aSupporting Information

n-Type Polymer Semiconductors Based on Conformation-Locked π-Extended Bithieno[3,4-c]pyrrole-4,6-dione (BTPD) Acceptor Units for Organic Thermoelectrics

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DOI: xxxxxxxxxxxxxxxx

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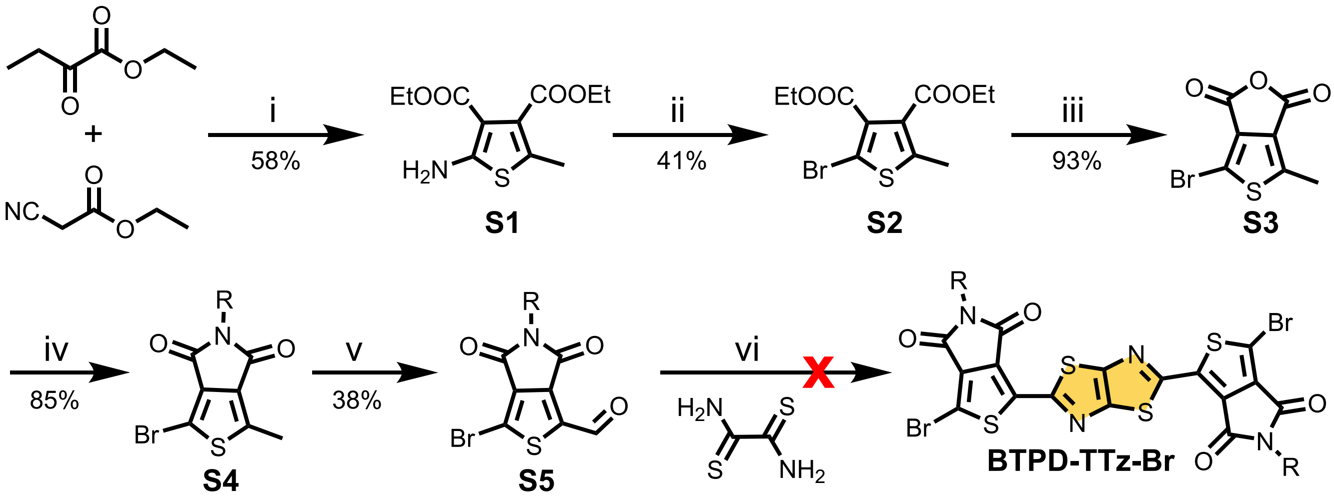
1. General methods

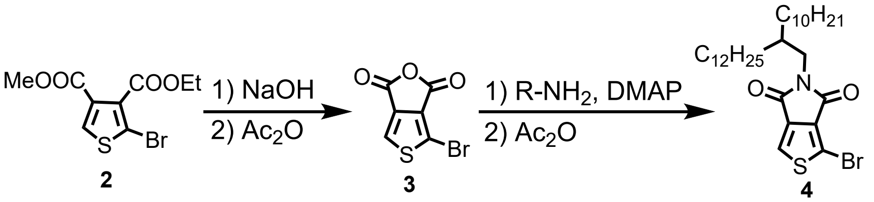
Column chromatography was performed on silica gel (200 - 300 mesh), and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates to visualize the course of reaction. ^{1}H-NMR and ^{13}C-NMR data were collected on a 400 or 600 MHz spectrometer. All chemical shifts are reported in ppm, relative to tetramethylsilane, using residual solvent peak as a reference standard. The following abbreviations were used to explain the multiplicities: *s* = singlet, *d* = doublet, *m* = multiplet. Cyclic voltammetry (CV) was performed on a Chenhua 650D electrochemical analyzer using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode in anhydrous solvents containing tetra-*n*-butyl-ammoniumhexa-fluorophosphate (TBAPF$_6$, 0.1 M) as supporting electrolyte at 298 K. The potential was externally calibrated against the ferrocene/ferrocenium couple. Absorption spectra were recorded on a Shimadzu UV-3600 plus. Polymer molecular weights were characterized using a Polymer Laboratories GPC-PL220 high-temperature GPC/SEC system (Agilent Technologies) at 150 °C, with polystyrene standards and trichlorobenzene as the eluent. Differential scanning calorimetry (DSC) curves were recorded on a NETZSCH STA449F5 in a nitrogen atmosphere with a heating rate of 10 °C /min, and thermogravimetric analysis (TGA) curves were collected on a NETZSCH DSC204F1 under the same conditions. The samples of AFM and GIWAXS were prepared under the optimized device fabrication conditions.AFM measurements were conducted using a Bruker Dimension Icon. The molecular packing and film crystallinity of the polymeric films were characterized by the grazing incidence wide-angle X-ray scattering (GIWAXS) at Shanghai Synchrotron Radiation Facility (SSRF).

2. Experimental and Material Characterization



Scheme S1. Failed synthetic attempts. i) Ethyl cyanoacetate, S$_8$, Et$_3$N, DMF; ii) 10% HBr (aq), CuBr$_2$, then NaOH (aq) 80 °C; iii) Ac$_2$O, reflux; iv) RNH$_2$, DMAP, 1, 4-dioxane, 90 °C, then Ac$_2$O, 140 °C; v) SeO$_2$, Celite, 1, 4-dioxane, 170 °C; vi) Dithiooxamide, DMF, reflux

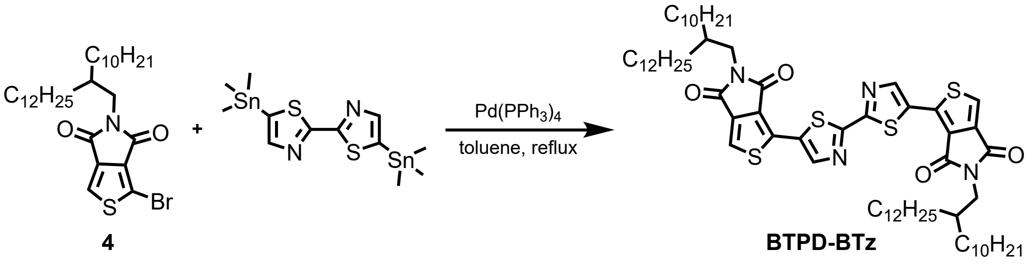
Synthesis of compound 4



Compound **4** was synthesized following a modified literature procedure.[1] Compound 2 (4.00 g, 13.65 mmol) was added to NaOH (1 M, 100 mL). The reaction mixture was stirred at 80 °C in a round-bottom flask overnight, acidified to pH = 3 with dilute HCl, and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to afford a crude white solid. This solid was refluxed in acetic anhydride (30 mL) for 12 h. After cooling to room temperature, the resulting precipitate was collected by filtration, washed with methanol, and dried in vacuo to yield compound **3** as a white solid (3.00 g, 95%). The product was used directly in the next step without further purification.

To a flask were added 4-dimethylaminopyridine (1.57 g, 12.87 mmol), R-NH_2 (4.55 g, 12.87 mmol), compound 3 (2.00 g, 8.58 mmol), and anhydrous 1,4-dioxane (20 mL). The reaction mixture was heated to 80 °C and stirred at this temperature overnight. After cooling to room temperature, acetic anhydride (20 mL) was added in one portion, and the mixture was reheated to 80 °C for 6 h. Upon completion, the mixture was cooled to room temperature, diluted with ethyl acetate (200 mL) and water (50 mL), and washed with brine (10 mL). After solvent removal, the residue was purified by silica gel chromatography (petroleum ether/dichloromethane = 1:5) to afford compound **4** as a colorless oil (2.50 g, 51%). ^{1}H NMR (600 MHz, chloroform-*d*): δ 7.72 (s, 1H), 3.48 (t, J = 7.20 H$_Z$, 2H), 1.82 (m, 1H), 1.33~1.23 (m, 40H), 0.87 (t, J = 6.84 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*): δ 161.89, 161.56, 136.63, 134.11, 126.53, 113.33, 42.88, 36.82, 31.90, 31.39, 29.92, 29.67, 29.65, 29.62, 29.59, 29.35, 29.33, 26.23, 22.68, 14.12. HRMS (MALDI TOF, m/z) calcd for $C_{30}H_{50}BrNO_2S$ $[M]^+$, 567.2746; found 567.2750. (error = +0.7 ppm).

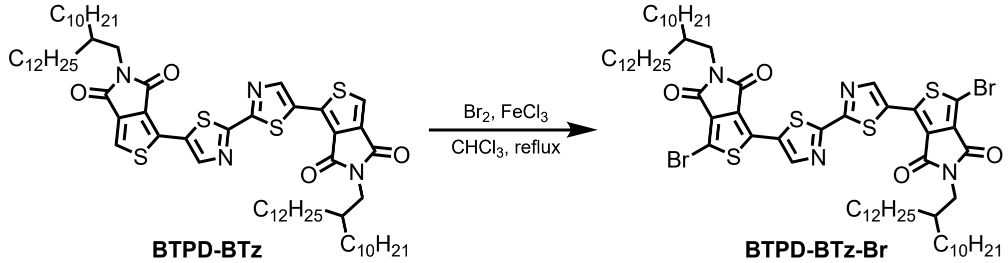
Synthesis of compound BTPD-BTz



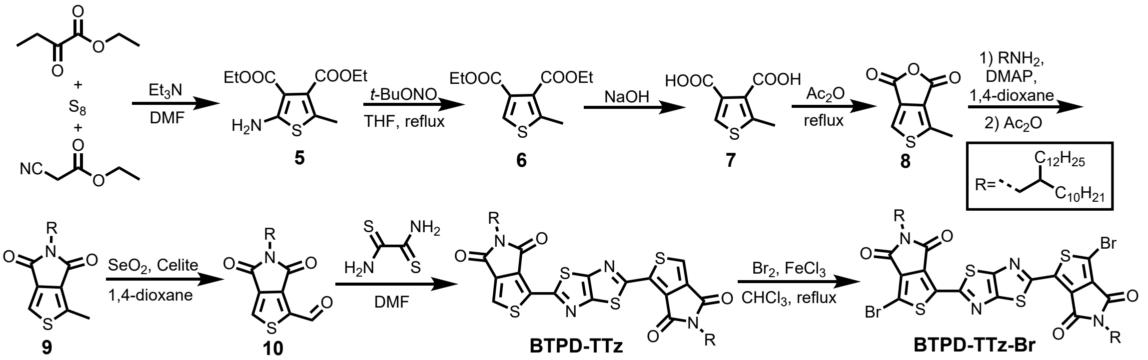
Compound **4** (864 mg, 1.52 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiazole (250 mg, 0.51 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and anhydrous toluene (20 mL) were added to a Schlenk tube under argon. The mixture was degassed via three freeze-pump-thaw cycles and backfilled with argon.

Triethylamine (0.74 mL, 5.32 mmol) was added, and the reaction mixture was stirred at 110 °C for 12 h. Reaction progress was monitored by TLC. Upon completion, the mixture was cooled to room temperature, diluted with dichloromethane (50 mL), and washed with brine (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 1:1) to afford **BTPD-BTz** as a yellow solid (498 mg, 86%). ^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.68 (s, 2H), 7.74 (s, 2H), 3.55 (d, *J* = 7.32 Hz, 4H), 1.87 (m, 2H), 1.32~1.16 (m, 80H), 0.87 (t, *J* = 6.84 Hz, 12H). ^{13}C NMR (150 MHz, Chloroform-*d*): δ 162.71, 162.33, 161.62, 145.32, 137.51, 134.49, 130.61, 130.38, 124.03, 42.98, 36.91, 31.91, 31.42, 29.97, 29.68, 29.65, 29.64, 29.60, 29.36, 29.34, 26.25, 22.68, 14.12. HRMS (MALDI TOF, m/z) calcd for $C_{66}H_{102}N_4O_4S_4[M]^+$, 1143.6784; found 1143.6744. (error = -3.8 ppm).

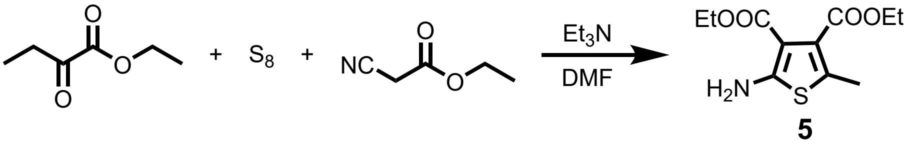
Synthesis of compound BTPD-BTz-Br



To a solution of BTPD-BTz (200 mg, 0.15 mmol) in chloroform (15 mL), Br_2 (74 mg, 0.46 mmol) and iron(III) chloride ($FeCl_3$, 3 mg) were added successively. The reaction mixture was stirred at room temperature in the dark for 8 h and monitored by TLC for consumption of starting material. Upon completion, a saturated aqueous $NaHSO_3$ solution (10 mL) was added, and stirring was continued for 0.5 h. The mixture was diluted with DCM (20 mL) and water (10 mL), then washed with brine (10 mL). After solvent removal, the residue was purified by silica gel chromatography (petroleum ether/ dichloromethane = 1/1) to afford BTPD-BTz-Br as a yellow solid (100 mg, 50%). ^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.59 (s, 2H), 3.53 (d, *J* = 7.20 Hz, 4H), 1.86 (m, 2H), 1.32~1.16 (m, 80H), 0.87 (t, *J* = 6.78 Hz, 12H). ^{13}C NMR (150 MHz, Chloroform-*d*): δ 161.75, 161.37, 161.27, 145.49,135.17, 135.02, 130.34, 129.87, 111.98, 43.15, 36.92, 31.90, 31.46, 29.97, 29.94, 29.68, 29.64, 29.60, 29.35, 26.28, 22.67, 14.10. HRMS (MALDI TOF, m/z) calcd for $C_{66}H_{100}Br_2N_4O_4S_4[M]^+$, 1301.4974; found 1301.4958. (error = -2.1 ppm).

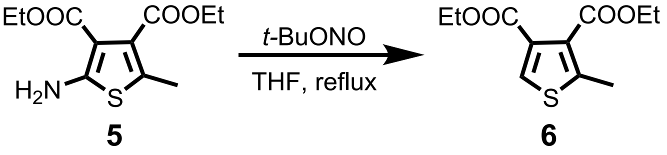


Synthesis of compound 5



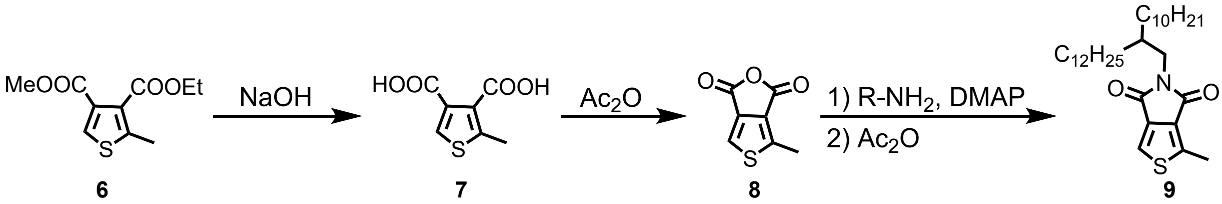
The compound was synthesized following a literature procedure with slight modifications.[1] Ethyl 3-oxobutanoate sodium salt (2.93 g, 22.54 mmol), sulfur (1.12 g, 34.72 mmol), and ethyl cyanoacetate (4.14 g, 31.84 mmol) were stirred in DMF (20 mL) in a 100 mL three-necked flask. A solution of triethylamine (7.5 mL, 54.06 mmol) in DMF (10 mL) was then added dropwise over 30 min. After complete addition, the mixture was heated to 50 °C and stirred for 10 h. Upon reaction completion, the system was cooled to room temperature, poured into water, and the precipitated solid was collected by suction filtration. The crude product was dried under vacuum to afford a yellow solid (3.36 g, 58%) without further purification.

Synthesis of compound 6



tert-Butyl nitrite (0.84 g, 8.16 mmol) was dissolved in anhydrous THF (100 mL) in a 250 mL three-neck flask under argon. A solution of compound 5 (2.00 g, 7.77 mmol) in anhydrous THF (75 mL) was added dropwise to this mixture. After complete addition, the reaction was heated to reflux and stirred for 3 h, with progress monitored by TLC. Upon completion, the mixture was cooled to room temperature, and solvents were removed in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford compound 6 as a pale yellow oil that solidified (0.93 g, 49%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.68 (s, 1H), 4.35 (m, 2H), 4.29 (m, 2H), 2.53 (s, 3H), 1.35 (t, J = 7.20 Hz, 3H), 1.33 (t, J = 7.08 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*): δ 164.89, 162.67, 143.56, 133.20, 130.47, 128.81, 61.27, 61.01, 14.21, 14.17, 14.13. HRMS (MALDI TOF, m/z) calcd for $C_{11}H_{14}O_4S$ [M]+, 242.0613; found 242.0618. (error = +2.0 ppm).

Synthesis of compound 9

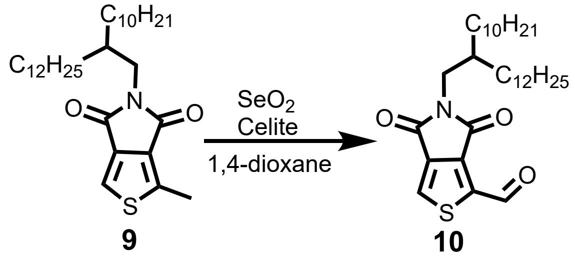


Compound 6 (0.93 g, 3.84 mmol) were added to NaOH aqueous (25 mL, 1M) in a 100 mL flask. The mixture was heated to 80 °C and stirred for overnight. Upon completion, the mixture was cooled to room temperature and added dilute hydrochloric acid (HCl) to adjust the pH ~ 2 and diluted with ether (50 mL × 3) and washed with brine (15 mL). The organic layer was dried by anhydrous Na_2SO_4. After filtration, organic solvents were evaporated under reduce pressure, the residue was then dried under vacuum to afford Compound 7 as white solid (686 mg, 95%), which can be directly used for the next coupling step without further purification.

