.95-0.90 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.78, 141.66, 139.70, 137.74, 137.04, 129.70, 127.25, 126.57, 119.44, 77.35, 77.03, 76.71, 58.06, 31.59, 31.41, 29.67, 29.06, 28.55, 28.35, 22.60, 22.04, 14.10, 13.88.

General procedure for the synthesis of 4a and 4b

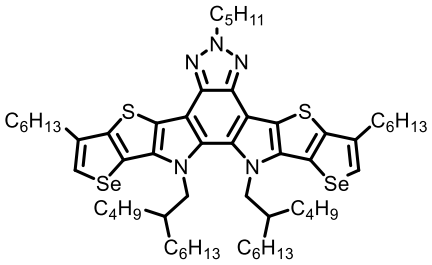
To a dry flask (100 mL) was added compound **3a** or **3b** (2.00 mmol), distilled $P(OEt)_3$ (7.08 mL, 40.0 mmol), and 1,2-dicholorobenzene (15 mL) under the argon atmosphere. The reaction mixture was refluxed overnight and cooled to room temperature. The solvent was evaporated under reduced pressure and resulting dark red oils. Then the oils were dissolved in anhydrous DMF (15 mL). 2-butyloctyl iodide (2.37 g, 8.00 mmol) and sodium hydroxide (640 mg, 16.0 mmol) were added to the solution under the protection of argon. The reaction mixtures were

stirred overnight at 70 °C and cooled to room temperature. The organic layer was extracted by diethyl ether (3×50 mL) and dried over with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude products were further purified by silica gel column chromatography with hexane/dichloromethane (10:1) as the eluent to afford reddish orange oils of **4a** or **4b**.



4a

Synthesis of 12,13-bis(2-butyloctyl)-3,9-dihexyl-6-propyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole (4a) : Yield: 765 mg, 36%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, 2H), 4.79 (t, *J* = 7.3 Hz, 2H), 4.53 (d, *J* = 7.5 Hz, 4H), 2.83-2.75 (m, 4H), 2.27-2.22 (m, 2H), 2.01 (s, 2H), 1.87-1.81 (m, 4H), 1.45 (s, 4H), 1.35 (d, *J* = 3.6 Hz, 8H), 1.08-0.89 (m, 38H), 0.68-0.56 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.69, 140.31, 138.65, 136.02, 131.20, 122.35, 121.18, 120.80, 109.06, 77.35, 77.03, 76.71, 57.58, 54.63, 53.42, 38.62, 31.69, 31.56, 31.17, 30.40, 30.24, 30.08, 29.35, 29.32, 29.23, 28.77, 28.05, 27.81, 25.27, 25.03, 23.86, 22.76, 22.70, 22.65, 22.46, 22.43, 14.12, 13.94, 13.75, 13.70, 11.30. HRMS (ESI): calcd for $C_{57}H_{85}N_5S_2Se_2$ (M+), 1063.4577; found, 1063.4556.

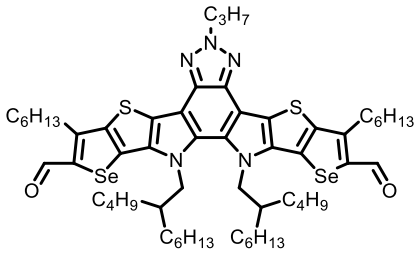


4b

Synthesis of 12,13-bis(2-butyloctyl)-3,9-dihexyl-6-pentyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole (4b): Yield: 829 mg, 38%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 2H), 4.86-4.78 (m, 2H), 4.54 (d, *J* = 7.6 Hz, 4H), 2.79 (t, *J* = 7.7 Hz, 4H), 2.28-2.18 (m, 2H), 2.08-1.97 (m, 2H), 1.90-1.81 (m, 4H), 1.48-1.32 (m, 18H), 1.00-0.75 (m, 36H), 0.90-0.56 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.71, 140.32, 138.67, 136.02, 131.21, 122.36, 121.17, 120.82, 109.08, 77.35, 77.03, 76.71, 56.11, 54.64, 38.63, 31.70, 31.57, 31.18, 30.41, 30.25, 30.15, 29.36, 29.33, 29.24, 28.91, 28.78, 22.76, 22.71, 22.66, 22.47, 22.45, 22.31, 14.13, 13.97, 13.95, 13.76, 13.71. HRMS (ESI): calcd for $C_{59}H_{89}N_5S_2Se_2$ (M+), 1091.4890; found, 1091.4890.

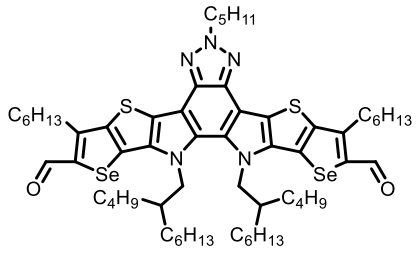
General procedure for the synthesis of 5a and 5b

A mixture of anhydrous DMF (619 μL, 8.00 mmol) and anhydrous dichloromethane (5 mL) were added into a flask (50 mL) under the protection of argon. $POCl_3$ (559 μL, 6.00 mmol) was added dropwise to the solution under the ice bath and the reaction mixture was stirred at 0 °C for 0.5 h. Then the mixture was added slowly to the solution of compound **4a** or **4b** (0.50 mmol) and anhydrous dichloromethane (5 mL) in another flask (100 mL). The reaction mixtures were stirred overnight at room temperature, quenched by adding a saturated aqueous solution of sodium carbonate to the mixtures. The organic layer was extracted by dichloromethane (3×50 mL) and dried over with $MgSO_4$. The solvent was removed under the reduced pressure and the crude products were then purified by silica gel column chromatography with hexane/dichloromethane (2:1) as the eluent to afford orange solids of **5a** or **5b**.



5a

Synthesis of 12,13-bis(2-butyloctyl)-3,9-dihexyl-6-propyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-dicarbaldehyde (5a) : Yield: 498 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 2H), 4.80 (t, *J* = 7.3 Hz, 2H), 4.56 (d, *J* = 7.7 Hz, 4H), 3.17 (t, *J* = 7.7 Hz, 4H), 2.28-2.23 (m, 2H), 1.96-1.90 (m, 6H), 1.51-1.45 (m, 4H), 1.35 (d, *J* = 3.5 Hz, 8H), 1.09-0.89 (m, 38H), 0.68-0.53 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.15, 149.06, 143.87, 140.50, 140.46, 135.84, 132.60, 132.58, 128.67, 125.46, 125.41, 110.01, 77.35, 77.03, 76.71, 57.64, 54.69, 53.36, 38.79, 31.44, 31.39, 30.55, 30.27, 30.08, 29.84, 29.46, 29.23, 29.19, 29.16, 27.91, 27.64, 25.07, 24.75, 23.70, 22.63, 22.56, 22.43, 22.33, 22.30, 13.93, 13.82, 13.80, 13.60, 13.55, 11.14. HRMS (ESI): calcd for $C_{59}H_{85}N_5O_2S_2Se_2$ (M+), 1119.4475; found, 1119.4454.



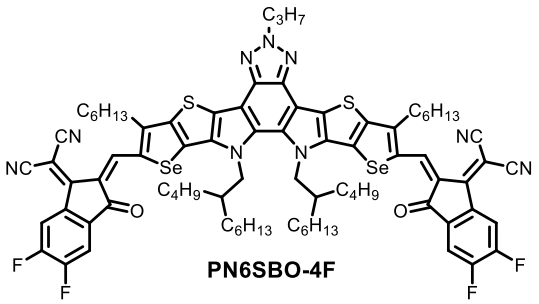
5b

Synthesis of 12,13-bis(2-butyloctyl)-3,9-dihexyl-6-pentyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-dicarbaldehyde (5b): Yield: 493 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 2H), 4.82 (t, *J* = 7.5 Hz, 2H), 4.56 (d, *J* = 7.7 Hz, 4H), 3.17 (t, *J* = 7.7 Hz, 4H), 2.26-2.18 (m, 2H), 1.96-1.90 (m, 6H), 1.50-1.42 (m, 8H), 1.36-1.33 (m, 10H), 0.94-0.89 (m, 36H), 0.68-0.54 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.29, 149.21, 143.96,

140.57, 140.49, 135.90, 132.68, 128.79, 125.57, 125.52, 110.09, 77.35, 77.03, 76.71, 56.25, 54.76, 53.40, 38.86, 31.51, 31.46, 30.63, 30.33, 30.14, 30.04, 29.91, 29.55, 29.32, 29.26, 29.23, 28.79, 27.97, 27.71, 24.84, 22.69, 22.63, 22.50, 22.40, 22.37, 22.20, 14.00, 13.89, 13.67, 13.62. HRMS (ESI): calcd for $C_{61}H_{89}N_5O_2S_2Se_2$ (M+), 1147.4788; found, 1147.4771.

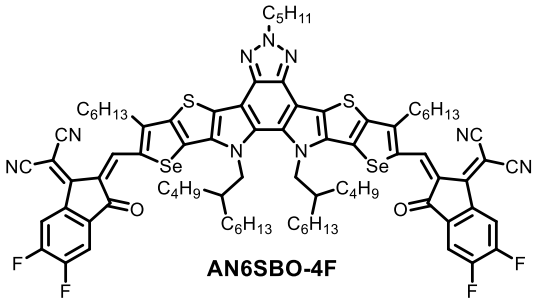
General procedure for the synthesis of acceptors

A mixture of compound **5a, 5b,** or **5c** (0.15 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene) malononitrile (138 mg, 0.60 mmol) were added into in a flask (100 mL) and were dissolved in chloroform (15 mL). Pyridine (200 μL) was added to the mixture and the reaction was stirred overnight at room temperature. The solvent was removed under the reduced pressure and the crude product were purified by silica gel column chromatography with hexane/chloroform (1:1) as the eluent to afford acceptor solids in black.

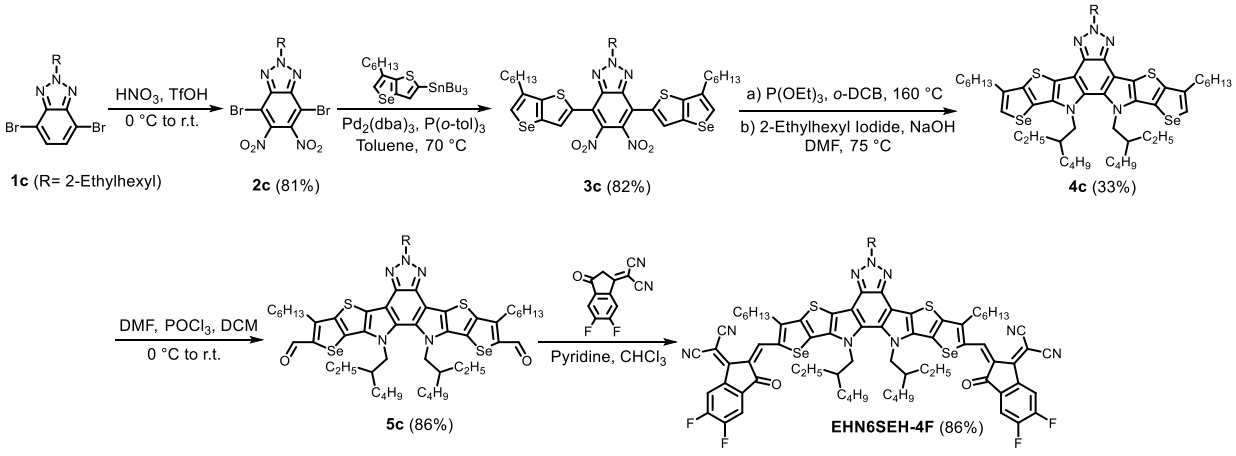


PN6SBO-4F

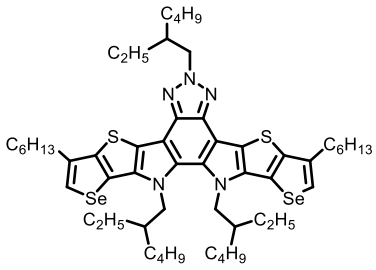
Synthesis of 2,2'-((2*Z*,2'*Z*)-((12,13-bis(2-butyloctyl)-3,9-dihexyl-6-propyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (PN6SBO-4F): Yield: 208 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 2H), 8.56 (dd, *J* = 10.0, 6.5 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 2H), 4.81 (t, *J* = 7.3 Hz, 2H), 4.67 (d, *J* = 7.6 Hz, 4H), 3.30-3.19 (m, 4H), 2.26 (dd, *J* = 14.7, 7.3 Hz, 2H), 2.07 (d, *J* = 6.4 Hz, 2H), 1.91-1.83 (m, 4H), 1.56-1.49 (m, 4H), 1.39-1.30 (m, 8H), 1.11-0.89 (dt, *J* = 14.0, 7.2 Hz, 38H), 0.72- 0.57 (m, 15H). HRMS (ESI): calcd for $C_{83}H_{89}F_4N_9O_2S_2Se_2$ (M+), 1543.4847; found, 1543.4846.



Synthesis of 2,2'-((2*Z*,2'*Z*)-((12,13-bis(2-butyloctyl)-3,9-dihexyl-6-pentyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile AN6SBO-4F): Yield: 212 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 2H), 8.56 (dd, *J* = 10.0, 6.4 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 2H), 4.83 (t, *J* = 7.5 Hz, 2H), 4.66 (d, *J* = 7.6 Hz, 4H), 3.30-3.19 (m, 4H), 2.27-2.19 (m, 2H), 2.08 (s, 2H), 1.91-1.82 (m, 4H), 1.56-1.50 (m, 4H), 1.48-1.42 (m, 4H), 1.40-1.31 (m, 8H), 1.15- 0.82 (m, 38H), 0.73-0.57 (m, 15H). HRMS (ESI): calcd for $C_{85}H_{93}F_4N_9O_2S_2Se_2$ (M+), 1571.5160; found, 1571.5153.



