Electronic Supplementary Information

Fine-tuning of Side-chain Orientations on Nonfullerene Acceptors Enables Organic Solar Cells with 17.7% Efficiency

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General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ^{1}H NMR and ^{13}C NMR spectra were referenced to tetramethylsilane (0 ppm) for $CDCl_3$. Mass spectra were collected on a MALDI Micro MX mass spectrometer, or an API QSTAR XL System.

DFT calculations. The calculations were performed on a Gauss software package on B3LYP/6-31G(d,p) level.

TGA Measurements. Thermogravimetric analysis (TGA) plots were measured with a Discovery series instrument under a nitrogen atmosphere at heating and cooling rates of 10 ℃ min^{-1}.

Optical characterizations. Film UV-Vis absorption spectra were acquired on a Perkin Elmer Lambda 20 UV/VIS Spectrophotometer. The films were cast from the solutions of the acceptors with a concentration of 20 mg/mL in chloroform. UV-Vis absorption spectra were collected from the solution of two small molecules with the concentration of 1.0×10^{-5} M in chloroform and a cuvette with a stopper (Sigma Z600628) was used to avoid volatilization during the measurement. The films were spin-coated from the chloroform solution (13-15 mg mL^{-1}) on a quartz substrate at 1000 rpm for 30 s.

Electrochemical characterizations. Cyclic voltammetry was carried out on a CHI610E electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The solid films were drop-casted on the working electrode from a chloroform solution with a concentration of 5 mg/mL. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as external standards in acetonitrile solutions. The scan rate is 0.05 V s^{-1}. The LUMO levels were estimated by $-(E_{re} - E_{fc} + 4.8)$ eV and the HOMO levels were estimated by $-(E_{ox} - E_{fc} + 4.8)$ eV.

Solar cell fabrications and testing. Devices were fabricated on the indium tin oxide (ITO) patterned glass with a conventional configuration of ITO/PEDOT:PSS/active layers/PNDIT-F3N/Ag. PEDOT:PSS was spin-coated onto the ITO substrates at 5000 rpm for 30 s, then the

substrates were moved to a hot plate and dried at 150°C for 15 min. PTQ10:*o*-BTP-PhC6, PTQ10:*m*-BTP-PhC6, and PTQ10:*p*-BTP-PhC6 blends (D:A=1:1.2) were dissolved in chloroform (the donor concentration of the solution was 9 mg/mL). The blend solution was spin-coated on the top of PEDOT:PSS layer and then thermal annealing was utilized to optimize the morphology of active layer. The optimal method for active layer was to deposit the solution with 0.70% CN at 3000 rpm and annealed at 100 °C for 5 minutes. Atop the active layer, a thin electron transporting layer of PNDIT-F3N (0.5 mg/mL in methanol, 2000 rpm for 30 s, about 5-10 nm) was spin-coated. Finally, the Ag electrodes were thermally deposited on the top of devices, the thickness of which was about 100 nm. The current density voltage (*J*-*V*) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm^{-2}) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity).

EQE measurements. EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

TRPL Measurements. Time-resolved Photoluminescence (TRPL) spectra were recorded using Time-correlated single-photon counting (TCSPC) technique with the exciton pulse from a mode-locked Ti:sapphire laser (Mira 900).

SCLC measurements. The electron and hole mobilities were measured by using the method called space-charge limited current (SCLC) for electron-only and hole-only devices. The structure of electron-only devices was ITO/ZnO/active layer/PNDIT-F3N/Ag and the hole-only devices were fabricated with the structure of ITO/PEDOT:PSS/active layer/MoO_3/Ag. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the Mott–Gurney law: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J is the measured current density, L is the film thickness of the active layer, μ is the mobility of charge carrier, ε_r is the relative dielectric constant of the transport medium component, and ε_0 is the permittivity of vacuum (8.85419×10^{-12} CV^{-1} m^{-1}), V is the difference of applied voltage (V_{app}) and offset voltage (V_{BI}). The mobility of charge carriers can be calculated from the slope of the $J^{1/2} \sim V$ curves.

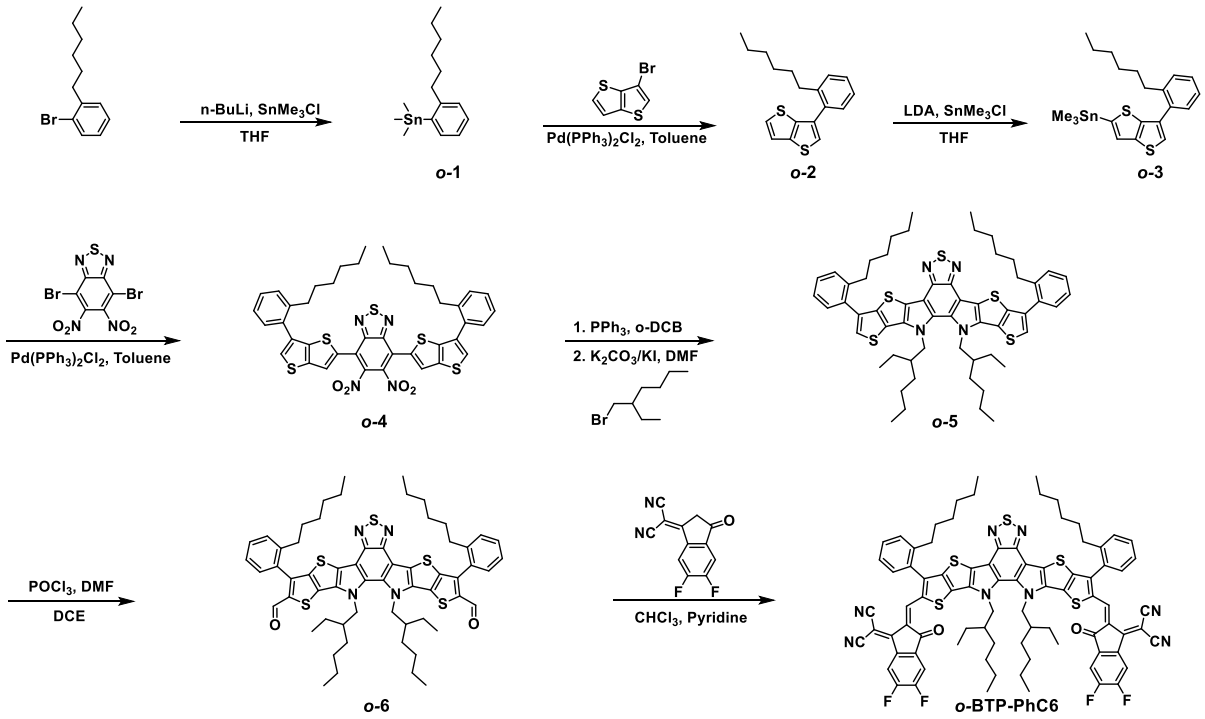
AFM characterizations. The AFM images were recorded using a Bruker multimode 8 AFM.

TEM characterizations. TEM experiments were performed on a JEM-2100 transmission electron microscope operated at 200 kV. For TEM experiments, the films were obtained by transferring the floated blend films from the water onto the Cu grid.

GIWAXS characterizations. GIWAXS measurements were performed at the Complex Materials Scattering (CMS) beamline of National Synchrotron Light Source II (NSLS-II), Brookhaven National Lab. The X-ray beam with an energy of 13.5 KeV shone upon the samples with the incident angle of 0.1° with respect to the substrate between the critical angles of the organic films and the Si substrate. A custom-made Pilatus-800K detector was placed at the distance of 257 mm from the sample center to capture GIWAXS images with the exposure time of 10 s. The data analysis was performed by SciAnalysis program. The coherence length was calculated using the Scherrer equation: $L_c = 2\pi K/\Delta q$, where Δq is the full width at half-maximum of the peak and K is a shape factor.

Materials and Synthesis

All chemicals, unless otherwise specified, were purchased from commercial resources and used as received.



Scheme S1 Synthetic route of *o*-BTP-PhC6.

Synthesis of compound *o*-1

To a solution of compound 1-bromo-3-hexylbenzene (3.50 g, 14.51 mmol) in tetrahydrofuran (90 mL), 2.0 **M** n-butyllithium (8.7 mL, 17.41 mmol) was added dropwise at −78 °C under argon. After stirring at the same temperature for 1.5 h, 1.0 **M** trimethyltin chloride (17.4 mL, 17.41 mmol) was added to the mixture at −78 °C, and the mixture was gradually warmed to room temperature. After stirring overnight, the mixture was quenched with saturated KF aqueous solution and extracted with hexane. The organic layer was dried with Na_2SO_4. Removing the solvent under reduced pressure gave the crude compound ***o*-1**. Without any further purification, the product was used into the following reaction.

Synthesis of compound *o*-2

A mixture of compound ***o*-1** (3.70 g, 11.38 mmol), 3-bromothieno[3,2-b]thiophene (1.08 g, 4.95 mmol), and $Pd(PPh_3)_2Cl_2$ (175.5 mg, 0.25 mmol) were dissolved in anhydrous toluene (50.0 mL) and stirred at 110 °C overnight under argon atmosphere. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed

with water and extracted with hexane. The crude product was purified with column chromatography on silica gel using hexane as the eluent to give a white solid ***o*-2** (892.4 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.33-7.32 (m, 2H), 7.28 (d, *J* = 5.2 Hz, 1H), 7.26-7.22 (m, 1H), 7.19 (d, *J* = 1.6 Hz, 1H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.50-1.44 (m, 2H), 1.22-1.11 (m, 6H), 0.79 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.59, 141.18, 138.60, 134.92, 134.37, 129.79, 129.68, 128.23, 127.43, 125.96, 124.37, 119.93, 33.38, 31.64, 31.54, 29.14, 22.60, 14.17. HR-MS (MALDI-TOF) m/z calcd. for ($C_{18}H_{20}S_2$): 300.1006. Found: 300.1005.

Synthesis of compound *o*-3

To a solution of compound ***o*-2** (890.0 mg, 2.96 mmol) in tetrahydrofuran (40 mL), 2.0 **M** lithium diisopropylamide (1.8 mL, 3.55 mmol) was added dropwise at −78 °C under argon. After stirring at the same temperature for 1.5 h, 1.0 **M** trimethyltin chloride (3.6 mL, 3.55 mmol) was added to the mixture at −78 °C, and the mixture was gradually warmed to room temperature. After stirring overnight, the mixture was quenched with saturated KF aqueous solution and extracted with hexane. The organic layer was dried with Na_2SO_4. Removing the solvent under reduced pressure gave the crude compound ***o*-3**. Without any further purification, the product was used into the following reaction.