Compound 7 (4.00 g, 21.48 mmol) was dissolved in acetic anhydride (100 mL) in a 250 mL two-necked flask. The mixture was heated to reflux with stirring overnight. After completion, the reaction mixture was cooled to room temperature, and volatile components were removed under reduced pressure. The residue was dried in vacuo to afford Compound 8 as a brown solid (3.52 g, 97%), which was used directly in the next coupling step without purification.

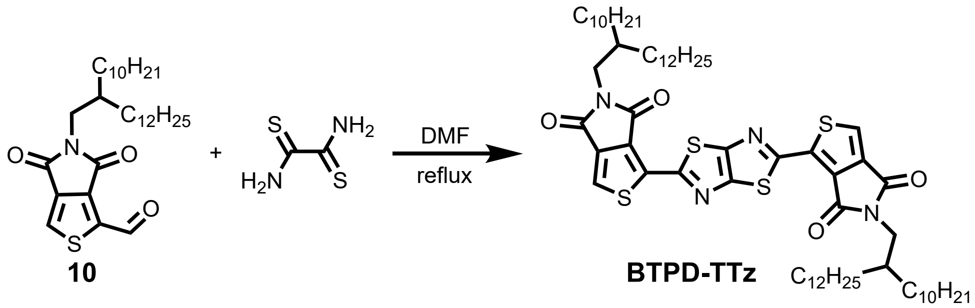
4-dimethylaminopyridine (2.73 g, 22.3 mmol), R-NH_2 (7.89 g, 22.3 mmol), and compound 8 (2.50 g, 14.87 mmol) were charged into a flask, followed by anhydrous 1,4-dioxane (100 mL). The reaction mixture was heated to 90 °C and stirred at this temperature overnight. After cooling to room temperature, acetic anhydride (20 mL) was added in one portion, and the mixture was heated to 140 °C for 6 h. Upon reaction completion, the mixture was cooled to room temperature, diluted with ethyl acetate (100 mL) and water (50 mL), and transferred to a separatory funnel. The organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1) to afford compound 9 as a yellow oil (6.50 g, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.54 (s, 1H), 3.46 (d, *J* = 7.24 Hz, 2H), 2.69 (s, 3H), 1.82(m, 1H), 1.32~1.16 (m, 40H), 0.87 (t, *J* = 6.44 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*): δ 163.77, 162.90, 143.63, 136.10, 131.66, 122.78, 42.50, 36.89, 31.90, 31.47, 29.94, 29.66, 29.63, 29.62, 29.58, 29.34, 29.32, 26.29, 22.66, 14.08, 13.44. HRMS (MALDI TOF, m/z) calcd for $C_{31}H_{53}NO_2S$ [M]+, 503.3797; found 503.3794. (error = -0.6 ppm).

Synthesis of compound 10



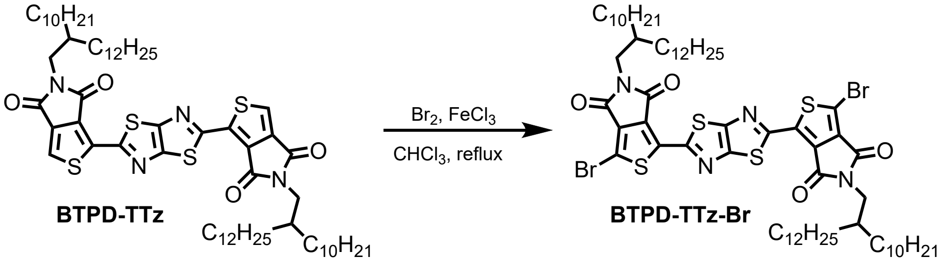
To a solution of compound 9 (6.49 g, 12.88 mmol) in 1,4-dioxane (50 mL) contained in a 250 mL pressure vessel, were added selenium dioxide (SeO_2) (4.29 g, 38.64 mmol) and celite (0.2 g) under argon. The mixture was heated to reflux (internal temperature monitored) and stirred overnight. Reaction progress was monitored by TLC to confirm complete consumption of starting material. After completion, the mixture was cooled to room temperature and filtered through a celite pad. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10/1) to afford compound 10 as a yellow oil (2.70 g, 40%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 10.34 (s, 1H), 7.54 (s, 1H), 3.55 (d, *J* = 7.20 Hz, 2H), 1.85 (m, 1H), 1.32~1.16 (m, 40H), 0.87 (t, *J* = 6.44 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*): δ 180.55, 162.11, 161.81, 140.49, 140.00, 137.32, 131.32, 43.04, 36.94, 31.88, 31.42, 29.90, 29.65, 29.63, 29.61, 29.59, 29.55, 29.32, 29.30, 26.22, 22.65, 14.07. HRMS (MALDI TOF, m/z) calcd for $C_{31}H_{51}NO_3S$ [M]+, 517.3590; found 517.3598. (error = +1.5 ppm).

Synthesis of compound BTPD-TTz



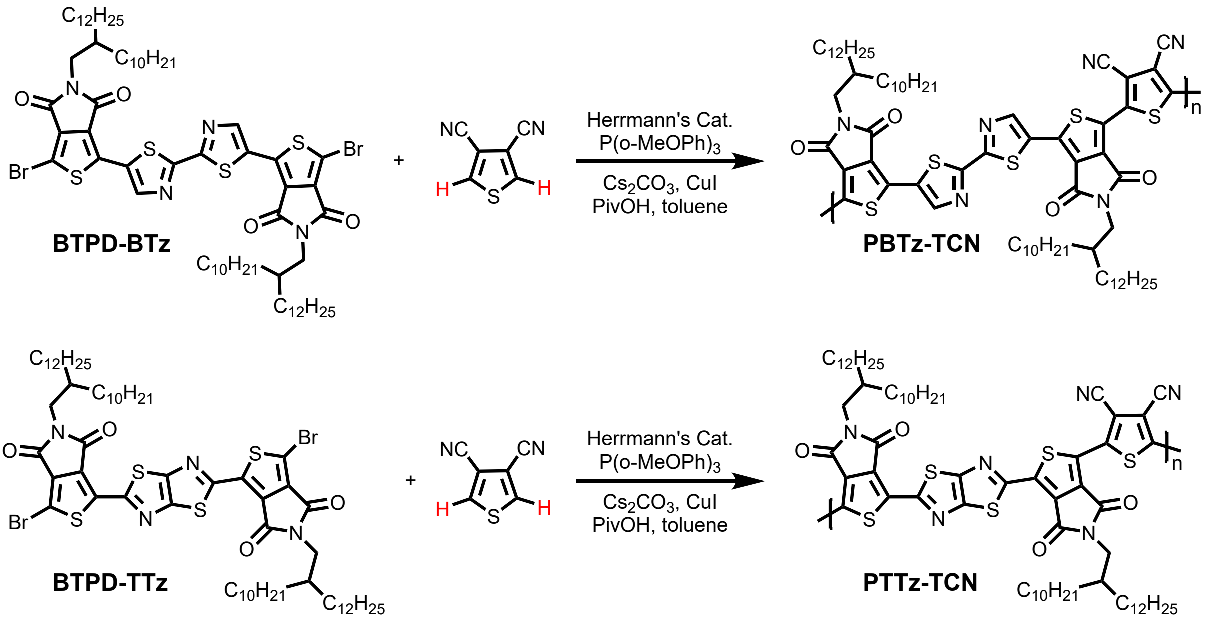
To a solution of compound 10 (1.2 g, 2.96 mmol) in anhydrous DMF (50 mL) under argon, dithiooxamide (177.79 mg, 1.48 mmol) was added. The mixture was refluxed for 10 h with stirring, and reaction progress was monitored by TLC. After completion, the solution was cooled to ambient temperature, poured into water (100 mL), and extracted with CH_2Cl_2 (20 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ dichloromethane = 1/2) to yield BTPD-TTz as a yellow solid (1.12 g, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.89 (s, 2H), 3.57 (d, *J* = 7.20 Hz, 4H), 1.89 (m, 1H), 1.32~1.16 (m, 80H), 0.87 (t, *J* = 6.44 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.58, 162.21, 159.40, 154.01, 137.96, 137.19, 131.10, 126.99, 43.04, 36.93, 31.91, 31.47, 29.97, 29.69, 29.65, 29.59, 29.35, 26.25, 22.68, 14.10. HRMS (MALDI TOF, m/z) calcd for $C_{64}H_{100}N_4O_4S_4[M]^+$, 1117.6627; found 1117.6607. (error = -1.8 ppm).

Synthesis of compound BTPD-TTz-Br



To a solution of BTPD-TTz (240 mg, 0.22 mmol) in chloroform (15 mL), iron(III) chloride (3.60 mg, 0.02 mmol) and Br_2 (107 mg, 0.67 mmol) in chloroform (5 mL) were added successively. The bromine solution was added dropwise to the mixture. The reaction was heated to reflux and stirred for 24 h under dark conditions. Reaction progress was monitored by TLC until complete consumption of starting materials was observed. After cooling to room temperature, saturated aqueous $NaHSO_3$ solution (10 mL) was added, and stirring continued for 0.5 h. The mixture was diluted with CH_2Cl_2 (20 mL) and water (10 mL), then washed with brine (10 mL). The organic layer was concentrated under reduced pressure, and the residue purified by flash chromatography on silica gel (petroleum ether/dichloromethane =1/1) to afford BTPD-TTz-Br as a yellow solid (143 mg, 50%). ^{1}H NMR (600 MHz, Chloroform-*d*): δ 3.56 (d, *J* = 7.26 Hz, 4H), 1.88 (m, 1H), 1.37~1.23 (m, 80H), 0.87 (t, *J* = 6.78 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 161.75, 161.31, 161.22, 158.61, 154.16, 138.44, 134.71, 130.91, 116.05, 111.98, 43.18, 36.92, 31.91, 31.46, 29.97, 29.94, 29.69, 29.65, 29.60, 29.35, 26.26, 22.68, 14.11. HRMS (MALDI TOF, m/z) calcd for $C_{66}H_{100}Br_2N_4O_4S_4[M]^+$, 1274.4817; found 1274.4805. (error = -1.2 ppm).

3. General Synthesis of the Polymers



General synthesis of the polymers: A glass tube was charged with monomer (60 mg, 47.04 μmol), 3,4-dicyanothiophene (6.31 mg, 1.0 equiv), Herrmann's catalyst (0.88 mg, 0.94 μmol), tris(2-methoxyphenyl)phosphine (0.66 mg, 1.88 μmol), CuI (1.79 mg, 9.41 μmol), Cs_2CO_3 (46 mg, 14.11 μmol), and pivalic acid (4.80 mg, 47.04 μmol). The system underwent three argon purge/pump cycles before adding freshly distilled anhydrous toluene (3 mL). The solution was frozen in liquid nitrogen, evacuated, and thawed – a process repeated three times. After sealing, the tube was heated at reflux for 7 h and cooled to room temperature. The crude mixture was precipitated by dropwise addition into vigorously stirred methanol (100 mL). The solids were subjected to sequential Soxhlet extraction with methanol, acetone, hexane, and chloroform. The chloroform-soluble fraction was concentrated and reprecipitated in methanol to yield the final product as a dark solid.

PBTz-TCN: (31 mg, yield: 53%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (s, 2H), 3.54 - 3.57 (m, 4H), 2.33 - 2.34 (m, 2H), 1.25 - 1.26 (m, 80H), 0.86 - 0.88 (m, 12H).

PTTz-TCN: (45 mg, yield: 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.58 - 3.64 (m, 4H), 1.91 (m, 2H), 1.23 - 1.24 (m, 80H), 0.82 - 0.87 (m, 12H).

3. Gel permeation chromatography (GPC) results of polymers

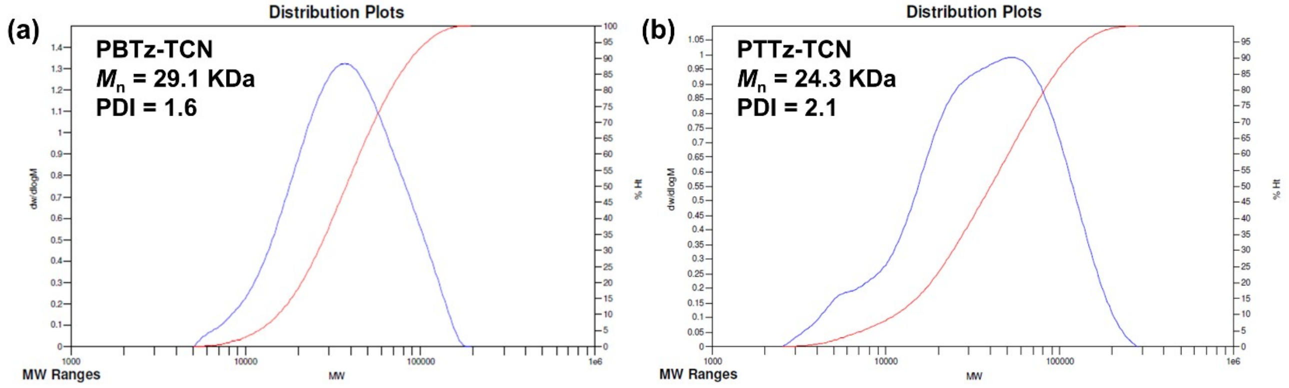


Figure S1. Molecular weights and polymer dispersity index (PDI) of PBTz-TCN (a) and PTTz-TCN (b) determined by high-temperature GPC at 150 °C

4. Polymer Thermal Properties

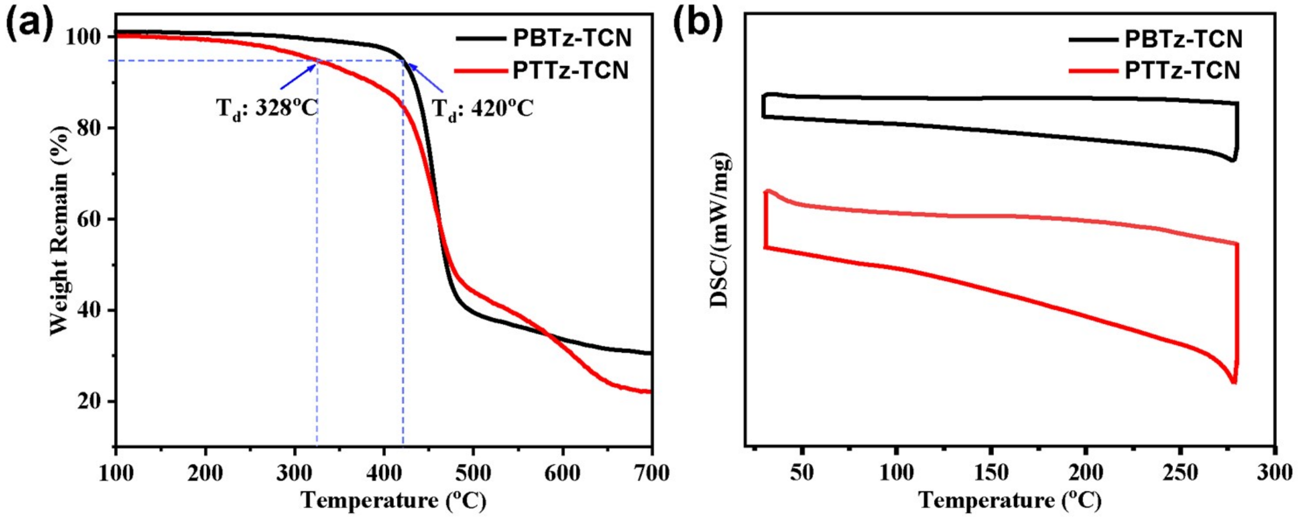


Figure S2. The TGA curves (a) and DSC measurement (b) of PBTz-TCN and PTTz-TCN.

5. Theoretical calculations of polymers

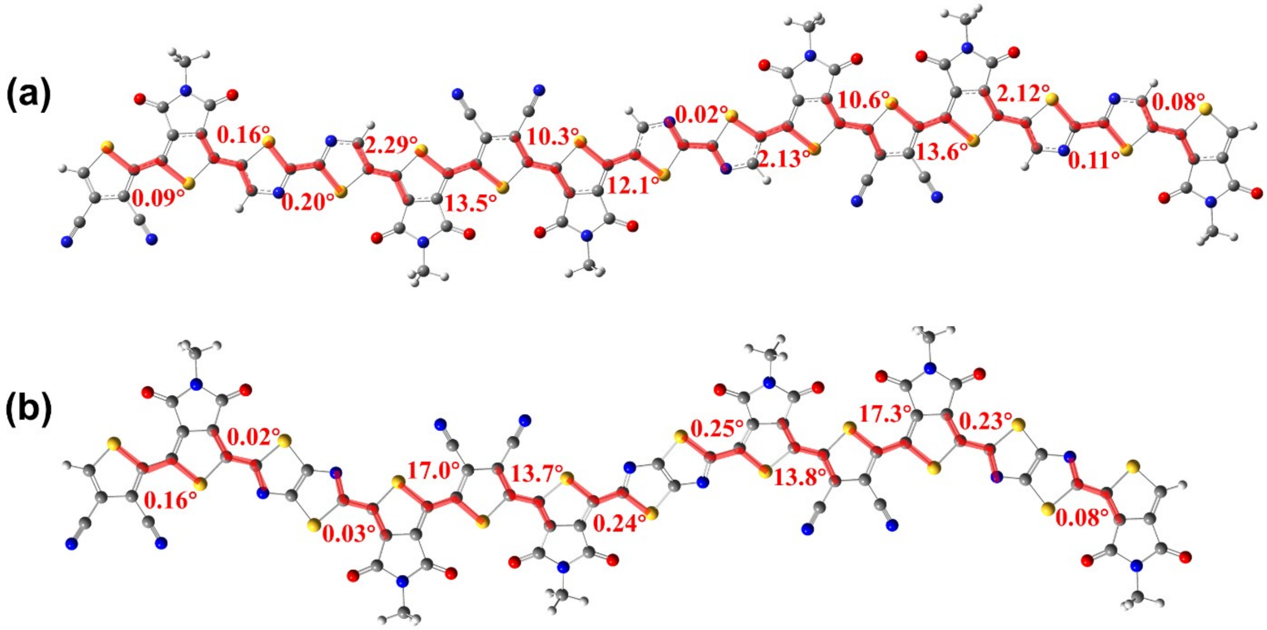


Figure S3. The dihedral angles of trimers of PBTz-TCN (a) and PTTz-TCN (b) under optimized molecular geometries. Calculations were performed at B3LYP/6-31G(d, p) level.