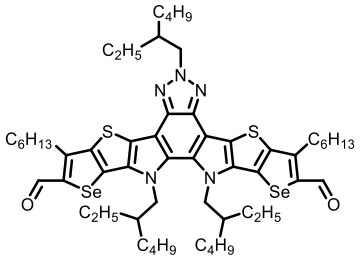
Scheme S2 Synthesis route of **EHN6SEH-4F**.



4c

Synthesis of 6,12,13-tris(2-ethylhexyl)-3,9-dihexyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole (4c)

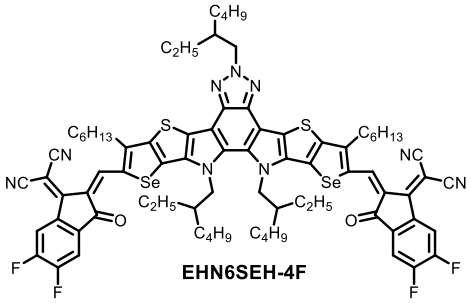
To a dry flask (100 mL) was added compound **3c** (1.72 g, 2.00 mmol), distilled $P(OEt)_3$ (7.08 mL, 40.0 mmol), and 1,2-dicholorobenzene (15 mL) under the argon atmosphere. The reaction mixture was refluxed overnight and cooled to room temperature. The solvent was evaporated under reduced pressure to obtain a dark red oil. Then the oil was dissolved in anhydrous DMF (15 mL). 2-ethylhexyl iodide (1.92 g, 8.00 mmol) and sodium hydroxide (640 mg, 16.0 mmol) were added to the solution under the protection of argon. The reaction mixture was stirred overnight at 70 °C and cooled to room temperature. The organic layer was extracted by diethyl ether (3×50 mL) and dried over with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was further purified by silica gel column chromatography with hexane/dichloromethane (10:1) as the eluent to afford a reddish orange oil (694 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (s, 2H), 4.75 (d, J = 7.2 Hz, 2H), 4.56 (d, J = 7.7 Hz, 4H), 2.86-2.75 (m, 4H), 2.46-2.34 (m, 1H), 2.08-1.95 (m, 2H), 1.92-1.82 (m, 4H), 1.48-1.31 (m, 20H), 1.04-0.79 (m, 28H), 0.66-0.51 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.65, 140.28, 138.66, 135.93, 130.96, 122.29, 121.16, 120.59, 109.05, 77.45, 77.03, 76.61, 59.44, 54.54, 40.26, 39.86, 31.67, 31.14, 30.41, 29.54, 29.22, 28.74, 28.38, 27.61, 23.92, 23.13, 22.95, 22.65, 14.12, 14.02, 13.65, 10.52, 10.10. HRMS (ESI): calcd for $C_{54}H_{79}N_5S_2Se_2$ (M+), 1021.4107; found, 1021.4091.



5c

Synthesis of 6,12,13-tris(2-ethylhexyl)-3,9-dihexyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-dicarbaldehyde (5c)

A mixture of anhydrous DMF (619 μL, 8.00 mmol) and anhydrous dichloromethane (5 mL) were added into a flask (50 mL) under the protection of argon. $POCl_3$ (559 μL, 6.00 mmol) was added dropwise to the solution under the ice bath and the reaction was stirred at 0 °C for 0.5 h. Then the mixture was added slowly to the solution of compound **4c** (510 mg, 0.50 mmol) and anhydrous dichloromethane (5 mL) in another flask (100 mL). The reaction mixture was stirred overnight at room temperature, quenched by adding a saturated aqueous solution of sodium carbonate. The organic layer was extracted by dichloromethane (3×50 mL) and dried over with $MgSO_4$. The solvent was removed under the reduced pressure and the crude product was then purified by silica gel column chromatography with hexane/dichloromethane (2:1) as the eluent to afford an orange solid (463 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 2H), 4.73 (d, *J* = 7.2 Hz, 2H), 4.58 (d, *J* = 7.7 Hz, 4H), 3.17 (t, *J* = 7.7 Hz, 4H), 2.41-2.31 (m, 1H), 1.97-1.89 (m, 6H), 1.48-1.24 (m, 22H), 1.03-0.82 (m, 26H), 0.66-0.59 (m, 6H), 0.56-0.50 (m, 6H).^{13}C NMR (75 MHz, $CDCl_3$): δ 182.27, 149.22, 143.95, 140.57, 140.47, 135.86, 132.48, 128.75, 125.36, 110.13, 77.35, 77.03, 76.71, 59.55, 54.73, 40.29, 40.13, 31.51, 30.64, 30.38, 29.55, 29.50, 29.45, 29.31, 28.32, 27.51, 27.38, 23.92, 23.20, 23.12, 22.88, 22.60, 22.56, 22.50, 14.01, 13.95, 13.57, 13.54, 10.48, 10.17, 10.03. HRMS (ESI): calcd for $C_{56}H_{79}N_5O_2S_2Se_2$ (M+), 1077.4006; found, 1077.4006.



Synthesis of 2,2'-((2*Z*,2'*Z*)-((6,12,13-tris(2-ethylhexyl)-3,9-dihexyl-12,13-dihydro-6*H*-selenopheno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]selenopheno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (EHN6SEH-4F)

A mixture of compound **5c** (161 mg, 0.15 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene) malononitrile (138 mg, 0.60 mmol) were added into in a flask (100 mL) and were dissolved in chloroform (15 mL). Pyridine (200 μL) was added to the mixture and the reaction mixture was stirred at room temperature overnight. The solvent was removed under the reduced pressure and the crude product was purified by silica gel column chromatography with hexane/chloroform (1:1) as the eluent to afford a red solid (194 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 2H), 8.55 (dd, *J* = 9.6, 6.7 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 2H), 4.74 (d, *J* = 7.2 Hz, 2H), 4.67 (d, *J* = 7.6 Hz, 4H), 3.31-3.20 (m, 4H), 2.37 (s, 1H), 2.08-2.00 (m, 2H), 1.92-1.83 (m, 4H), 1.55-1.25 (m, 20H), 1.08-0.82 (m, 28H), 0.74-0.70 (m, 6H), 0.61-0.57 (m, 6H). HRMS (ESI): calcd for $C_{80}H_{83}F_4N_9O_2S_2Se_2$ (M+), 1501.4378; found, 1501.4375.

Device fabrication and measurements

The device was fabricated with a conventional structure ITO/PEDOT:PSS/PM6:acceptors/ PNDIT-F3N/Ag. The ITO/glass substrates were ultrasonically cleaned with detergent, deionized water, acetone, and isopropanol. After drying in an oven at 110 °C overnight, the ITO glasses were treated with plasma for 25 min. A thin layer of PEDOT:PSS was spin-cast onto the ITO substrates at 5000 rpm for 25 s, then annealed at 150 °C for 15 min in air. The mixture of PM6 and NFA blends (1:1.2 weight ratio) were dissolved in chloroform (the total concentration of blend solutions was 7 mg mL^{-1} for all blends), with the addition of 0.5% CN

as additive, and stirred 2 hours on a hotplate at 55°C in a nitrogen filled glove box. The solution were spin-casted on the PEDOT:PSS layer at 3000 rpm for 39 s and accompanied by a thermal annealing process at 90 °C for 5 min. After a PNDIT-F3N layer was spin-coated, Ag (90 nm) layer was sequentially deposited under a high vacuum. Current density–voltage (*J–V*) curves of the devices were performed by a Keithley 2400 source meter in a glove box with nitrogen atmosphere. The simulated sunlight was calibrated by an AM 1.5G solar simulator (Enlitech, SS-F5, Taiwan), which was measured with a calibrated Si diode by National Renewable Energy Laboratory. The EQE curves were tested by an EQE measurement system manufactured by EnLi Technology (Taiwan).

SCLC device fabrication and characterization

The electron-only devices were fabricated by the structure: ITO/ZnO/blend film/PNDIT-F3N/Al. The mobilities were calculated according to the equation listed below:

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

where J is the current density, ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant, μ is the mobility, V is the voltage, and L is the film thickness.

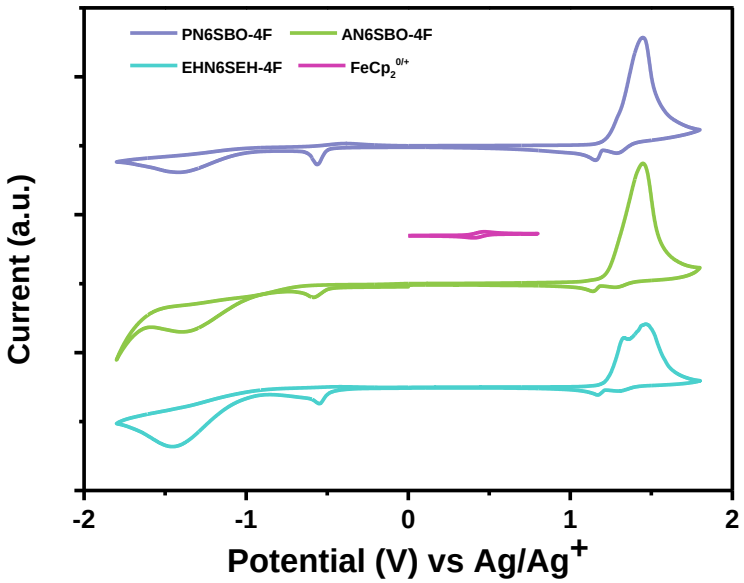


Fig. S1 Electrochemical cyclic voltammogram curves of **PN6SBO-4F**, **AN6SBO-4F, EHN6SEH-4F** and $FeCp_2^{0/+}$.

Table S1 Optical parameters of **mBzS-4F**, **PN6SBO-4F**, **AN6SBO-4F**, and **EHN6SEH-4F**.

NFAs	$\lambda_{s,max}$ a) [nm]	$\lambda_{f,max}$ b) [nm]	λ_{onset} c) [nm]	E_g^{opt} d) [eV]
mBzS-4F	770	877	989	1.25
PN6SBO-4F	773	877	969	1.28
AN6SBO-4F	774	880	978	1.27
EHN6SEH-4F	774	876	962	1.29

a) Absorption maximum in solution, b) absorption maximum in film, c) absorption edge in film, d) optical bandgap estimated from thin-film absorption

Single-Crystal Characteristics.

Single-crystal growth using ternary solvent diffusion technique.

A solution prepared from about 1 mg of NFA in 0.3 mL $CHCl_3$ was transferred into an NMR tube. Around 0.2 mL of CH_2Cl_2 was carefully layered on top of the $CHCl_3$ solution, followed by carefully layering acetone or hexanes on top. The CH_2Cl_2 portion plays an important role as a buffer layer to create a gradient of solubility, which modulates growth kinetics of crystals and suppresses random crystallizations. The NMR tube was then sealed and left to stand for few days (3-7 days) until the color of the solution faded. **mBzS-4F**, **AN6SBO-4F** and **EHN6SEH-4F** were grown using this method.

Single-crystal X-ray diffraction of **mBzS-4F**

A black lustrous needle, measuring 0.17 x 0.03 x 0.02 mm^3 was mounted on a loop with oil. Data was collected at -173 ^oC on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 53 mm and exposure time was 120 seconds per frame for all sets. The scan width was 0.5^o. Data collection was 99.9% complete to 23.26^o in ϑ. A total of 65010 reflections were collected covering the indices, -15<=h<=15, -57<=k<=57, -35<=l<=35. 32824 reflections were symmetry independent and the R_{int} = 0.1923 indicated that the data was appropriate considering the large cell size. Indexing and unit cell refinement indicated a primitive monoclinic lattice. The space group was found to be $P2_1/c$ (No. 14).

Single-crystal X-ray diffraction of **AN6SBO-4F**

A black prism, measuring 0.40 x 0.37 x 0.20 mm^3 was mounted on a loop with oil. Data was collected at -173 ^oC on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 40 mm and exposure time was 20 seconds per frame for all sets. The scan width was 0.5^o. Data collection was 98.7% complete to 25^o in ϑ. A total of 42117 merged reflections were collected covering the indices, -25<=h<=25, -39<=k<=39, -41<=l<=41. 21415 reflections were symmetry independent and the low R_{int} = 0.0426 indicated

that the data was excellent. Indexing and unit cell refinement indicated a C-centered monoclinic lattice. The space group was found to be C 2/c (No. 15).

Single-crystal X-ray diffraction of **EHN6SEH-4F**

A lustrous brown needle, measuring 0.60 x 0.07 x 0.05 mm^3 was mounted on a loop with oil. Data was collected at -173 ^oC on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 40 mm and exposure time was 20 seconds per frame for all sets. The scan width was 0.5^o. Data collection was 99.8% complete to 25^o in ϑ. A total of 31189 merged reflections were collected covering the indices, -14<=h<=14, -21<=k<=21, -24<=l<=24. 15876 reflections were symmetry independent and the R_{int} = 0.0784 indicated that the data was of average quality (0.07). Indexing and unit cell refinement indicated a triclinic lattice. The space group was found to be P $\bar{1}$ (No. 2).

Table S2 Crystallographic data for **mBzS-4F**.

Empirical formula	C81 H85 F4 N9 O2 S2 Se2	
Formula weight	1514.61	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.938(5) Å	α= 90.000(5)°.
	b = 52.166(5) Å	β= 99.927(5)°.
	c = 31.942(5) Å	γ = 90.000(5)°.
Volume	22877(9) $Å^3$	
Z	12	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	1.087 mm^{-1}	
F(000)	9432	
Crystal size	0.170 x 0.030 x 0.020 mm^3	
Theta range for data collection	1.294 to 23.257°.	
Index ranges	-15<=h<=15, -57<=k<=57, -35<=l<=35	
Reflections collected	65010	
Independent reflections	32824 [R(int) = 0.1923]	
Completeness to theta = 23.257°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	32824 / 4511 / 2680	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.1209, wR2 = 0.2666	
R indices (all data)	R1 = 0.3045, wR2 = 0.3277	
Largest diff. peak and hole	0.802 and -0.700 $e.Å^{-3}$	

Table S3 Crystallographic data for **AN6SBO-4F**.

