Supporting Information

Spectra Tunable Non-Fused Ring Electron Acceptors via Incorporation of Electron-deficient Unit and Side-Chain Engineering

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Experimental Procedures

1. General characterization

All commercial chemicals were used without further purification. Column chromatography was carried out on silica gel (300-400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. ^{1}H and ^{13}C NMR spectra were obtained using $CDCl_3$ as solvent and measured on 300 MHz or 400 MHz spectrometer (Bruker). HRMS spectra (MALDI/DHB) were recorded on mass spectrometer Thermo Fisher Scientific LTQ FT Ultra. UV-visible absorption spectra were recorded on a UV-1900pc spectrophotometer. Electrochemical measurements were conducted using a CHI 600E Electrochemical Analyzer under nitrogen in anhydrous 0.1 M n-Bu4NPF6 acetonitrile solutions at a scan rate of 100 mV/s. $Ag/AgNO_3$ electrode was used as the reference electrode. All potentials were referenced to Fc/Fc^{+}. Atomic force microscopy (AFM) images of films were obtained on a Bruker Dimension Icon instrument. Transmission electron microscopy (TEM) images were obtained with a JEM-F200 transmission electron microscopy. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at BL14B1 Diffuse X-ray Scattering Station, Shanghai Synchrotron Radiation Facility (SSRF-BL14B1).

2. Materials and Synthesis

Synthesis of compound **3**: compound 1 (534 mg, 0.97 mmol), compound 2 (938 mg, 2.91 mmol), $Pd(PPh_3)_4$ (80 mg, 0.097) and K_2CO_3 (804 mg, 5.82 mmol) were added in a 100 mL Schlenk flask followed by several cycles of nitrogen degassing, and THF (20 mL) and H_2O (1 mL) were added under argon protection. The reaction mixture was then transferred to a 90 °C oil bath and stirred for 12 h. Subsequently, the solvent was removed under pressure and the remaining residue was purified by column chromatography (eluent: Hex) and obtained compound 3 (562 mg, yield = 74%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.96 (s, 2H), 7.08 (s, 2H), 3.92 (d, J = 6.9 Hz, 4H), 2.64 (d, J = 6.6 Hz, 4H), 1.93-1.85 (m, 2H), 1.69-1.59 (m, 2H), 1.54-1.25 (m, 32H),

0.97-0.84 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 153.93, 151.17, 141.39, 133.33, 132.30, 123.10, 117.63, 77.92, 40.30, 40.27, 34.59, 32.48, 30.21, 29.06, 28.88, 25.60, 23.54, 23.08, 14.15, 14.08, 10.97, 10.82.

Synthesis of compound **4**: compound 3 (450 mg, 0.575 mmol) was added to a round-bottom flask with 30 mL $CHCl_3$.After that, the flask was placed in an ice-water bath, and NBS (235 mg, 1.324 mmol) was added in portions and stirred for 12 h. At the end of the reaction, the mixture was quenched with saturated Na_2SO_3 solution, extracted with DCM, the solution was dried and removed under reduced pressure, and the crude product was purified by column chromatography (eluent: Hex) and obtained compound 4 (473 mg, yield = 88%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.01 (s, 2H), 3.94 (d, *J* = 6.9 Hz, 4H), 2.59 (d, *J* = 7.2 Hz, 4H), 1.98-1.90 (m, 2H), 1.73-1.67 (m, 2H), 1.57-1.23 (m, 32H), 0.97-0.87 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 152.62, 150.61, 140.78, 133.33, 132.06, 116.93, 112.96, 78.31, 40.30, 40.01, 33.80, 32.47, 30.25, 29.03, 28.76, 25.68, 23.56, 23.09, 14.15, 10.98, 10.84.

Synthesis of compound **4a**: compound 3 (362 mg, 0.463 mmol) was added in a 25 mL Schlenk flask followed by several cycles of nitrogen degassing, and THF (10 mL) was added under argon protection. After that, LDA (3.706 mmol) was slowly added dropwise at -78 °C and reacted for 2 h. Boronic ester (0.756 mL, 3.706 mmol) was then added dropwise at -78 °C under argon protection and the reaction was allowed to room temperature for 12 h. The reaction was quenched with cold methanol and removed the solvent under pressure. The residue was washed with H_2O and extracted with EA, obtaining the crude product.

Synthesis of compound **6b**: compound 4 (176 mg, 0.187 mmol), Compound 5b (181 mg, 0.561 mmol), $Pd(PPh_3)_4$ (22 mg, 0.0187 mmol) and K_2CO_3 (160 mg, 1.122 mmol) were added in a 25 mL Schlenk flask followed by several cycles of nitrogen degassing, and THF (10 mL) and H_2O (1 mL) were added under argon protection. The reaction mixture was then transferred to a 90 °C oil bath and stirred for 12 h. Subsequently, the solvent was removed under pressure and the remaining residue was dissolved in DCM, washed with H_2O and extracted with DCM, obtaining the crude product. The crude product was further purified by column chromatography (eluent:

Hex:DCM = 20:1, v/v), yielding the compound 6b (175 mg, yield = 80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.14 (s, 2H), 7.31 (d, *J* = 5.1 Hz, 2H), 6.96 (d, *J* = 5.1 Hz, 2H), 3.98-3.95 (m, 4H), 2.52 (d, *J* = 7.2 Hz, 8H), 1.00-1.94 (m, 2H), 1.63-1.56 (m, 4H), 1.30-1.13 (m, 48H), 0.90-0.84 (m, 18H), 0.82-0.74 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 152.80, 151.02, 141.24, 140.93, 133.50, 132.64, 131.94, 129.55, 128.80, 125.21, 117.27, 78.17, 40.39, 40.31, 33.21, 33.18, 32.75, 32.69, 32.66, 30.33, 29.69, 29.14, 28.87, 28.79, 28.75, 25.80, 25.76, 23.62, 23.12, 23.06, 23.01, 14.16, 14.10, 14.08, 11.03, 10.87, 10.78, 10.74.

Synthesis of compound **6c**: compound 4 (93 mg, 0.1 mmol), compound 5c (95 mg, 0.297 mmol), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), and K_2CO_3 (82 mg, 0.59 mmol) were added in a 25 mL Schlenk flask followed by several cycles of nitrogen degassing, and THF (10 mL) and H_2O (1 mL) were added under argon protection. The flask was then transferred to a 90 °C oil bath and stirred for 12 h. Subsequently, the solvent was removed under pressure and the remaining residue was dissolved in DCM, washed with H_2O and extracted with DCM, obtaining the crude product. The crude product was further purified by column chromatography (eluent: Hex:DCM = 8:1, v/v), yielding the compound 6c (102 mg, yield = 88%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.13 (s, 2H), 7.04 (s, 2H), 6.91 (s, 2H), 4.00 (d, *J* = 6.6 Hz, 4H), 2.82 (d, *J* = 7.2 Hz, 4H), 2.57 (d, *J* = 6.9 Hz, 4H), 2.05-1.97 (m, 2H), 1.80-1.72 (m, 2H),1.65-1.55 (m, 2H), 1.53-1.26 (m, 48H), 1.01-0.81 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 152.72, 151.03, 142.25, 137.99, 135.77, 134.30, 133.71, 131.42, 127.87, 121.00, 117.17, 78.24, 40.38, 40.17, 34.57, 33.47, 32.53, 30.35, 29.20, 28.95, 28.64, 25.69, 23.64, 23.14, 23.05, 14.16, 14.12, 11.07, 10.88, 10.72.

Synthesis of compound **7a**: compound 4a (154 mg, 0.149 mmol), compound 4b (110 mg, 0.344 mmol), $Pd(PPh_3)_4$ (17 mg, 0.01 mmol) and K_2CO_3 (123 mg, 0.89 mmol) were taken into a 25 mL Schlenk flask and purged with argon for 0.5 hours. Under an argon atmosphere, THF (10 mL) and H_2O (1 mL) were added. The flask was then transferred to a 90°C oil bath and stirred for 12 hours. Subsequently, the solvent was removed under pressure and the remaining residue was dissolved in DCM, washed with H_2O and extracted with DCM, obtaining the crude product. The crude product was

further purified by column chromatography (eluent: Hex:DCM = 1.5:1, v/v), yielding the compound 7a (462 mg, yield = 80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 9.81 (s, 2H), 8.05 (s, 2H), 7.56 (s, 2H), 4.03 (d, *J* = 5.7 Hz, 4H), 3.96 (d, *J* = 6.9 Hz, 4H), 2.84 (d, *J* = 7.2 Hz, 4H), 1.94-1.85 (m, 2H), 1.80-1.72 (m, 4H), 1.64-1.22 (m, 48H), 0.94-0.81 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 182.02, 154.27, 153.14, 150.94, 141.06, 137.59, 134.45, 133.56, 129.77, 128.10, 125.88, 123,35, 117.28, 78.14, 74.53, 40.29, 40.02, 39.61, 34.28, 32.51, 30.27, 30.23, 29.66, 29.01, 28.65, 25.69, 23.71, 23.51, 23.06, 22.98, 14.13, 14.04, 11.11, 10.91, 10.69.

Synthesis of compound **7b**: a 100 mL Schlenk flask was evacuated and purged with argon for 0.5 h. DMF (4 mL) was added under argon protection, followed by slow dropwise addition of 0.5 mL of $POCl_3$. The reaction was carried out at 0 °C for 1 hour. Compound 6b (226 mg, 0.19 mmol) was placed in a 100 mL round-bottom flask under vacuum for 0.5 h. DCM (20 mL) was added under argon protection, and the DCM solution of 6b was added in portions to the 100 mL Schlenk flask. The reaction was allowed to proceed at room temperature for 2 h, followed by overnight reaction at 80 °C. The reaction was quenched with $NaHCO_3$ in an ice bath. Subsequently, the solvent was removed under pressure and the residue was dissolved in DCM, washed with H_2O and extracted with DCM, obtaining the crude product. The crude product was further purified by column chromatography (eluent: Hex:DCM = 2:1, v/v), yielding the compound 7b (179 mg, yield = 77%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 9.90 (s, 2H), 8.23 (s, 2H), 7.66 (s, 2H), 4.00-3.98 (m, 4H), 2.59-2.55 (m, 8H), 1.99-1.95 (m, 2H), 1.66-1.57 (m, 4H), 1.39-1.13(m, 48H), 0.92-0.85 (m, 14H), 0.84-0.76 (m, 22H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 182.85, 152.88, 150.77, 142.68, 142.42, 141.76, 140.86, 137.94, 134.74, 133.00, 130.12, 117.10, 78.36, 40.41, 40.36, 40.30, 33.33, 33.11, 32.60, 30.30, 29.09, 28.76, 28.71, 25.74, 25.67, 23.59, 23.07, 22.99, 22.93, 14.10, 14.04, 10.99, 10.74, 10.70.