Synthesis of compound *o*-4

Compound ***o*-3** (1.10 g, 2.37 mmol), 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (349.4 mg, 0.91 mmol), and $Pd(PPh_3)_2Cl_2$ (35.10 mg, 0.05 mmol) were dissolved in anhydrous toluene (8.0 mL) and stirred at 110 °C overnight under argon atmosphere. Then, the reaction mixture was cooled and poured into a saturated KF aqueous solution. The mixture was extracted with diethyl ether for three times. The combined organic phase was washed with water followed by brine. Then, the solution was dried over Na_2SO_4 and concentrated under reduced pressure. Compound ***o*-4** was purified by chromatography in on a silica gel column eluting with hexane/dichloromethane (4/1, *v*/*v*), which yielding a red powder as product (561.8 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.34-7.32 (m, 6H), 7.26-7.21 (m, 2H), 2.66 (t, *J* = 8.0 Hz, 4H), 1.56-1.48 (m, 4H), 1.26-1.14 (m, 12H), 0.80 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.09, 145.34, 141.77, 141.51, 138.85, 134.43, 133.89, 130.93, 129.78, 129.62, 128.56, 127.65, 126.10, 123.95, 121.34, 33.33, 31.61, 31.58,

29.12, 22.59, 14.17. HR-MS (MALDI-TOF) m/z calcd. for ($C_{42}H_{38}N_4O_4S_5$): 822.1497. Found: 822.1571.

Synthesis of compound *o*-5

Compound ***o*-4** (560.0 mg, 0.68 mmol) and triphenylphosphine (2.68 g, 10.20 mmol) were dissolved in anhydrous 1,2-dichlorobenzene (*o*-DCB, 6 mL) under argon and the mixture was stirred at 180 °C overnight. After cooling to room temperature, methanol was added and the mixture was filtered under reduced pressure to yield an orange solid. Subsequently, the orange intermediate was then mixed with K_2CO_3 (432.3 mg, 3.13 mmol), KI (2.1 mg, 0.01 mmol), 1-bromo-3-ethylheptane (1.21 g, 6.26 mmol), and anhydrous DMF (10 mL) were mixed under argon and stirred at 80 °C overnight. The mixture was extracted with diethyl ether for three times. The combined organic phase was washed with water followed by brine. Then, the solution was dried over Na_2SO_4 and concentrated under reduced pressure to yield an orange oil. Compound ***o*-5** was obtained by column chromatography on silica gel using hexane/dichloromethane (7/1, *v*/*v*) as the eluent to give an orange solid (307.6 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 4.0 Hz, 4H), 7.31-7.27 (m, 2H), 7.22 (s, 2H), 4.67 (d, *J* = 8.0 Hz, 4H), 2.74 (t, *J* = 8.0 Hz, 4H), 2.13-2.10 (m, 2H), 1.54-1.51 (m, 4H), 1.26-1.09 (m, 16H), 1.02-0.86 (m, 12H), 0.77 (t, *J* = 6.8 Hz, 6H), 0.70 (td, *J* = 7.2, 2.4 Hz, 6H), 0.63 (td, *J* = 7.2, 2.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.75, 143.35, 141.68, 137.00, 136.28, 133.95, 131.53, 129.91, 129.81, 128.52, 126.06, 123.53, 123.24, 121.45, 111.77, 55.10, 40.12, 33.50, 31.60, 29.77, 29.13, 27.79, 27.76, 23.32, 22.86, 22.59, 14.13, 13.85, 10.29. HR-MS (MALDI-TOF) m/z calcd. for ($C_{58}H_{70}N_4S_5$): 982.4204. Found: 983.4277.

Synthesis of compound *o*-6

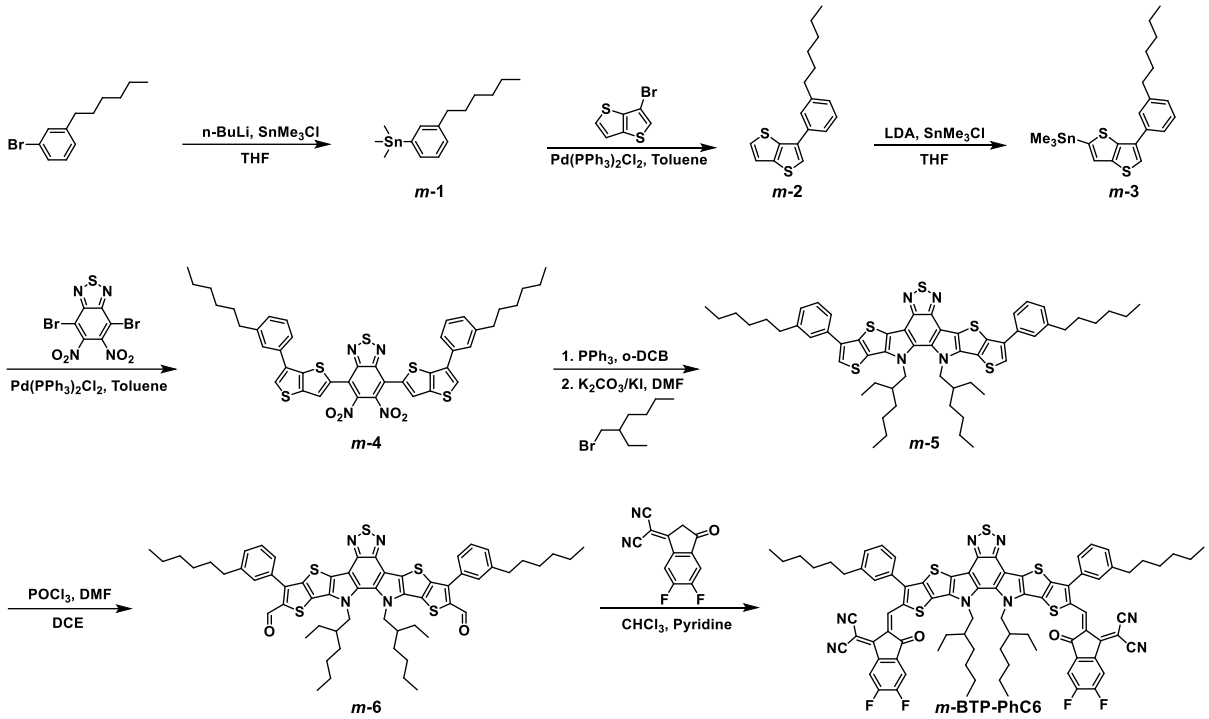
Compound ***o*-5** (200 mg, 0.20 mmol) was dissolved in 20 mL dichloroethane under argon, then the fresh Vilsmeier reagent (0.4 mL $POCl_3$ in 2.0 mL DMF) was added dropwise at 0 °C. After stirring for 20 min at 0 °C, the mixture was heated to 80 °C and reacted overnight. The reaction was quenched with saturated Na_2CO_3 solution and allowed to stir at room temperature for 20 min. The organic layer was separated, and the aqueous phase was extracted with diethyl ether for three times. The combined organic layer was washed with brine, dried over Na_2SO4, filtered, and concentrated under reduced pressure. The crude product was purified with column chromatograph on silica gel using dichloromethane/hexane (1/1, *v*/*v*) as the eluent to give an orange solid ***o*-6** (167.0 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 2H), 7.51-7.44 (m, 6H), 7.40-7.36 (m, 2H), 4.73 (d, *J* = 7.6 Hz, 4H), 2.71-2.66 (m, 4H), 2.11 (s, 2H), 1.50 (s, 4H), 1.14-0.90 (m, 28H), 0.78-0.62 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.93, 147.58, 145.83, 144.25, 142.07, 138.06, 136.90, 136.87, 132.82, 132.70, 130.78, 130.53, 129.98, 129.88, 129.00, 128.08, 126.25, 112.75, 55.38, 55.28, 40.38, 40.25, 33.59, 31.44, 31.40, 31.21, 29.70, 29.65, 28.93, 23.42, 23.38, 23.18, 22.86, 22.77, 22.75, 22.47, 14.04, 13.79, 10.58, 10.46, 10.17, 10.06. HR-MS (MALDI-TOF) m/z calcd. for ($C_{60}H_{70}N_4O_2S_5$): 1038.4102. Found: 1038.4176.

Synthesis of *o*-BTP-PhC6

Compound ***o*-6** (100.0 mg, 0.096 mmol), 2-(5, 6-difluoro-3-oxo-2, 3-dihydro-1*H*-inden-1-ylidene) malononitrile (110.7 mg, 0.48 mmol), pyridine (1.0 mL), and chloroform (10.0 mL) were dissolved in a round bottom flask under nitrogen. The mixture was stirred at 65 °C for 2 h. After cooling to room temperature, the mixture was poured into methanol and filtered. The residue was purified with column chromatography on silica gel using dichloromethane/hexane (3/1, *v*/*v*) as the eluent to give a dark blue solid ***o*-BTP-PhC6** (98.6 mg, 70% yield, purity >99% confirmed from high-performance gel permeation chromatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 2H), 8.51-8.47 (m, 2H), 7.75-7.72 (m, 2H), 7.56-7.54 (m, 2H), 7.50-7.48 (m, 2H), 7.43-7.39 (m, 4H), 4.84 (d, *J* = 8.0 Hz, 4H), 2.55 (t, *J* = 7.6 Hz, 4H), 2.21-2.18 (m, 2H), 1.46-1.45 (m, 4H), 1.25-1.05 (m, 28H), 0.86-0.79 (m, 6H), 0.74-0.64 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.23, 158.08, 153.18, 151.85, 147.50, 146.14, 142.20, 137.85, 137.81 137.78, 136.83, 135.11, 135.10, 134.67, 134.57, 131.31, 131.22, 131.18, 130.48, 130.41, 126.75, 121.03, 115.05, 114.84, 114.53, 113.86, 113.83, 113.34, 112.72, 112.53, 69.86, 55.85, 55.73, 40.57, 40.47, 33.61, 31.47, 31.42, 30.99, 29.85, 29.80, 29.00, 28.98, 28.97, 27.90, 27.65, 27.60, 23.53, 23.36, 22.99, 22.92, 22.48, 14.03, 13.88, 10.63, 10.58, 10.29, 10.24. HR-MS (MALDI-TOF) m/z calcd. for ($C_{84}H_{74}F_4N_8O_2S_5$): 1462.4474. Found: 1462.4550.



Scheme S2 Synthetic route of *m*-BTP-PhC6.