Empirical formula	C88 H99 F4 N9 O3 S2 Se2	
Formula weight	1628.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 18.8244(12) Å	α= 90°.
	b = 29.3244(18) Å	β= 95.951(3)°.
	c = 31.439(2) Å	γ = 90°.
Volume	17261(2) $Å^3$	
Z	8	
Density (calculated)	1.254 Mg/m^3	
Absorption coefficient	0.966 mm^{-1}	
F(000)	6800	
Crystal size	0.400 x 0.370 x 0.200 mm^3	
Theta range for data collection	1.290 to 28.466°.	
Index ranges	-25<=h<=25, -39<=k<=39, -41<=l<=41	
Reflections collected	42450	
Independent reflections	21585 [R(int) = 0.0420]	
Completeness to theta = 25.000°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21585 / 484 / 1026	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0702, wR2 = 0.1925	
R indices (all data)	R1 = 0.1362, wR2 = 0.2391	
Largest diff. peak and hole	1.030 and -0.742 $e.Å^{-3}$	

Table S4 Crystallographic data for **EHN6SEH-4F**.

Empirical formula	C83 H89 F4 N9 O3 S2 Se2	
Formula weight	1558.67	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.7514(12) Å	α= 102.675(6)°.
	b = 17.3977(17) Å	β= 98.649(6)°.
	c = 19.925(2) Å	γ = 99.031(5)°.
Volume	3852.2(7) $Å^3$	
Z	2	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	1.079 mm^{-1}	
F(000)	1620	
Crystal size	0.600 x 0.070 x 0.050 mm^3	
Theta range for data collection	1.067 to 26.562°.	
Index ranges	-14<=h<=14, -21<=k<=21, -24<=l<=24	
Reflections collected	31189	
Independent reflections	15876 [R(int) = 0.0784]	
Completeness to theta = 25.000°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15876 / 1203 / 1003	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0774, wR2 = 0.2064	
R indices (all data)	R1 = 0.1415, wR2 = 0.2464	
Largest diff. peak and hole	1.518 and -1.008 $e.Å^{-3}$	

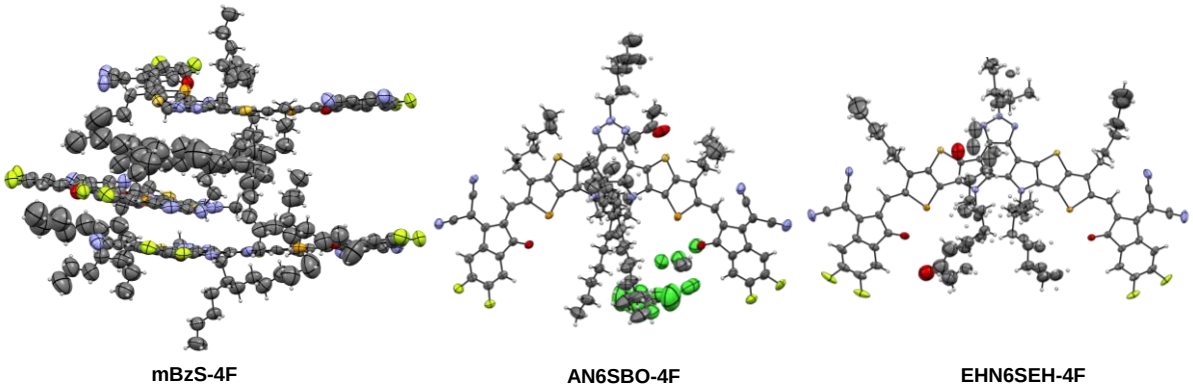


Fig. S2 ORTEP view of **mBzS-4F**, **AN6SBO-4F** and **EHN6SEH-4F** with atomic displacement parameters shown at the 50% probability level.

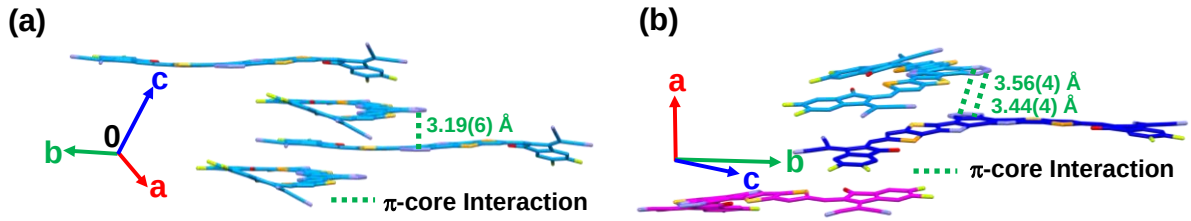


Fig. S3 π-core interaction of (a) **AN6SBO-4F** and (b) **EHN6SEH-4F**.

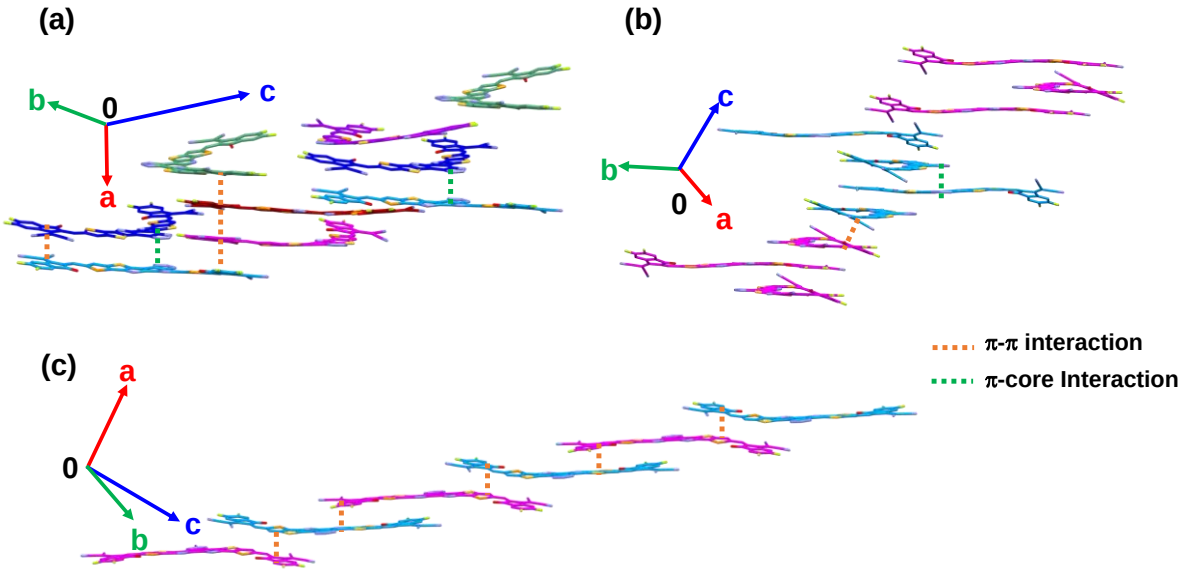


Fig. S4 Long-range order in the crystal of (a) **mBzS-4F**, (b) **AN6SBO-4F** and (c) **EHN6SEH-4F**.

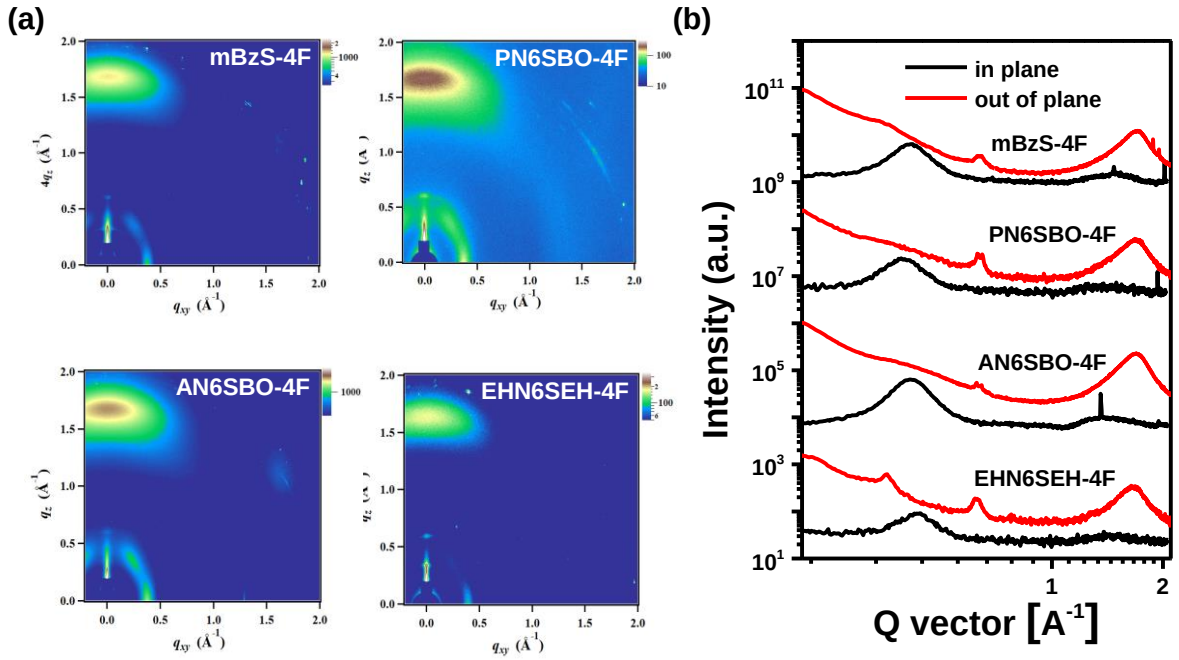


Fig. S5 (a) 2D-GIWAXS images of **mBzS-4F**, **PN6SBO-4F**, **AN6SBO-4F** and **EHN6SEH-4F** films. (b) The corresponding out-of-plane and in-plane 1D line-cut profiles of **mBzS-4F**, **PN6SBO-4F**, **AN6SBO-4F** and **EHN6SEH-4F** films.

Table S5 Coherence lengths of the (100) and (010) peaks and the *d*-spacings for the NFAs.

	Out-of-Plane				In-Plane			
	π-π stacking cell axis (*010*)				Unit cell long axis (*100*)			
	q (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	Coherence length (Å)	*q* (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	Coherence length (Å)
mBzS-4F	1.69	3.72	0.2542	22.50	0.41	15.20	0.093	61.01
PN6SBO-4F	1.67	3.76	0.261	21.94	0.40	15.87	0.093	60.96
AN6SBO-4F	1.68	3.75	0.259	22.10	0.42	15.13	0.096	58.84
EHN6SEH-4F	1.65	3.81	0.245	23.31	0.43	14.65	0.097	58.34

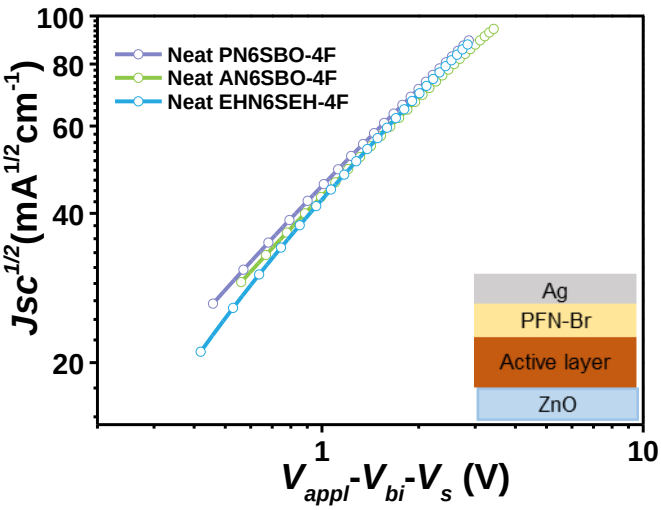


Fig. S6 SCLC characteristics of electron-only devices of **PN6SBO-4F**, **AN6SBO-4F** and **EHN6SEH-4F**.

Table S6 Summary of SCLC characteristics of **PN6SBO-4F**, **AN6SBO-4F** and **EHN6SEH-4F**.

	Thickness (nm)	μ_e ($cm^2/V \cdot s$)
PN6SBO-4F	80	9.2×10^{-5}
AN6SBO-4F	79	8.0×10^{-5}
EHN6SEH-4F	83	1.4×10^{-4}

Table S7 The electronic couplings for the dimers of **mBzS-4F**.

Dimer	e-coupling / meV
AB	0
AC	0.02
AD	2.28
AE	22.2
AF	37.4
AG	0.70
AH	0.18

Table S8 The electronic couplings for the dimers of **AN6SBO-4F**.

Dimer	e-coupling / meV
AB	5.04
AC	5.04
AD	17.4
AE	45.2

Table S9 The electronic couplings for the dimers of **EHN6SEH-4F**.