6. Device Fabrication and Characterization

The substrates were first cleaned by sonication in acetone and water for 10 min, then immersed in Piranha solution (7:3 mixture of sulfuric acid and 30% hydrogen peroxide) for 30 min. After rinsing with deionized water and isopropyl alcohol three times, the substrates were blow-dried with nitrogen and treated with UV ozone for 10 min. The substrates were placed in a petri dish, and one drop of *n*-octadecyltrichlorosilane (OTS) was placed in the center. The system was heated under vacuum at 120 ^{o}C for 2 h to form an OTS self-assembled monolayer. The modified substrates were sequentially washed with *n*-hexane, $CHCl_3$, and isopropyl alcohol. Thin films of PBTz-TCN and PTTz-TCN were spin-coated from chloroform solutions (8.0 mg/mL, 200 μL) at 2000 rpm for 60 s. Annealing was performed in a nitrogen-filled glovebox for 10 min at 140 ^{o}C. Gold drain-source (D-S) electrodes (~30 nm thickness) were deposited by vacuum thermal evaporation. Transfer and output curves of the FETs were measured at room temperature in the glovebox using a Keithley 2636B parameter analyzer.

$$I_{DS} = \mu C_i \, (V_{GS} - V_{th})^2 \, W/2L$$

I_{DS} is the current collected by the drain electrode; L and W are the channel length and width, respectively; μ is the mobility of the device; C_i is the capacitance per unit area of the gate dielectric layer (11.0 nF/cm^2); V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively. The V_{th} of the device was obtained by extrapolating the $(I_{DS,\ sat})^{1/2}$ vs. V_{GS} plot to $I_{DS} = 0$.

For electrical conductivity characterization, glass substrates were sequentially cleaned by sonication in deionized water, isopropanol and acetone. The patterned electrode (5 nm Cr and 30 nm Au) was then thermally evaporated onto the substrates. For n-doping studies, polymers PTTz-TCN and PBTz-TCN were co-dissolved with N-DMBI in chloroform, with the polymer concentration fixed at 8 mg mL^{-1}. Solutions with N-DMBI:polymer mass ratios of 2:10 or 3:10 were vortex-mixed at room temperature, spin-coated onto pre-patterned gold electrodes (1 cm × 1 cm glass substrates) at 2000 rpm for 1 min, and annealed at 140 °C for 1 h. Electrical conductivity was acquired via standard four-point probe method using a Keithley 2636B semiconductor parameter analyzer within an N_2 glovebox. A temperature gradient (ΔT) was generated between electrodes using paired Peltier devices (separation: 1 mm), with temperatures monitored by thermocouples. ΔT was systematically varied from 0 to 1 K (step: 0.25 K). The resultant thermal voltage responses were recorded by the Keithley system in the N_2-filled glovebox. Seebeck coefficients were extracted through linear regression of thermal voltage versus ΔT data.

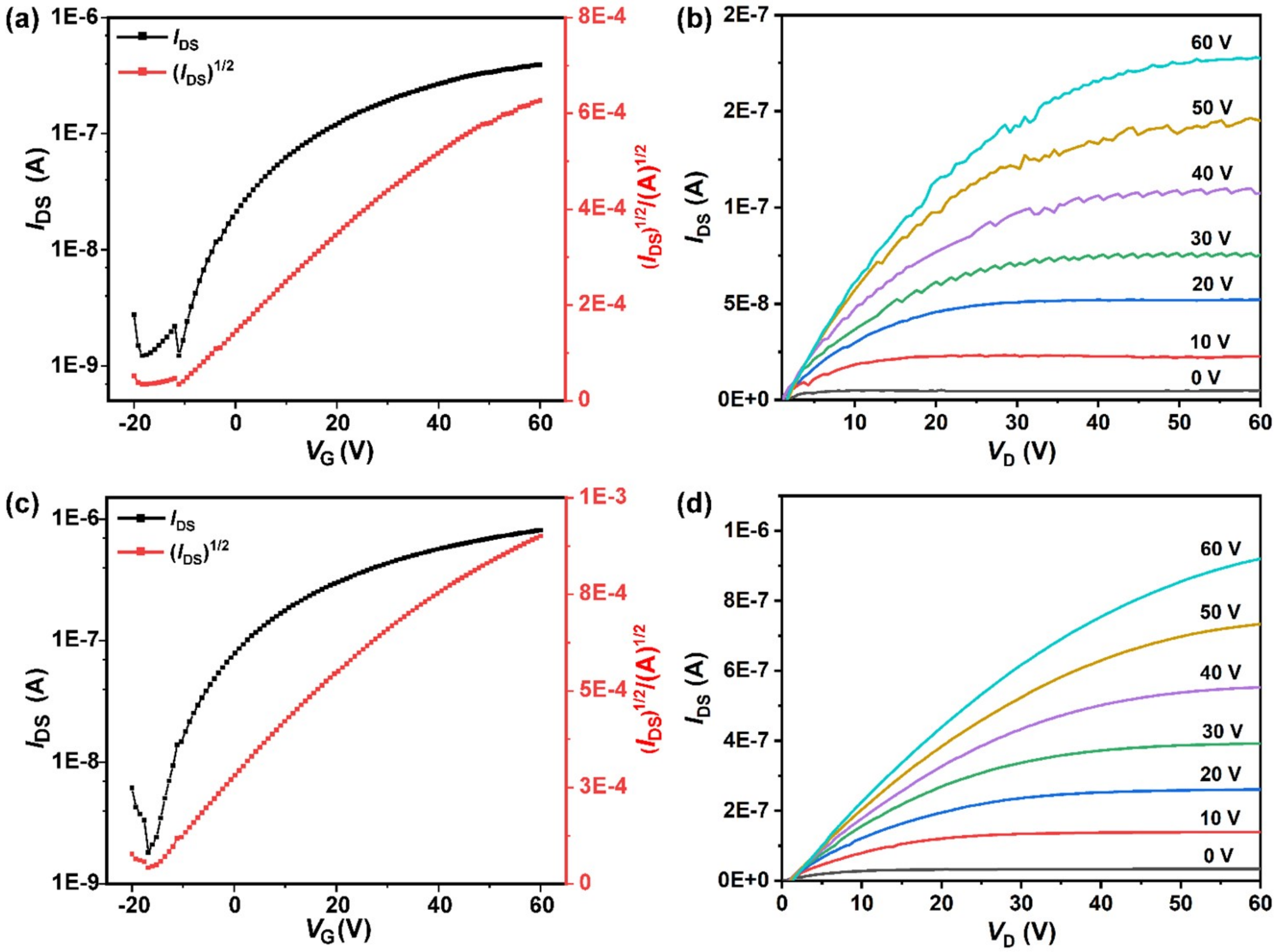


Figure S4. Transfer and output curves of polymers (a, b) PBTz-TCN, and (c, d) PTTz-TCN (L = 100 μm, W = 4500 μm).

Table S1 OFET performance parameters of the polymers.

Polymer	μ_e (cm^2 V^{-1} s^{-1})	V_{th}	I_{on}/I_{off}
PBTZ-TCN	1.97×10^{-4}	-16.4	10^2
PTTZ-TCN	2.69×10^{-3}	-20.2	10^2

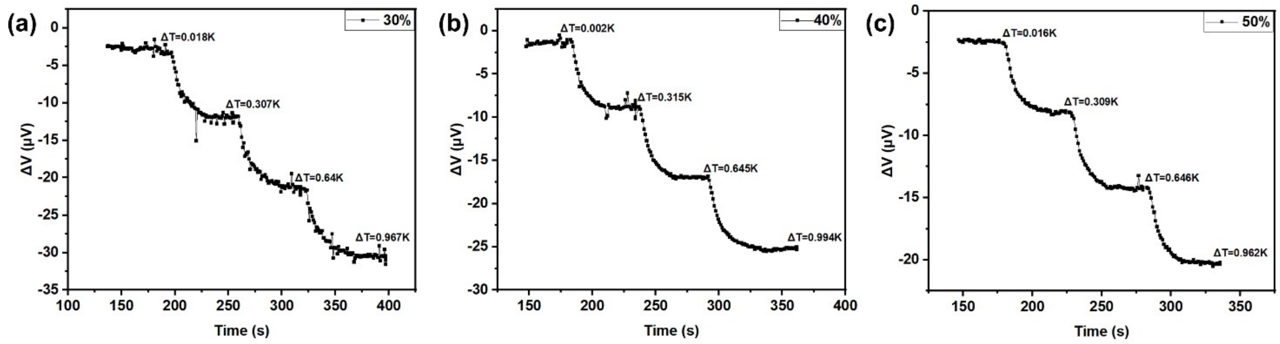


Figure S5. Seebeck coefficient measurement of N-DMBI doped polymer for PTTz-TCN: temperature difference dependent thermal voltage in thermal voltage measurement.

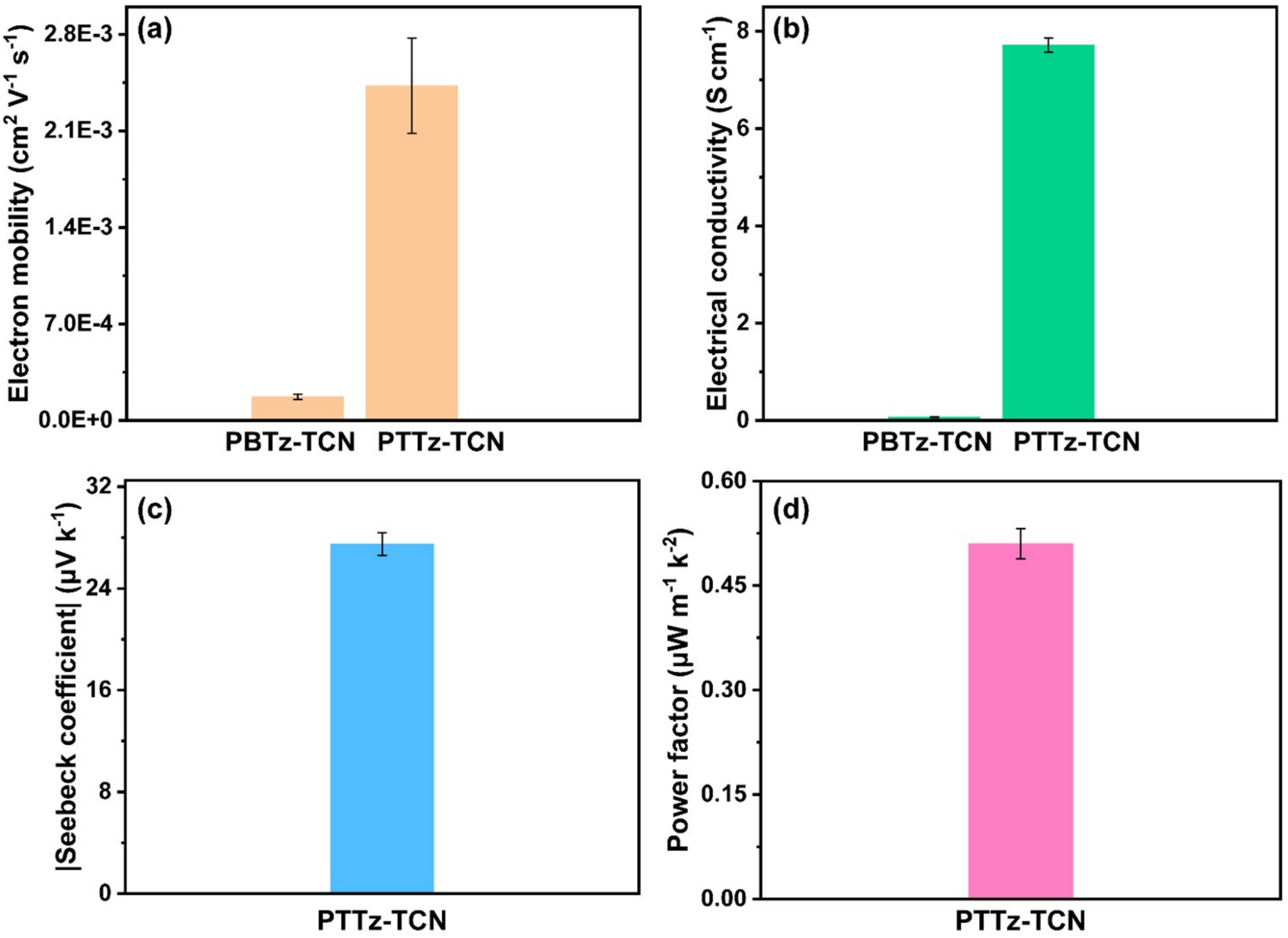


Figure S6. OFET and OTE devices performance data with standard deviation error bars (five devices per data point. Electron mobility (a), Electrical conductivity (b), Seebeck coefficient (c), and Power factor (d).

Table S2. Comparison of thermoelectric performance of this work with that of the representative typical n-type organic thermoelectric polymers reported in literature.

Polymer	$\sigma_{\max}$ (S cm^{-1})	$PF_{\max}$ (μW m^{-1} k^{-2})	Reference
PBTz-TCN	0.08	–	This work
PTTz-TCN	7.91	0.54	This work
BBL	2.4	0.43	[2]
P(BTP-DPP)	0.45	–	[3]
N2200	0.008	0.06	[4]
TEG-N2200	0.17	0.40	[4]
P(gNDI-gT2)	0.29	0.41	[5]
LPPV	1.1	1.96	[6]

7. Grazing-Incident Wide-Angle X-Ray Scattering (GIWAXS) analysis

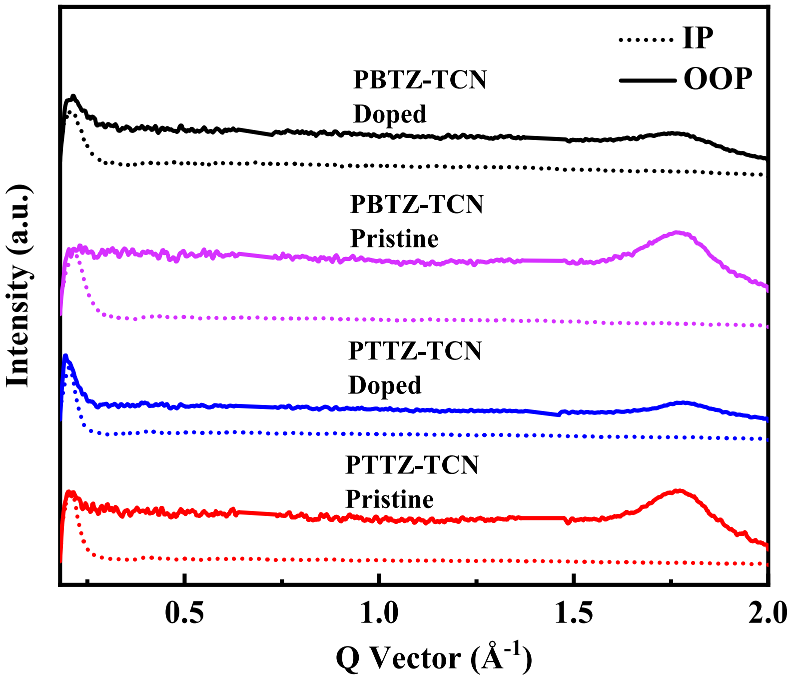


Figure S7. 1D-GIWAXS plots of OOP and IP directions two polymer films before and after doping with N-DMBI.

Table S3. GIWAXS lamellar and π-π stacking parameters of the polymer films before and after n-doping.