Synthesis of compound **7c**: a 25 mL Schlenk flask was evacuated and purged with argon for 0.5 h, and DMF (3 mL) was added under argon protection, followed by slow dropwise addition of 0.4 mL $POCl_3$ at 0 °C for 1 h. compound 6c (120 mg, 0.10 mmol) was added in a 100 mL round-bottom flask followed by several cycles of nitrogen

degassing. After that, DCM (10 mL) was added under argon protection and the DCM solution of 6c was added in portions to the 25 mL Schlenk flask and reacted for 2 h at room temperature, followed by overnight reaction at 80 °C. The reaction was quenched with $NaHCO_3$ in an ice bath. Subsequently, the solvent was removed under pressure and the residue was dissolved in DCM, washed with H_2O and extracted with DCM, obtaining the crude product. The crude product was further purified by column chromatography (eluent: Hex:DCM = 2:1, v/v), yielding the compound 7c (110 mg, yield = 82%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 10.02 (s, 2H), 8.21 (s, 2H), 7.12 (s, 2H), 4.01 (d, *J* = 6.9 Hz, 4H), 2.90-2.86 (m, 8H), 2.05-1.96 (m, 2H), 1.83-1.75 (m, 2H),1.70-1.64 (m, 2H), 1.62-1.27 (m, 48H), 0.95-0.86 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 181.71, 152.96, 152.49, 150.72, 145.27, 140.71, 137.12, 134.94, 133.50, 132.21, 129.12, 117.11, 78.46, 41.58, 40.38, 40.07, 33.90, 32.74, 32.51, 32.45, 30.30, 29.14, 28.79, 28.59, 25.70, 23.59, 23.07, 23.04, 22.93, 14.08, 14.05, 14.04, 11.03, 10.76, 10.69.

Synthesis of **BT-4T-1**: compound 7a (32 mg, 0.025 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-2F) (13 mg, 0.058 mmol) were added in a 25 mL Schlenk flask followed by several cycles of nitrogen degassing, and CF (5 mL) and pyridine (0.1 mL) were added under argon protection. The reaction proceeded overnight at room temperature. The residue was washed with methanol to get a solid. After column chromatography (eluent: Hex:DCM = 1:1, v/v), BT-4T-1 was obtained (31 mg, yield = 75%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.73 (s, 2H), 8.55-8.50 (m, 2H), 8.10 (s, 2H), 7.71-7.64 (m, 4H), 4.14 (d, *J* = 5.1 Hz, 4H), 4.00 (d, *J* = 6.6 Hz, 4H), 3.08 (d, *J* = 7.5 Hz, 4H), 1.94-1.81 (m, 6H), 1.57-1.19 (m, 48H), 1.01-0.94 (m, 8H), 0.93-0.81 (m, 28H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 185.58, 158.48, 155.68, 153.63, 150.84, 143.64, 137.39, 136.80, 136.59, 136.52, 134.82, 132.51, 131.19, 128.76, 121.15, 117.52, 114.96, 114.66, 114.56, 112.52, 112.28, 78.35, 74.82, 68.52, 40.38, 39.73, 35.68, 32.35, 30.35, 30.25, 29.12, 29.00, 28.55, 25.39, 23.88, 23.53, 23.19, 23.08, 23.02, 14.206, 14.08, 14.07, 11.29, 10.89, 10.56. HRMS (ESI) m/z Calcd for $C_{96}H_{113}F_4N_6O_6S_5^+$ $[M+H]^+$ 1681.7183, found 1681.7256.

Synthesis of **BT-4T-2**: compound 7b (100 mg, 0.081 mmol) and IC-2F (47 mg, 0.2025 mmol) were added in a 25 mL Schlenk flask followed by several cycles of nitrogen degassing, and CF (5 mL) and pyridine (0.1 mL) were added under argon protection. The reaction proceeded overnight at room temperature. The residue was washed with methanol to get a solid. After column chromatography (eluent: Hex:DCM = 1:1, v/v), BT-4T-2 was obtained (103 mg, yield = 78%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.86 (s, 2H), 8.59-8.53 (m, 2H), 8.31 (s, 2H), 7.78 (s, 2H), 7.72-7.67 (m, 2H), 4.08-4.00 (m, 4H), 2.71-2.62 (m, 8H), 2.06-1.95 (m, 2H), 1.68-1.61 (m, 4H), 1.37-1.16 (m, 48H), 0.95-0.86 (m, 12H), 0.84-0.77 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 185.55, 158.61, 153.04, 150.71, 149.99, 147.25, 143.25, 142.22, 138.18, 136.20, 135.71, 134.59, 133.55, 130.32, 122.10, 117.12, 115.12, 114.83, 114.11, 113.97, 112.88, 112.64, 78.47, 70.35, 40.62,40.37, 33.66, 32.93, 32.59, 30.31, 29.11, 28.72, 25.67, 23.62, 23.12, 23.04, 22.98, 14.15, 14.08, 14.06, 11.02, 10.70. HRMS (ESI) m/z Calcd for $C_{96}H_{113}F_4N_6O_4S_5^+$ $[M+H]^+$ 1649.7289, found 1649.7358.

Synthesis of **BT-4T-3**: compound 7c (60 mg, 0.049 mmol) and IC-2F (26 mg, 0.112 mmol) were added in a 25 mL Schlenk flask followed by several cycles of nitrogen degassing, and CF (5 mL) and pyridine (0.1 mL) were added under argon protection. The reaction proceeded overnight at room temperature. The residue was washed with methanol to get a solid. After column chromatography (eluent: Hex:DCM = 1:1, v/v), BT-4T-3 was obtained (64 mg, yield = 80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.99 (s, 2H), 8.56-8.51 (m, 2H), 8.34 (s, 2H), 7.69-7.64 (m, 2H), 7.33 (s, 2H), 4.06 (d, J = 6.3 Hz, 4H), 3.01 (d, J = 7.2 Hz, 4H), 2.94 (d, J = 7.5 Hz, 4H), 2.12-2.02 (m, 2H), 1.93-1.82 (m, 2H),1.75-1.68 (m, 2H), 1.53-1.25 (m, 48H), 0.98-0.85 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ: 185.56, 161.29, 159.38, 153.28, 152.26, 150.56, 143.29, 136.14, 135.69, 134.70, 132.80, 132.54, 128.99, 119.90, 117.23, 114.98, 114.91, 114.63, 112.48, 112.25, 78.77, 68.50, 41.95, 40.53, 39.96, 34.95, 34.46, 32.42, 32.21, 30.35, 29.22, 28.71, 28.58, 25.55, 25.44, 23.68, 23.18, 23.16, 23.01, 14.19, 14.11, 11.14, 10.68, 10.62. HRMS (ESI) m/z Calcd for $C_{96}H_{113}F_4N_6O_4S_5^+$ $[M+H]^+$ 1649.7292, found 1649.7358.

Results and discussion

1. Device fabrication and measurements

OSC devices were made with an inverted configuration of ITO/ZnO/active layer/MoO_3/Ag. The ITO-coated glass substrates were cleaned by ultrasonicating sequentially in deionized water, detergent, and isopropanol for 20 min each. After the substrates were dried at 200 ^oC for 10 minutes, followed by plasma treatment for 10 minutes, then thin layers of sol-gel ZnO (30 nm) were spin-coated onto ITO glass (3500 rpm for 30 s). The films were annealed at 200 ^oC in air for 15 minutes. Subsequently, the substrates were transferred into a N_2-filled glove box for spin-coating the active layer. The active layer was dissolved with o-dichlorobenzene and stirred at 110 ^oC for at least 1 h to ensure a sufficient dissolution and spin coated on the top of ZnO modified glass substrates in the N_2-filled glove box with a donor concentration of 5.5 mg mL^{-1}. Finally, 4.5 nm thick MoO_3 film and 100 nm thick Ag layer were deposited sequentially by thermal evaporation at a pressure of 1.0×10^{-4} Pa. Six cells were fabricated on one substrate with an effective area of 0.04 cm^2. Current-voltage characteristics were recorded using an Enli Technology Ltd., Taiwan (SS-F53A) AAA class solar simulator under AM 1.5G with an intensity of 100 mW cm^{-2} as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 ^oC. The EQE measurements of OSCs are performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

Table S1. Photovoltaic parameters of PBDB-T:**BT-4T-1**, PBDB-T:**BT-4T-2** and PBDB-T:**BT-4T-3** OSCs with different blend ratios.

Active layer	D:A	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PBDB-T:BT-4T-1	1:0.8	0.80	7.99	46.49	2.98
PBDB-T:BT-4T-1	1:1.0	0.80	8.50	48.11	3.27
PBDB-T:BT-4T-1	1:1.2	0.79	7.65	48.74	2.94
PBDB-T:BT-4T-1	1:1.4	0.79	6.43	50.10	2.54
PBDB-T:BT-4T-2	1:0.8	0.92	9.67	53.94	4.78
PBDB-T:BT-4T-2	1:1.0	0.93	11.61	54.67	5.90
PBDB-T:BT-4T-2	1:1.2	0.93	12.24	56.00	6.40
PBDB-T:BT-4T-2	1:1.4	0.93	12.78	51.93	6.17
PBDB-T:BT-4T-3	1:0.8	0.92	13.92	49.43	6.30
PBDB-T:BT-4T-3	1:1.0	0.89	14.44	50.92	6.52
PBDB-T:BT-4T-3	1:1.2	0.89	15.35	49.99	6.86
PBDB-T:BT-4T-3	1:1.4	0.89	15.54	47.41	6.58

Table S2. Photovoltaic parameters of PBDB-T:**BT-4T-1**, PBDB-T:**BT-4T-2** and PBDB-T:**BT-4T-3** OSCs with different additive concentration.

Active layer	Additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PBDB-T:BT-4T-1	-	0.80	8.50	48.11	3.27
PBDB-T:BT-4T-1	0.2%DIO	0.79	8.27	48.34	3.16
PBDB-T:BT-4T-1	0.5%DIO	0.79	5.97	48.79	2.30
PBDB-T:BT-4T-1	0.7%DIO	0.78	4.41	45.64	1.57
PBDB-T:BT-4T-2	-	0.93	12.24	56.00	6.40
PBDB-T:BT-4T-2	0.2% DIO	0.92	11.71	58.58	6.32
PBDB-T:BT-4T-2	0.5% DIO	0.92	13.16	55.44	6.71
PBDB-T:BT-4T-2	0.7% DIO	0.92	12.19	54.46	6.12
PBDB-T:BT-4T-3	-	0.89	15.35	49.99	6.86
PBDB-T:BT-4T-3	0.2% DIO	0.89	14.54	52.90	6.83
PBDB-T:BT-4T-3	0.5% DIO	0.84	16.95	64.87	9.28
PBDB-T:BT-4T-3	0.7% DIO	0.82	15.98	62.23	8.15
PBDB-T:BT-4T-3	1.0% DIO	0.78	15.68	62.30	7.65

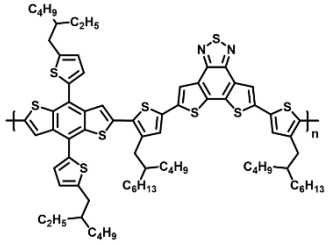
Table S3. Photovoltaic parameters of PBDB-T:**BT-4T-1**, PBDB-T:**BT-4T-2** and PBDB-T:**BT-4T-3** OSCs with different annealing temperature for 3 min.