Dimer	e-coupling / meV
AB	12.5
AC	19.3
AD	0.16
AE	0.53
AF	0.02
AG	19.3
AH	20.2
AI	0.16
AJ	0.48

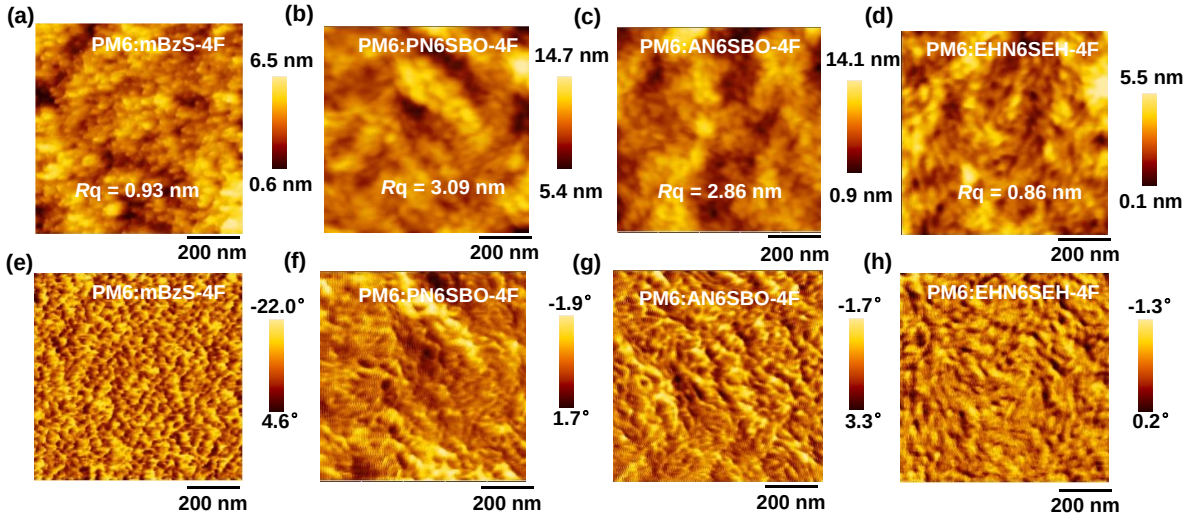


Fig. S7 AFM height images (1 μm × 1 μm) of a) PM6:**mBzS-4F**, b) PM6:**PN6SBO-4F**, c) PM6:**AN6SBO-4F**, and d) PM6:**EHN6SEH-4F** blend films. AFM phase images (1 μm × 1 μm) of e) PM6:**mBzS-4F**, f) PM6:**PN6SBO-4F**, g) PM6:**AN6SBO-4F**, and h) PM6:**EHN6SEH-4F** blend films.