Synthesis of compound *m*-1

To a solution of compound 1-bromo-3-hexylbenzene (4.50 g, 18.66 mmol) in tetrahydrofuran (100 mL), 2.0 **M** n-butyllithium (11.2 mL, 22.39 mmol) was added dropwise at −78 °C under argon. After stirring at the same temperature for 1.5 h, 1.0 **M** trimethyltin chloride (22.4 mL, 22.39 mmol) was added to the mixture at −78 °C, and the mixture was gradually warmed to room temperature. After stirring overnight, the mixture was quenched with saturated KF aqueous solution and extracted with hexane. The organic layer was dried with Na_2SO_4. Removing the solvent under reduced pressure gave the crude compound ***m*-1**. Without any further purification, the product was used into the following reaction.

Synthesis of compound *m*-2

A mixture of compound ***m*-1** (3.92 g, 12.06 mmol), 3-bromothieno[3,2-b]thiophene (1.15 g, 5.24 mmol), and $Pd(PPh_3)_2Cl_2$ (182.5 mg, 0.26 mmol) were dissolved in anhydrous toluene (50.0 mL) and stirred at 110 °C overnight under argon atmosphere. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed with water and extracted with hexane. The crude product was purified with column chromatography on silica gel using hexane as the eluent to give a white solid ***m*-2** (1.23 g, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.57 (m, 2H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.43 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.39-7.35 (m, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 2.70-2.66 (m, 2H), 1.71-1.64 (m, 2H), 1.40-1.26 (m, 6H), 0.91-0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.81, 139.60, 138.20, 134.84, 134.83, 128.97, 127.98, 127.30, 126.59, 123.84, 122.48, 119.93, 36.15, 31.88, 31.57, 29.14, 22.75, 14.24. HR-MS (MALDI-TOF) m/z calcd. for ($C_{18}H_{20}S_2$): 300.1006. Found: 300.1003.

Synthesis of compound *m*-3

To a solution of compound ***m*-2** (1.23 g, 4.09 mmol) in tetrahydrofuran (50 mL), 2.0 **M** lithium diisopropylamide (2.5 mL, 4.91 mmol) was added dropwise at −78 °C under argon. After stirring at the same temperature for 1.5 h, 1.0 **M** trimethyltin chloride (4.9 mL, 4.91 mmol) was added to the mixture at −78 °C, and the mixture was gradually warmed to room temperature. After stirring overnight, the mixture was quenched with saturated KF aqueous solution and extracted with hexane. The organic layer was dried with Na_2SO_4. Removing the solvent under reduced pressure gave the crude compound ***m*-3**. Without any further purification, the product was used into the following reaction.

Synthesis of compound *m*-4

Compound ***m*-3** (1.71 g, 3.69 mmol), 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (545.2 mg, 1.42 mmol), and $Pd(PPh_3)_2Cl_2$ (49.1 mg, 0.07 mmol) were dissolved in anhydrous toluene (10.0 mL) and stirred at 110 °C overnight under argon atmosphere. Then, the reaction mixture was cooled and poured into a saturated KF aqueous solution. The mixture was extracted with diethyl ether for three times. The combined organic phase was washed with water followed by brine. Then, the solution was dried over Na_2SO_4 and concentrated under reduced pressure. Compound ***m*-4** was purified by chromatography in on a silica gel column eluting with hexane/dichloromethane (4/1, *v*/*v*), which yielding a red powder as product (946.7 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.65 (s, 2H), 7.59-7.57 (m, 4H), 7.43-7.39 (m, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 2.72-2.68 (m, 4H), 1.72-1.64 (m, 4H), 1.40-1.29 (m, 12H), 0.90-0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.29, 144.05, 142.47, 142.02, 139.84, 135.16, 134.13, 130.76, 129.17, 128.44, 126.70, 125.58, 123.94, 123.92, 121.58, 36.12, 31.86, 31.53, 29.11, 22.74, 14.24. HR-MS (MALDI-TOF) m/z calcd. for ($C_{42}H_{38}N_4O_4S_5$): 822.1497. Found: 822.1569.

Synthesis of compound *m*-5

Compound ***m*-4** (940.0 mg, 1.14 mmol) and triphenylphosphine (4.48 g, 17.10 mmol) were dissolved in anhydrous 1,2-dichlorobenzene (*o*-DCB, 10 mL) under argon and the mixture was stirred at 180 °C overnight. After cooling to room temperature, methanol was added and the mixture was filtered under reduced pressure to yield an orange solid. Subsequently, the orange intermediate was then mixed with K_2CO_3 (756.3 mg, 5.47 mmol), KI (3.6 mg, 0.02 mmol), 1-bromo-3-ethylheptane (2.11 g, 10.94 mmol), and anhydrous DMF (10 mL) were mixed under argon and stirred at 80 °C overnight. The mixture was extracted with diethyl ether for three times. The combined organic phase was washed with water followed by brine. Then, the solution was dried over Na_2SO_4 and concentrated under reduced pressure to yield an orange oil. Compound ***m*-5** was obtained by column chromatography on silica gel using hexane/dichloromethane (7/1, *v*/*v*) as the eluent to give an orange solid (538.2 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 4H), 7.52 (s, 2H), 7.47-7.43 (m, 2H), 7.28-7.26 (m, 2H), 4.72-4.69 (m, 4H), 2.77 (t, *J* = 8.0, 4H), 2.12-2.10 (m, 2H), 1.77-1.71 (m, 4H), 1.47-1.36 (m, 12H), 1.11-0.90 (m, 22H), 0.71-0.63 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.88, 144.09, 140.36, 137.00, 136.84, 134.46, 131.94, 129.17, 128.40, 126.96, 124.72, 124.33, 123.37, 119.95, 111.72, 55.18, 40.22, 36.30, 31.98, 31.75, 29.88, 29.85, 29.29, 27.91, 23.31, 23.26, 22.94, 22.86, 14.35, 13.92, 10.22, 10.19. HR-MS (MALDI-TOF) m/z calcd. for ($C_{58}H_{70}N_4S_5$): 982.4204. Found: 982.4277.

Synthesis of compound *m*-6

Compound ***m*-5** (200 mg, 0.20 mmol) was dissolved in 20 mL dichloroethane under argon, then the fresh Vilsmeier reagent (0.4 mL $POCl_3$ in 2.0 mL DMF) was added dropwise at 0 °C. After stirring for 20 min at 0 °C, the mixture was heated to 80 °C and reacted overnight. The reaction was quenched with saturated Na_2CO_3 solution and allowed to stir at room temperature for 20 min. The organic layer was separated, and the aqueous phase was extracted with diethyl ether for three times. The combined organic layer was washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. The crude product was purified with column chromatograph on silica gel using dichloromethane/hexane (1/1, *v*/*v*) as the eluent to give an orange solid ***m*-6** (177.6 mg, 84% yield).

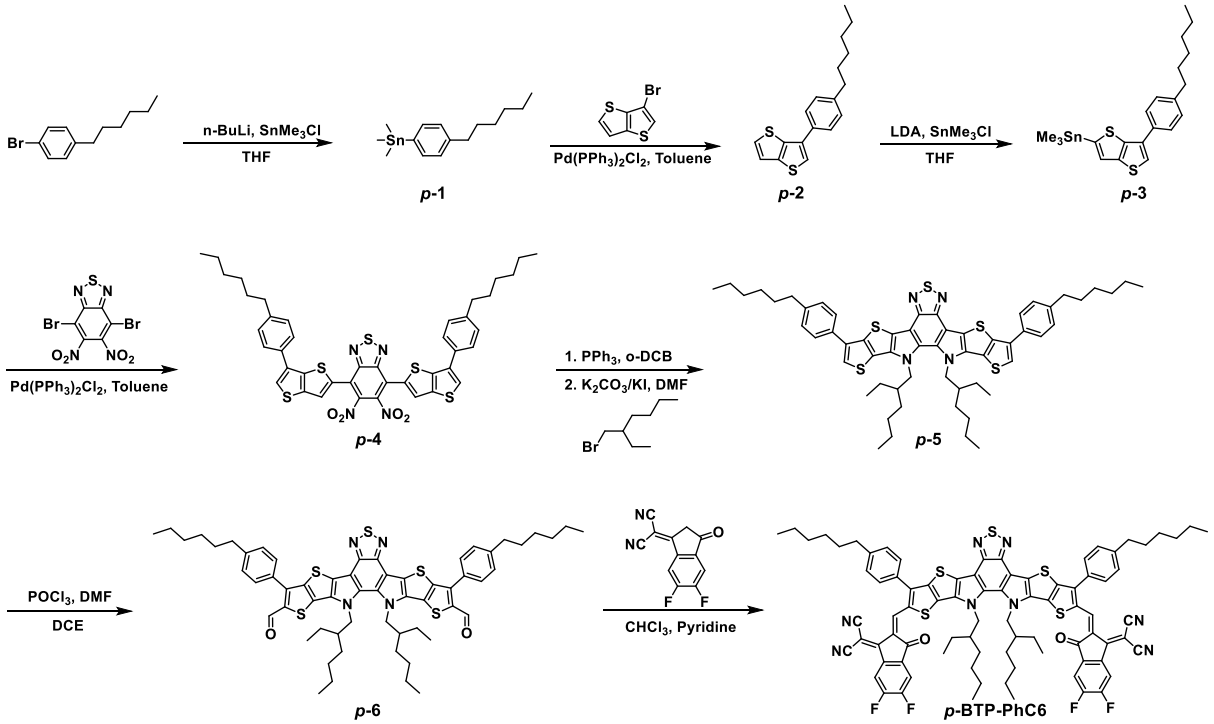
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 2H), 7.59-7.57 (m, 4H), 7.52-7.48 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 4.75-4.64 (m, 4H), 2.75 (t, *J* = 7.6 Hz, 4H), 2.06-2.03 (m, 2H), 1.75-1.68 (m, 4H), 1.43-1.34 (m, 12H), 1.10-0.89 (m, 22H), 0.69-0.62 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.36, 147.69, 146.11, 144.48, 143.19, 137.48, 136.99, 132.97, 132.94, 132.02, 130.19,

129.81, 129.39, 129.32, 128.07, 128.05, 127.20, 112.65, 55.39, 40.40, 36.12, 31.90, 31.60, 29.76, 29.22, 27.79, 23.23, 22.90, 22.82, 14.30, 13.87, 10.19. HR-MS (MALDI-TOF) m/z calcd. for ($C_{60}H_{70}N_4O_2S_5$): 1038.4102. Found: 1038.4175.