Active layer	TA	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PBDB-T:BT-4T-1	-	0.80	8.50	48.11	3.27
PBDB-T:BT-4T-1	90 °C	0.79	8.62	46.57	3.15
PBDB-T:BT-4T-1	110 °C	0.78	8.80	49.55	3.42
PBDB-T:BT-4T-1	130 °C	0.79	8.14	49.90	3.22
PBDB-T:BT-4T-2	-	0.92	13.16	55.44	6.71
PBDB-T:BT-4T-2	90 °C	0.90	13.45	58.80	7.15
PBDB-T:BT-4T-2	110 °C	0.90	14.39	60.55	7.84
PBDB-T:BT-4T-2	130 °C	0.90	13.66	61.36	7.50
PBDB-T:BT-4T-3	-	0.84	16.95	64.87	9.28
PBDB-T:BT-4T-3	90 °C	0.88	15.39	53.14	7.16
PBDB-T:BT-4T-3	110 °C	0.86	14.70	58.38	7.42
PBDB-T:BT-4T-3	130 °C	0.85	11.80	52.71	5.31

2. Space charge limited current (SCLC) measurements

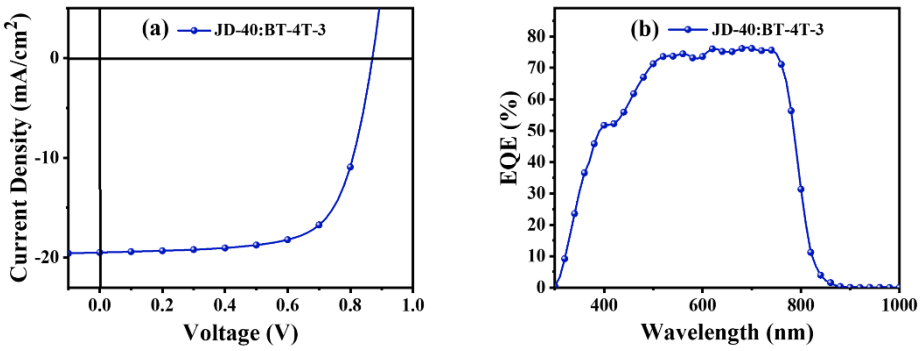
Hole-only/electron-only devices with a structure of ITO/PEDOT:PSS/Active Layer/MoO3/Ag and ITO/ZnO/Active Layer/PDINN/Ag were fabricated, respectively. Dark *J-V* curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method. The active layers were prepared under the same conditions as the optimal OSCs. Hole and electron mobilities of devices were calculated according to the Mott-Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, μ is electron mobility or hole mobility, ε_o is the permittivity of free space (ε_o =8.85×10^{-12} F/m), ε_r is the permittivity of the active layer (ε_r = 3 F/m), μ is mobility, and d is the thickness of the active layer.

3. Chemical structure of JD-40



JD-40

4. *J-V* (a)and EQE (b) curves of JD-40:BT-4T-3



5. Thermogravimetric (TGA) measurements

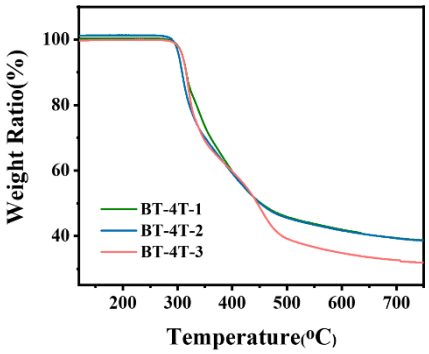


Figure S1. TGA curves of **BT-4T-1**, **BT-4T-2** and **BT-4T-3** under nitrogen atmosphere.

6. Quantum Chemistry Calculation

Table S4. Selected calculated absorption wavelength (nm), oscillator strength (f) and transition contributions of the acceptors in chloroform solvent at B3LYP/6-31G(d, p) level of theory.

Compound	Band	State	λ_{calc} (nm)	Oscillator strength (f)	Major transition contributions
BT-4T-1	I	1	846.4	2.7610	HOMO→LUMO (98%)
BT-4T-2	I	1	683.0	1.3575	HOMO→LUMO (95%)
	II	3	542.1	0.4980	HOMO→L+2 (85%), HOMO→L+4 (7%)
		7	490.0	0.2840	H-1→L+1 (64%), HOMO→L+4 (32%),
BT-4T-3	I	1	724.2	2.5360	HOMO→LUMO (96%)
	II	7	494.5	0.3672	HOMO→L+4 (71%), H-1→L+1 (23%)

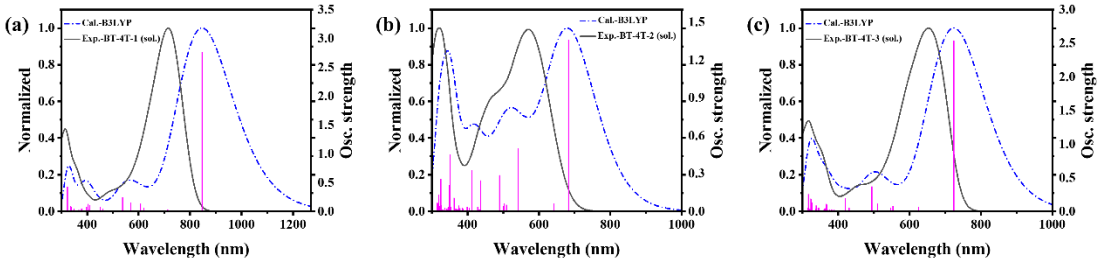


Figure S2. Normalized optical absorption spectra of (a) **BT-4T-1**, (b) **BT-4T-2** and (c) **BT-4T-3**: measured spectra in dilute CF solutions (black solid lines) and spectra computed within the TD-DFT approaches based on B3LYP (dash dot lines).

7. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements

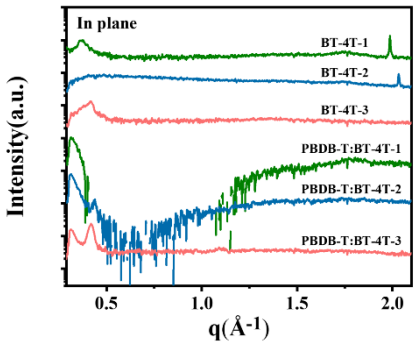


Figure S3. 1D intensity profiles for the corresponding films.