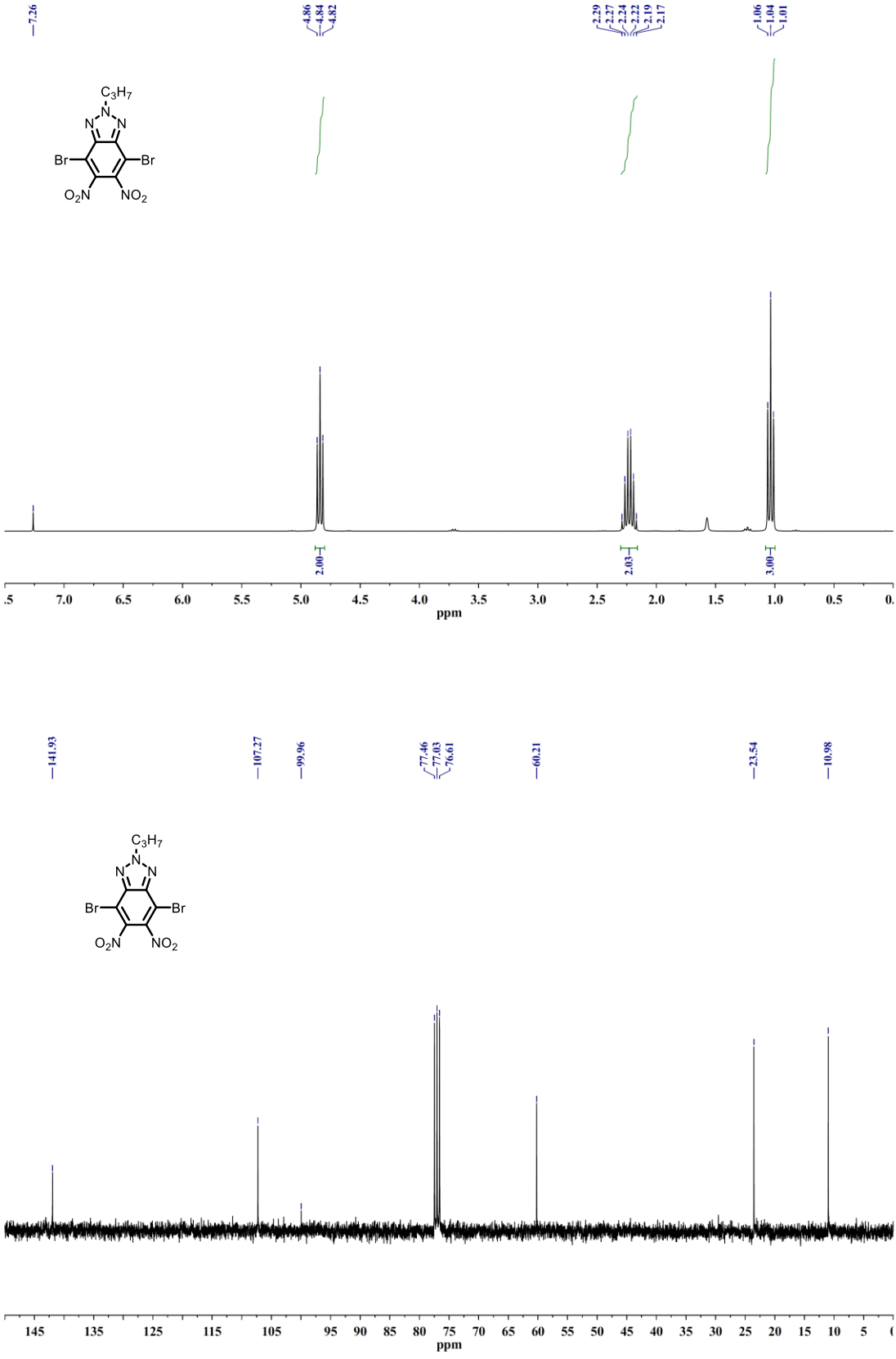


Fig. S8 ^{1}H and ^{13}C NMR spectra of **2a.**

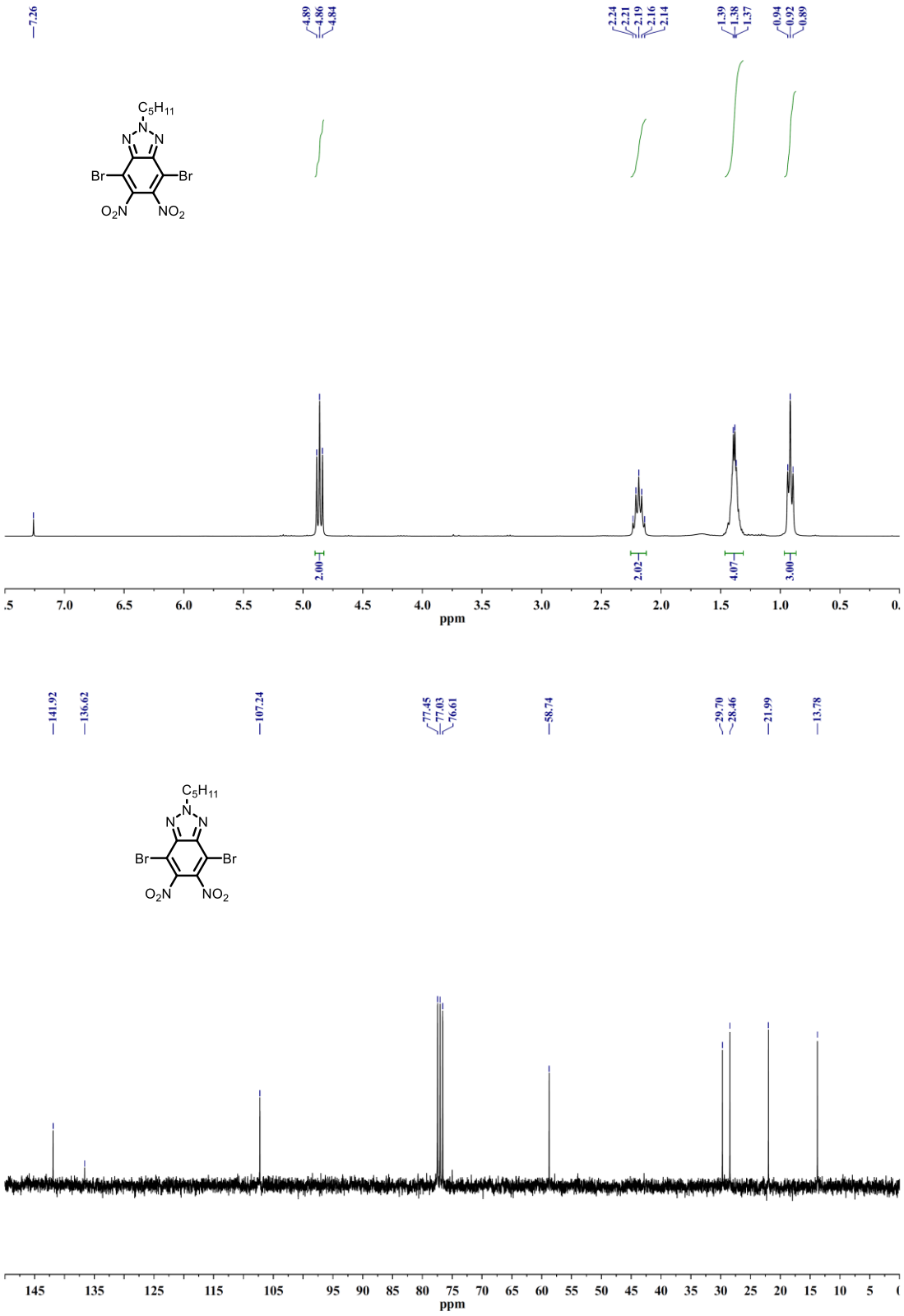


Fig. S9 ^{1}H and ^{13}C NMR spectra of **2b.**

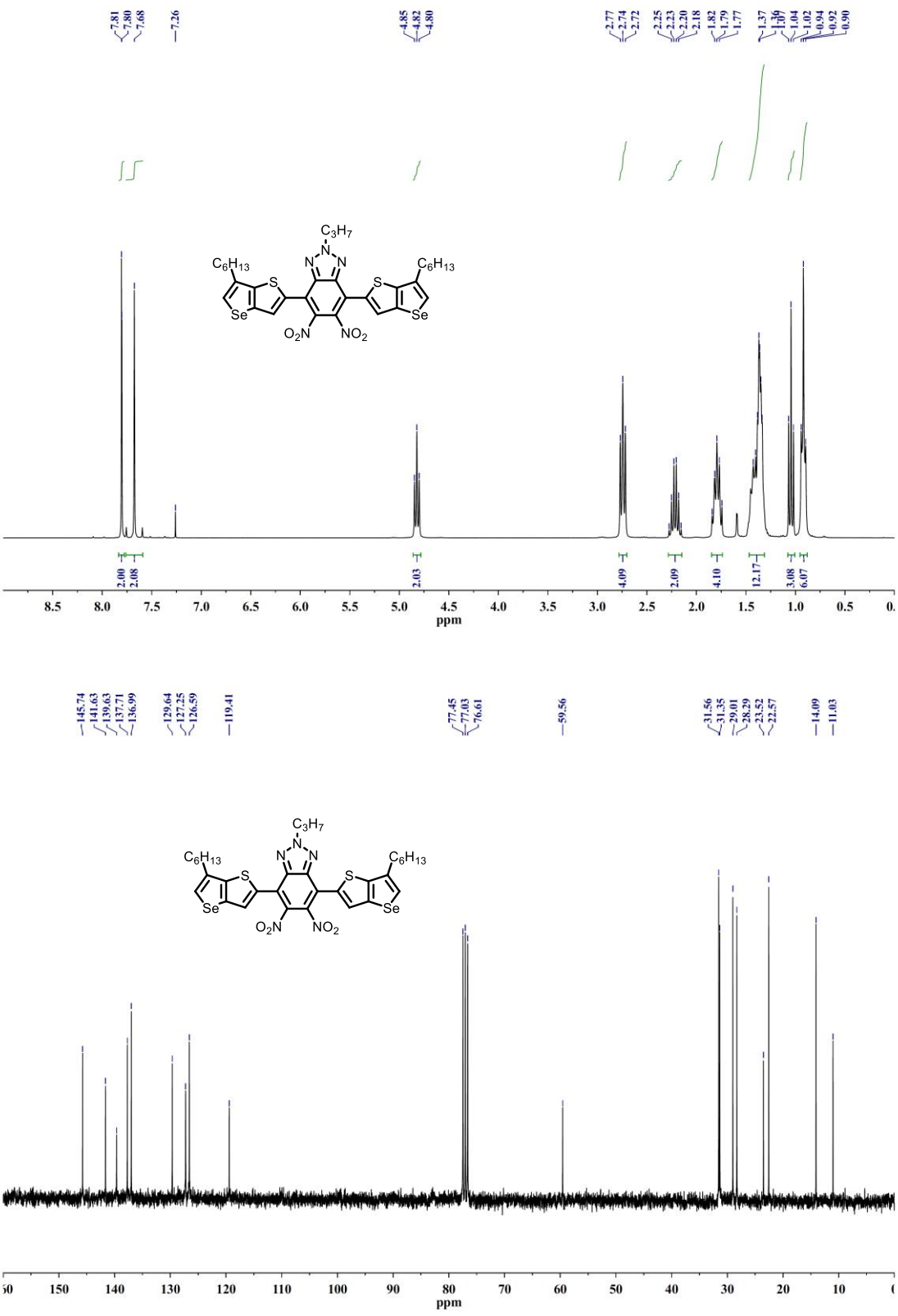


Fig. S10 ^{1}H and ^{13}C NMR spectra of **3a.**

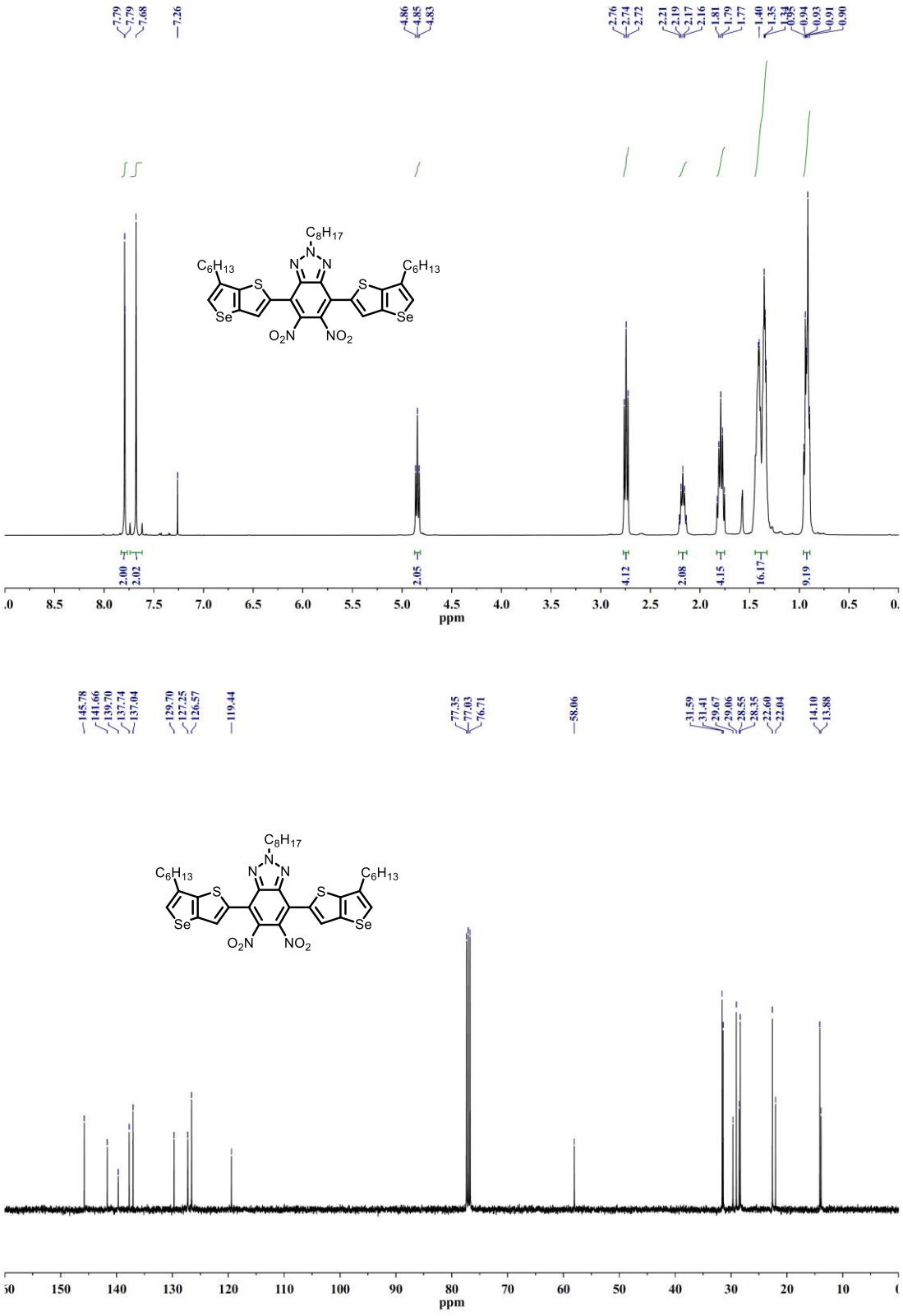


Fig. S11 ^{1}H and ^{13}C NMR spectra of **3b.**

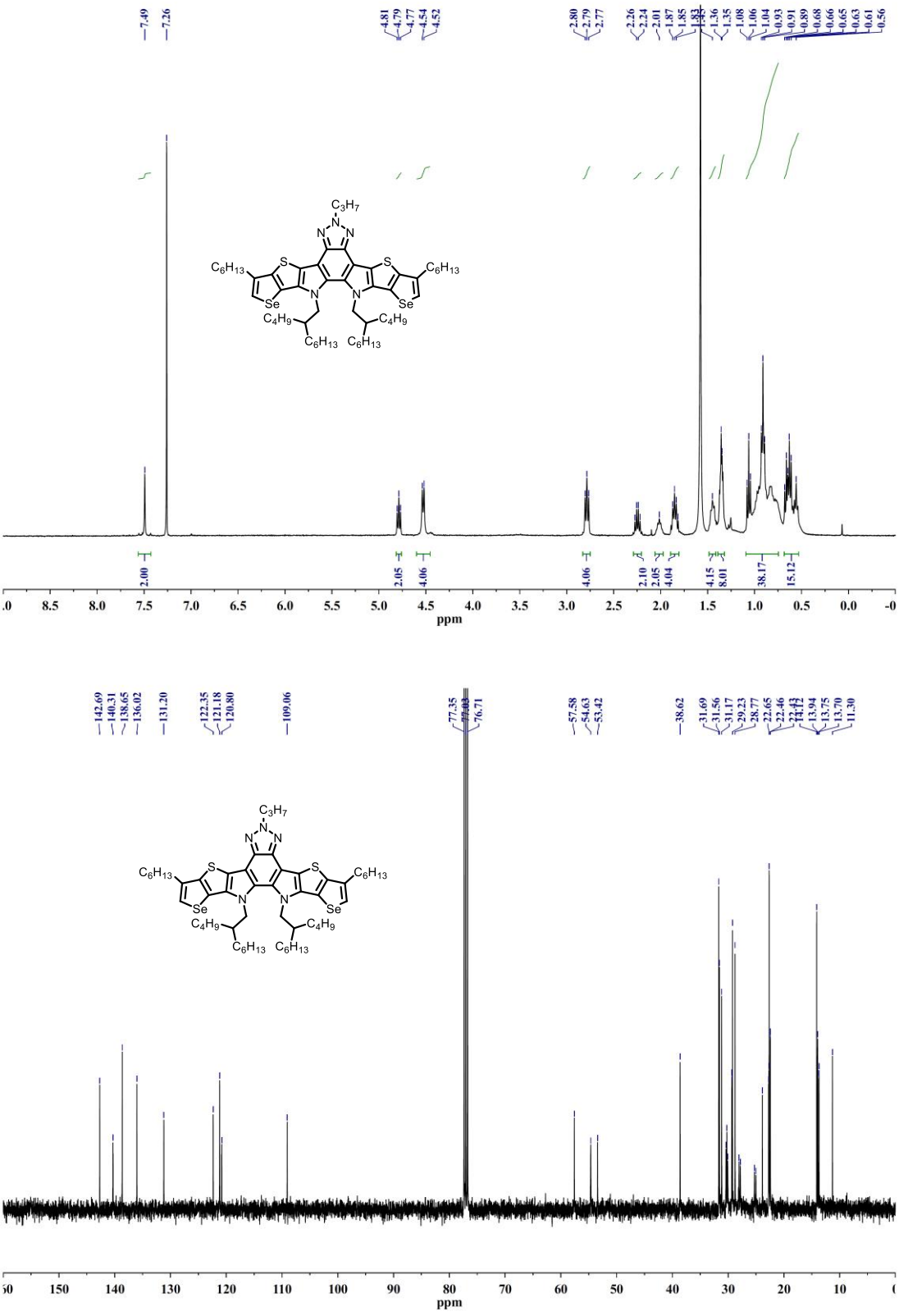


Fig. S12 ^{1}H and ^{13}C NMR spectra of **4a.**

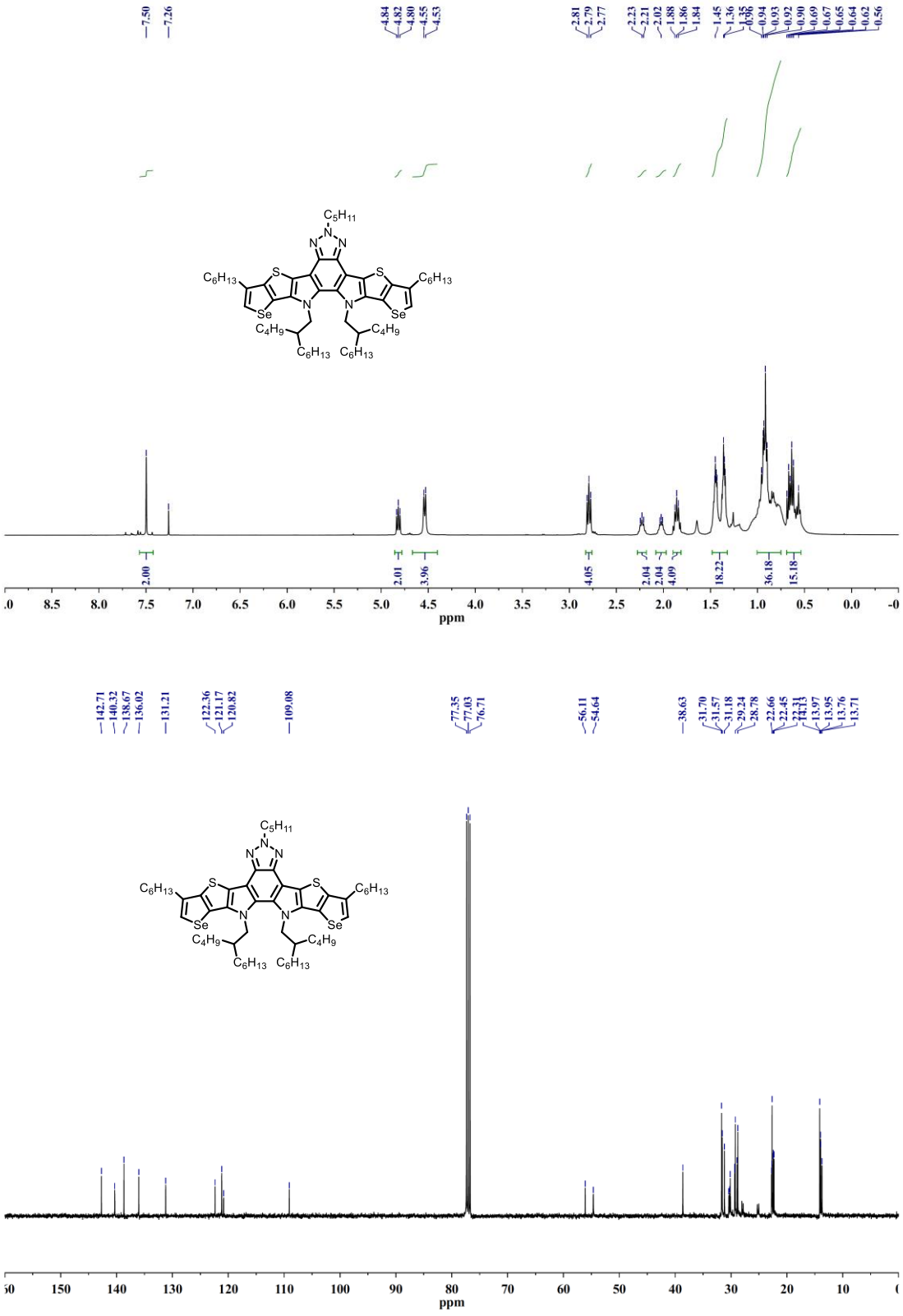