Polymer		lamellar spacing				π-π spacing			
		q_{xy}(100) (Å^{-1})	d_{xy}(100) (Å)	FWHM (Å^{-1})	CCL$_{xy}$ (100) (Å)	q_z(010) (Å^{-1})	d_z(010) (Å)	FWHM (Å^{-1})	CCL$_{xy}$ (010) (Å)
PBTz-TCN	pristine	0.2150	29.22	0.053	106.70	1.763	3.56	0.16	35.34
	doped	0.2075	30.28	0.041	137.92	1.733	3.63	0.14	40.39
PTTz-TCN	pristine	0.2075	30.28	0.047	120.32	1.773	3.54	0.15	37.70
	doped	0.2050	30.64	0.041	137.92	1.770	3.55	0.13	43.50

8. NMR/mass spectra for new compounds

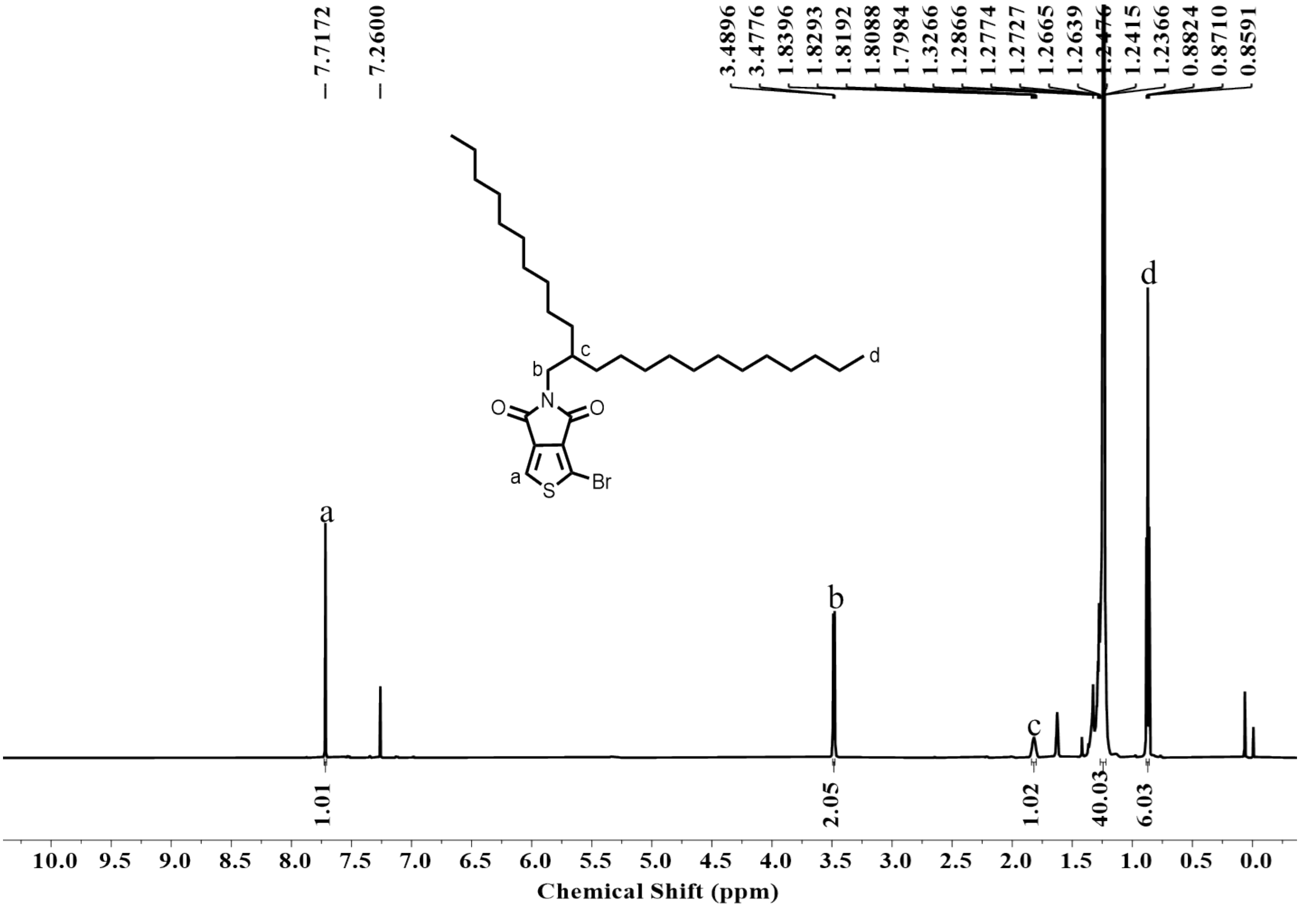


Figure S8. ^{1}H NMR spectrum (600 MHz) of compound **4** in $CDCl_3$ at 298 K.

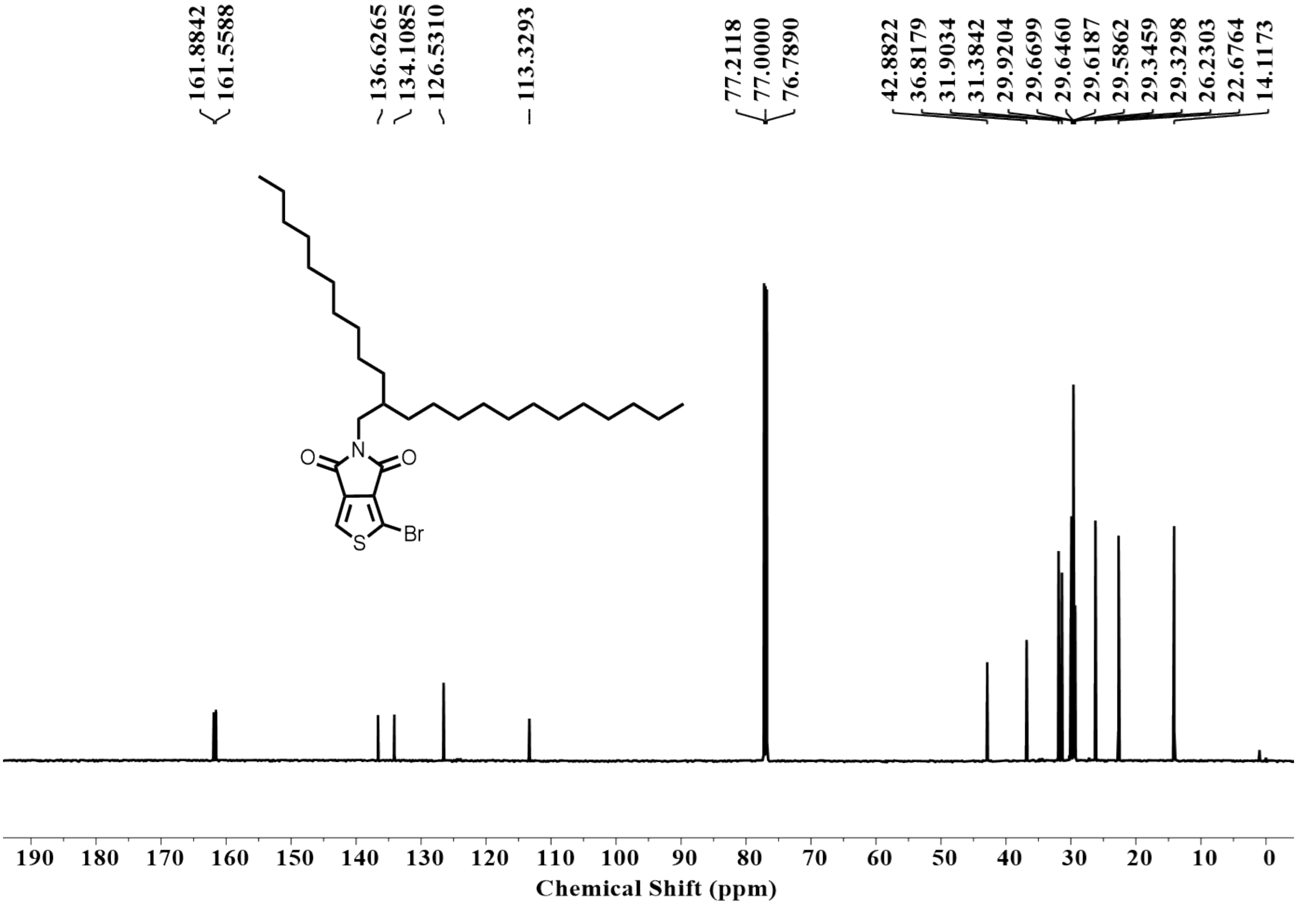


Figure S9. ^{13}C NMR spectrum (150 MHz) of compound **4** in $CDCl_3$ at 298 K.

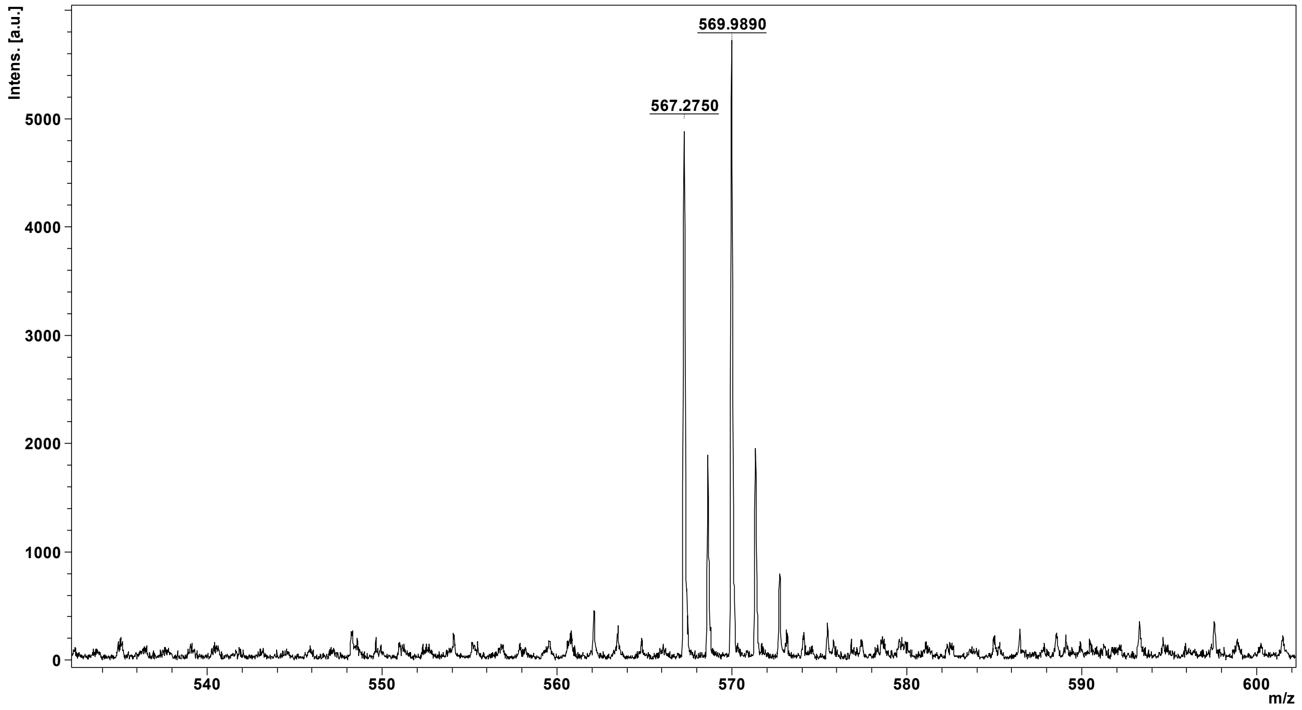


Figure S10. HR (MALDI-TOF) mass spectrum of compound **4**.

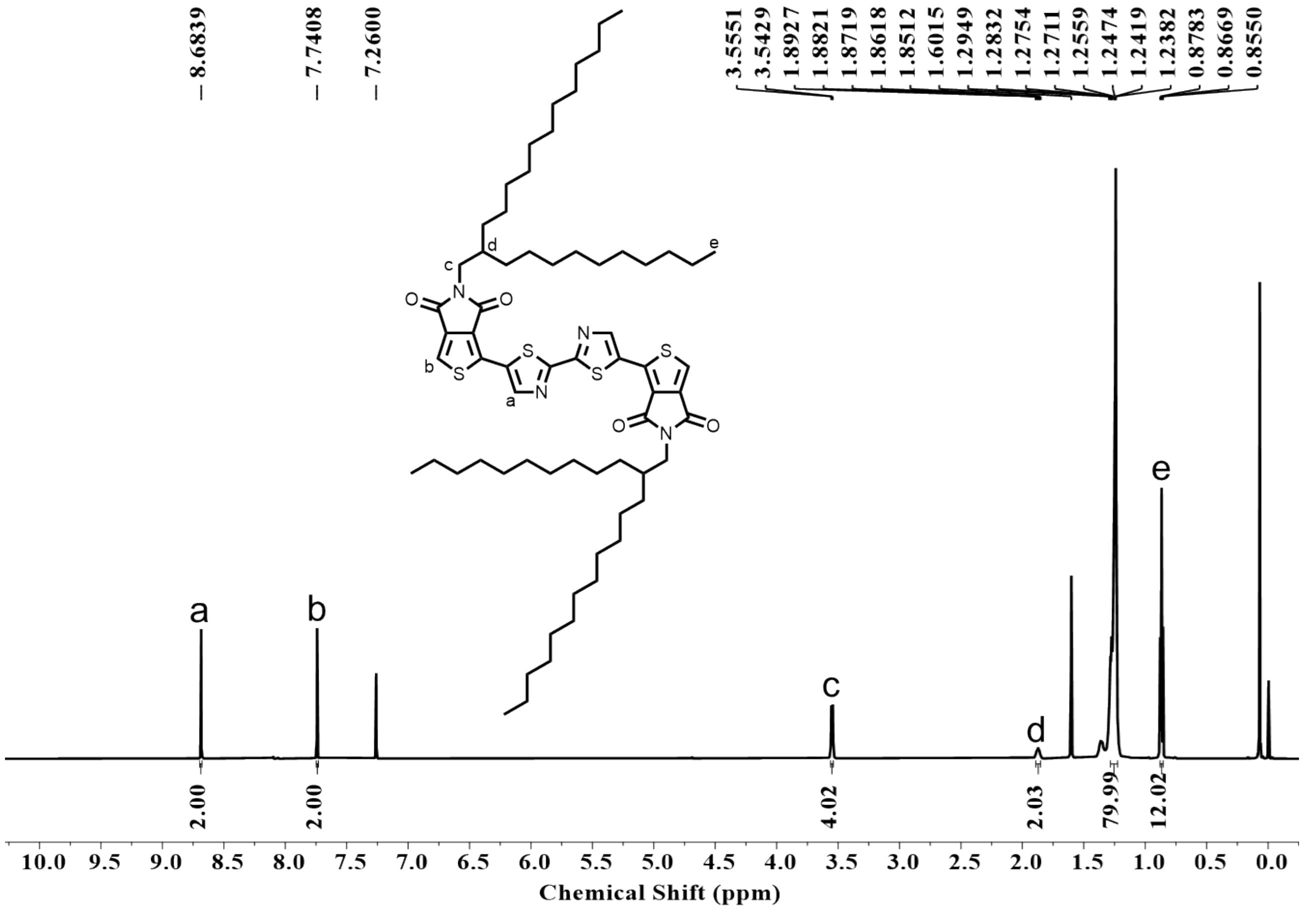


Figure S11. ^{1}H NMR spectrum (600 MHz) of compound **BTPD-BTz** in $CDCl_3$ at 298 K.

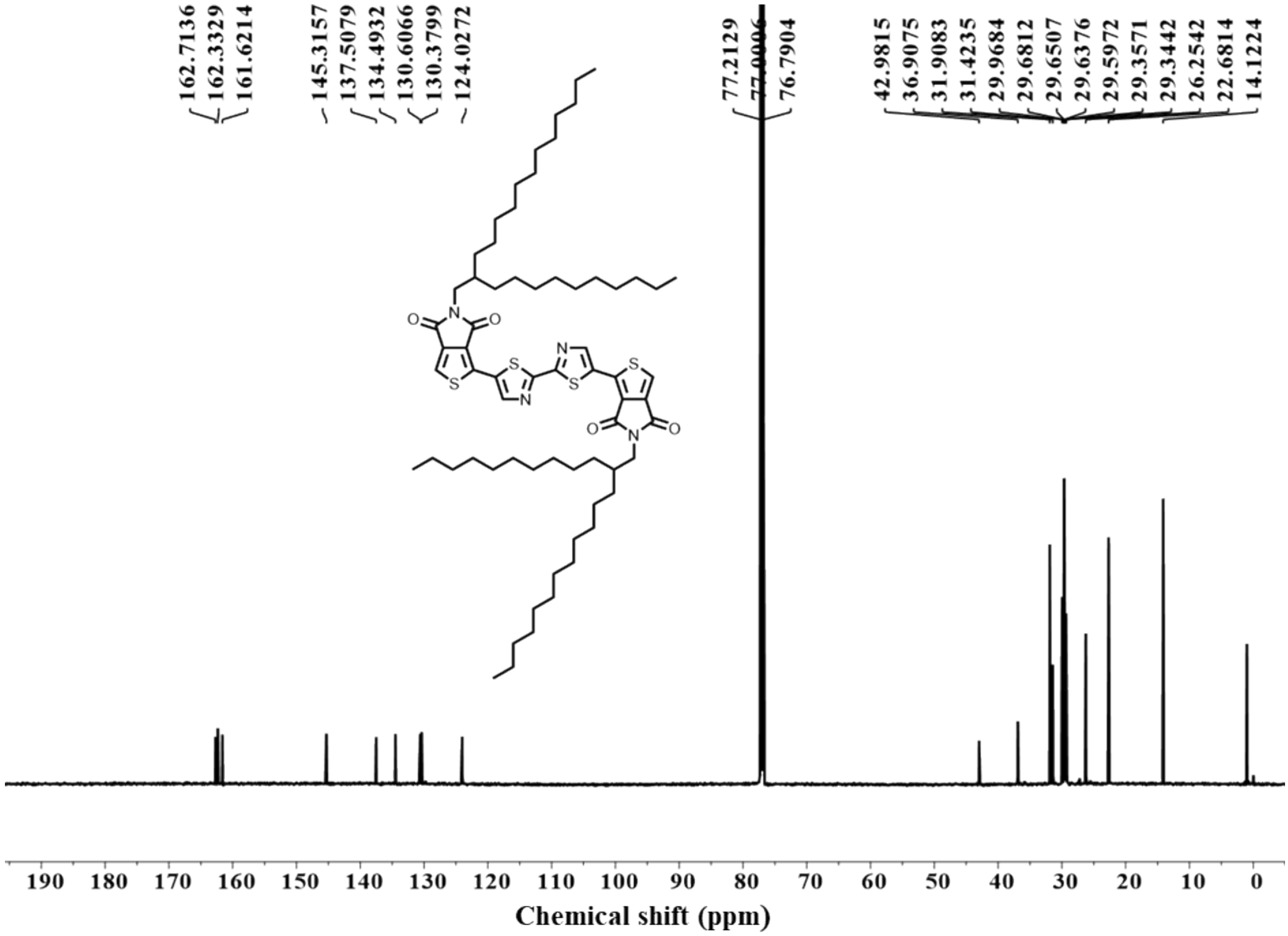


Figure S12. ^{13}C NMR spectrum (150 MHz) of compound **BTPD-BTz** in $CDCl_3$ at 298 K.