NMR and Mass Spectra

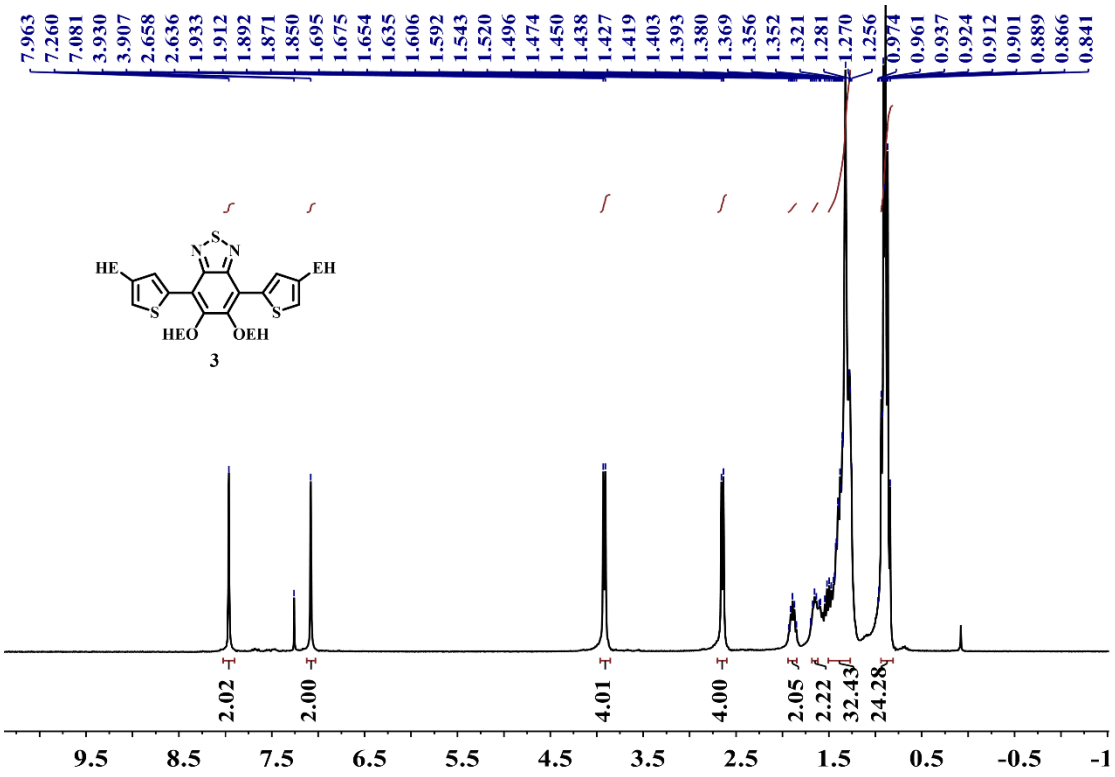


Figure S3. ^{1}H NMR of Compound **3**

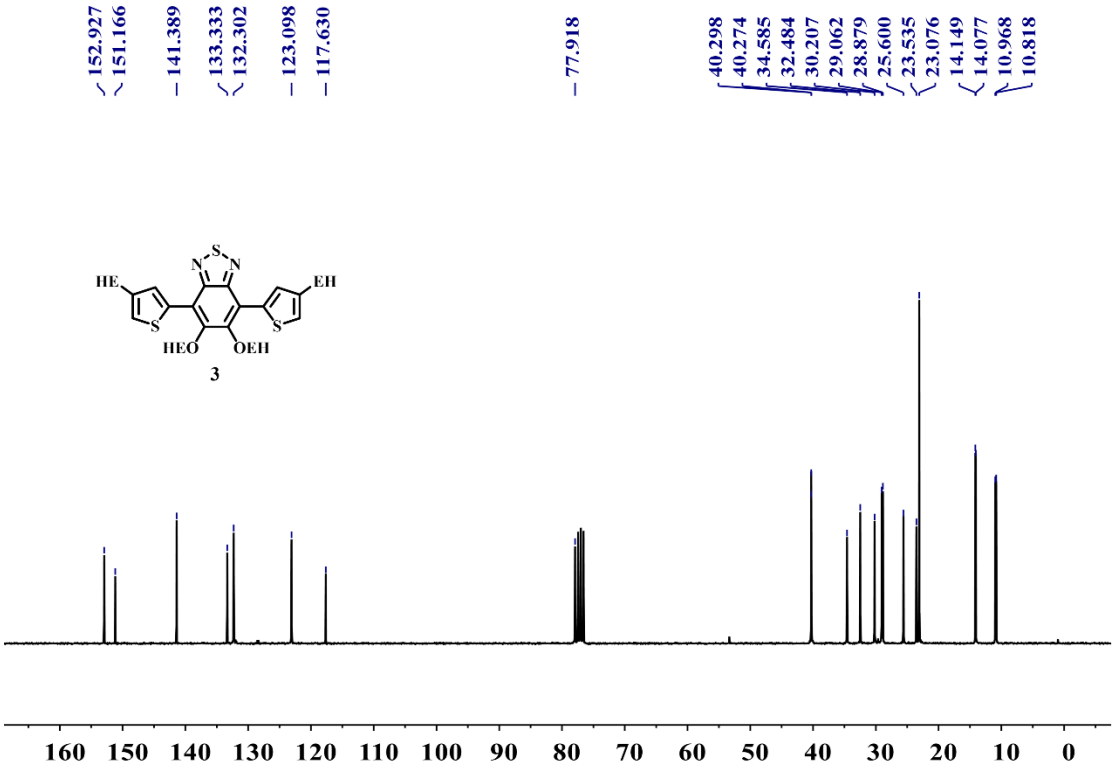


Figure S4. ^{13}C NMR of Compound **3**

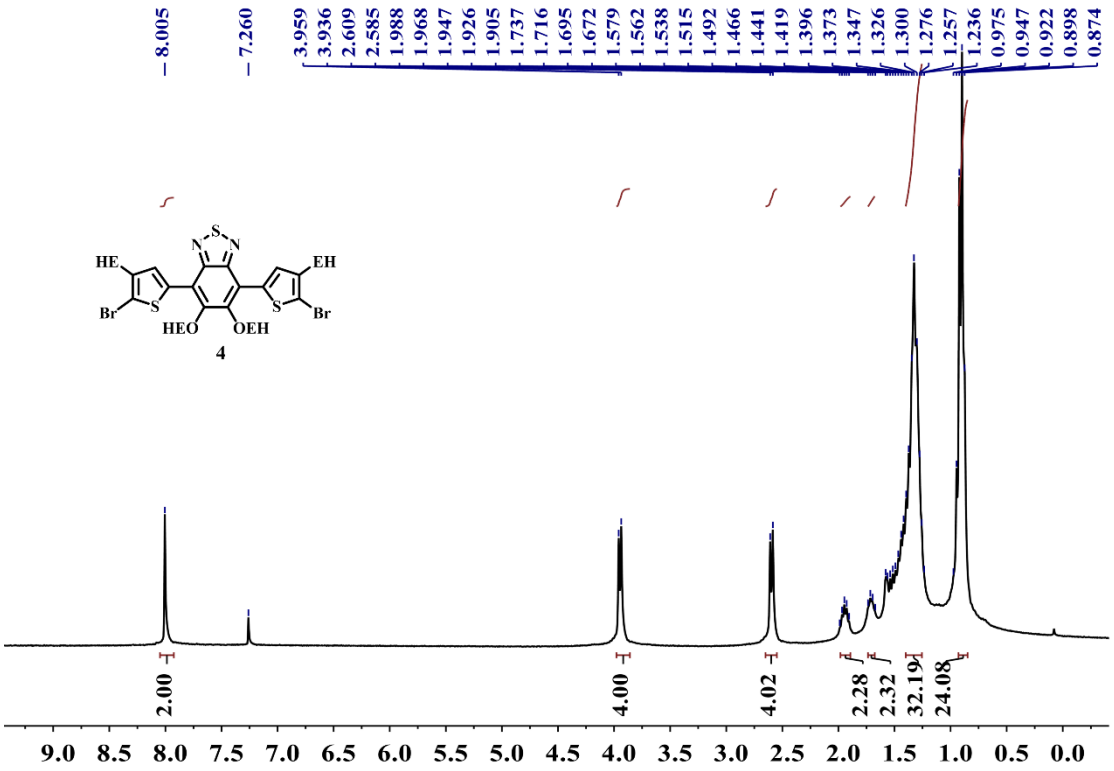


Figure S5. ^{1}H NMR of Compound **4**

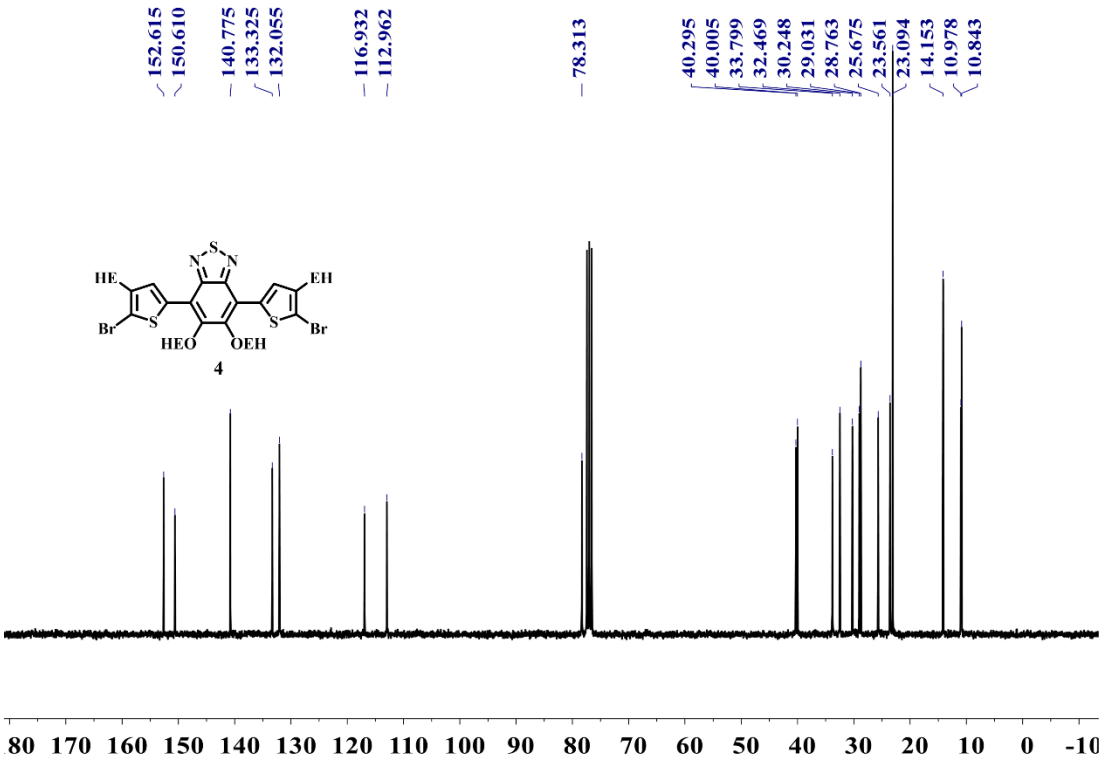


Figure S6. ^{13}C NMR of Compound **4**

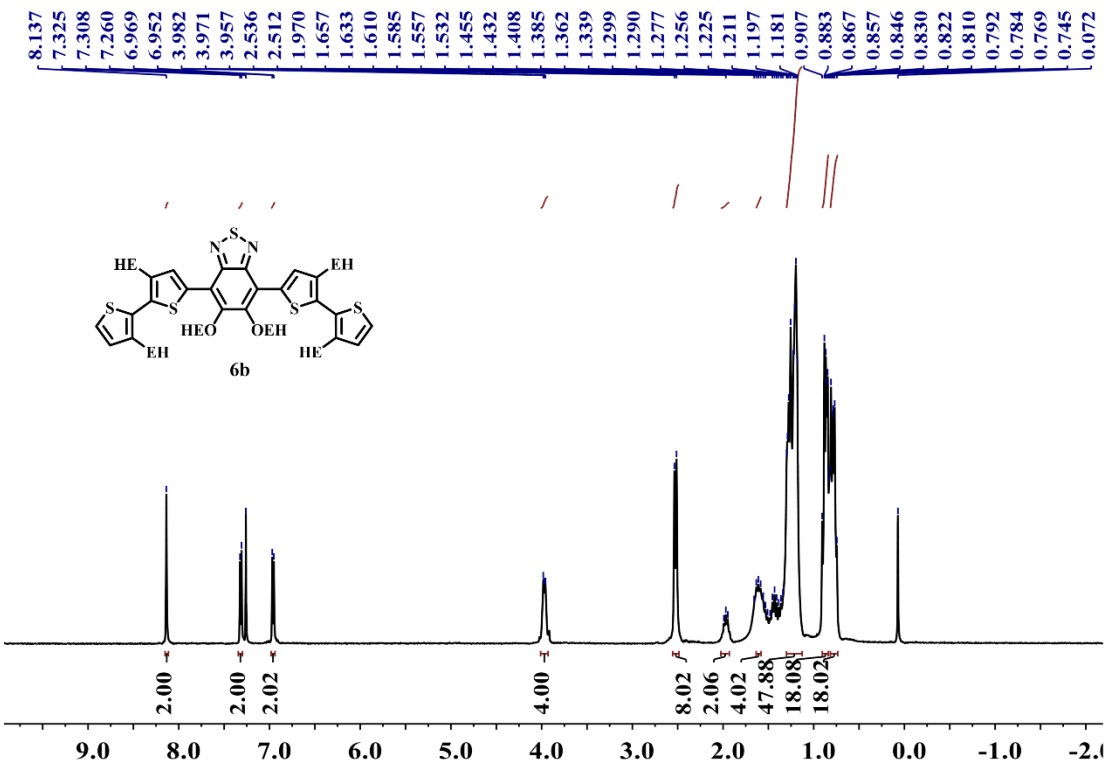