Fig. S13 ^{1}H and ^{13}C NMR spectra of **4b.**

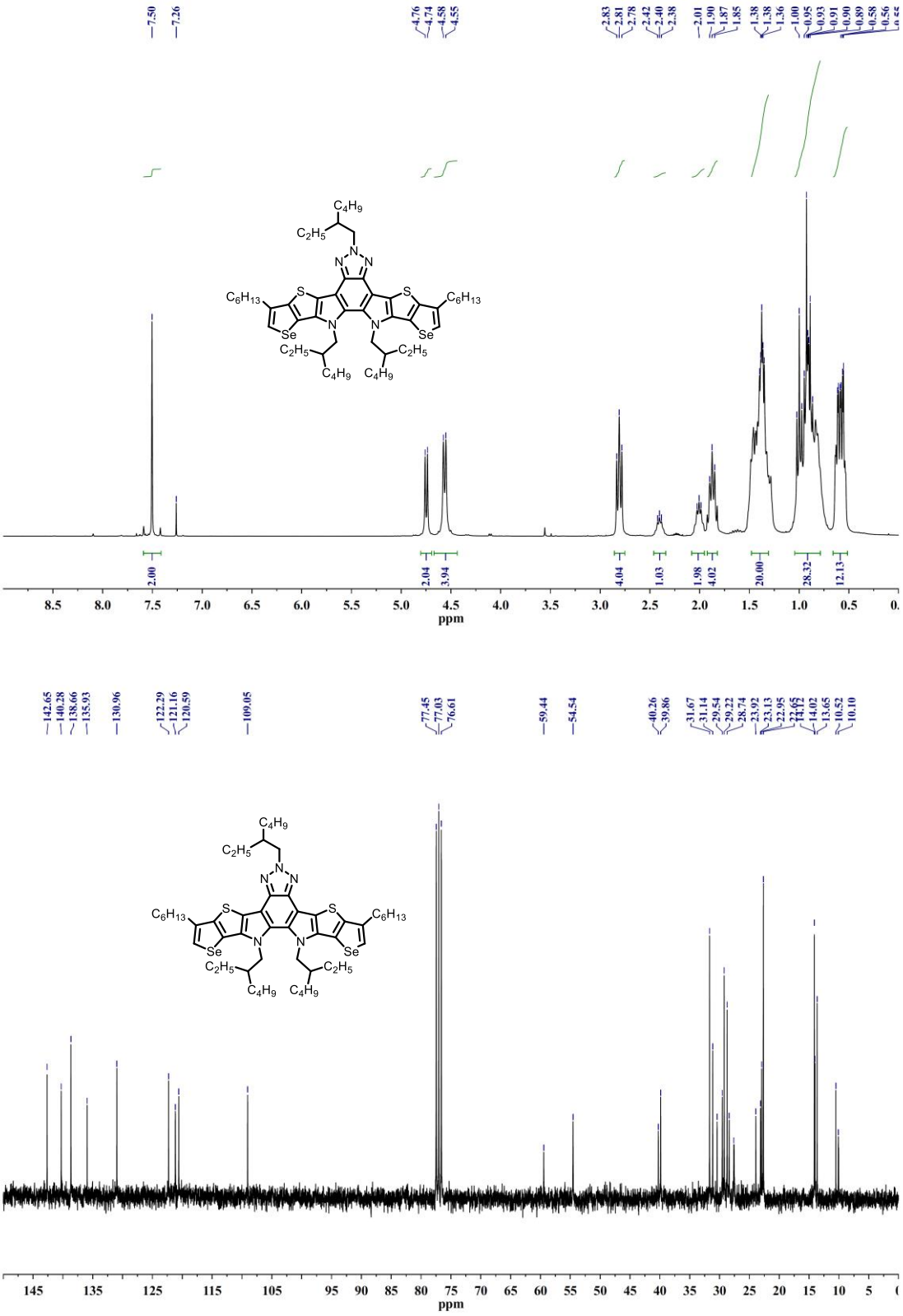


Fig. S14 ^{1}H and ^{13}C NMR spectra of **4c.**

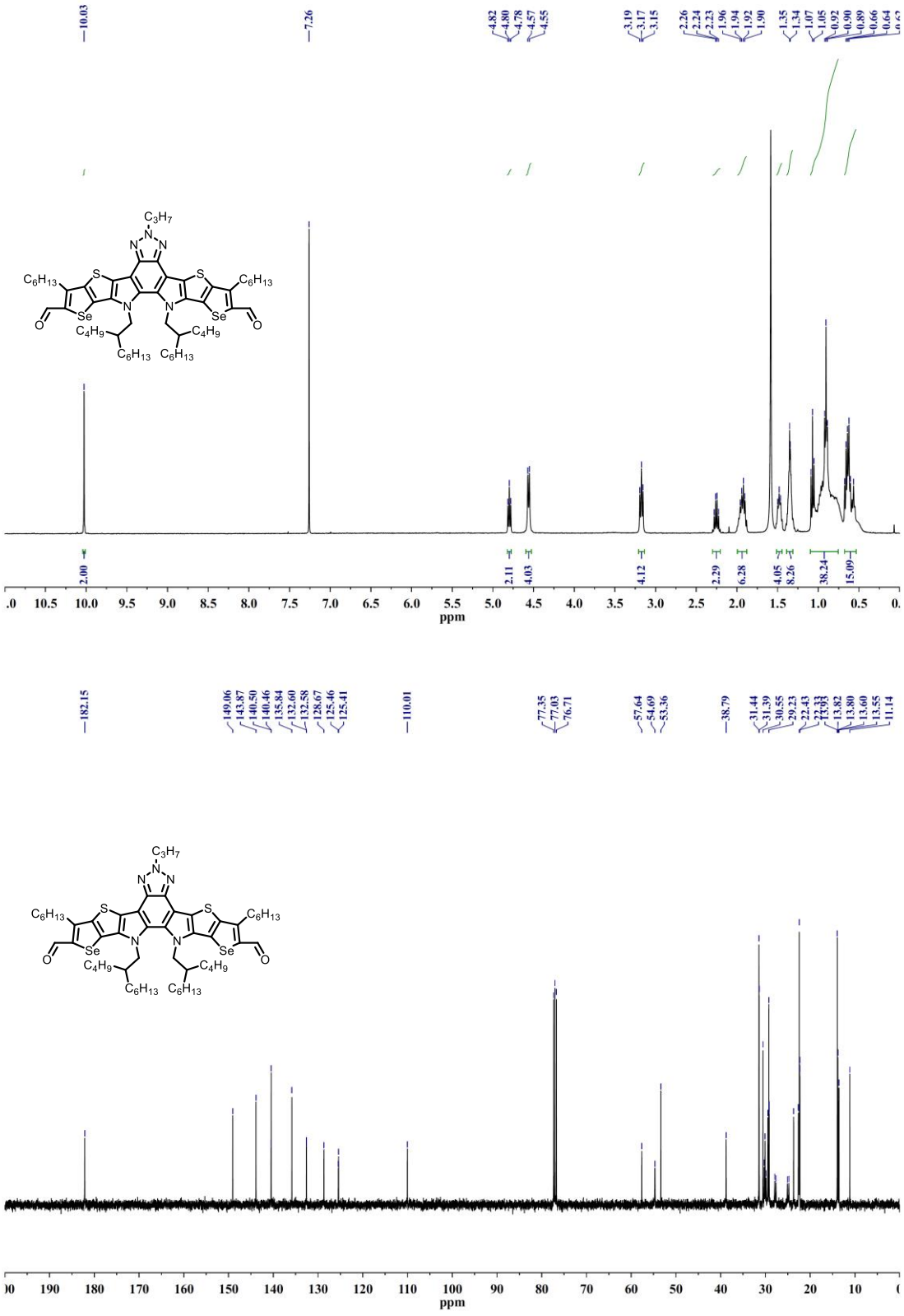


Fig. S15 ^{1}H and ^{13}C NMR spectra of **5a.**

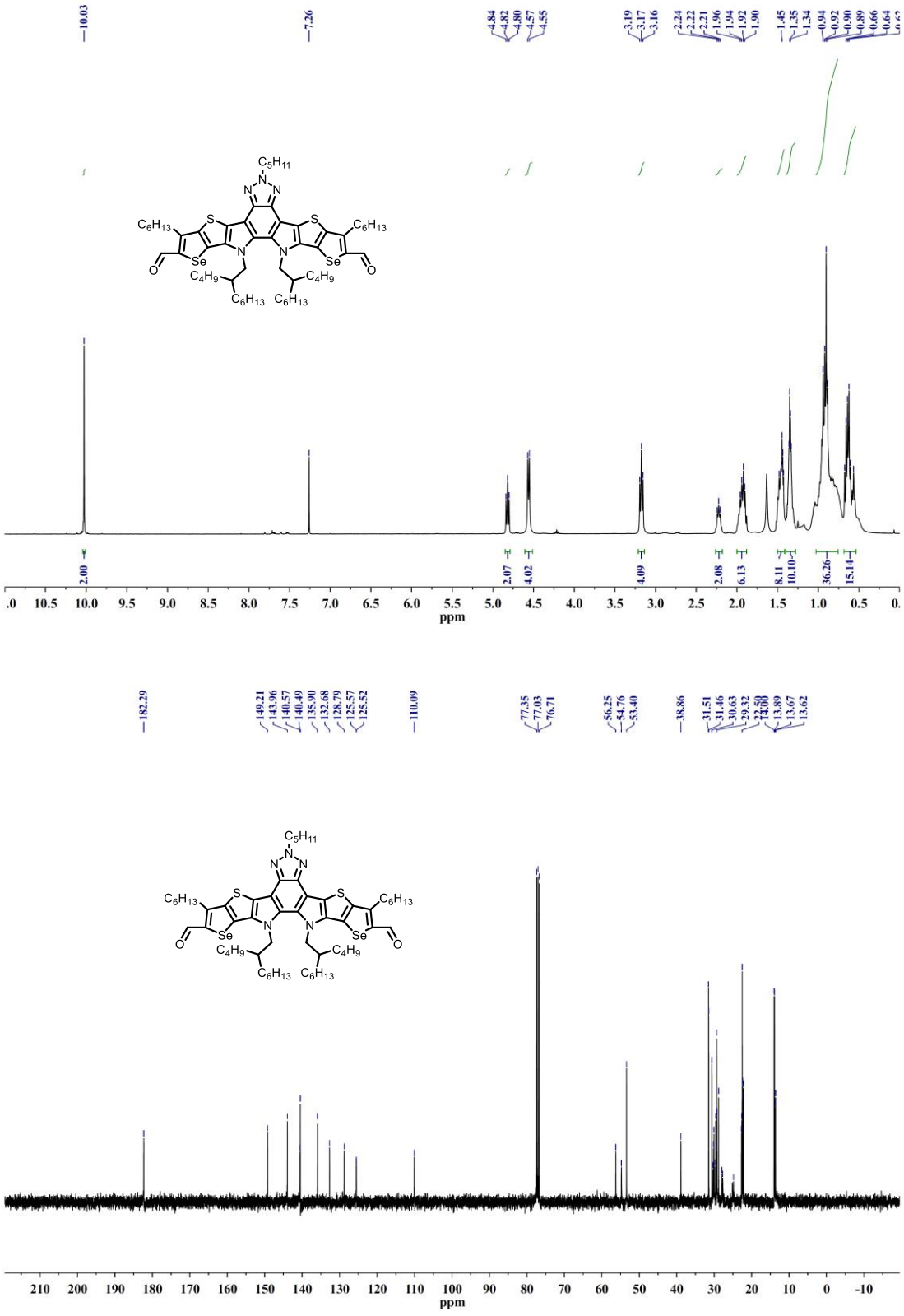


Fig. S16 ^{1}H and ^{13}C NMR spectra of **5b.**

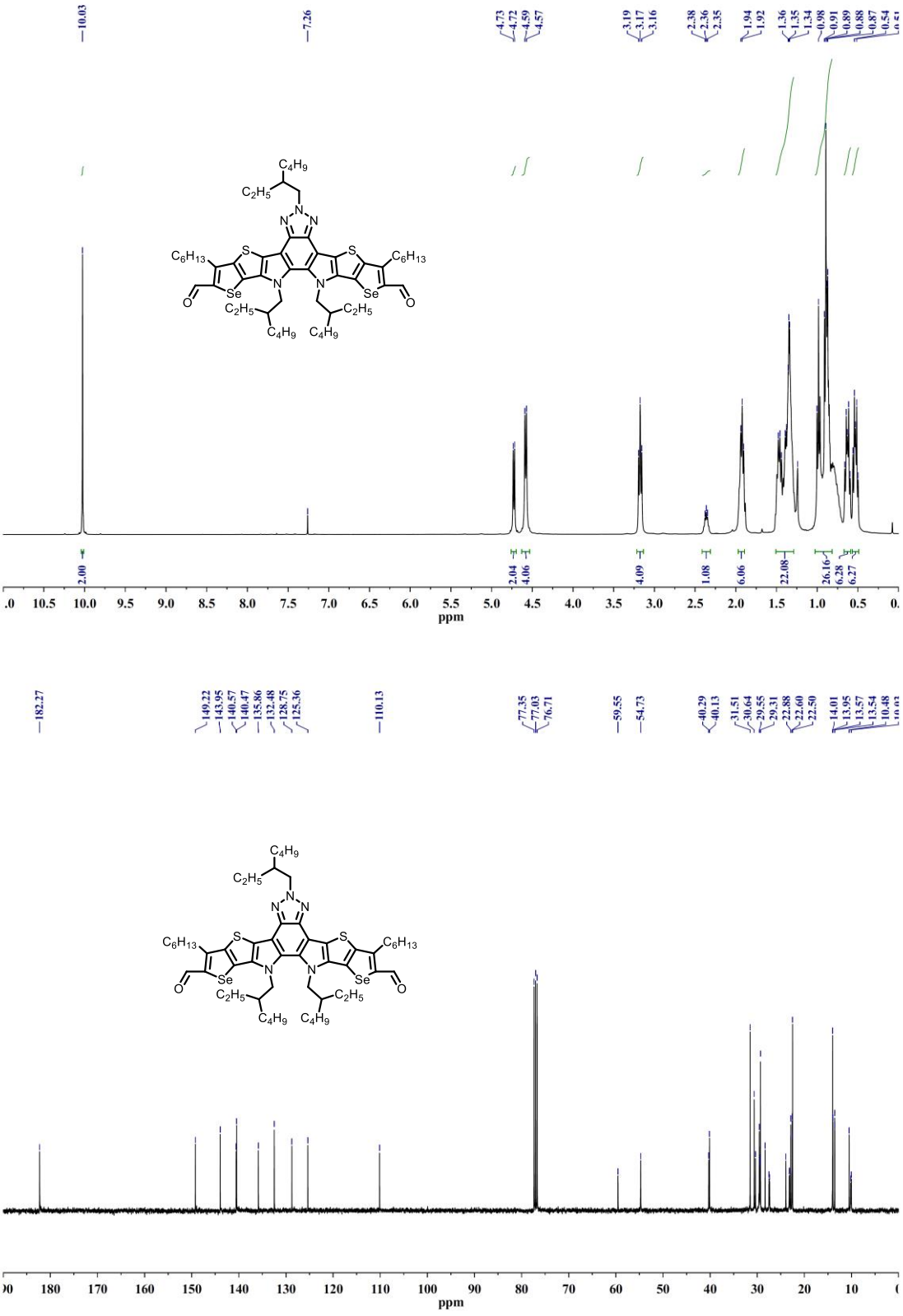


Fig. S17 ^{1}H and ^{13}C NMR spectra of **5c.**

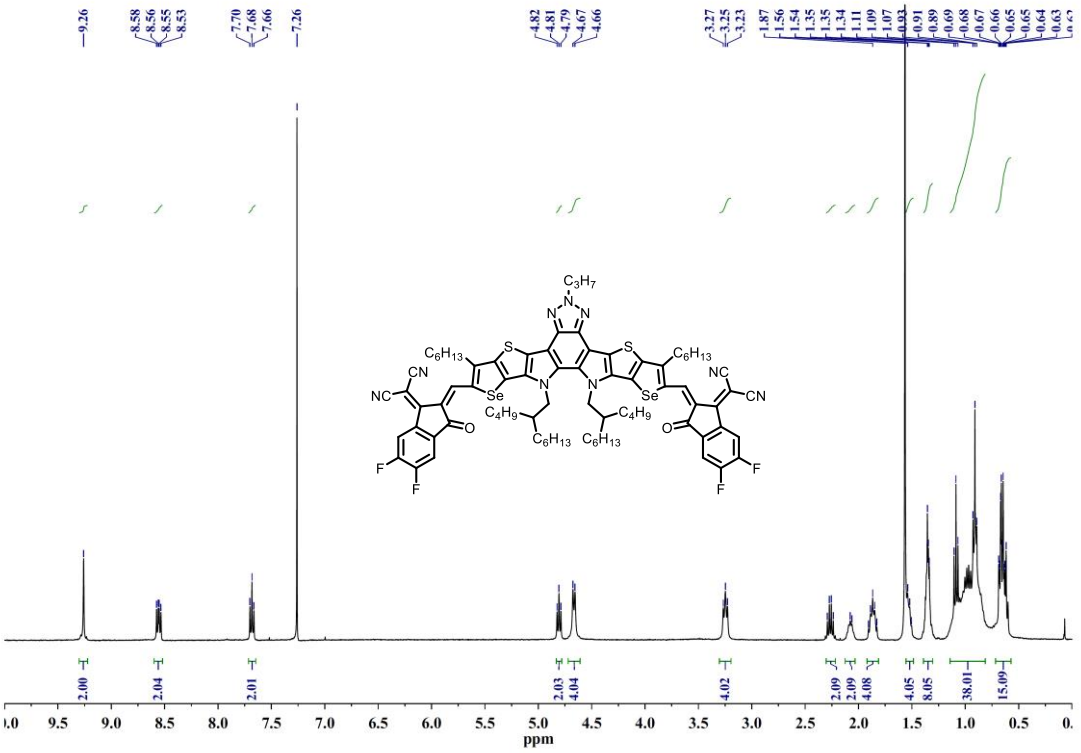