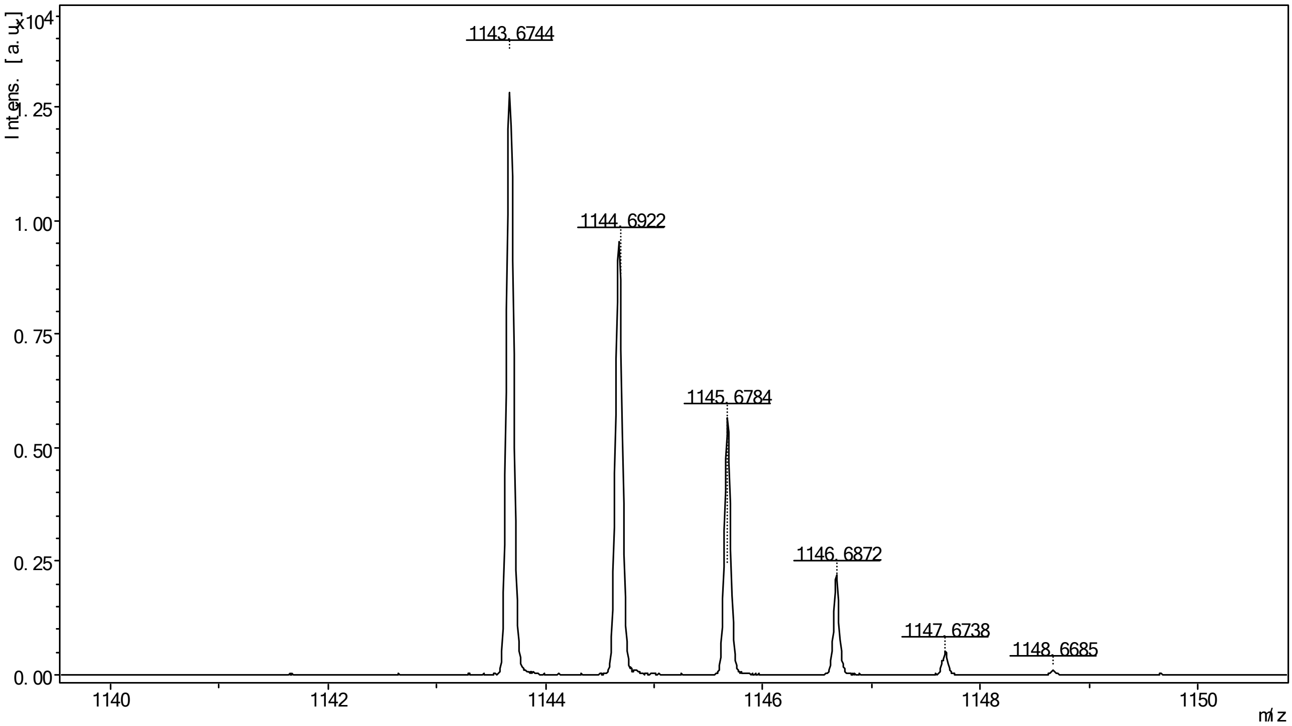


Figure S13. HR (MALDI-TOF) mass spectrum of compound **BTPD-BTz**.

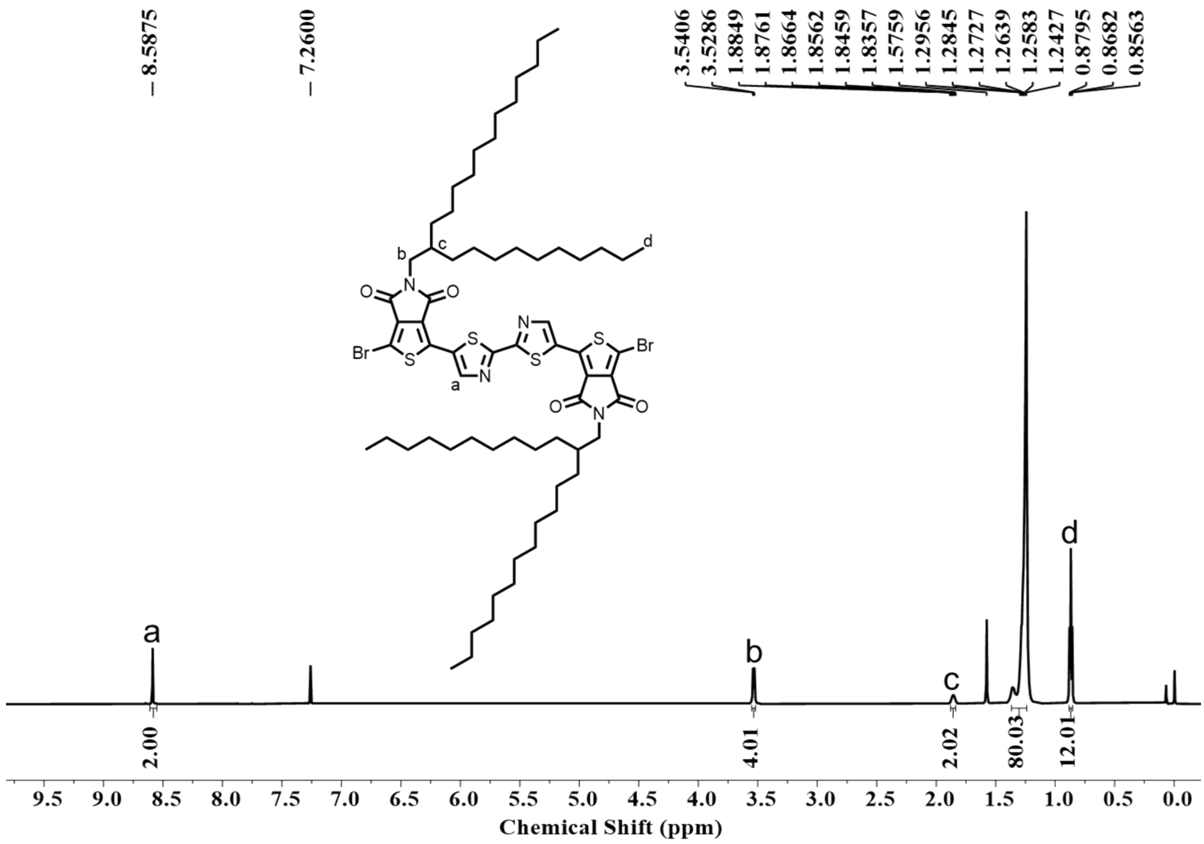


Figure S14. ^{1}H NMR spectrum (600 MHz) of compound **BTPD-BTz-Br** in $CDCl_3$ at 298 K.

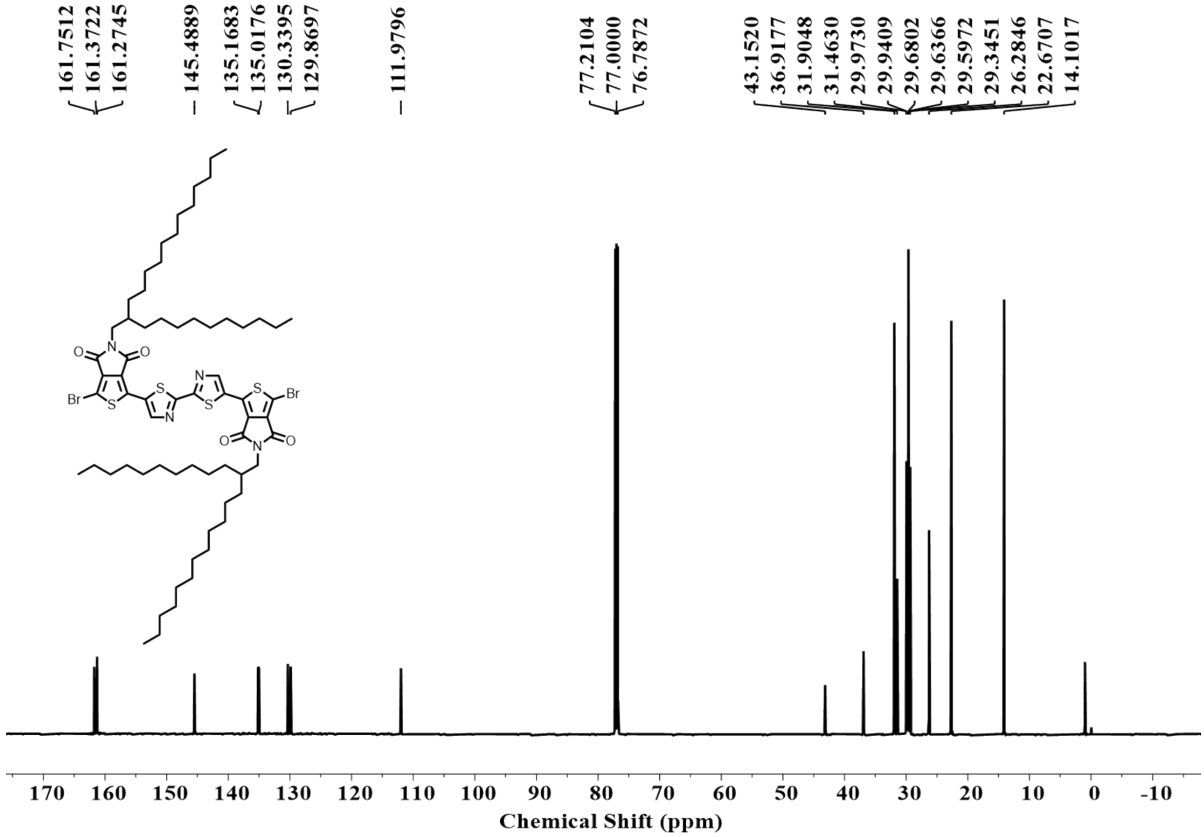


Figure S15. ^{13}C NMR spectrum (150 MHz) of compound **BTPD-BTz-Br** in $CDCl_3$ at 298 K.

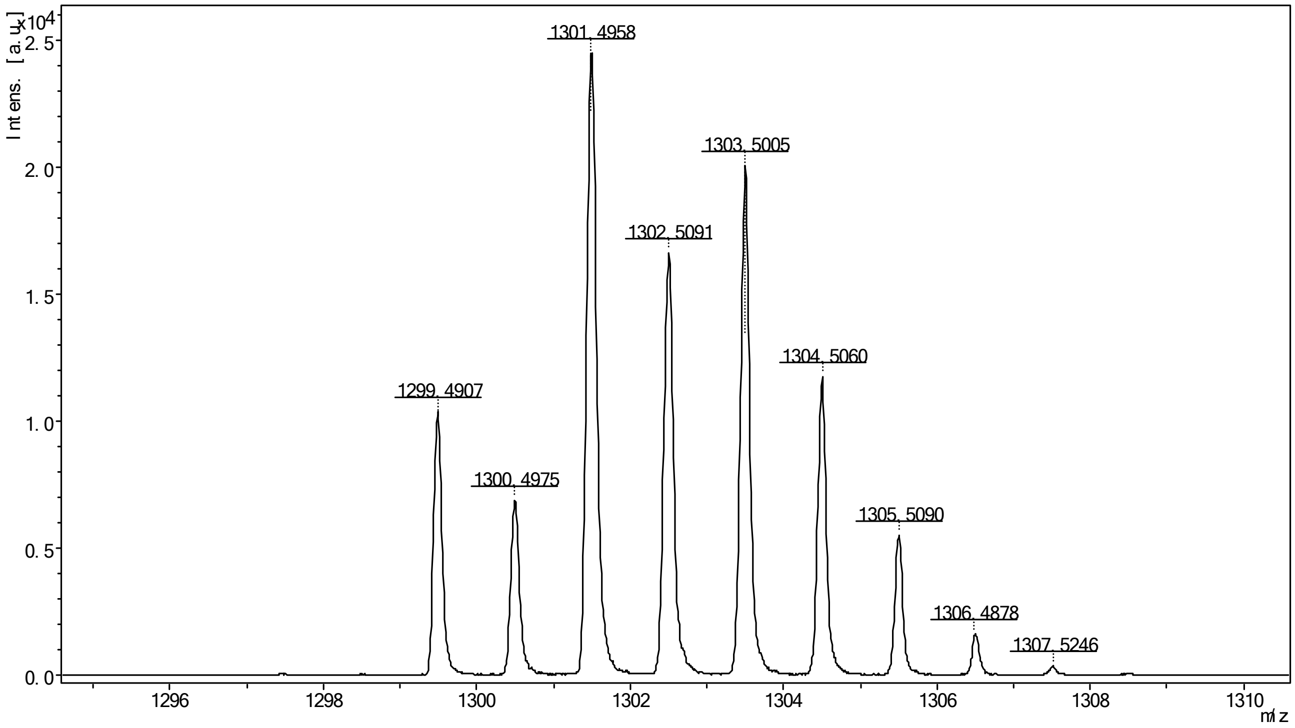


Figure S16. HR (MALDI-TOF) mass spectrum of compound **BTPD-BTz-Br**.

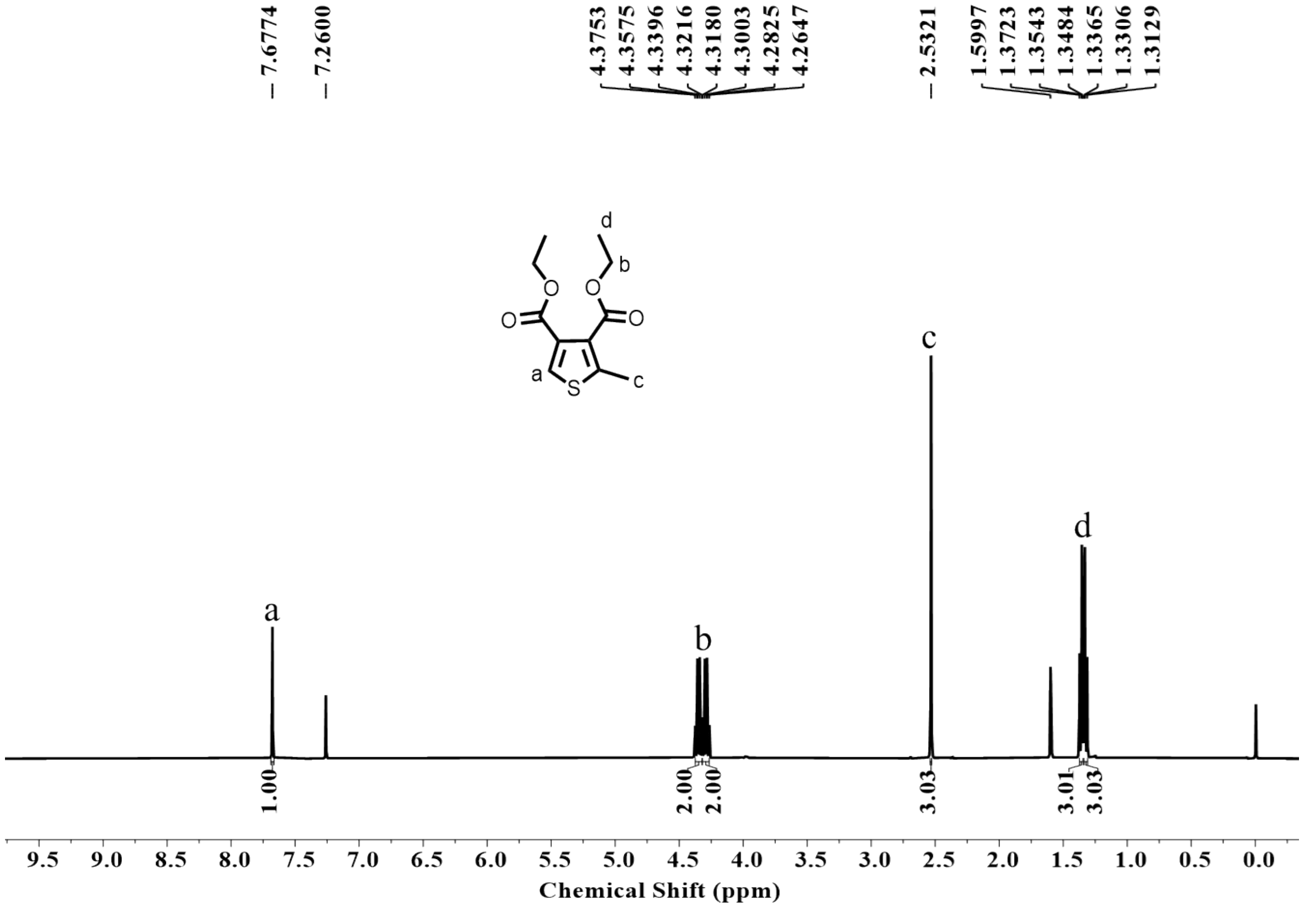


Figure S17. ^{1}H NMR spectrum (400 MHz) of compound **6** in $CDCl_3$ at 298 K.