Figure S7. ^{1}H NMR of Compound **6b**

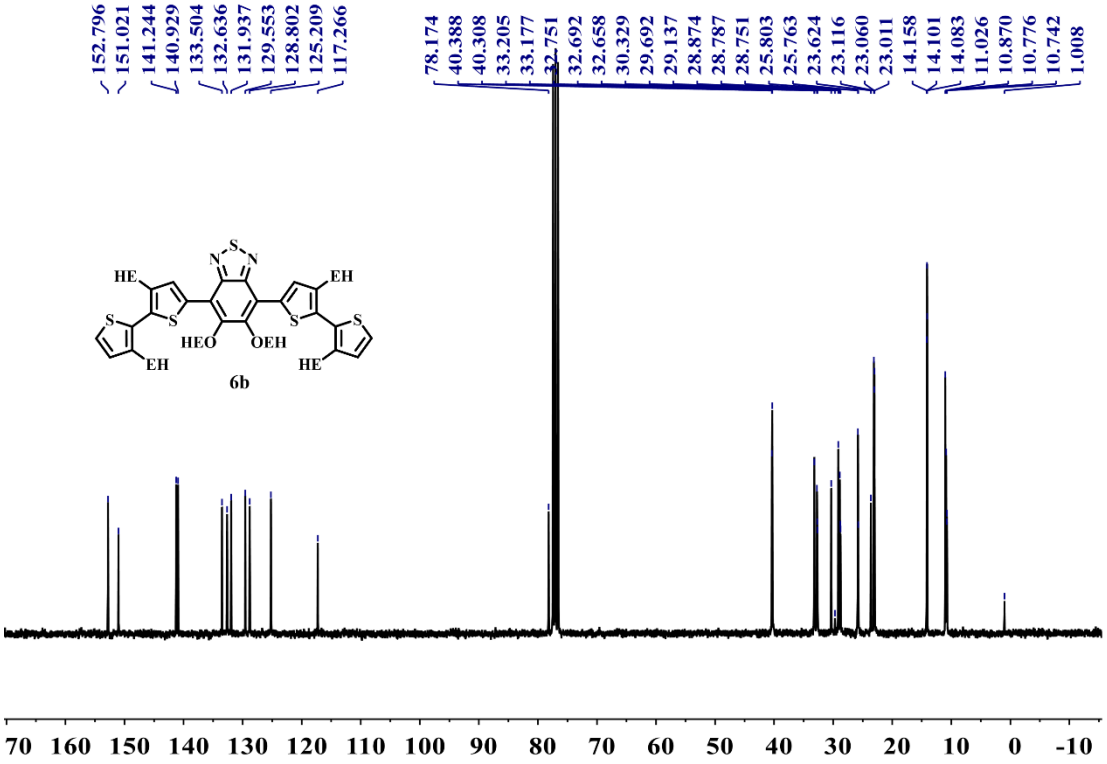


Figure S8. ^{13}C NMR of Compound **6b**

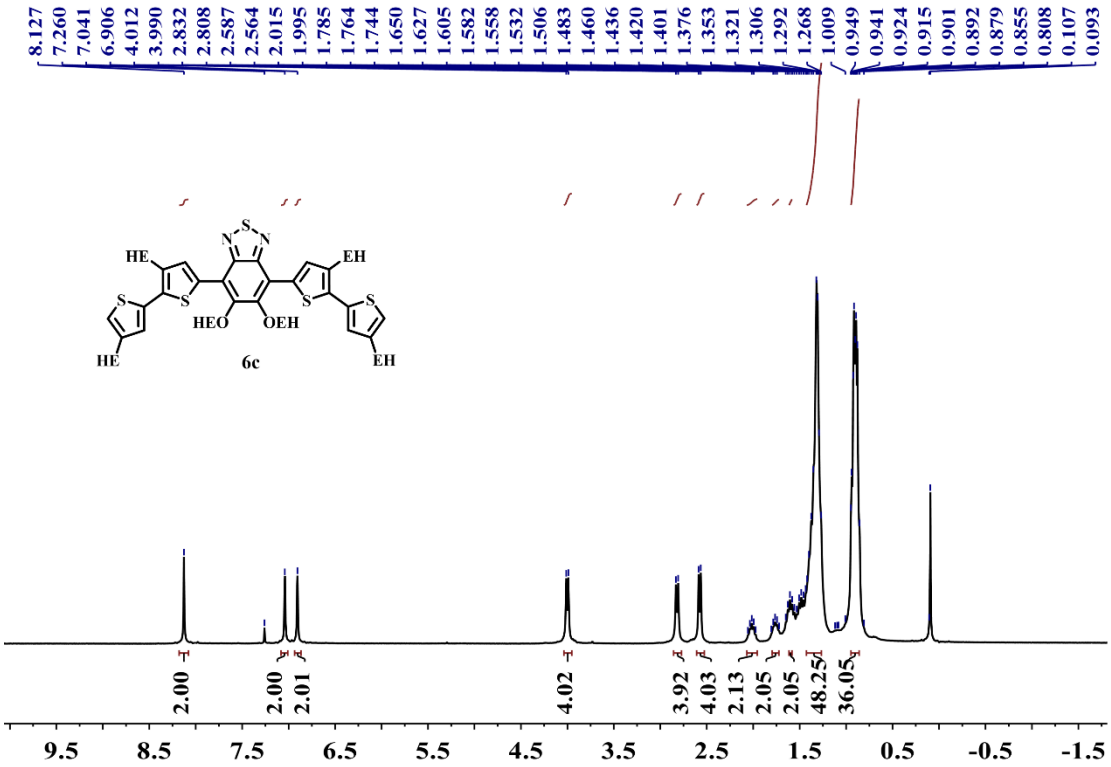


Figure S9. ^{1}H NMR of Compound **6c**

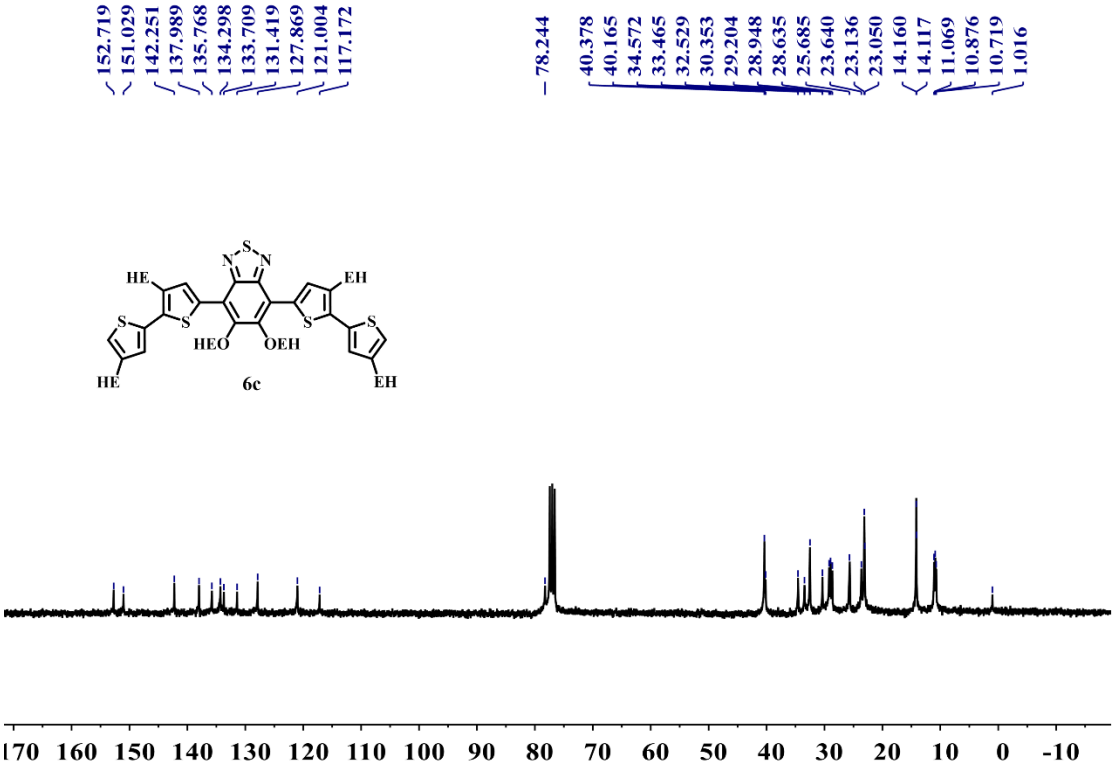


Figure S10. ^{13}C NMR of Compound **6c**

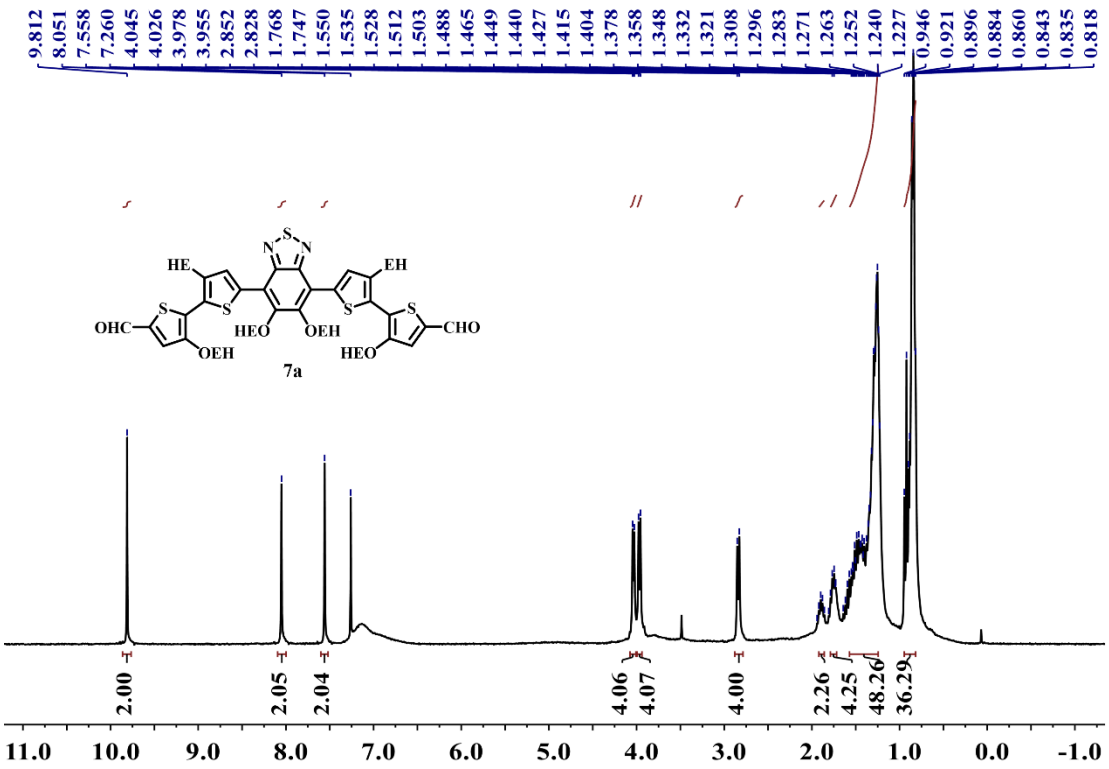


Figure S11. ^{1}H NMR of Compound **7a**