Fig. S18 ^{1}H NMR spectra of **PN6SBO-4F.**

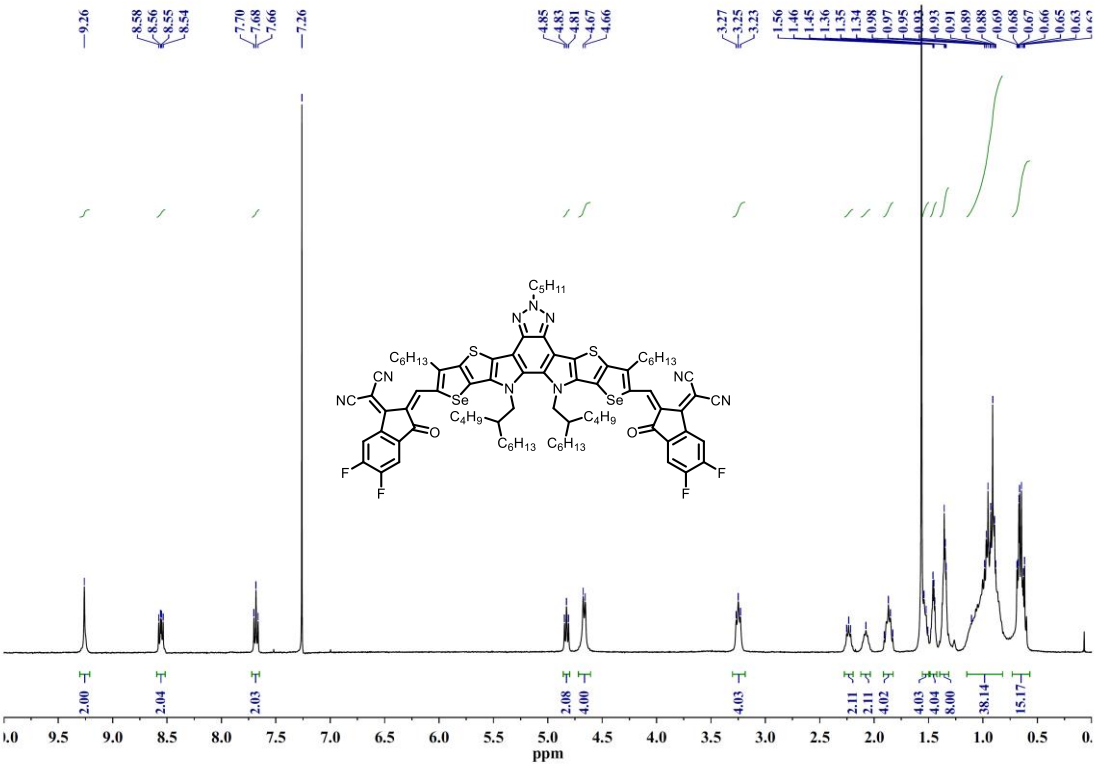


Fig. S19 ^{1}H NMR spectra of **AN6SBO-4F.**

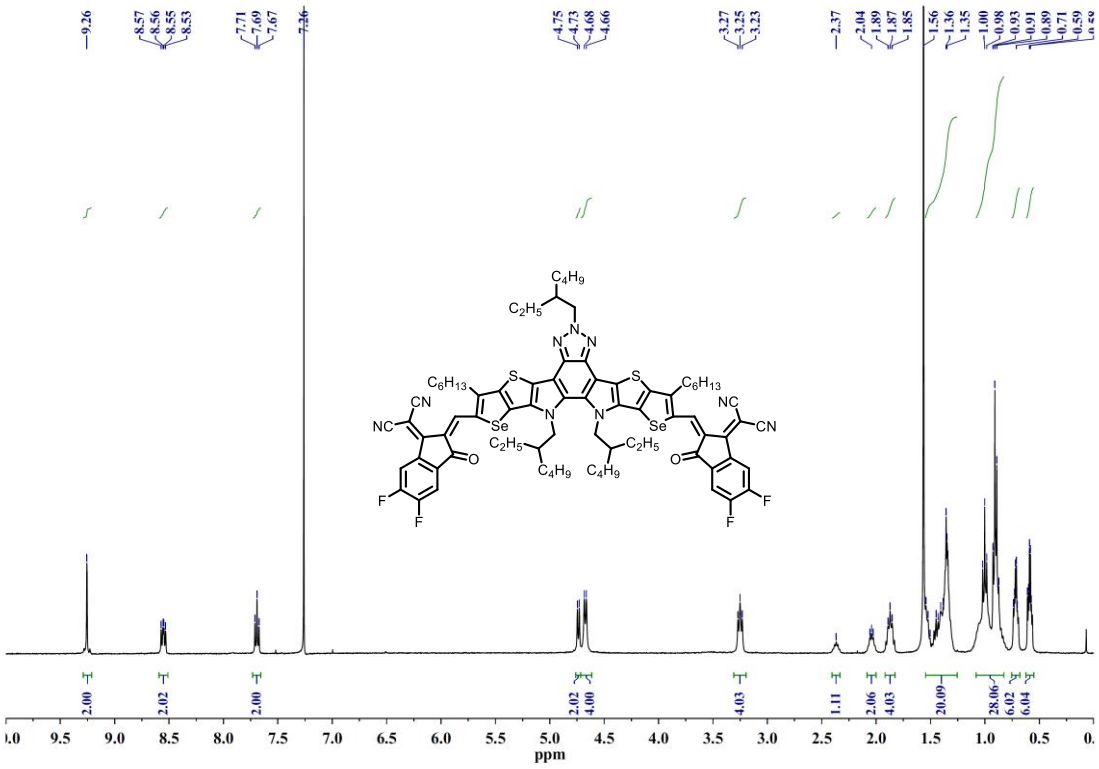


Fig. S20 ^{1}H NMR spectra of **EHN6SEH-4F.**

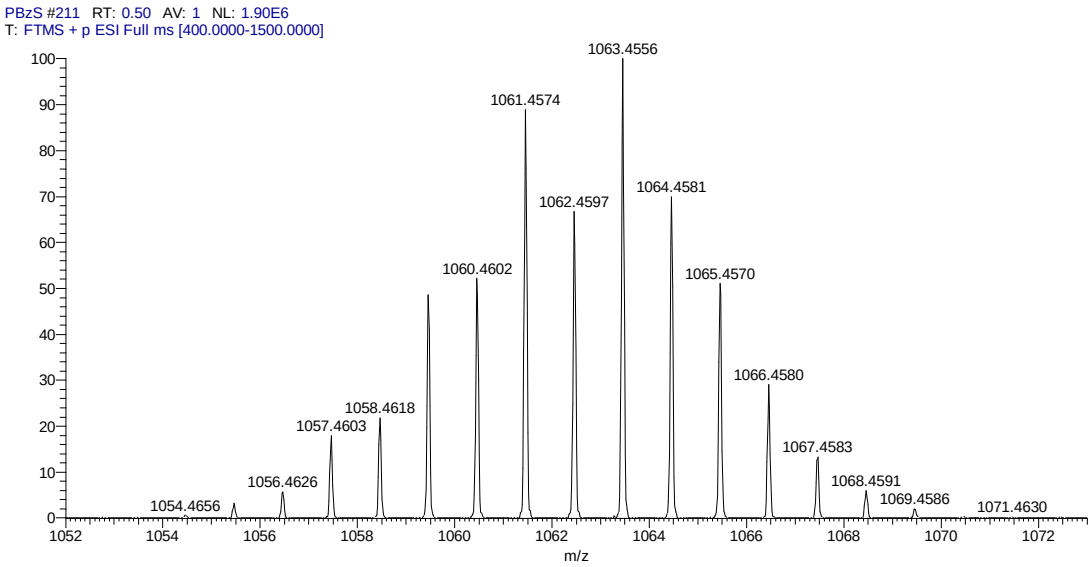


Fig. S21 HRMS spectrum (ESI) of compound **4a**.

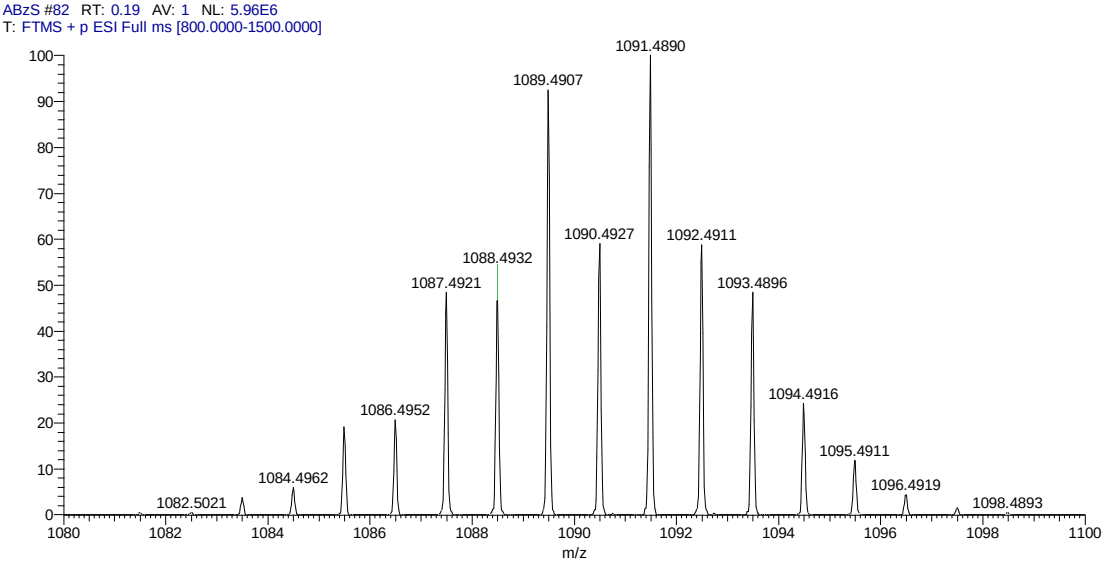


Fig. S22 HRMS spectrum (ESI) of compound **4b**.

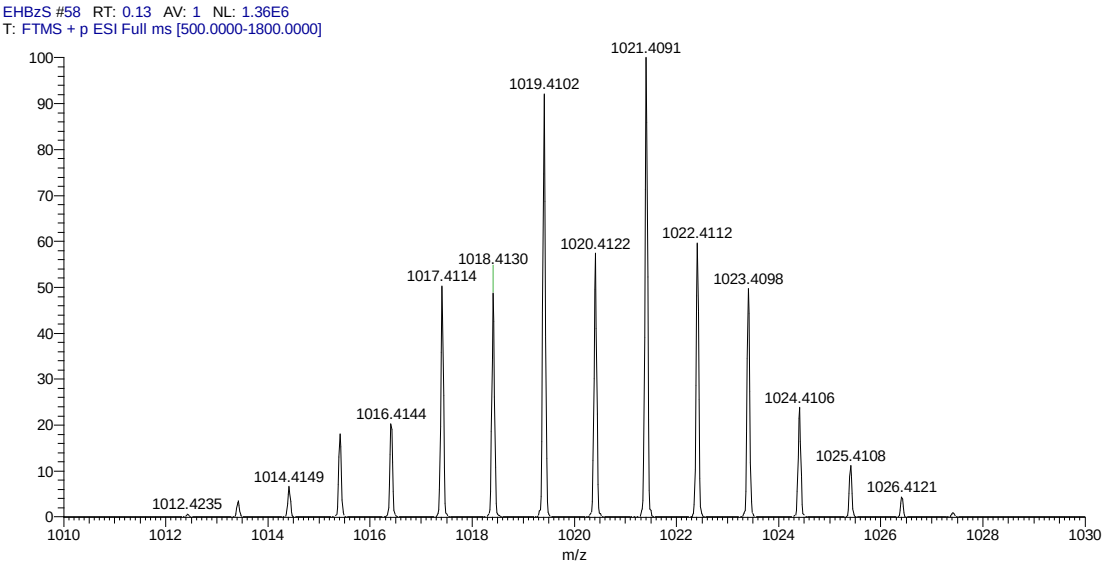


Fig. S23 HRMS spectrum (ESI) of compound **4c**.