Synthesis of *m*-BTP-PhC6

Compound ***m*-6** (100.0 mg, 0.096 mmol), 2-(5, 6-difluoro-3-oxo-2, 3-dihydro-1*H*-inden-1-ylidene) malononitrile (110.7 mg, 0.48 mmol), pyridine (1.0 mL), and chloroform (10.0 mL) were dissolved in a round bottom flask under nitrogen. The mixture was stirred at 65 °C for 2 h. After cooling to room temperature, the mixture was poured into methanol and filtered. The residue was purified with column chromatography on silica gel using dichloromethane/hexane (3/1, *v*/*v*) as the eluent to give a dark blue solid ***m*-BTP-PhC6** (109.83 mg, 78% yield, purity >99% confirmed from high-performance gel permeation chromatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 2H), 8.52-8.48 (m, 2H), 7.74-7.70 (m, 2H), 7.58-7.54 (m, 2H), 7.49-7.45 (m, 6H), 4.82-4.79 (m, 4H), 2.77 (t, *J* = 7.6 Hz, 4H), 2.15-2.10 (m, 2H), 1.76-1.70 (m, 4H), 1.44-1.34 (m, 12H), 1.22-0.89 (m, 22H), 0.79-0.67 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.96, 158.80, 153.19, 152.24, 147.60, 145.09, 144.80, 138.77, 137.79, 135.01, 133.87, 133.62, 132.45, 131.47, 130.83, 130.29, 129.76, 127.78, 121.26, 115.03, 114.81, 114.65, 113.73, 113.63, 112.57, 69.63, 55.79, 40.59, 36.08, 31.93, 31.45, 29.93, 29.88, 29.18, 27.96, 27.88, 23.41, 23.33, 23.01, 22.99, 22.81, 14.30, 13.93, 13.91, 10.33, 10.23. HR-MS (MALDI-TOF) m/z calcd. for ($C_{84}H_{74}F_4N_8O_2S_5$): 1462.4474. Found: 1462.4553.



Scheme S3 Synthetic route of *p*-BTP-PhC6.

Synthesis of compound *p*-1

To a solution of compound 1-bromo-3-hexylbenzene (4.00 g, 16.59 mmol) in tetrahydrofuran (90 mL), 2.0 **M** n-butyllithium (10.0 mL, 19.91 mmol) was added dropwise at −78 °C under argon. After stirring at the same temperature for 1.5 h, 1.0 **M** trimethyltin chloride (19.9 mL, 19.91 mmol) was added to the mixture at −78 °C, and the mixture was gradually warmed to room temperature. After stirring overnight, the mixture was quenched with saturated KF aqueous solution and extracted with hexane. The organic layer was dried with Na_2SO_4. Removing the solvent under reduced pressure gave the crude compound ***p*-1**. Without any further purification, the product was used into the following reaction.

Synthesis of compound *p*-2

A mixture of compound ***p*-1** (3.52 g, 10.83 mmol), 3-bromothieno[3,2-b]thiophene (1.03 g, 4.71 mmol), and $Pd(PPh_3)_2Cl_2$ (168.5 mg, 0.24 mmol) were dissolved in anhydrous toluene (50.0 mL) and stirred at 110 °C overnight under argon atmosphere. After being cooled to room temperature, the solvent was then removed under reduced pressure. The residue was washed with water and extracted with hexane. The crude product was purified with column chromatography on silica gel using hexane as the eluent to give a white solid ***p*-2** (1.12 g, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.44 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.32-7.30 (m, 2H), 7.28 (s, 1H), 2.66 (t, *J* = 8.0 Hz, 2H), 1.70-1.62 (m, 2H), 1.41-1.30 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.73, 139.60, 138.08, 134.59, 132.30, 129.11, 127.30, 126.35, 122.06, 119.93, 35.86, 31.88, 31.53, 29.17, 22.76, 14.25. HR-MS (MALDI-TOF) m/z calcd. for ($C_{18}H_{20}S_2$): 300.1006. Found: 300.1006.

Synthesis of compound *p*-3

To a solution of compound ***p*-2** (1.12 g, 3.73 mmol) in tetrahydrofuran (50 mL), 2.0 **M** lithium diisopropylamide (2.2 mL, 4.48 mmol) was added dropwise at −78 °C under argon. After stirring at the same temperature for 1.5 h, 1.0 **M** trimethyltin chloride (4.5 mL, 4.48 mmol) was added to the mixture at −78 °C, and the mixture was gradually warmed to room temperature. After stirring overnight, the mixture was quenched with saturated KF aqueous solution and extracted with hexane. The organic layer was dried with Na_2SO_4. Removing the solvent under reduced pressure gave the crude compound ***p*-3**. Without any further purification, the product was used into the following reaction.

Synthesis of compound *p*-4

Compound ***p*-3** (1.61 g, 3.48 mmol), 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (514.5 mg, 1.34 mmol), and $Pd(PPh_3)_2Cl_2$ (49.1 mg, 0.07mmol) were dissolved in anhydrous toluene (10.0 mL) and stirred at 110 °C overnight under argon atmosphere. Then, the reaction mixture was cooled and poured into a saturated KF aqueous solution. The mixture was extracted with diethyl ether for three times. The combined organic phase was washed with water followed by brine. Then, the solution was dried over Na_2SO_4 and concentrated under reduced pressure. Compound ***p*-4** was purified by chromatography in on a silica gel column eluting with hexane/dichloromethane (4/1, *v*/*v*), which yielding a red powder as product (948.5 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.67 (d, *J* = 8.4 Hz, 4H), 7.63 (s, 2H), 7.31 (d, *J* = 8.0 Hz, 4H), 2.67 (t, *J* = 8.0 Hz, 4H), 1.70-1.62 (m, 4H), 1.40-1.30 (m, 12H), 0.92-0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.31, 143.28, 142.38, 142.00, 139.88, 134.96, 131.59, 130.78, 129.31, 126.48, 125.21, 124.01, 121.55, 35.89, 31.88, 31.51, 29.16, 22.76, 14.26. HR-MS (MALDI-TOF) m/z calcd. for ($C_{42}H_{38}N_4O_4S_5$): 822.1497. Found: 822.1489.

Synthesis of compound *p*-5

Compound ***p*-4** (947.0 mg, 1.15 mmol) and triphenylphosphine (4.52 g, 17.25 mmol) were dissolved in anhydrous 1,2-dichlorobenzene (*o*-DCB, 10 mL) under argon and the mixture was stirred at 180 °C overnight. After cooling to room temperature, methanol was added and the mixture was filtered under reduced pressure to yield an orange solid. Subsequently, the orange intermediate was then mixed with K_2CO_3 (810.6 mg, 5.87 mmol), KI (3.9 mg, 0.02 mmol), 1-bromo-3-ethylheptane (2.27 g, 11.73 mmol), and anhydrous DMF (10 mL) were mixed under argon and stirred at 80 °C overnight. The mixture was extracted with diethyl ether for three times. The combined organic phase was washed with water followed by brine. Then, the solution was dried over Na_2SO_4 and concentrated under reduced pressure to yield an orange oil. Compound ***p*-5** was obtained by column chromatography on silica gel using hexane/dichloromethane (7/1, *v*/*v*) as the eluent to give an orange solid (576.8 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 4H), 7.47 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 4H), 4.69-4.61 (m, 4H), 2.69 (t, *J* = 7.6 Hz 4H), 2.10-2.07 (m, 2H), 1.72-1.65 (m, 4H), 1.42-1.29 (m, 12H), 1.12-0.85 (m, 22H), 0.68-0.60 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.82, 143.17, 140.26, 136.94, 136.53, 131.86, 131.81, 129.25, 126.77, 124.62, 123.28, 119.38, 111.66, 55.15, 40.17, 35.92, 31.90, 31.56, 29.84, 29.18, 27.87, 23.27, 23.22, 22.89, 22.79, 14.27, 13.87, 10.19. HR-MS (MALDI-TOF) m/z calcd. for ($C_{58}H_{70}N_4S_5$): 982.4204. Found: 982.4210.

Synthesis of compound *p*-6

Compound ***p*-5** (200 mg, 0.20 mmol) was dissolved in 20 mL dichloroethane under argon, then the fresh Vilsmeier reagent (0.4 mL $POCl_3$ in 2.0 mL DMF) was added dropwise at 0 °C. After stirring for 20 min at 0 °C, the mixture was heated to 80 °C and reacted overnight. The reaction was quenched with saturated Na_2CO_3 solution and allowed to stir at room temperature for 20 min. The organic layer was separated, and the aqueous phase was extracted with diethyl ether for three times. The combined organic layer was washed with brine, dried over Na_2SO4, filtered, and concentrated under reduced pressure. The crude product was purified with column chromatograph on silica gel using dichloromethane/hexane (1/1, *v*/*v*) as the eluent to give an orange solid ***p*-6** (171.2 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 2H), 7.69 (d, *J* = 8.0 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 4H), 4.74-4.64 (m, 4H), 2.74 (t, *J* = 8.0 Hz, 4H), 2.07-2.04 (m, 2H), 1.75-1.67 (m, 4H), 1.43-1.33 (m, 12H), 1.11-0.90 (m, 22H), 0.70-0.63 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.32, 147.66, 145.90, 145.28, 143.14, 137.23, 136.98, 132.87, 129.73, 129.53, 129.40, 129.27, 127.96, 127.94, 112.62, 55.38, 40.36, 36.00, 31.87, 31.43, 29.74, 29.17, 27.76, 23.22, 22.86, 22.76, 14.26, 13.82, 10.18. HR-MS (MALDI-TOF) m/z calcd. for ($C_{60}H_{70}N_4O_2S_5$): 1038.4102. Found: 1038.4108.