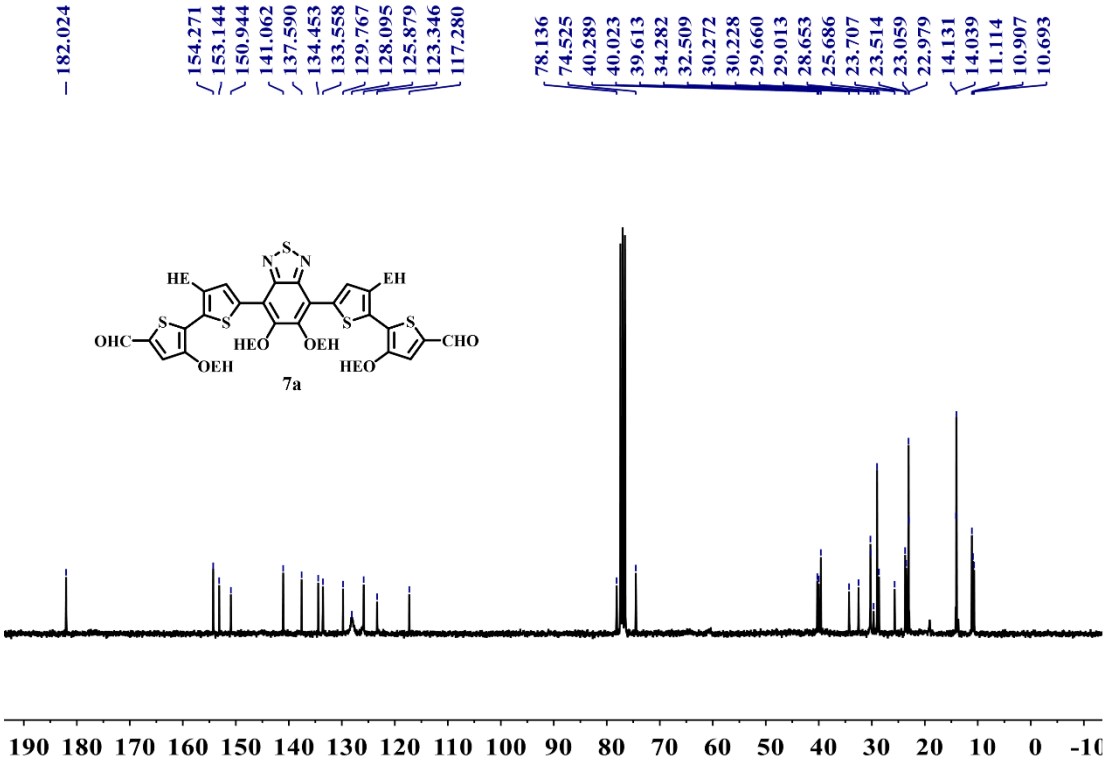


Figure S12. ^{13}C NMR of Compound **7a**

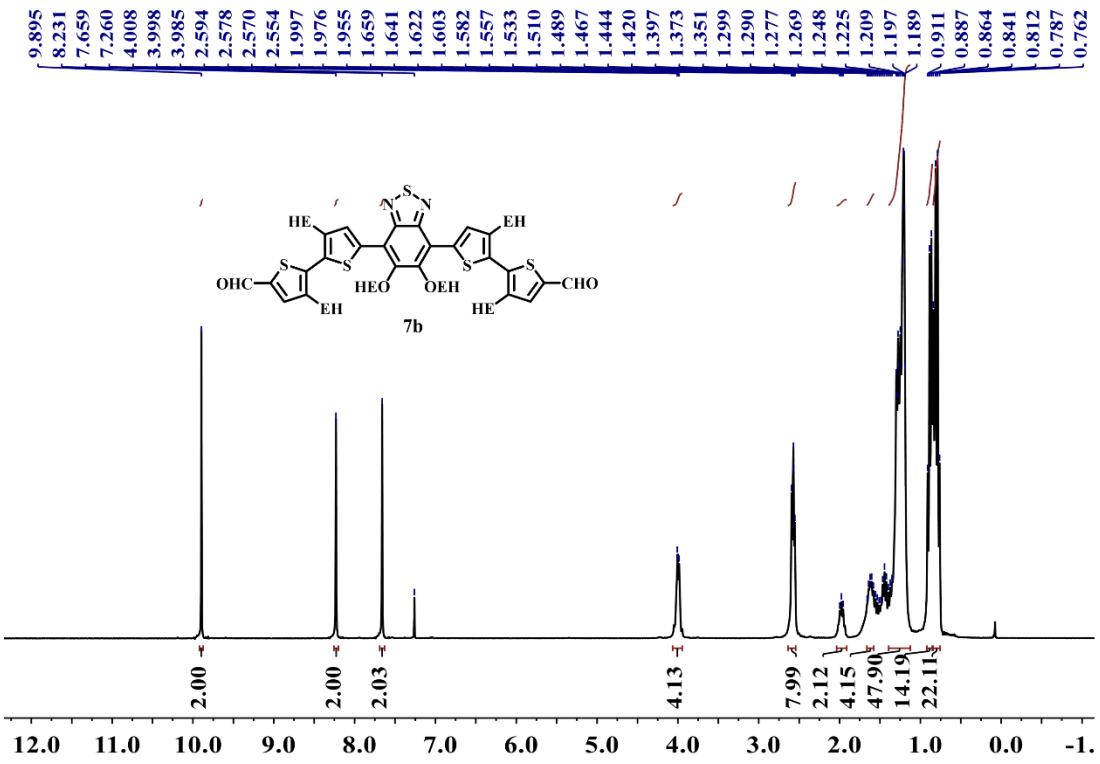


Figure S13. ^{1}H NMR of Compound **7b**

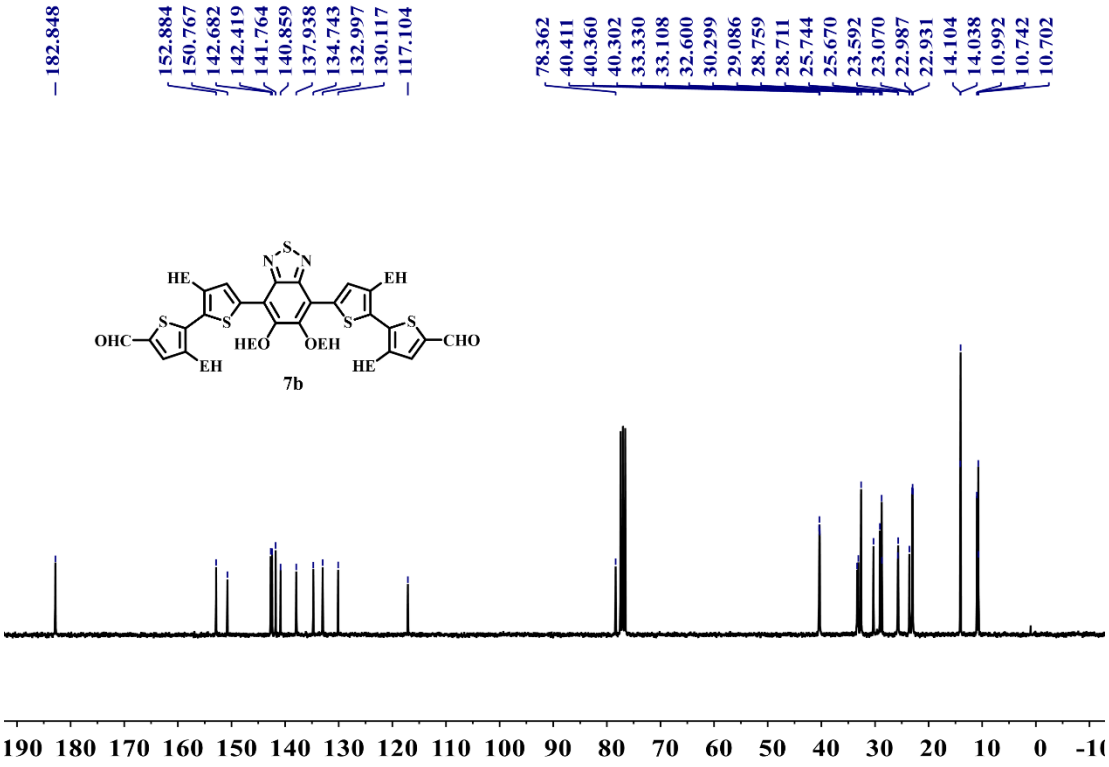


Figure S14. ^{13}C NMR of Compound **7b**

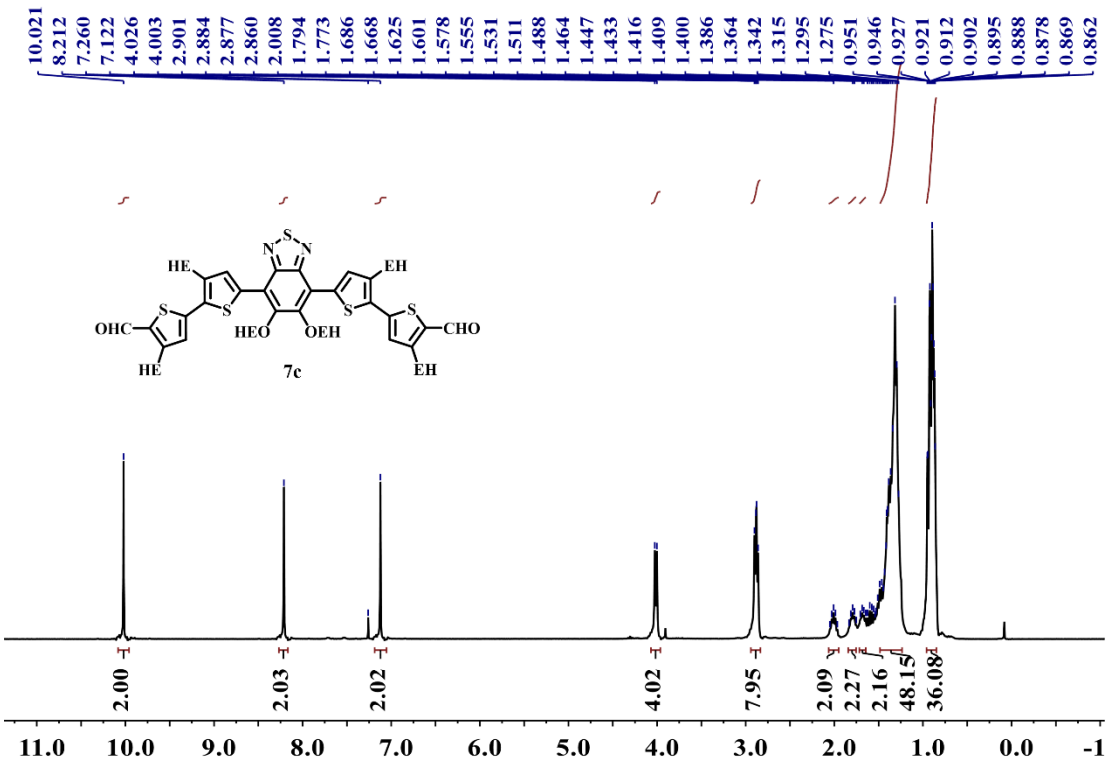


Figure S15. ^{1}H NMR of Compound **7c**

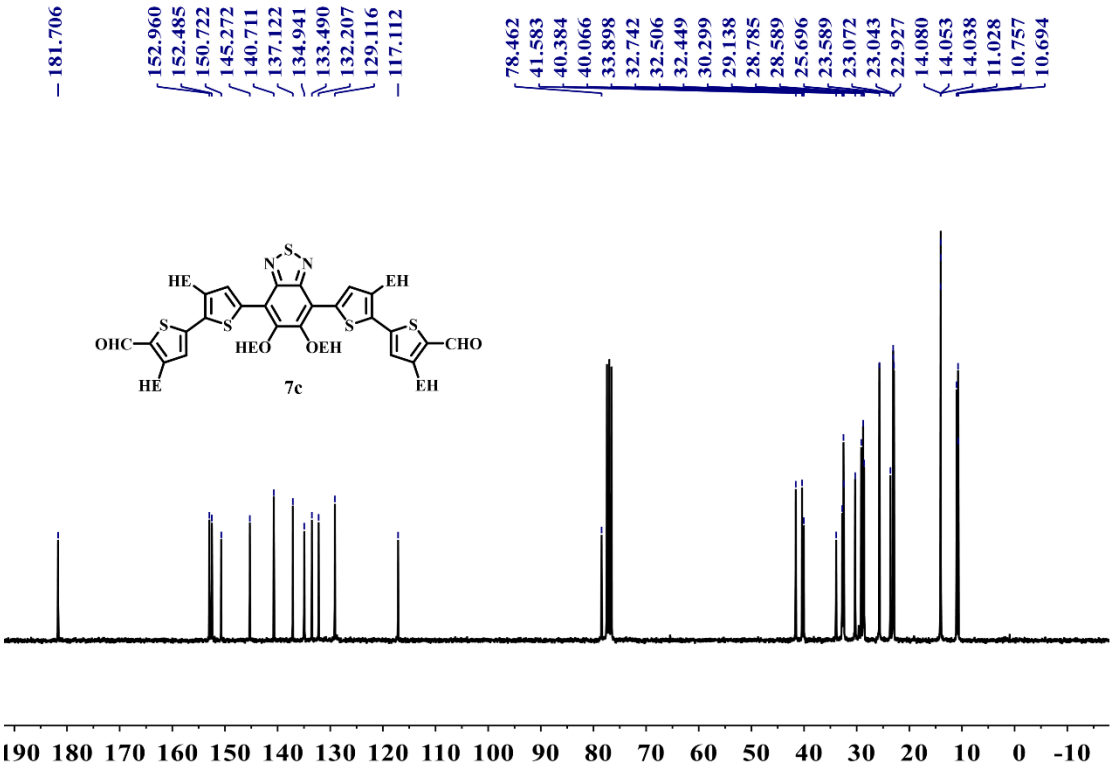