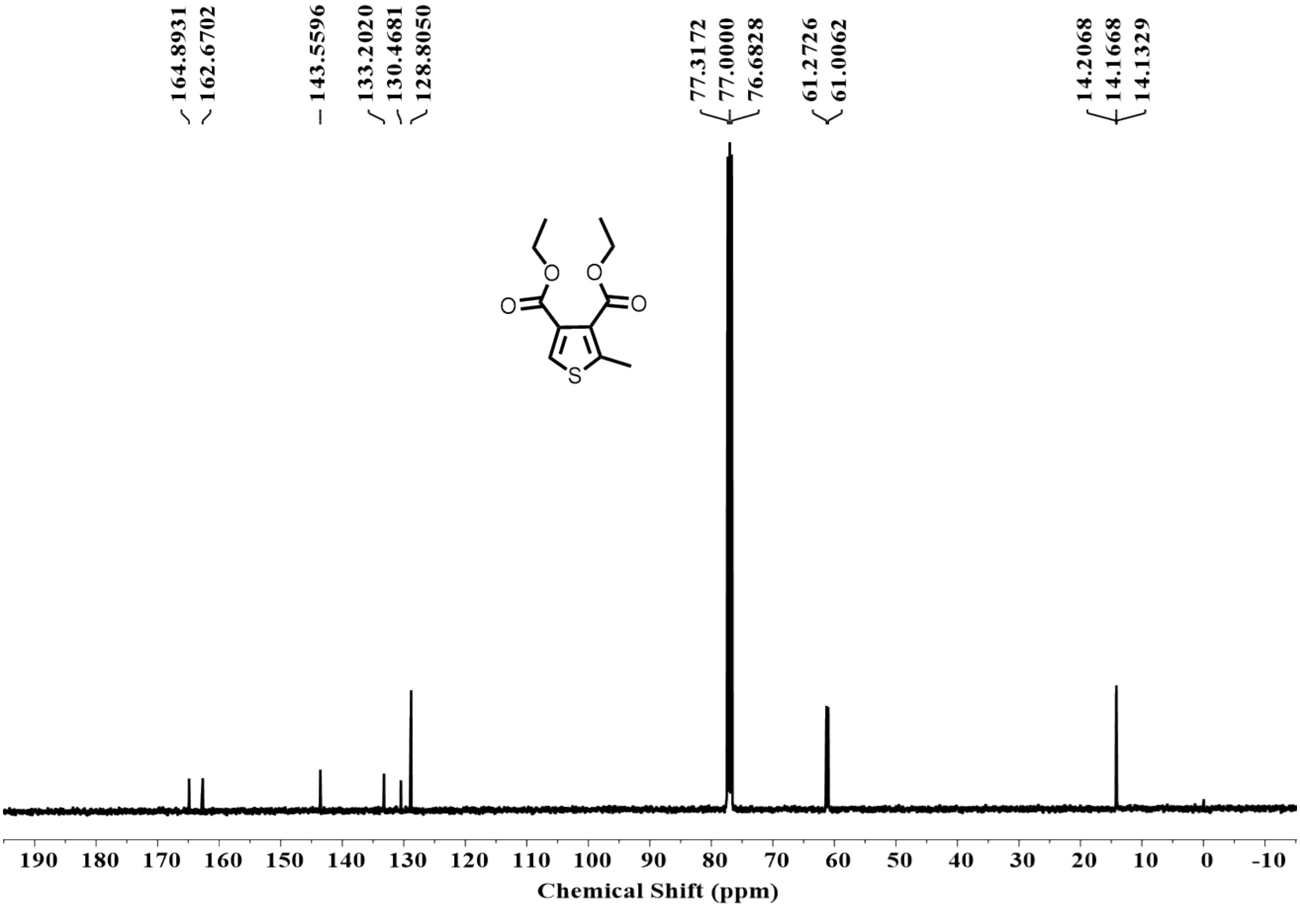


Figure S18. ^{13}C NMR spectrum (100 MHz) of compound **6** in CDCl$_3$ at 298 K.

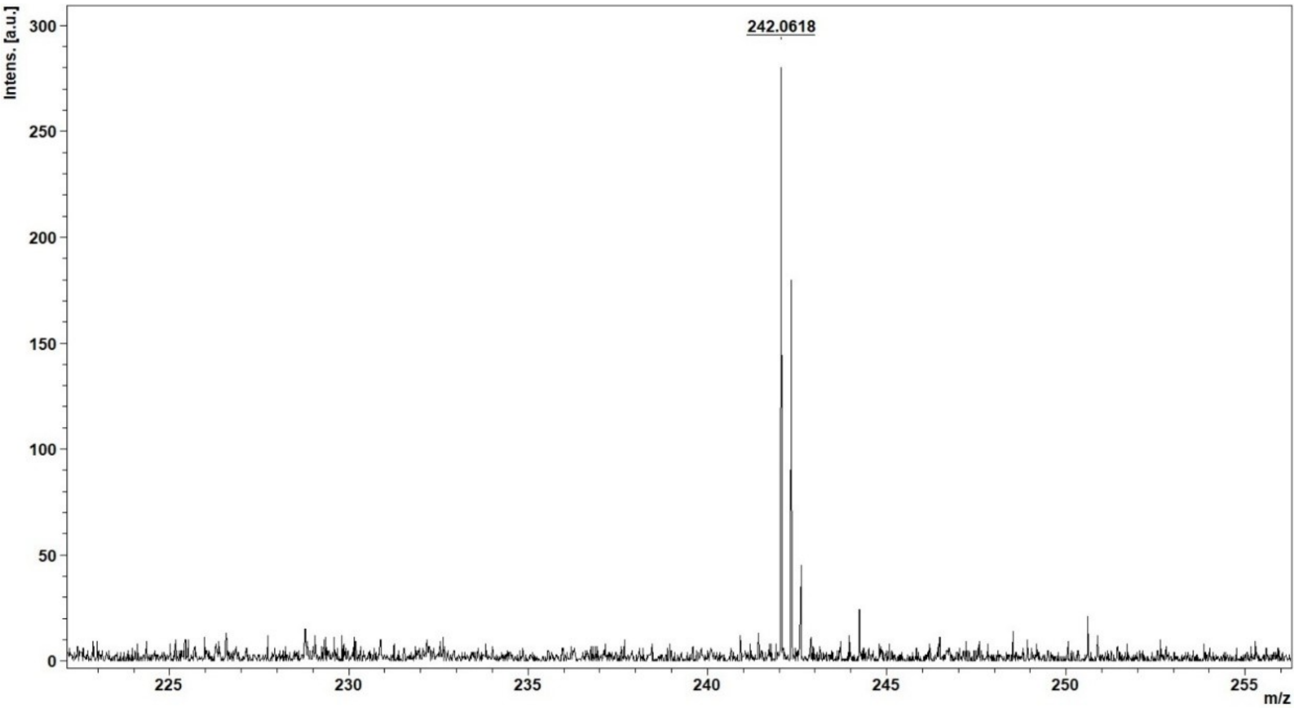


Figure S19. HR (MALDI-TOF) mass spectrum of compound **6**.

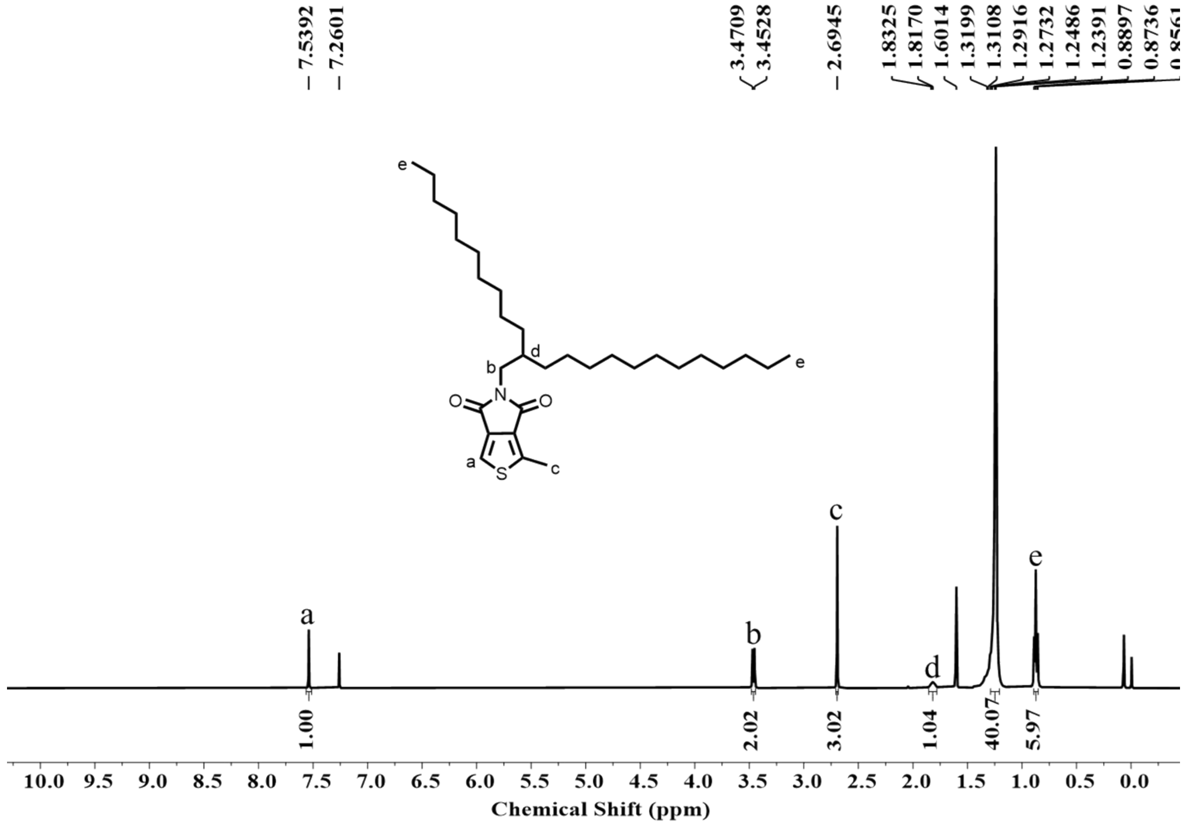


Figure S20. ^{1}H NMR spectrum (400 MHz) of compound **9** in $CDCl_3$ at 298 K.

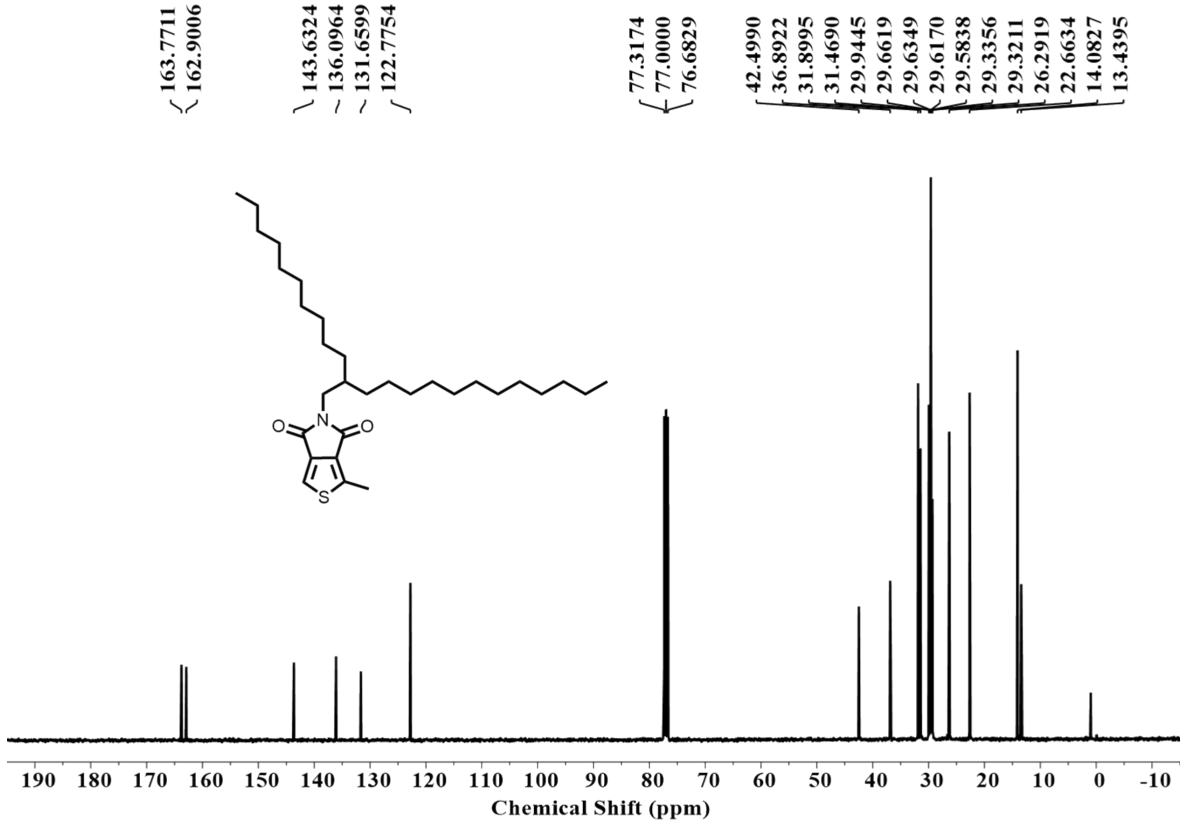


Figure S21. ^{13}C NMR spectrum (100 MHz) of compound **9** in $CDCl_3$ at 298 K.

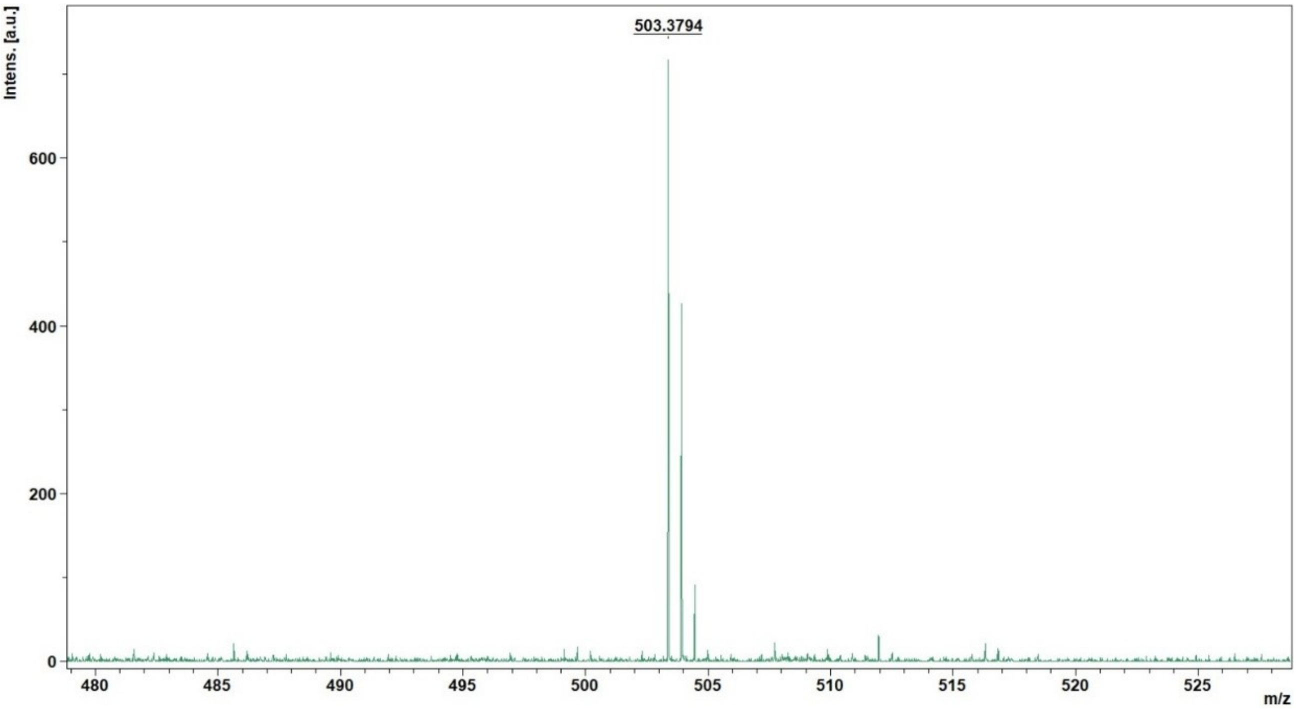


Figure S22. HR (MALDI-TOF) mass spectrum of compound **9**.

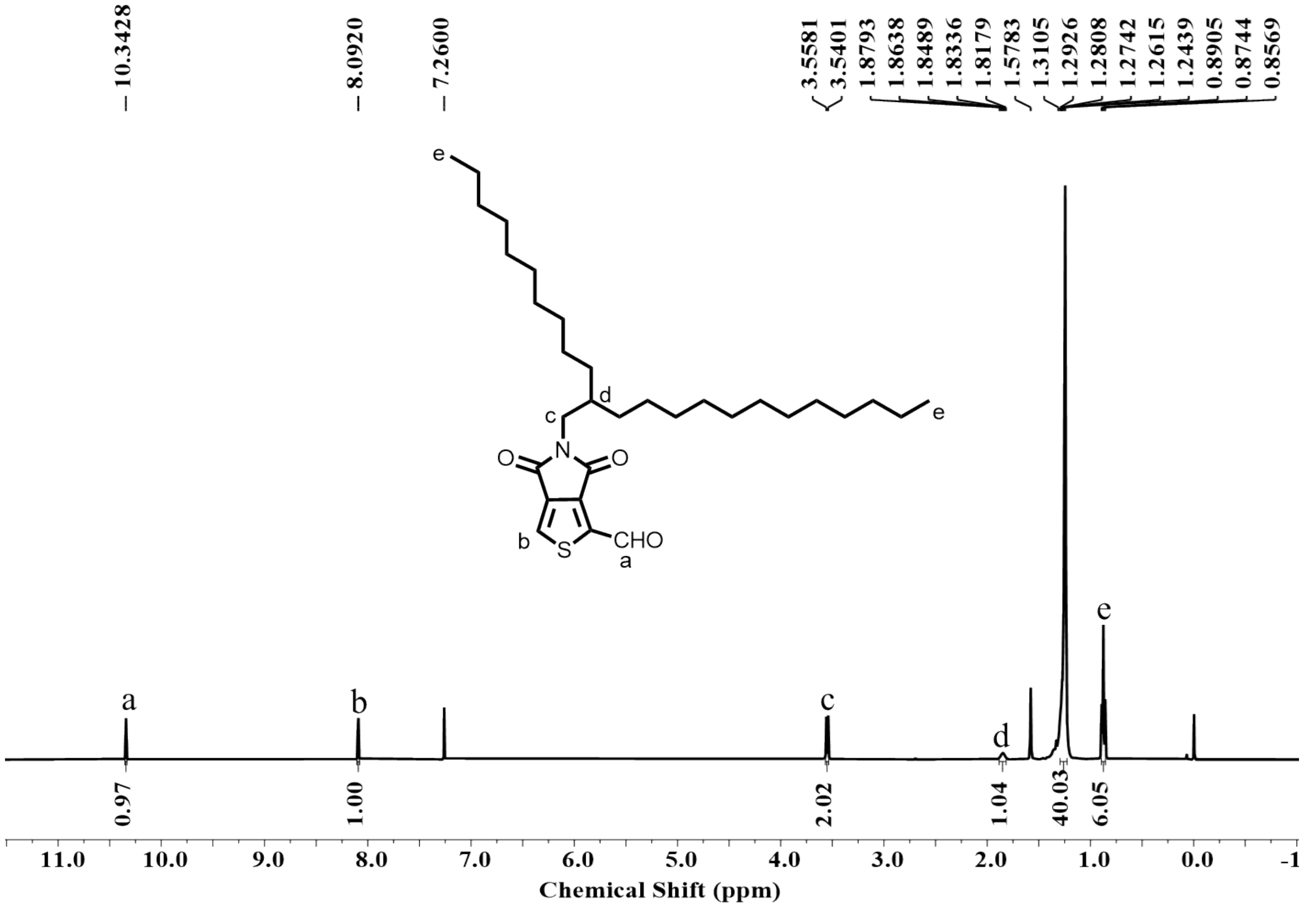


Figure S23. ^{1}H NMR spectrum (400 MHz) of compound **10** in $CDCl_3$ at 298 K.