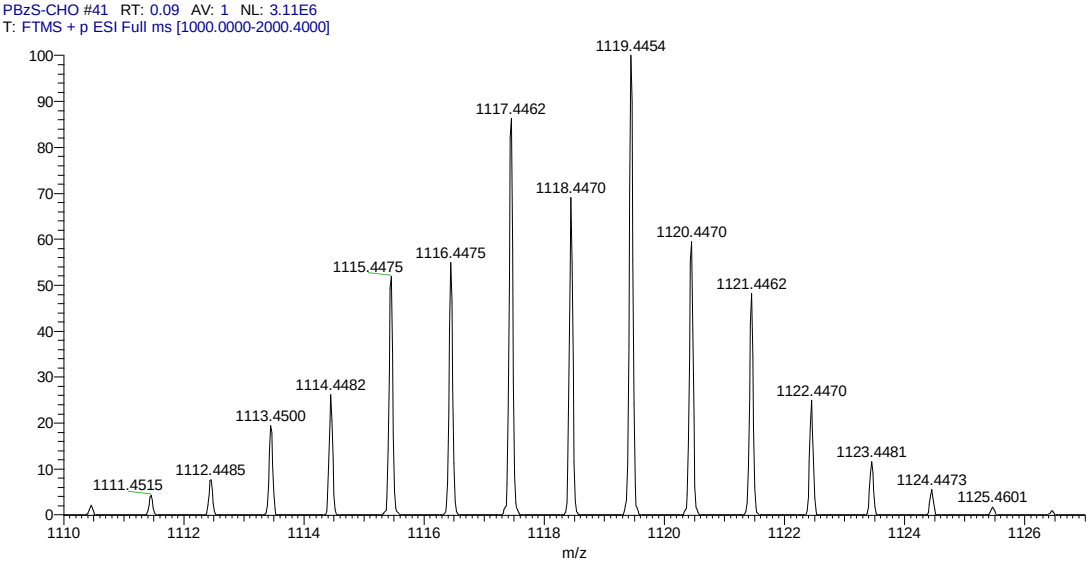


Fig. S24 HRMS spectrum (ESI) of compound **5a**.

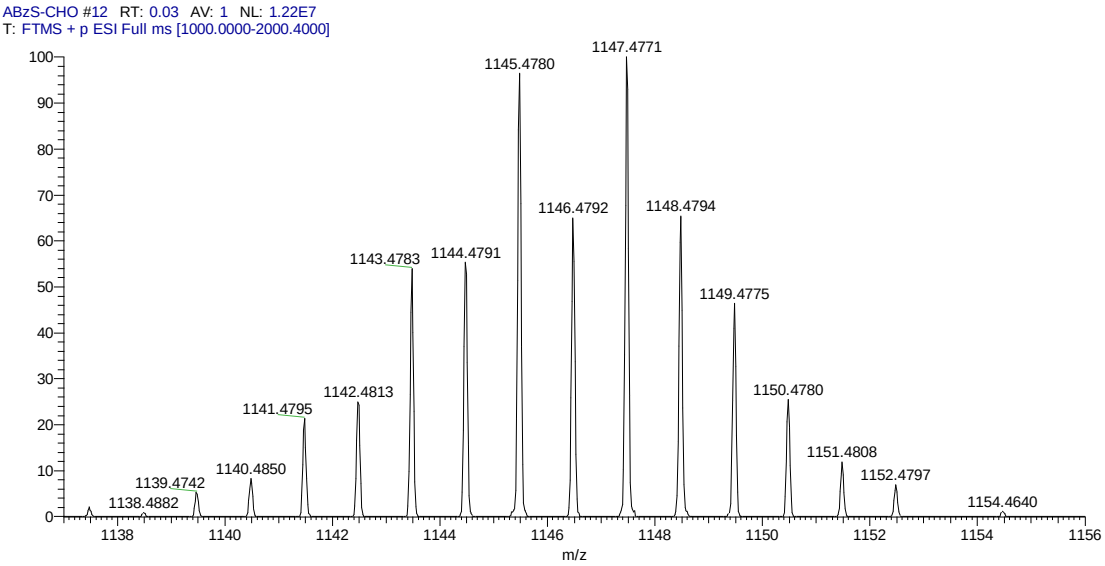


Fig. S25 HRMS spectrum (ESI) of compound **5b**.

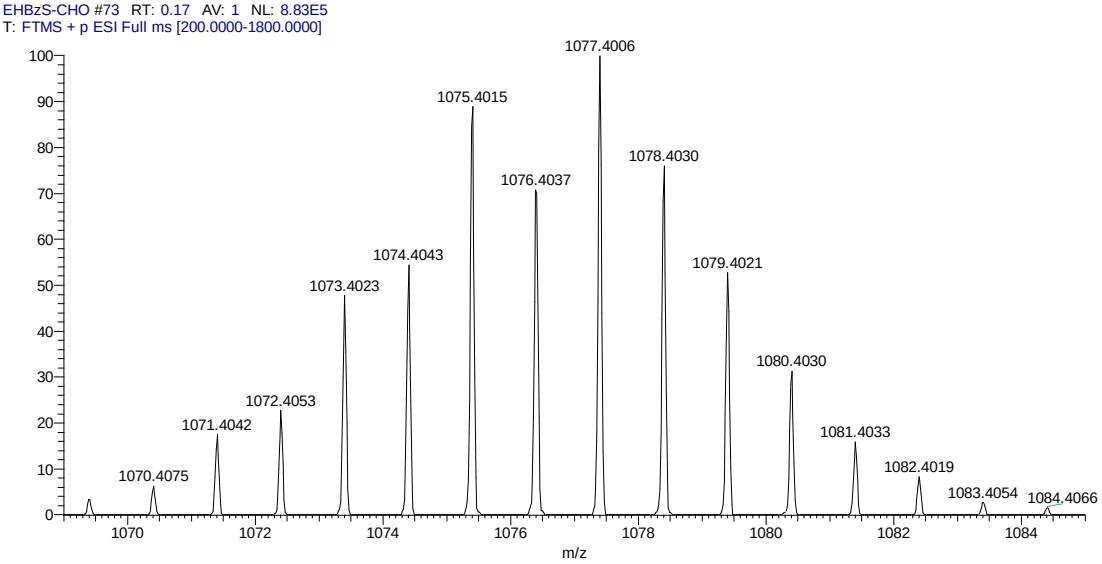


Fig. S26 HRMS spectrum (ESI) of compound **5c**.

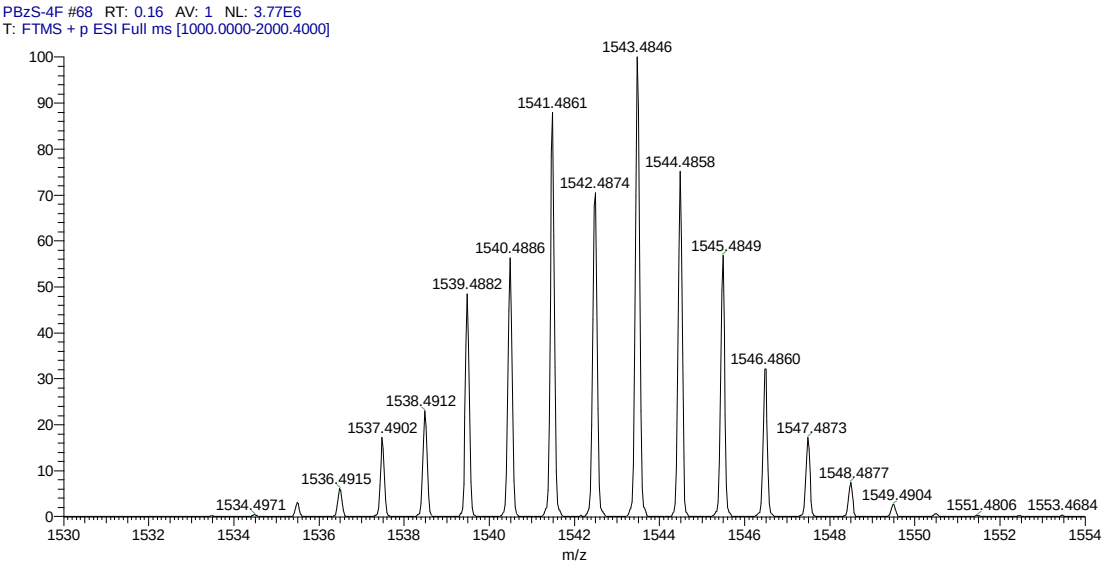


Fig. S27 HRMS spectrum (ESI) of compound **PN6SBO-4F**.

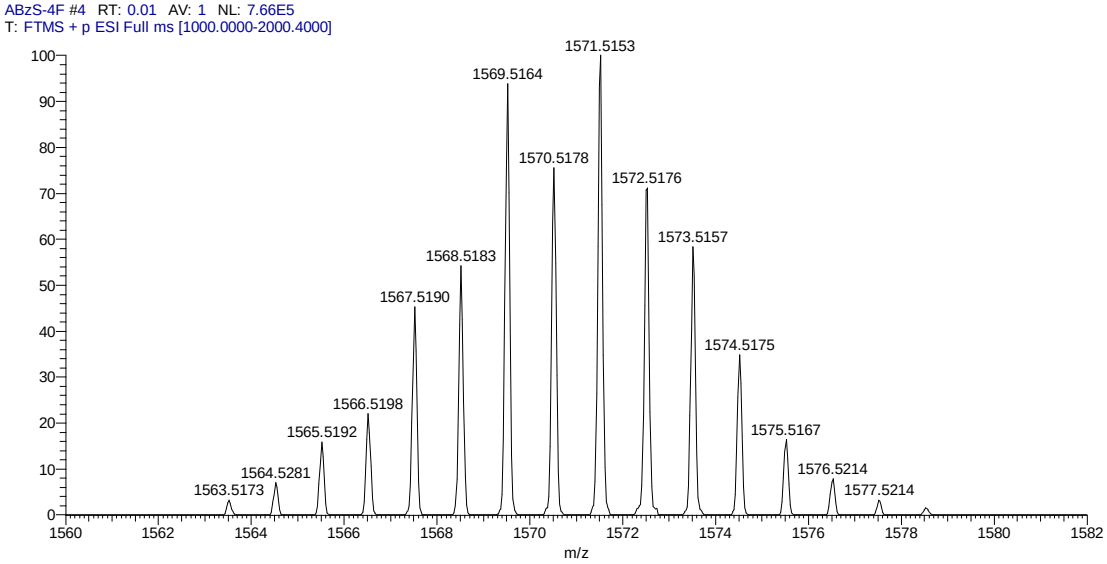


Fig. S28 HRMS spectrum (ESI) of compound **AN6SBO-4F**.

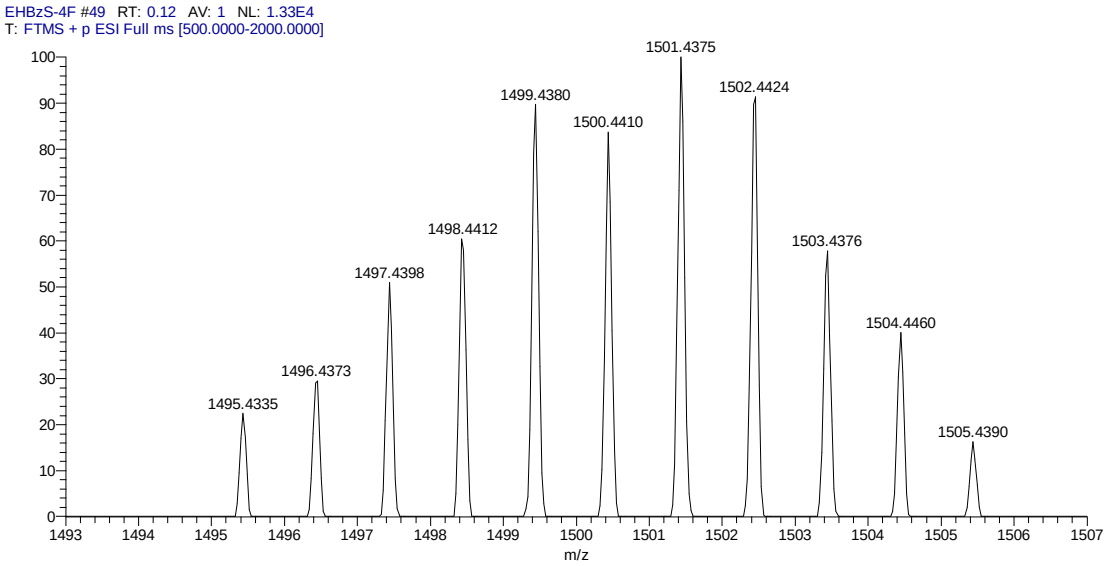


Fig. S29 HRMS spectrum (ESI) of compound **EHN6SEH-4F**.

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2. F. Lin, K. Jiang, W. Kaminsky, Z. Zhu, A. K. Jen, *J. Am. Chem. Soc.* **2020**, *142*, 15246-15251.
3. N. Shi, Y. Shi, J. Shao, X. Yang, X. Zhang, Y. Zhang, U. F. Warsame, J. Shao, X. Dong, *Dyes and Pigments* **2019**, *160*, 683-691.