Synthesis of *p*-BTP-PhC6

Compound ***p*-6** (100.0 mg, 0.096 mmol), 2-(5, 6-difluoro-3-oxo-2, 3-dihydro-1*H*-inden-1-ylidene) malononitrile (110.7 mg, 0.48 mmol), pyridine (1.0 mL), and chloroform (10.0 mL) were dissolved in a round bottom flask under nitrogen. The mixture was stirred at 65 °C for 2 h. After cooling to room temperature, the mixture was poured into methanol and filtered. The residue was purified with column chromatography on silica gel using dichloromethane/hexane (3/1, *v*/*v*) as the eluent to give a dark blue solid ***p*-BTP-PhC6** (105.6 mg, 75% yield, purity >99% confirmed from high-performance gel permeation chromatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 2H), 8.51 (dd, *J* = 10.0, 6.4 Hz, 2H), 7.74-7.70 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 4H), 4.85-4.75 (m, 4H), 2.77 (t, *J* = 7.6 Hz, 4H), 2.14-2.11 (m, 2H), 1.77-1.70 (m, 4H), 1.43-1.37 (m, 12H), 1.21-0.92 (m, 22H), 0.78-0.68 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.97, 158.88, 155.79, 153.31, 153.18, 153.04, 152.13, 147.64, 146.13, 144.99, 138.85, 137.81, 136.86, 136.81, 134.99, 134.63, 133.87, 133.46, 131.44, 130.32, 129.98, 129.81, 121.26, 115.02, 114.80, 114.73, 113.72, 113.65, 112.76, 112.58, 69.66, 55.79, 40.59, 36.12, 31.91, 31.73, 31.43, 29.92, 29.87, 29.12, 27.94, 27.87, 23.41,

23.34, 22.98, 22.81, 14.30, 13.92, 13.91, 10.33, 10.24. HR-MS (MALDI-TOF) m/z calcd. for ($C_{84}H_{74}F_4N_8O_2S_5$): 1462.4474. Found: 1462.4500.

Supplementary Tables

Table S1 The photovoltaic parameters of binary OSCs based on PTQ10 in previous reports.

	Donor:acceptor	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	Ref
1	PTQ10:*o*-BTP-PhC6	0.924	22.8	76.2	16.0	This work
2	PTQ10:*m*-BTP-PhC6	0.883	25.3	79.3	17.7	This work
3	PTQ10:*p*-BTP-PhC6	0.888	24.7	77.9	17.1	This work
4	PTQ10:Y6	0.826	26.65	75.1	16.53	1
5	PTQ10:Y6	0.87	24.81	75.1	16.21	2
6	PTQ10:Y6	0.849	24.49	72.63	15.10	3
7	PTQ10:Y6	0.851	24.64	71.67	15.03	4
8	PTQ10:N3	0.851	25.726	75.2	16.476	5
9	PTQ10:Y7	0.85	24.1	69.1	14.5	6
10	PTQ10:TPT10	0.890	22.30	66.20	13.14	7
11	PTQ10:TPT10	0.92	17.25	58.2	9.24	8
12	PTQ10:IDIC	0.969	17.81	73.6	12.70	9
13	PTQ10:IDIC	0.97	20.2	63.0	12.4	10
14	PTQ10:IDIC	0.943	18.75	69.66	12.32	11
15	PTQ10:IDIC	0.954	17.66	70.36	11.86	12
16	PTQ10:ITIC	1.029	16.13	60.01	10.90	12
17	PTQ10:IDIC	0.96	17.43	74.34	12.44	13
18	PTQ10:IDIC-2F	0.91	19.09	74.87	13.01	13
19	PTQ10:IDIC	0.956	17.11	72.15	11.80	14
20	PTQ10:IDIC-2F	0.904	18.95	75.99	13.02	14
21	PTQ10:IDIC-4F	0.810	18. 57	73.78	11.10	14
22	PTQ10:IT-4Cl	0.91	19.61	73.01	13.04	15
23	PTQ10:ZITI-C	0.93	20.42	68.9	13.13	16
24	PTQ10:ZITI-N	0.97	12.81	59.7	7.39	16
25	PTQ10:*m*-ITIC-2F	0.955	18.98	69.1	12.53	17
26	PTQ10:*m*-ITIC-4F	0.902	19.76	70.3	12.53	17
27	PTQ10:IDTCN	0.98	13.9	54.0	7.4	18
28	PTQ10:IDTPC	0.93	17.5	74.6	12.2	18
29	PTQ10:MO-IDIC	0.969	16.92	68.1	11.16	19
30	PTQ10:MO-IDIC-2F	0.906	19.87	74.8	13.46	19
31	PTQ10:IE4F-S	0.996	19.67	62.3	12.20	20
32	PTQ10:BFC-4F	0.81	20.50	72.35	12.05	21
33	PTQ10:BOC-4F	0.88	14.41	61.26	7.76	21
34	PTQ10:IDTPC	0.93	17.5	74.6	12.2	22
35	PTQ10:IDTPC-Me	0.95	13.8	70.3	9.2	22
36	PTQ10:IDTPC-DMe	1.02	13.5	68.0	9.3	22
37	PTQ10:ZITI-N	0.967	12.03	60.68	7.06	23
38	PTQ10:ZITI-S	0.960	16.94	65.75	10.69	23
39	PTQ10:TPTIC	0.90	17.17	67.45	10.42	24
40	PTQ10:HC-PCIC	0.94	15.99	67.96	10.42	25

Table S2 Photovoltaic performance of *o*-BTP-PhC6 based solar cells with different optimized conditions.

Conditions		V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
D:A	1:1	0.920 (0.914±0.003)	23.1 (22.7±0.18)	74.3 (71.9±1.25)	15.8 (15.4±0.18)
	1:1.2	0.924 (0.920±0.002)	22.8 (22.5±0.21)	76.2 (74.3±1.49)	16.0 (15.6±0.23)
	1:1.5	0.929 (0.922±0.003)	22.0 (21.6±0.25)	75.6 (73.1±1.34)	15.5 (15.0±0.30)
CN (%)	0.50	0.928 (0.924±0.003)	22.9 (22.6±0.29)	75.0 (73.2±1.28)	15.9 (15.5±0.21)
	0.75	0.924 (0.920±0.002)	22.8 (22.5±0.21)	76.2 (74.3±1.49)	16.0 (15.6±0.23)
	1.00	0.921 (0.916±0.004)	22.5 (22.1±0.23)	76.1 (74.5±1.43)	15.8 (15.3±0.27)
Annealing temperature (°C)	85	0.926 (0.923±0.003)	22.4 (22.0±0.28)	76.0 (73.7±1.32)	15.8 (15.3±0.34)
	100	0.924 (0.920±0.002)	22.8 (22.5±0.21)	76.2 (74.3±1.49)	16.0 (15.6±0.23)
	115	0.919 (0.915±0.003)	23.0 (22.7±0.25)	75.8 (73.2±1.47)	16.0 (15.5±0.31)

Table S3 Photovoltaic performance of *m*-BTP-PhC6 based solar cells with different optimized conditions.

Conditions		V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
D:A	1:1	0.880 (0.875±0.003)	25.7 (25.3±0.27)	76.2 (74.3±1.32)	17.2 (16.8±0.35)
	1:1.2	0.883 (0.878±0.003)	25.3 (24.8±0.26)	79.3 (77.4±1.21)	17.7 (17.3±0.22)
	1:1.5	0.887 (0.882±0.004)	25.1 (24.6±0.33)	77.8 (75.7±1.24)	17.3 (16.8±0.30)
CN (%)	0.50	0.888 (0.883±0.003)	25.6 (25.1±0.31)	75.9 (73.3±1.24)	17.3 (16.9±0.28)
	0.75	0.883 (0.878±0.003)	25.3 (24.8±0.26)	79.3 (77.4±1.21)	17.7 (17.3±0.22)
	1.00	0.878 (0.871±0.002)	25.2 (24.8±0.23)	77.4 (75.0±1.49)	17.1 (16.7±0.31)
Annealing temperature (°C)	85	0.884 (0.880±0.004)	25.0 (24.5±0.36)	77.0 (74.7±1.36)	17.0 (16.6±0.36)
	100	0.883 (0.878±0.003)	25.3 (24.8±0.26)	79.3 (77.4±1.21)	17.7 (17.3±0.22)
	115	0.878 (0.871±0.004)	25.6 (25.1±0.33)	78.1 (75.6±1.39)	17.5 (17.1±0.27)

Table S4 Photovoltaic performance of *p*-BTP-PhC6 based solar cells with different optimized conditions.

Conditions		V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
D:A	1:1	0.883 (0.877±0.003)	25.1 (24.7±0.25)	75.3 (73.2±1.46)	16.7 (16.3±0.21)
	1:1.2	0.888 (0.882±0.002)	24.7 (24.3±0.20)	77.9 (75.3±1.29)	17.1 (16.7±0.24)
	1:1.5	0.890 (0.883±0.002)	24.0 (23.5±0.31)	77.7 (75.0±1.33)	16.6 (16.1±0.31)
CN (%)	0.50	0.891 (0.886±0.003)	24.9 (24.4±0.29)	76.4 (74.1±1.24)	16.9 (16.4±0.29)
	0.75	0.888 (0.882±0.002)	24.7 (24.3±0.20)	77.9 (75.3±1.29)	17.1 (16.7±0.24)
	1.00	0.881 (0.876±0.004)	24.6 (24.1±0.31)	77.5 (75.3±1.36)	16.8 (16.3±0.26)
Annealing temperature (°C)	85	0.889 (0.882±0.003)	24.4 (24.0±0.31)	76.7 (74.6±1.32)	16.6 (16.1±0.32)
	100	0.888 (0.882±0.002)	24.7 (24.3±0.20)	77.9 (75.3±1.29)	17.1 (16.7±0.24)
	115	0.880 (0.872±0.003)	24.9 (24.5±0.25)	77.6 (75.2±1.24)	17.0 (16.5±0.27)

Table S5 SCLC mobilities of the pristine and blend films.

Materials combinations	μ_h (10^{-4} cm^2 V^{-1} s^{-1})	μ_e (10^{-4} cm^2 V^{-1} s^{-1})
o-BTP-PhC6	/	3.33
m-BTP-PhC6	/	6.41
p-BTP-PhC6	/	5.23
PTQ10:*o*-BTP-PhC6	1.28	2.96
PTQ10:*m*-BTP-PhC6	2.89	4.31
PTQ10:*p*-BTP-PhC6	1.99	3.64

Table S6 Summarized parameters for the ordering structures.

Film	Lamellar stacking			$\pi-\pi$ stacking		
	$d_l(q_{xy})$ (Å)((Å^{-1}))	FWHM[a] (Å^{-1})	CCL[b] (Å)	d_π (q_z) (Å)((Å^{-1}))	FWHM (Å^{-1})	CCL (Å)
PTQ10	23.3 (0.27)	0.091	69	3.49 (1.80)	0.243	26
o-BTP-PhC6	14.0 (0.45)	0.167	38	3.57 (1.76)	0.421	15
m-BTP-PhC6	23.3 (0.27)	0.081	78	3.45 (1.82)	0.228	28
	15.7 (0.40)	0.164	38			
p-BTP-PhC6	21.7 (0.29)	0.094	67	3.55 (1.77)	0.377	17
	15.0 (0.42)	0.148	42			
PTQ10:*o*-BTP-PhC6	22.4 (0.28)	0.091	69	3.51 (1.79)	0.282	22
PTQ10:*m*-BTP-PhC6	22.4 (0.28)	0.082	77	3.45 (1.82)	0.218	29
PTQ10:*p*-BTP-PhC6	22.4 (0.28)	0.079	80	3.45 (1.82)	0.229	27

[a] Full width at half-maximum (FWHM) of the diffraction peak.