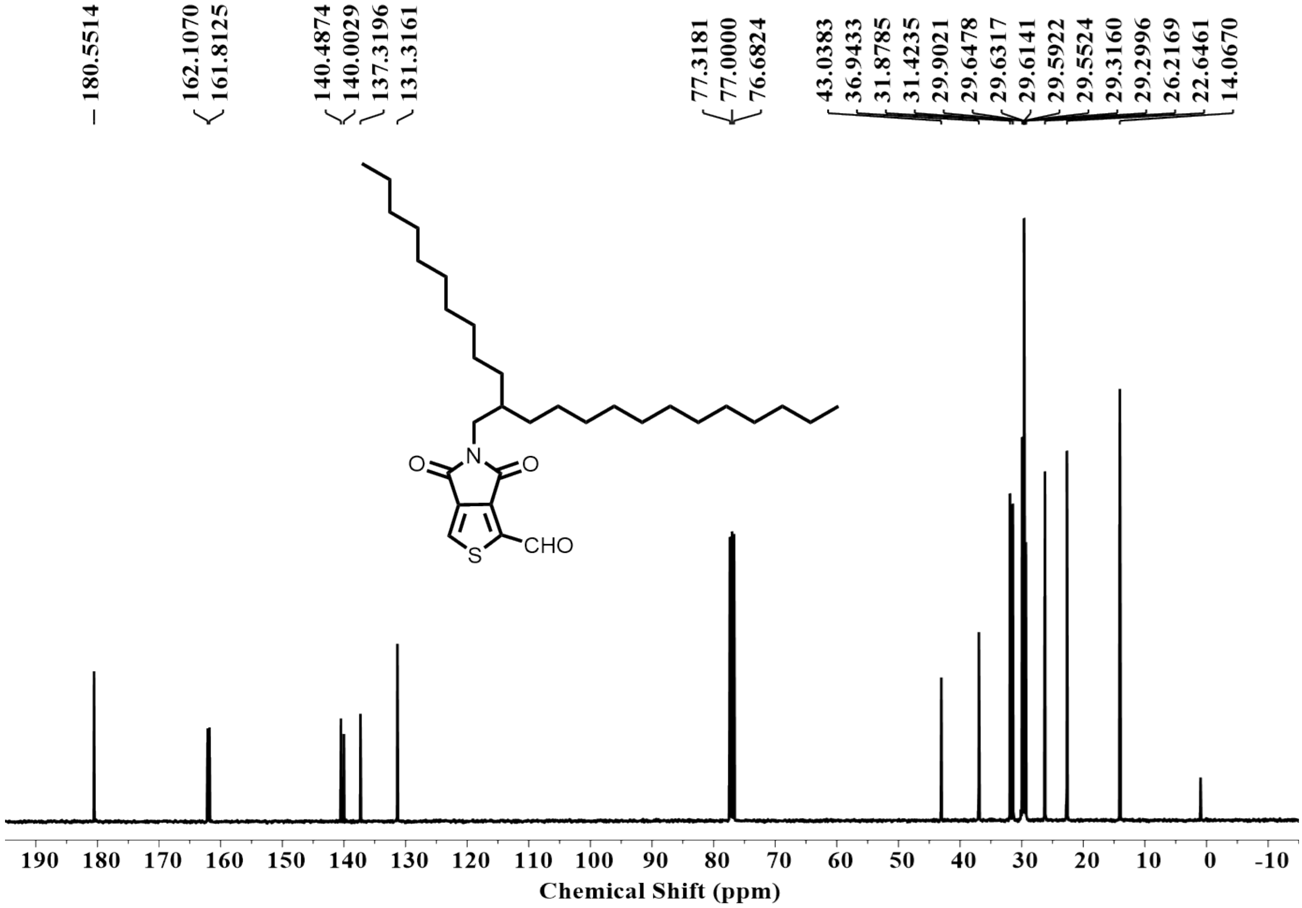


Figure S24. ^{13}C NMR spectrum (100 MHz) of compound **10** in $CDCl_3$ at 298 K.

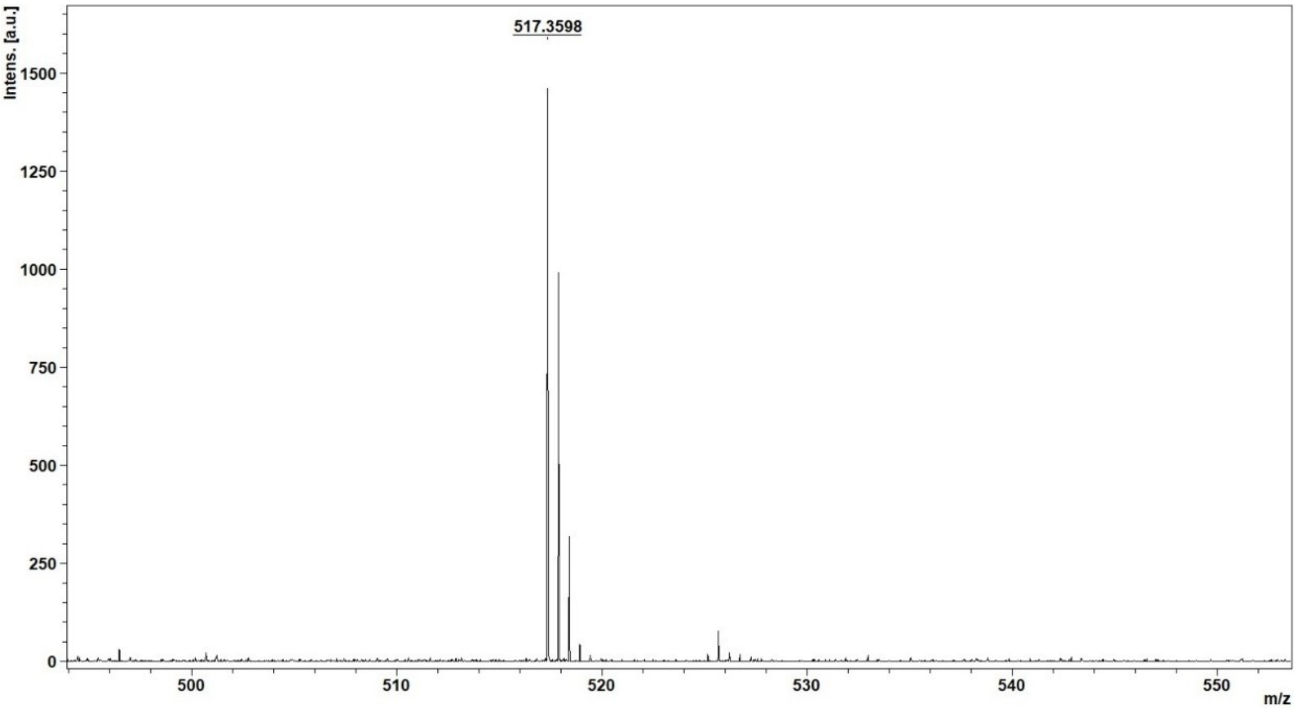


Figure S25. HR (MALDI-TOF) mass spectrum of compound **10**.

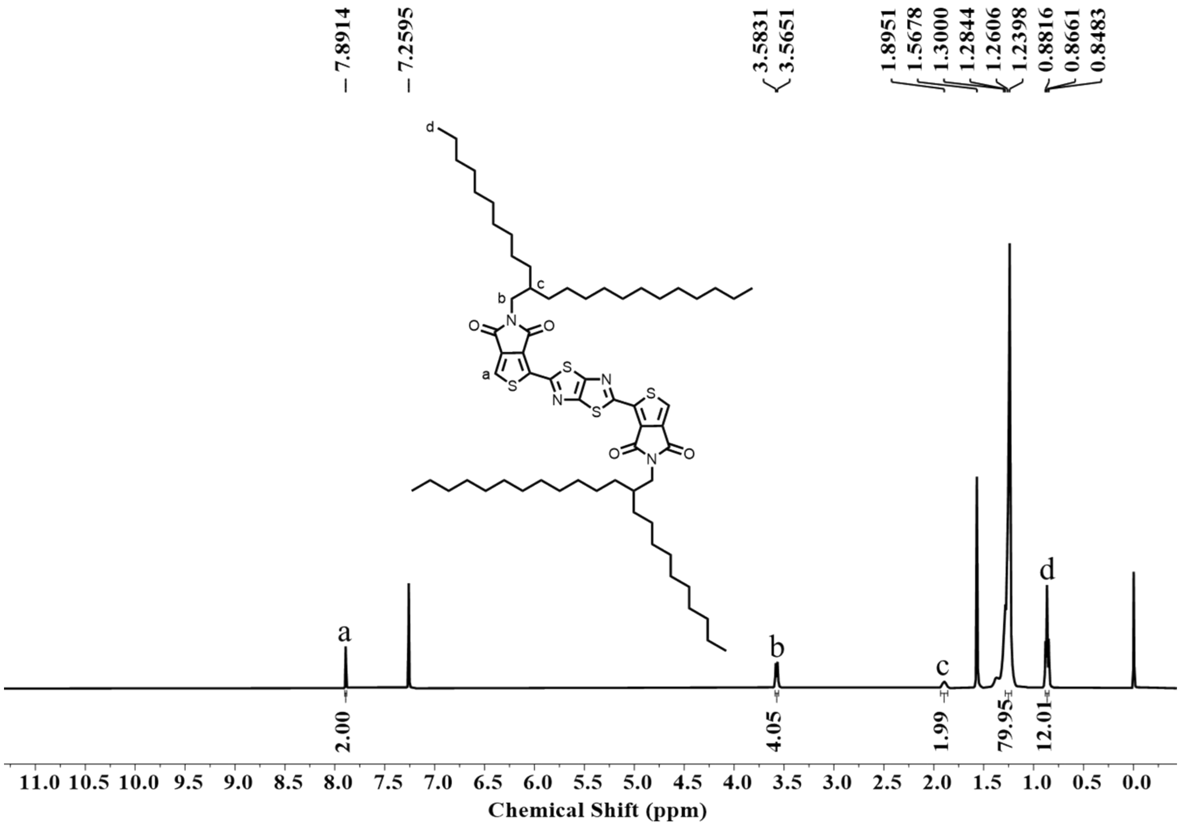


Figure S26. ^{1}H NMR spectrum (400 MHz) of compound **BTPD-TTz** in $CDCl_3$ at 298 K.

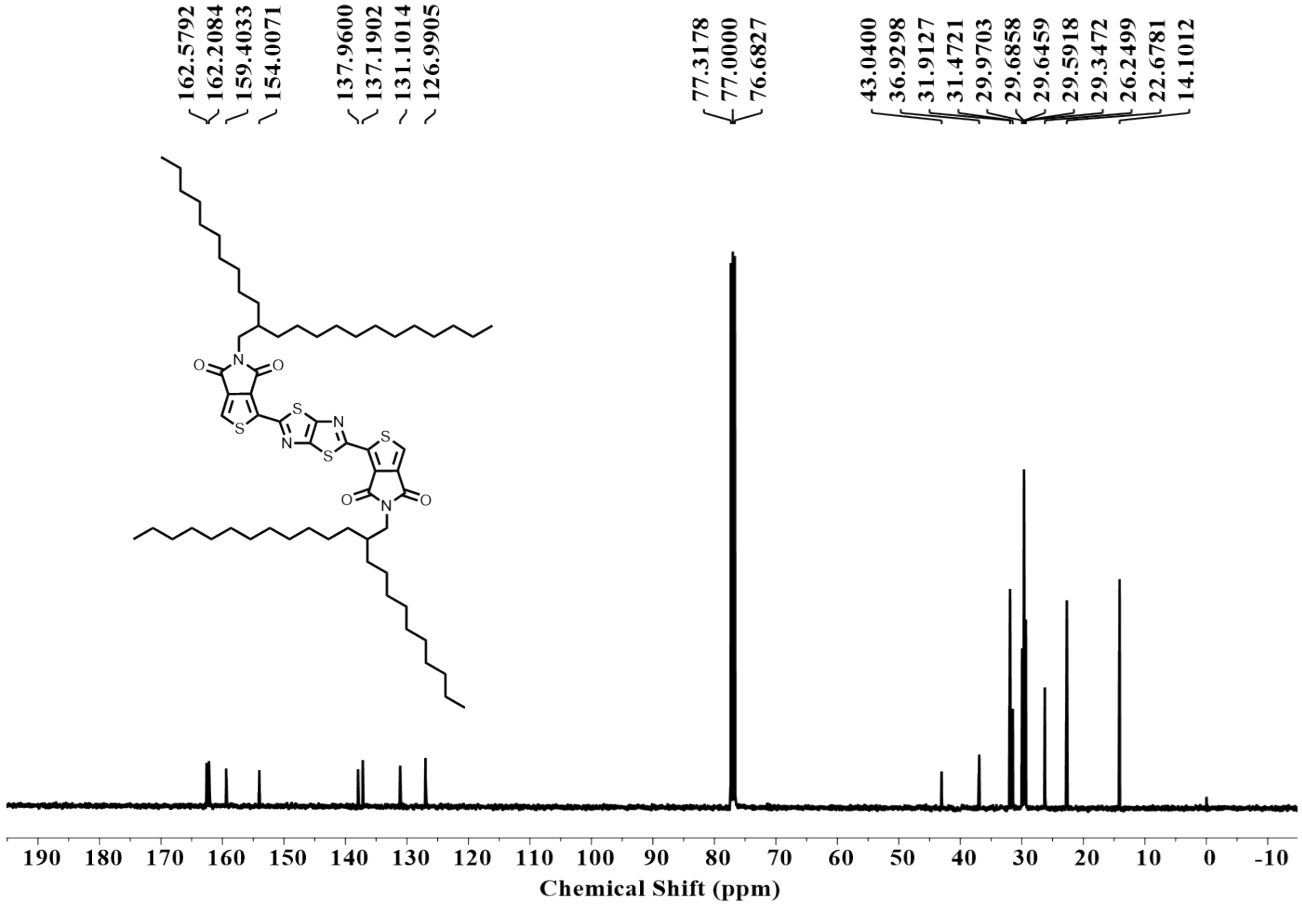


Figure S27. ^{13}C NMR spectrum (100 MHz) of compound **BTPD-TTz** in $CDCl_3$ at 298 K.

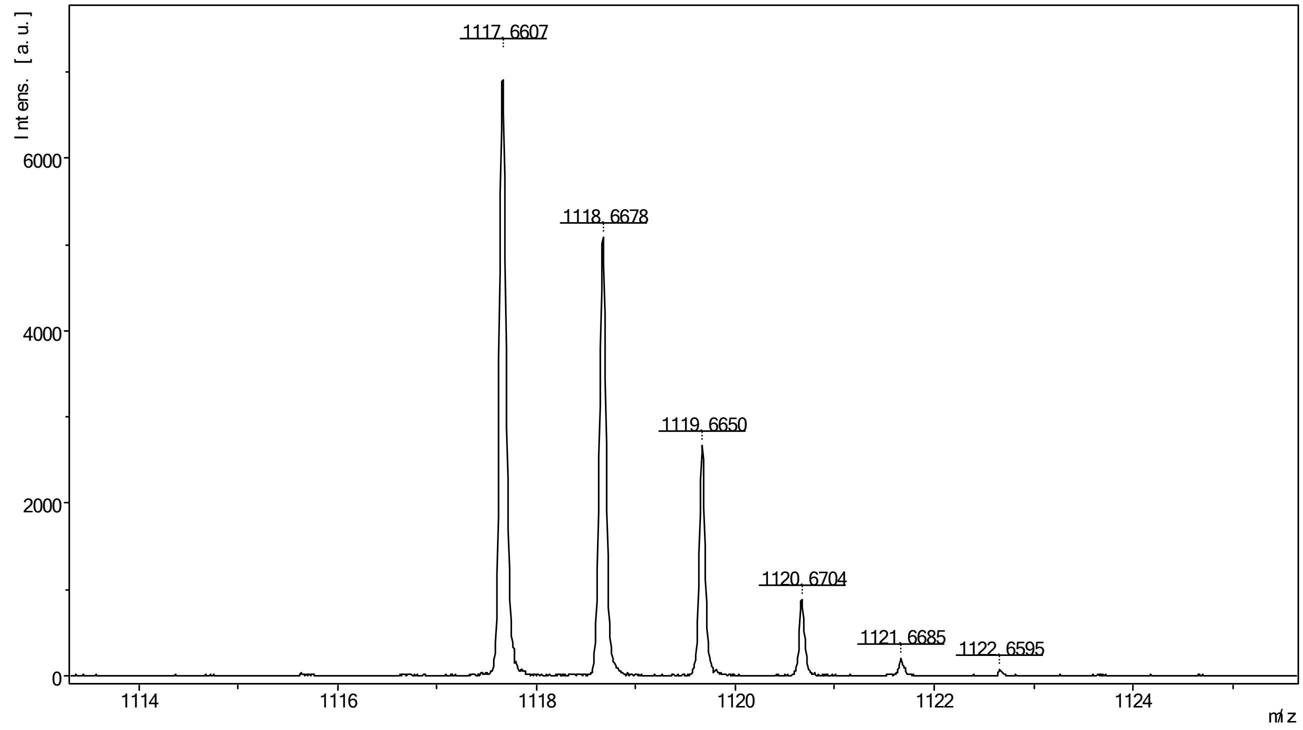


Figure S28. HR (MALDI-TOF) mass spectrum of compound **BTPD-TTz**.