Figure S16. ^{13}C NMR of Compound **7c**

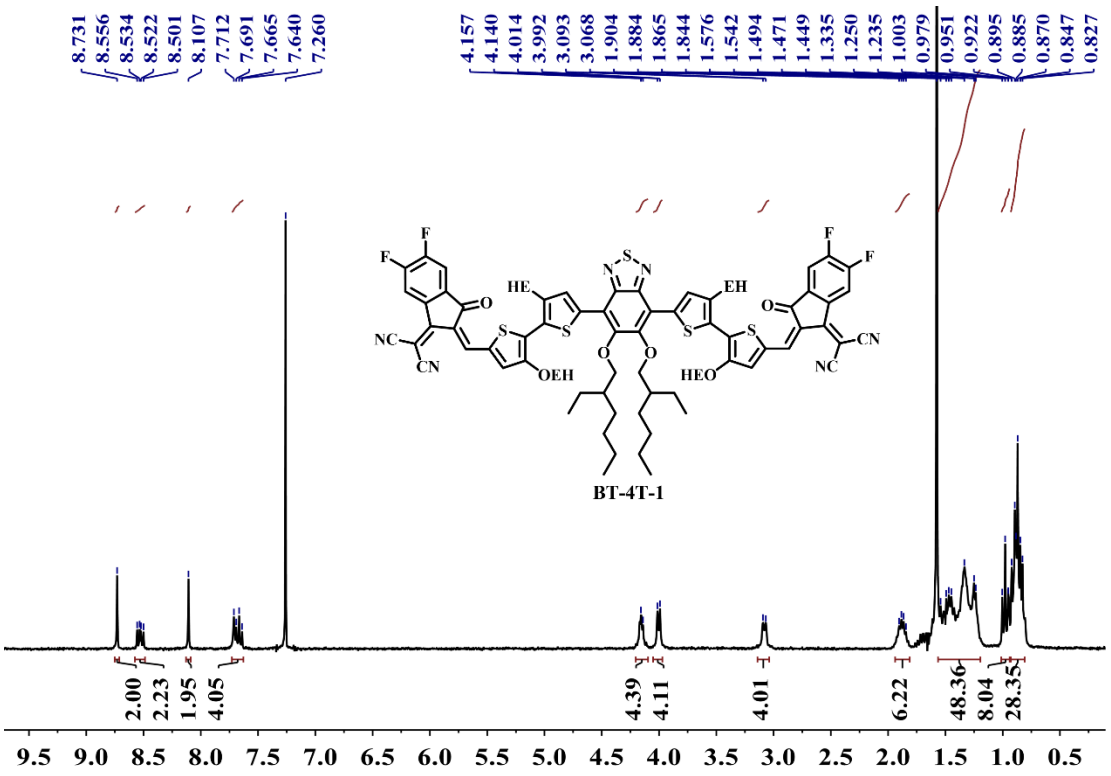


Figure S17. ^{1}H NMR of **BT-4T-1**

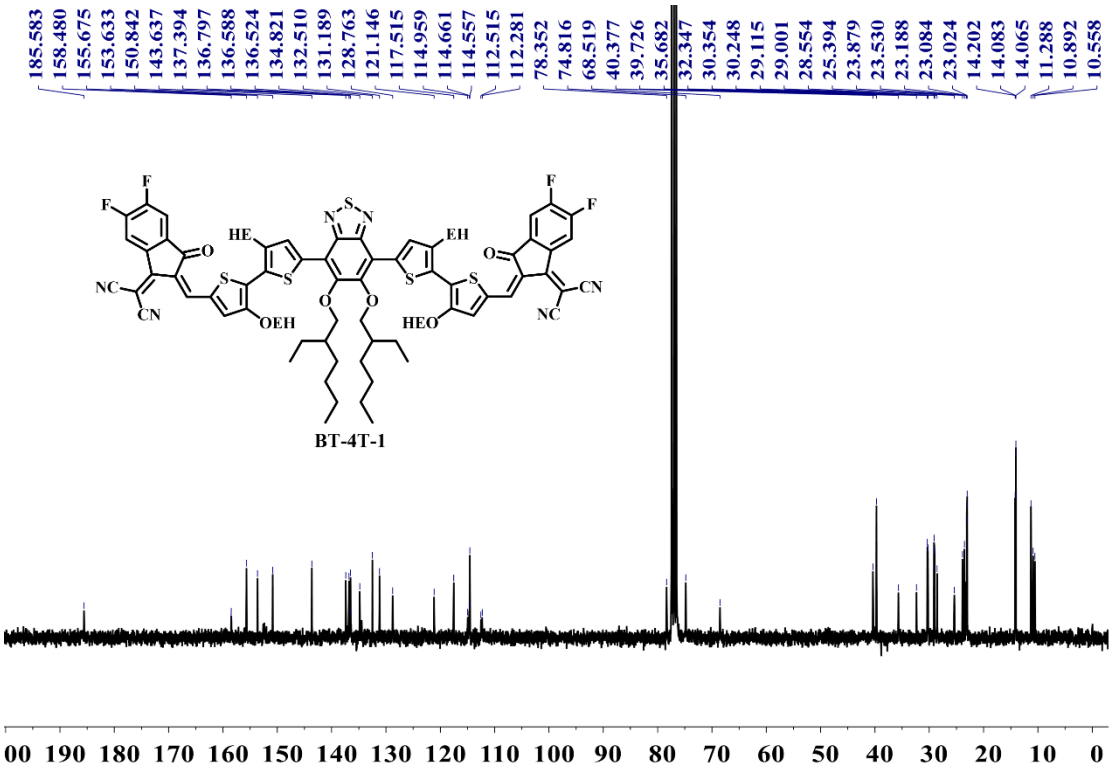


Figure S18. ^{13}C NMR of **BT-4T-1**

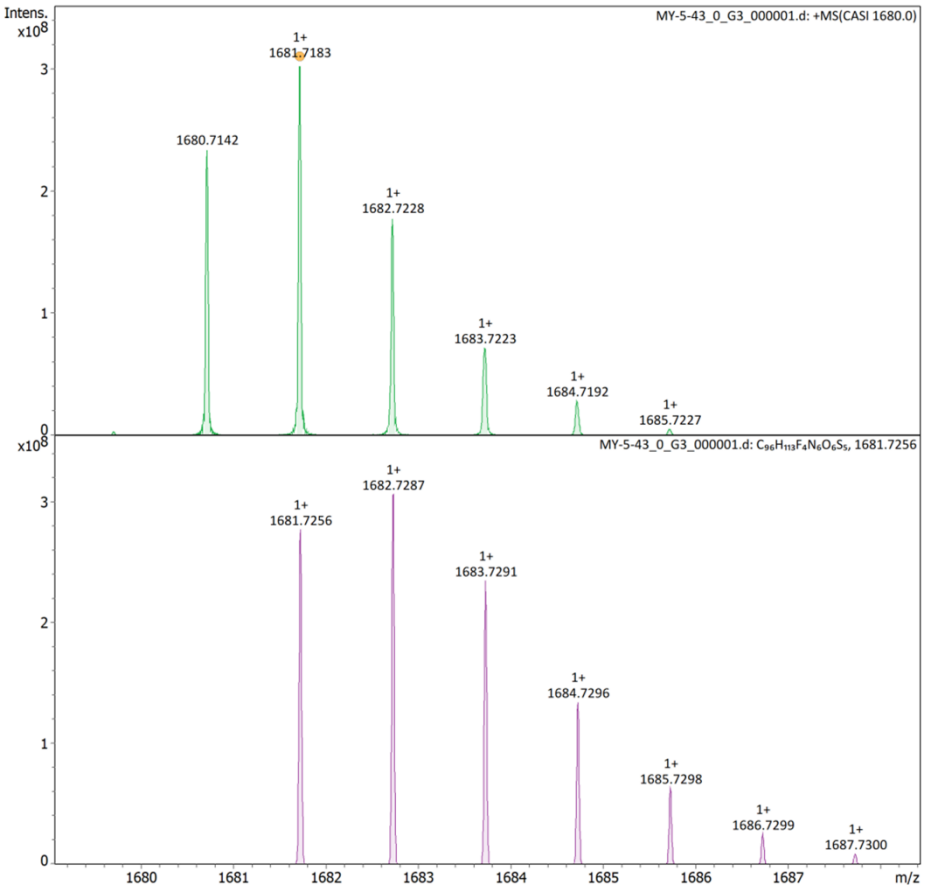


Figure S19. HR-FTMS of **BT-4T-1**

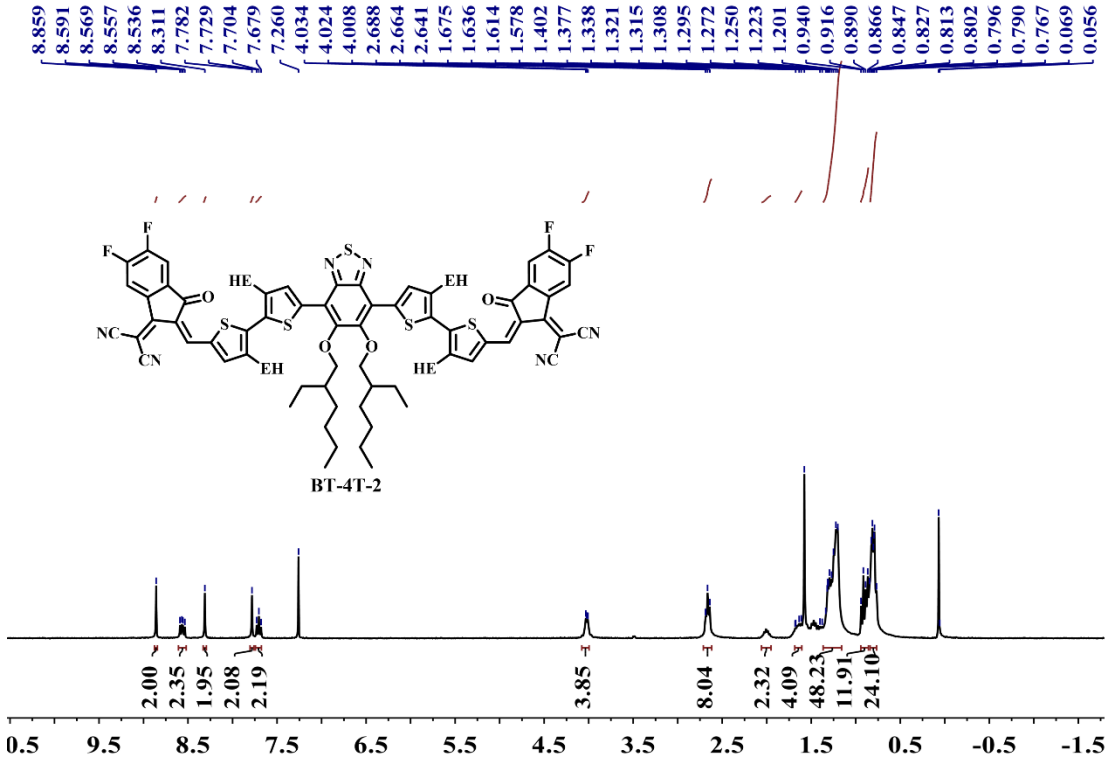


Figure S20. ^{1}H NMR of **BT-4T-2**