[b] Coherent length (CCL) estimated from the Scherrer equation (CCL = 2π/FWHM) for the $\pi-\pi$ stacking of the face-on crystallite.

Table S7 The parameters of exciton dissociation efficiency and charge collection efficiency.

Active layer	J_{sat} (mA/cm^2)	$J_{ph,\ SC}$ [a] (mA/cm^2)	$J_{ph,\ MPP}$ [b] (mA/cm^2)	η_{diss} (%)	η_{coll} (%)
PTQ10:*o*-BTP-PhC6	23.8	22.8	20.7	95.8	87.0
PTQ10:*m*-BTP-PhC6	25.6	25.3	23.3	98.8	91.0
PTQ10:*p*-BTP-PhC6	25.4	24.7	22.4	97.2	88.2

[a] Under short-circuit condition; [b] Under the maximum power output condition.

Supplementary Figures

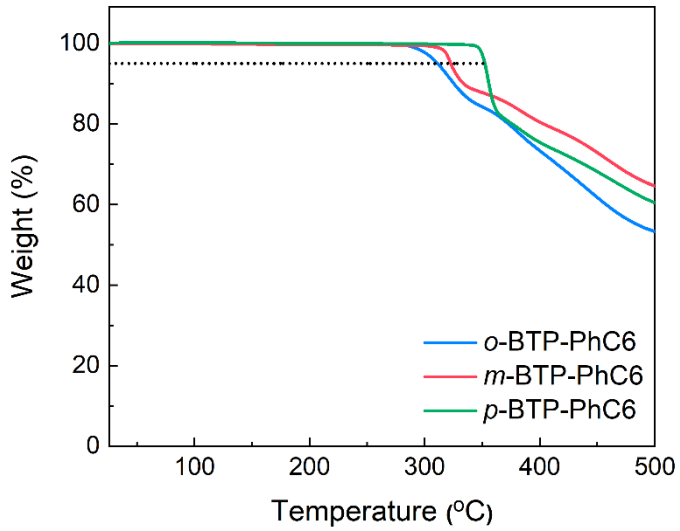


Fig. S1 Thermogravimetric analysis (TGA) curves of *o*-BTP-PhC6, *m*-BTP-PhC6, and *p*-BTP-PhC6.

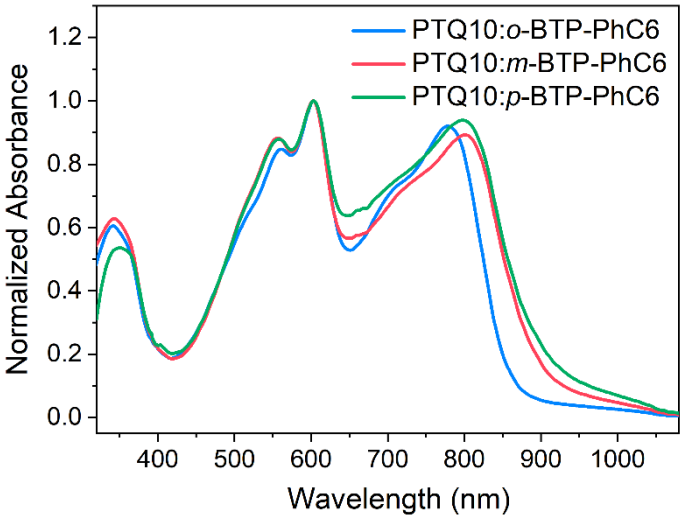


Fig. S2 UV-Vis absorption spectra of the PTQ10:*o*-BTP-PhC6, PTQ10:*m*-BTP-PhC6, and PTQ10:*p*-BTP-PhC6 blend films.

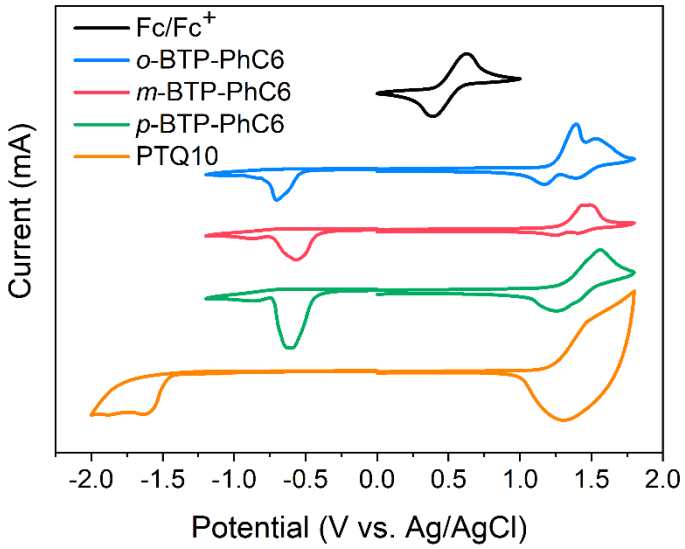


Fig. S3 Cyclic voltammetry curves of PTQ10, *o*-BTP-PhC6, *m*-BTP-PhC6, and *p*-BTP-PhC6.

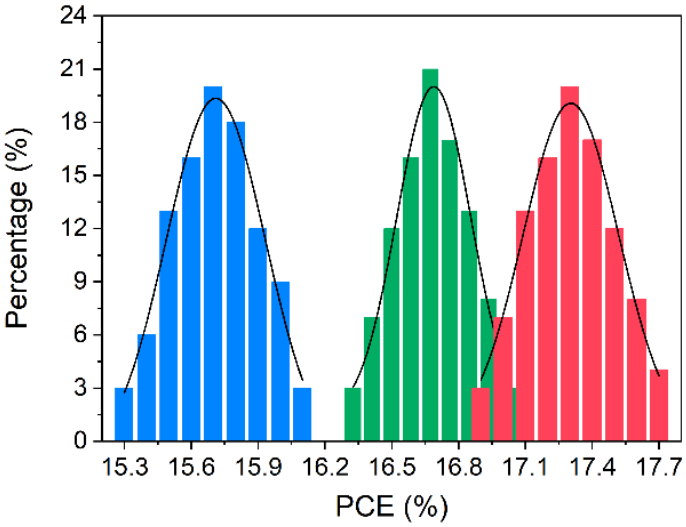


Fig. S4 Statistical PCE distribution histograms of the OSCs based on 20 cells of PTQ10:*o*-BTP-PhC6, PTQ10:*m*-BTP-PhC6, and PTQ10:*p*-BTP-PhC6.

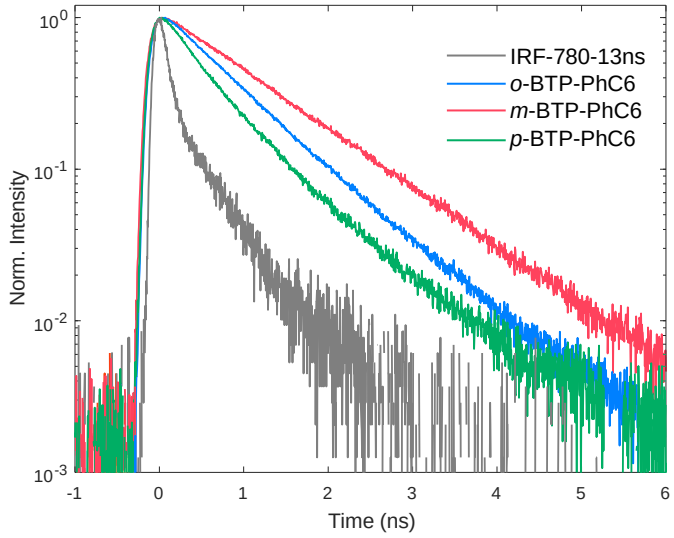


Fig. S5 TRPL decay spectra of pristine *o*-BTP-C6Ph, pristine *m*-BTP-PhC6, and pristine *p*-BTP-C6Ph films, the pump wavelength is 780 nm. The instrument response function (IRF) is also showed to indicate the time resolution limit of the system.

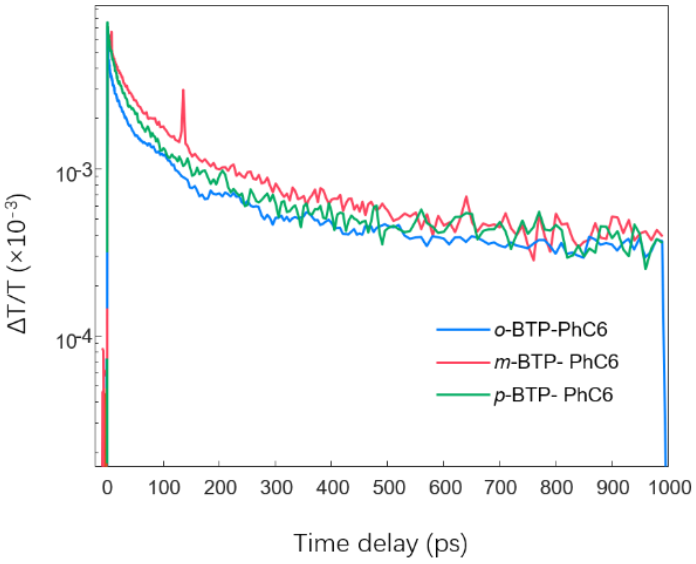


Fig. S6 Normalized kinetic traces of *o*-BTP-C6Ph, *m*-BTP-PhC6, and *p*-BTP-C6Ph ground state bleaching (GSB).