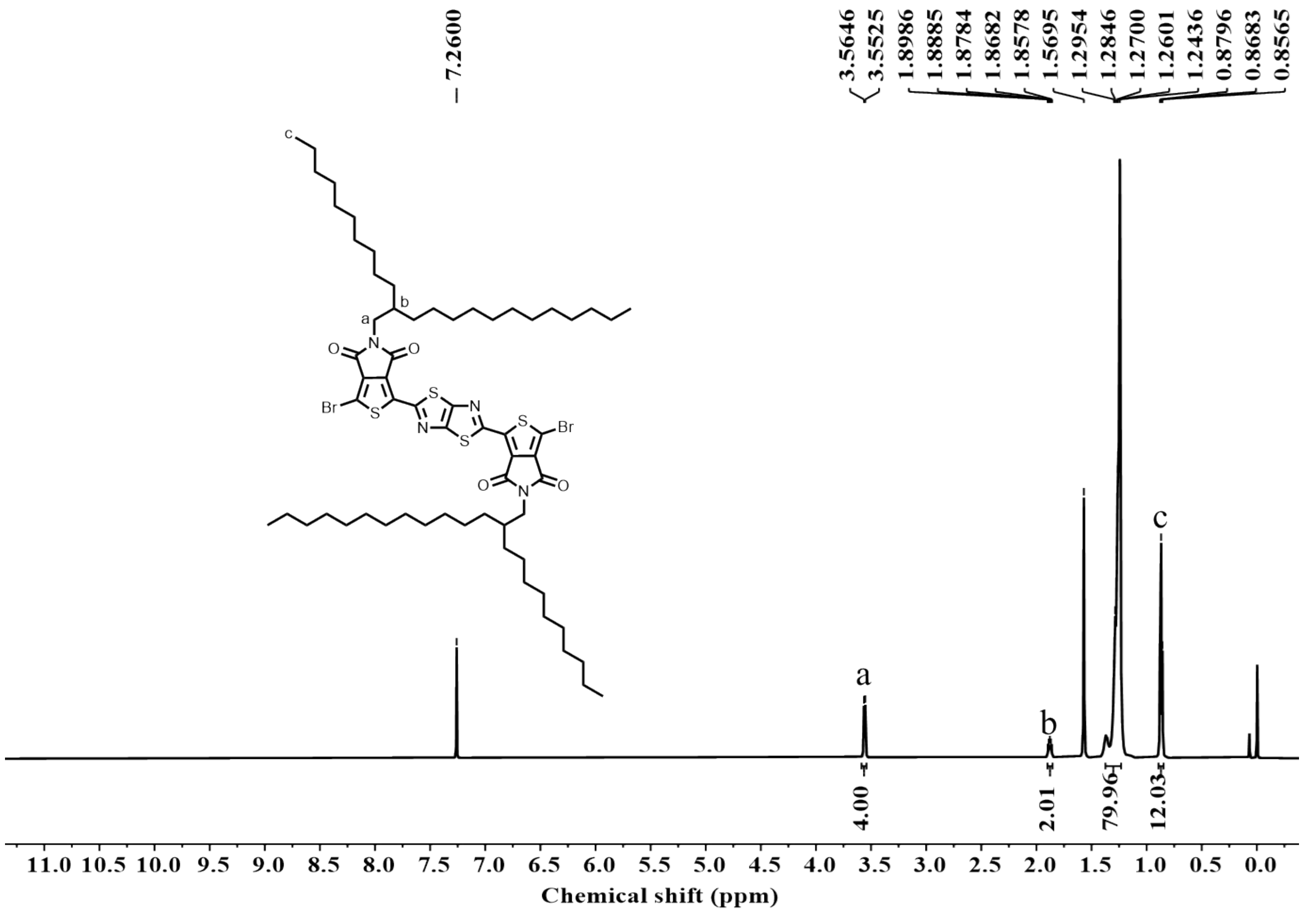


Figure S29. ^1H NMR spectrum (600 MHz) of compound **BTPD-TTz-Br** in $CDCl_3$ at 298 K.

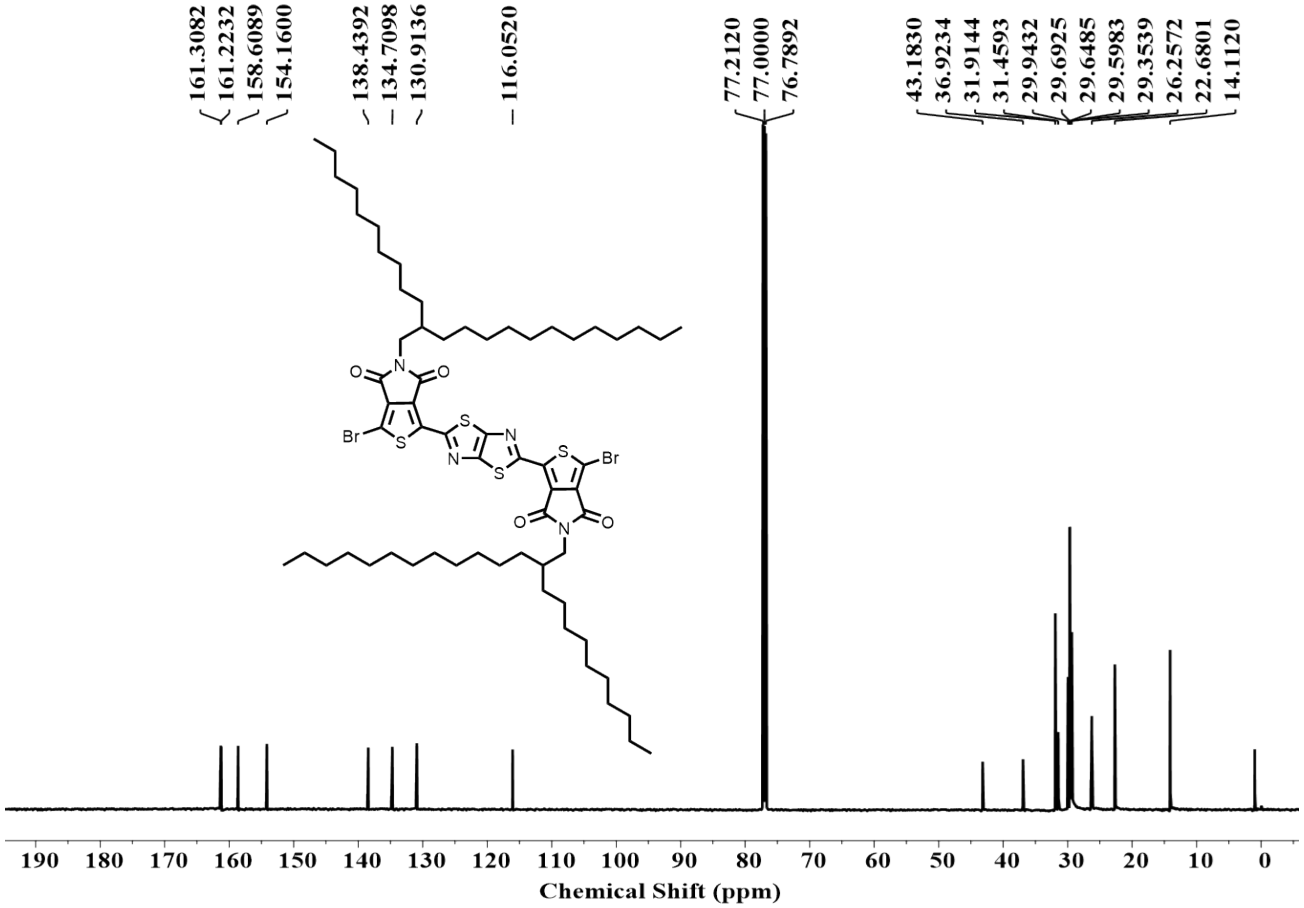


Figure S30. ^{13}C NMR spectrum (150 MHz) of compound **BTPD-TTz-Br** in $CDCl_3$ at 298 K.

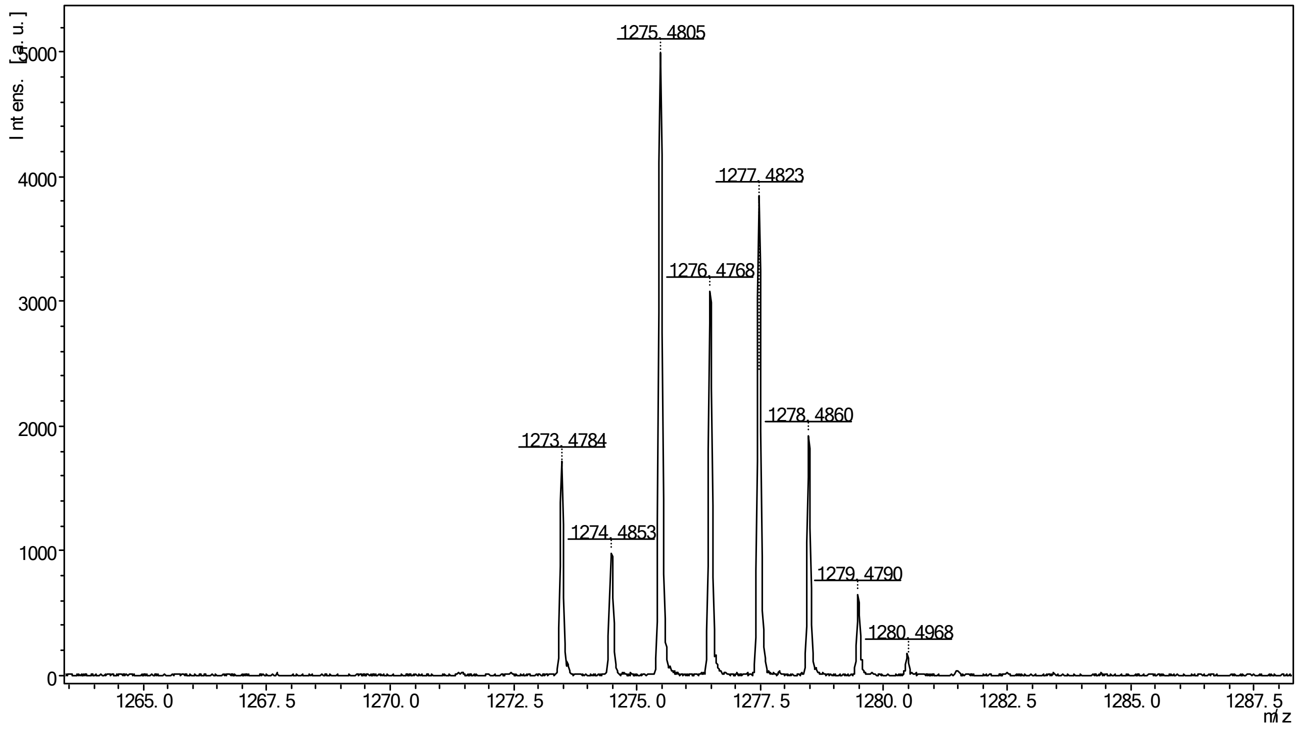


Figure S31. HR (MALDI-TOF) mass spectrum of compound **BTPD-TTz-Br**.

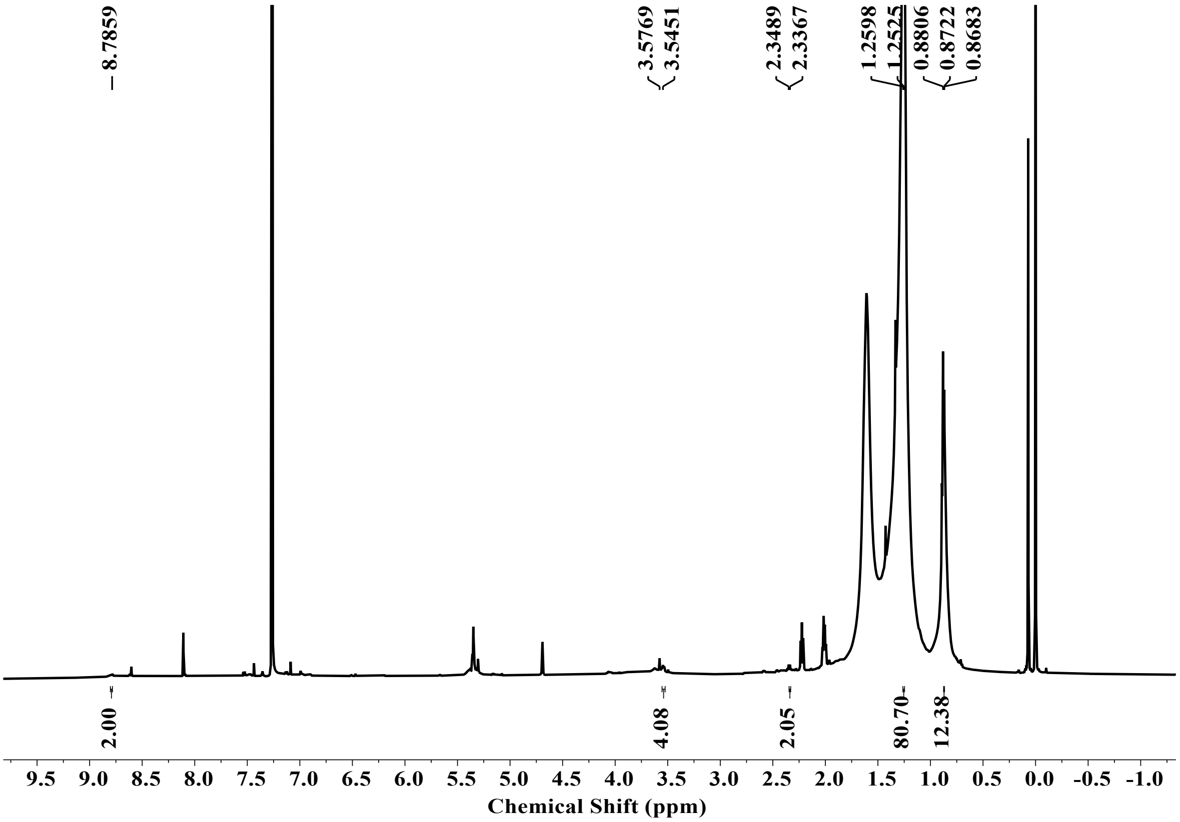


Figure S32. ^{1}H NMR spectrum (400 MHz) of polymer **PBTz-TCN** in CDCl$_3$ at 298 K

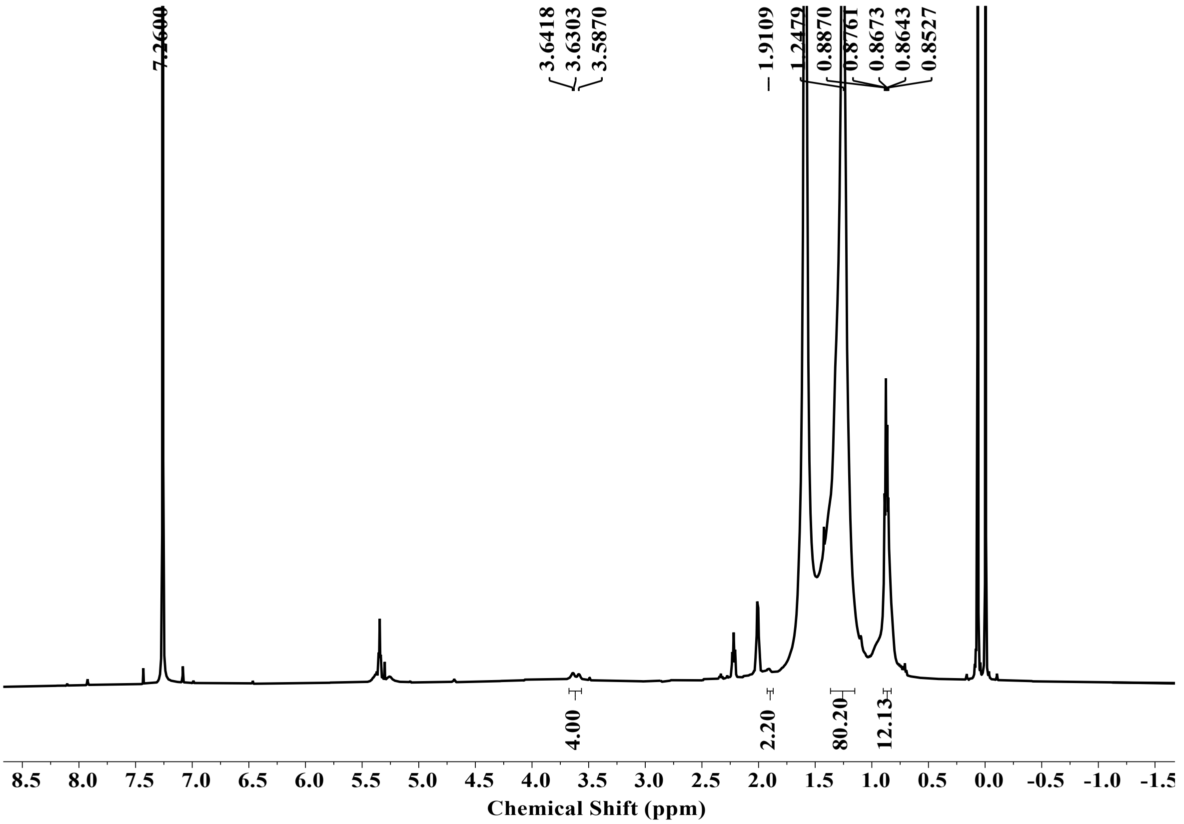


Figure S33. ^{1}H NMR spectrum (400 MHz) of polymer **PTTz-TCN** in CDCl$_3$ at 298 K

9. References

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