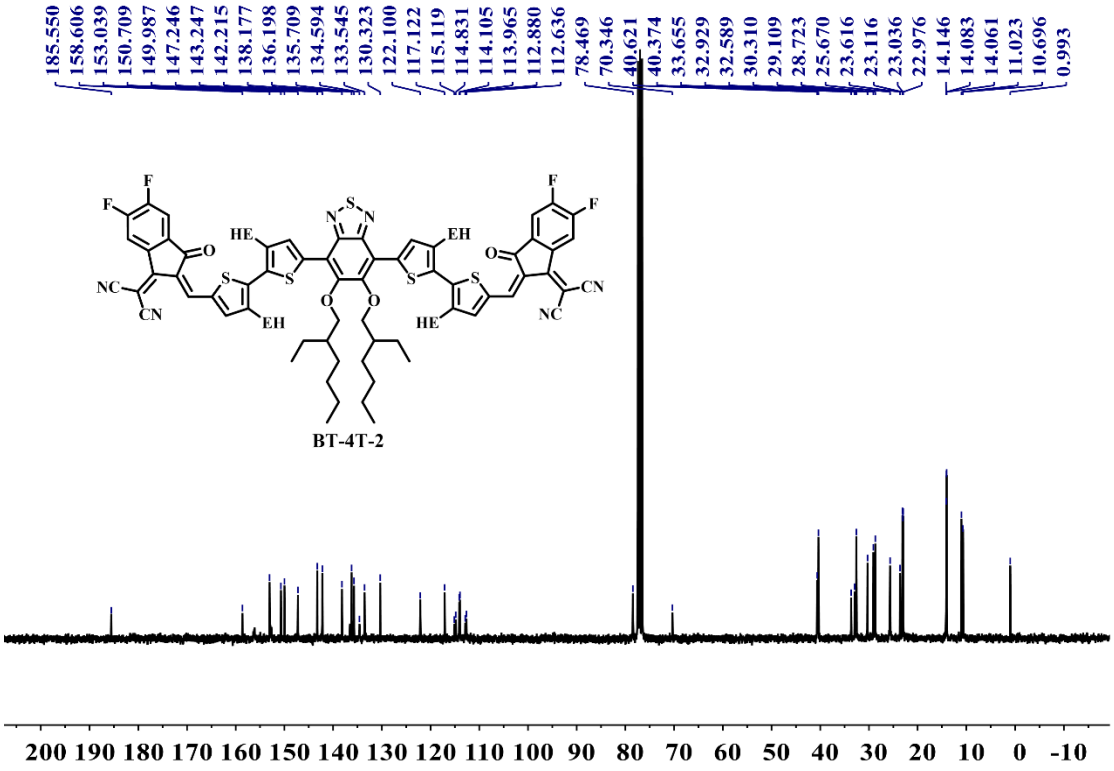


Figure S21. ^{13}C NMR of **BT-4T-2**

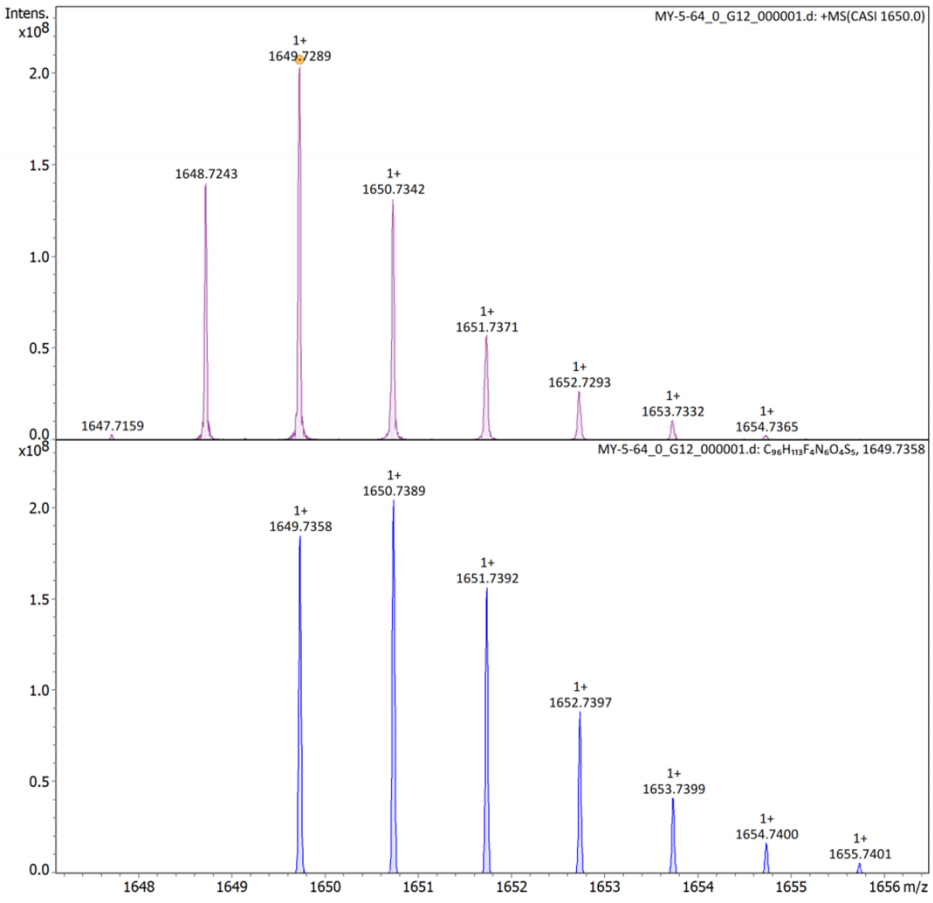


Figure S22. HR-FTMS of **BT-4T-2**

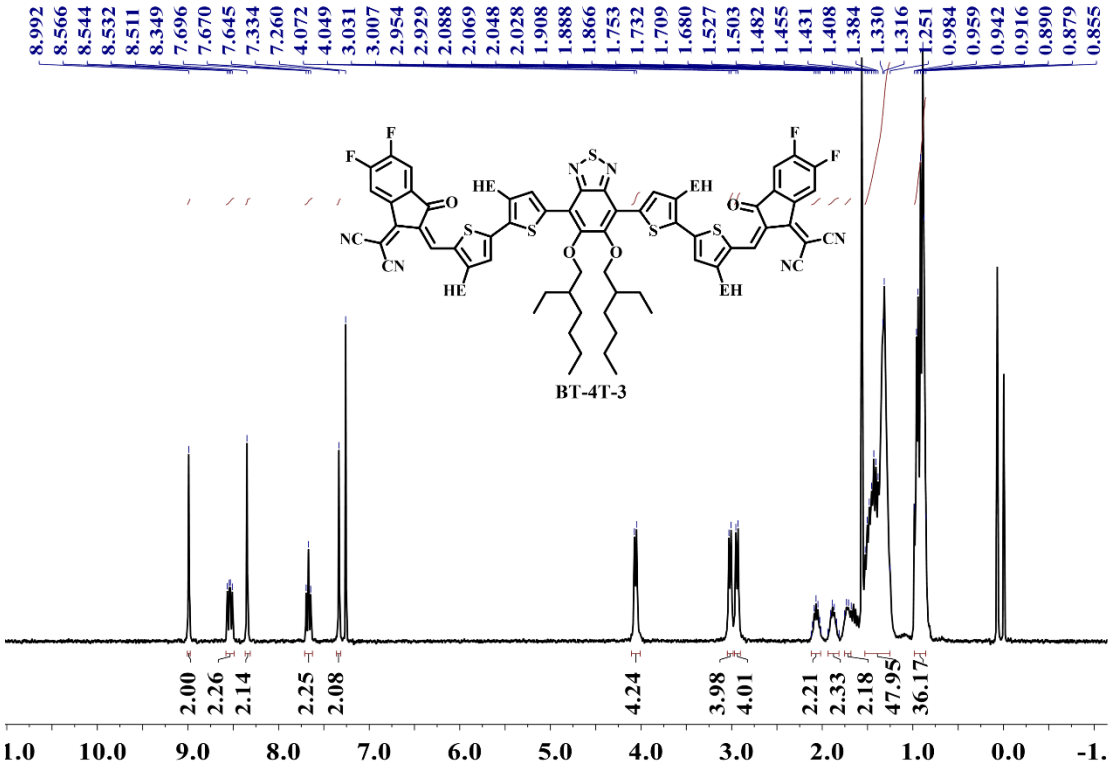


Figure S23. ^{1}H NMR of **BT-4T-3**

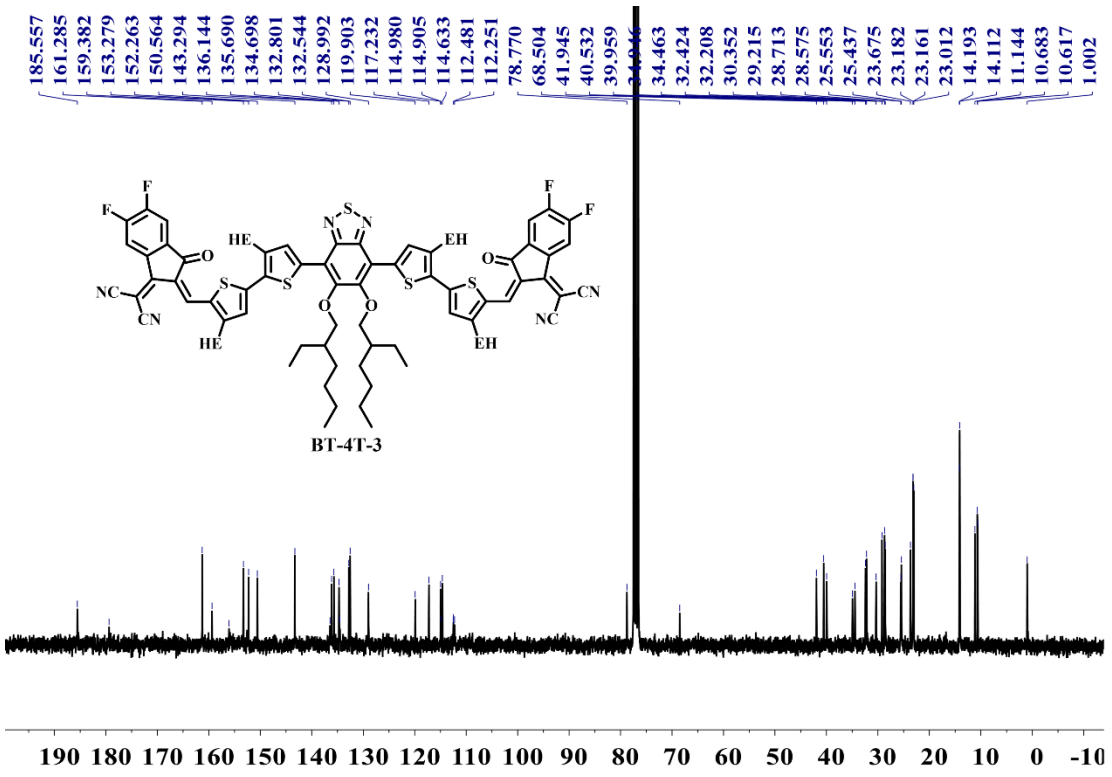


Figure S24. ^{13}C NMR of **BT-4T-3**

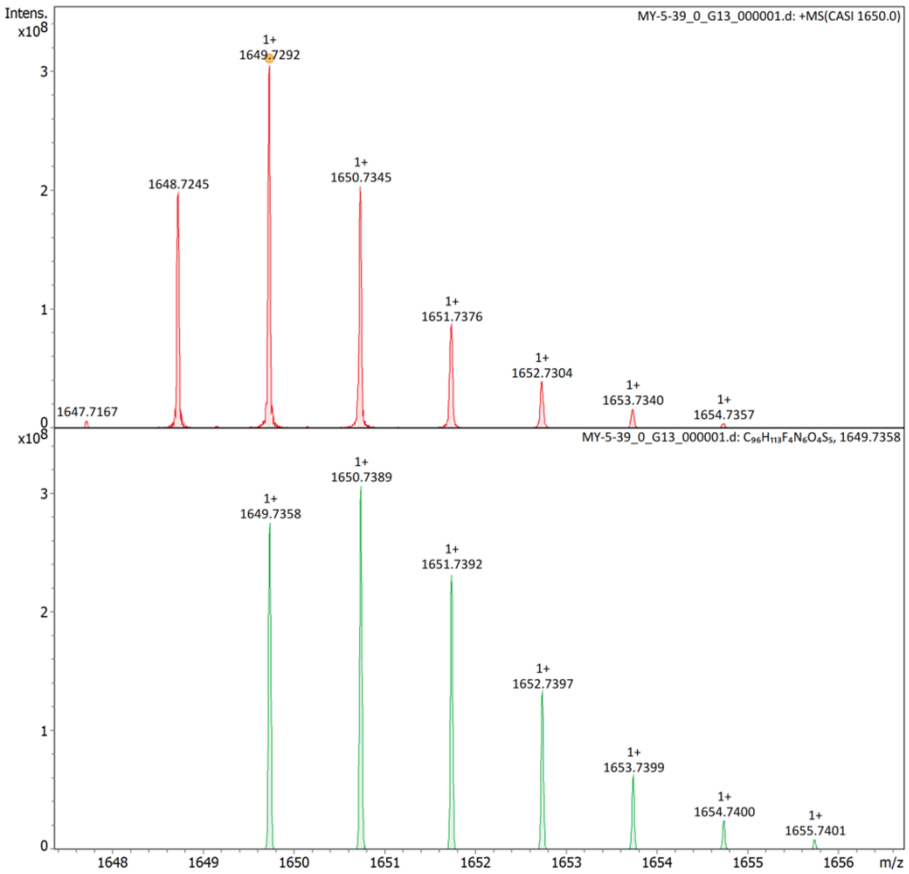


Figure S25. HR-FTMS of **BT-4T-3**