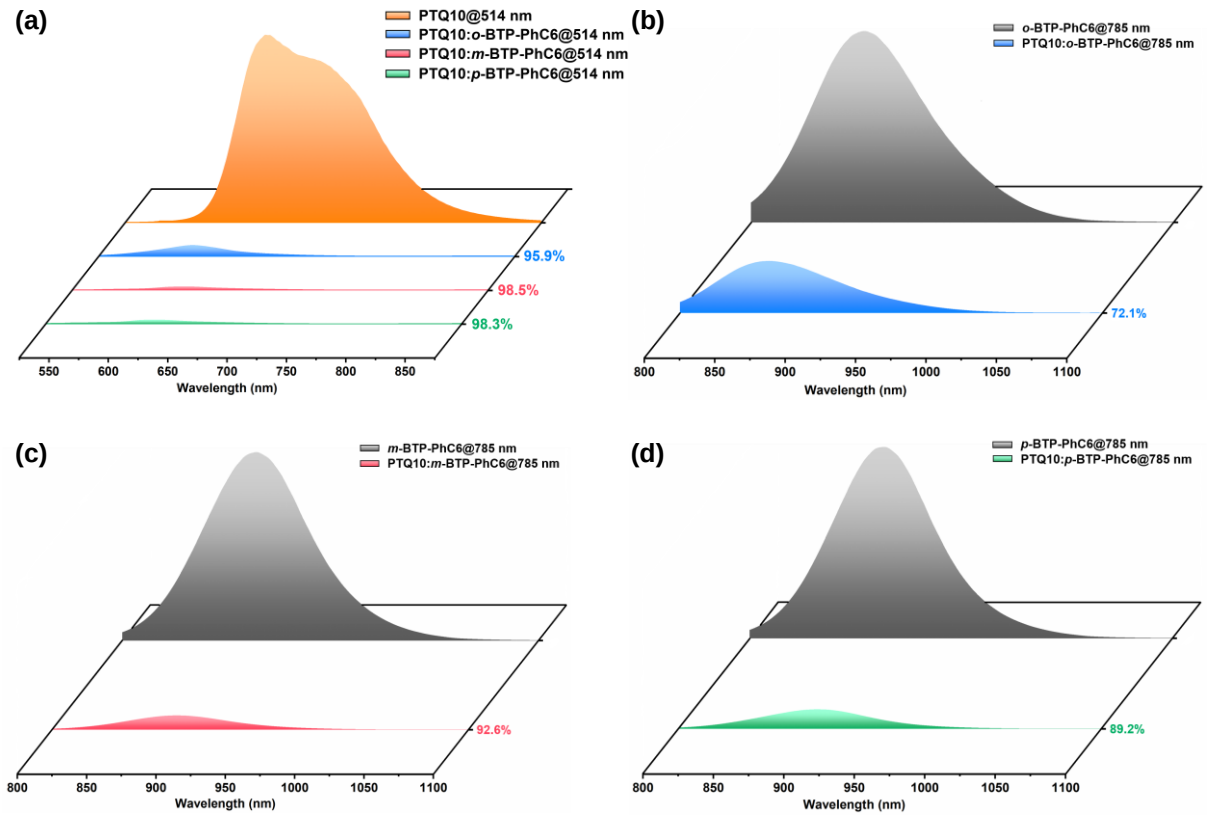


Fig. S7 (a) Photoluminescence (PL) spectra of pristine PTQ10, PTQ10:*o*-BTP-PhC6, PTQ10:*m*-BTP-PhC6, and the PTQ10:*p*-BTP-PhC6 blend films under 514 nm light excitation. Photoluminescence spectra of (b) the pristine *o*-BTP-PhC6 (excited at 785 nm) and the blend films of PTQ10:*o*-BTP-PhC6 (excited at 785 nm), (c) the pristine *m*-BTP-PhC6 (excited at 785 nm) and the blend films of PTQ10:*m*-BTP-PhC6 (excited at 785 nm), (d) the pristine *p*-BTP-PhC6 (excited at 785 nm) and the blend films of PTQ10:*p*-BTP-PhC6 (excited at 785 nm).

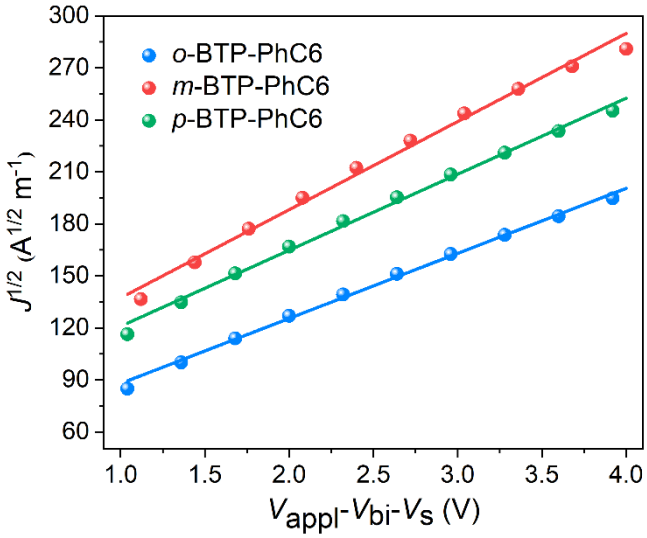


Fig. S8 Space-charge-limited (SCLC) $J^{1/2}$~V characteristics of pristine *o*-BTP-PhC6, *m*-BTP-PhC6, and *p*-BTP-PhC6 films.

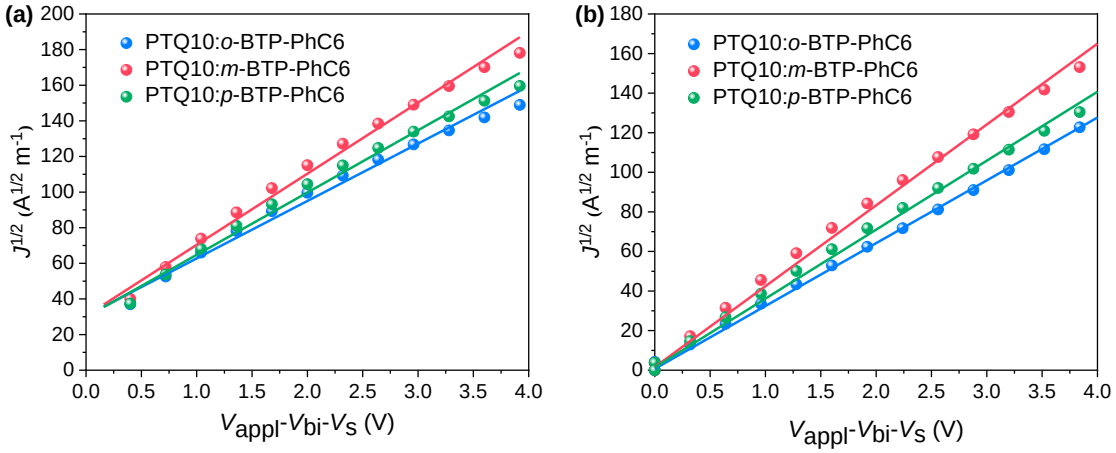


Fig. S9 $J^{1/2}$~V characteristics of (a) hole-only devices and (b) electron-only devices of the PTQ10:*o*-BTP-PhC6, PTQ10:*m*-BTP-PhC6, and PTQ10:*p*-BTP-PhC6 blend films.

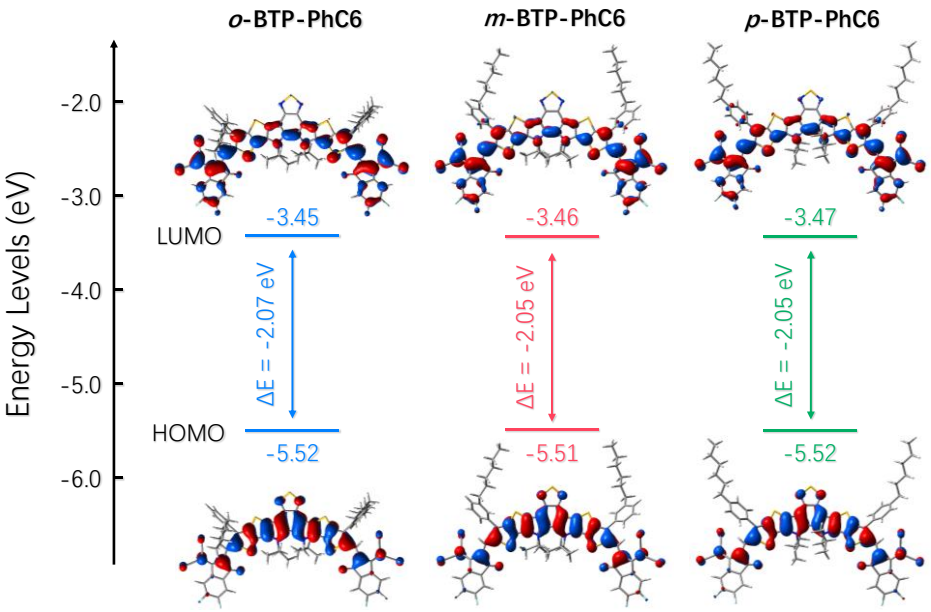


Fig. S10 DFT calculations of LUMO and HOMO levels of *o*-BTP-PhC6, *m*-BTP-PhC6, and *p*-BTP-PhC6.

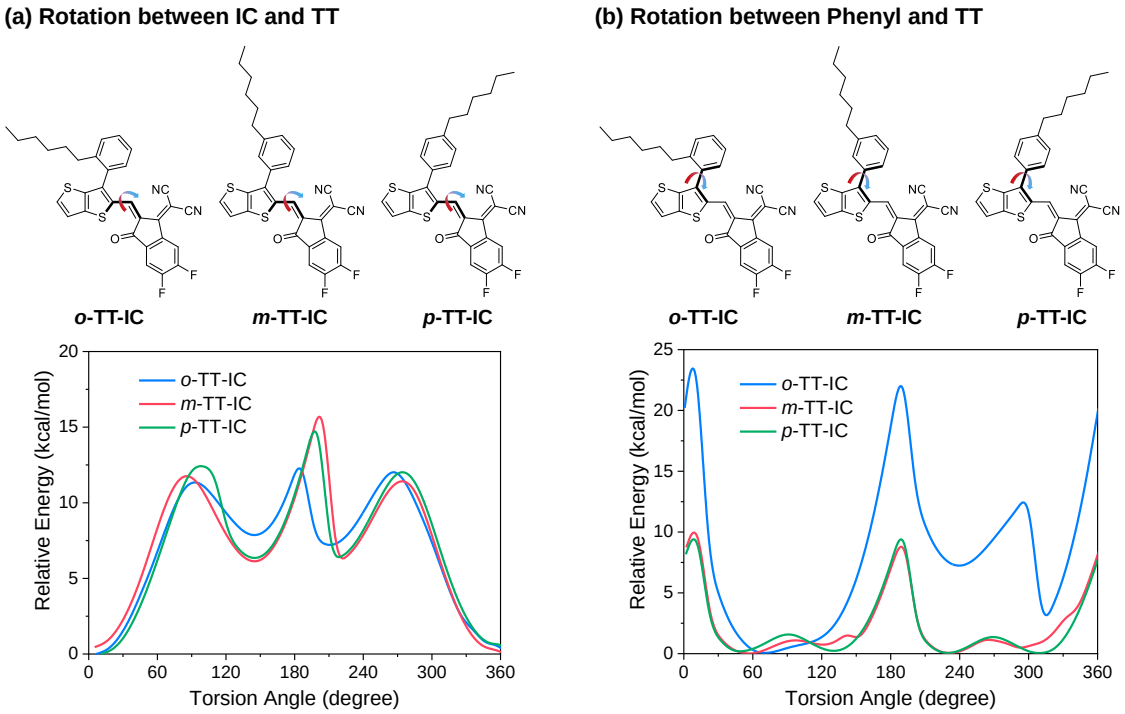


Fig. S11 Relaxed potential energy scans (PES) of the subunits of *o*-TT-IC, *m*-TT-IC, and *p*-TT-IC in terms of (a) the rotation between IC and TT, (b) the rotation between phenyl and TT.

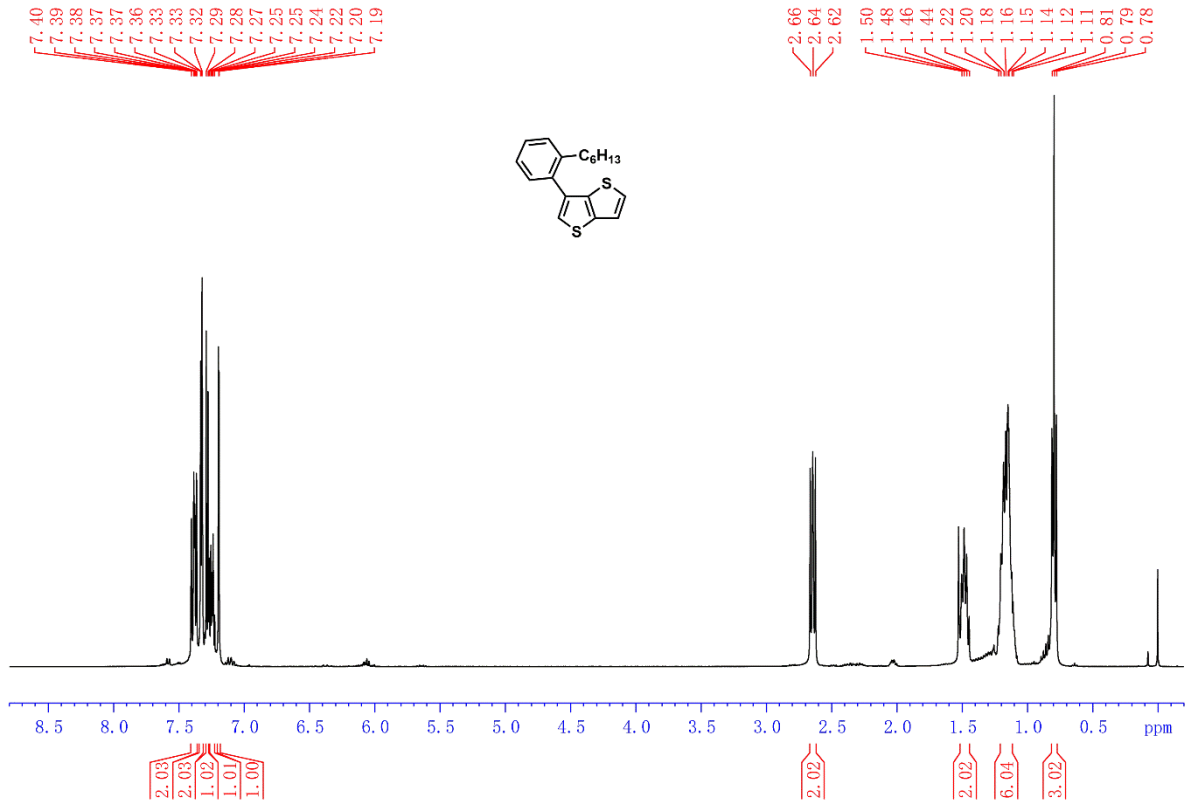


Fig. S12 ^{1}H NMR spectrum of compound *o*-2.

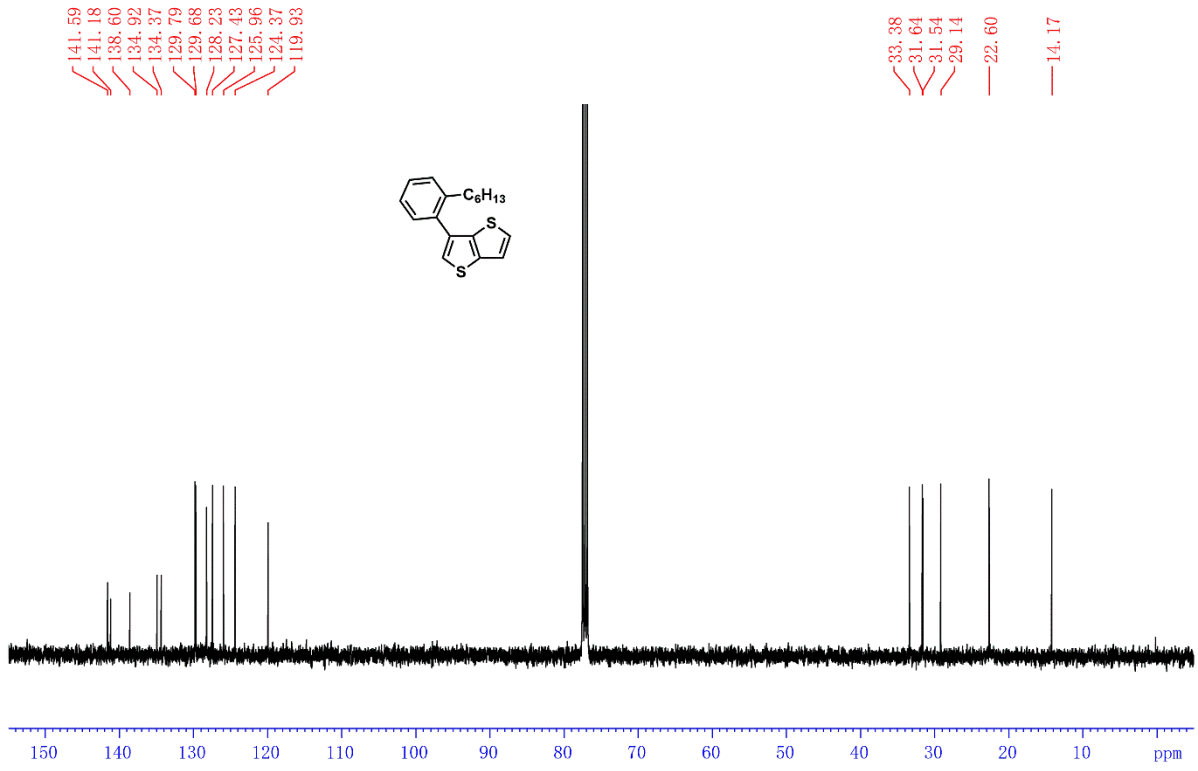


Fig. S13 ^{13}C NMR spectrum of compound *o*-2.

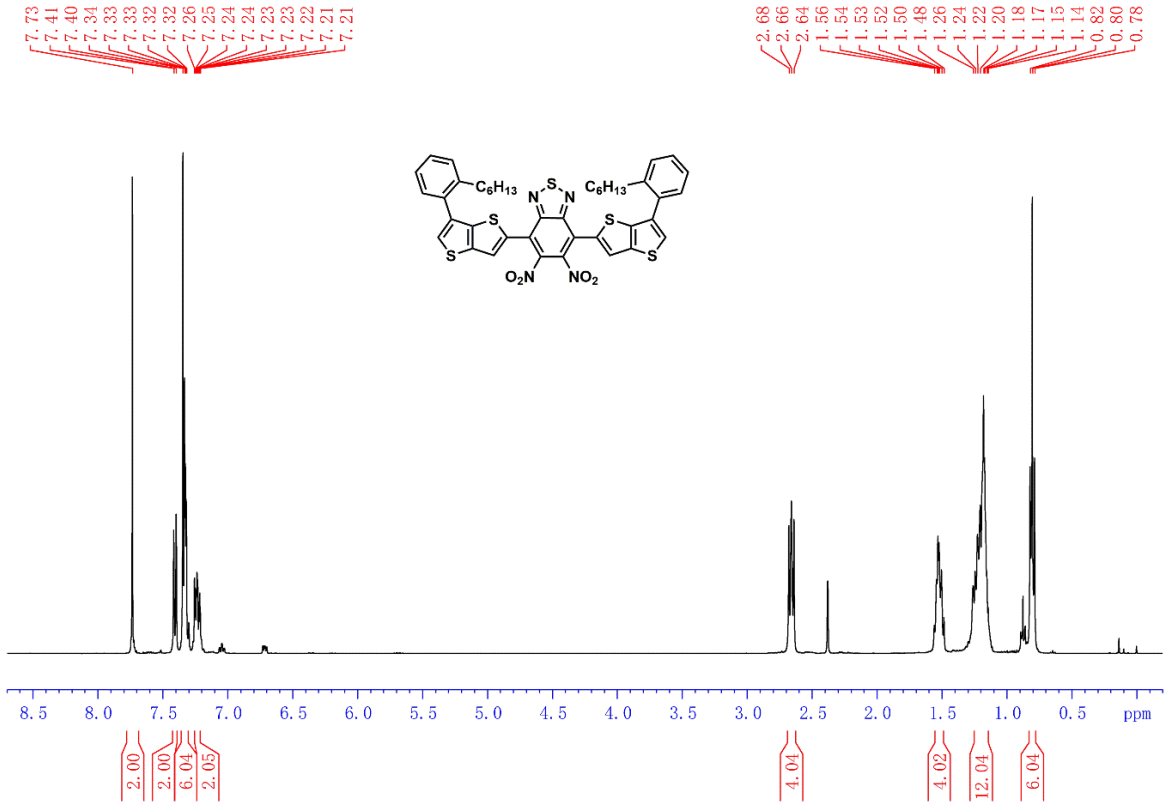


Fig. S14 ^{1}H NMR spectrum of compound *o*-4.

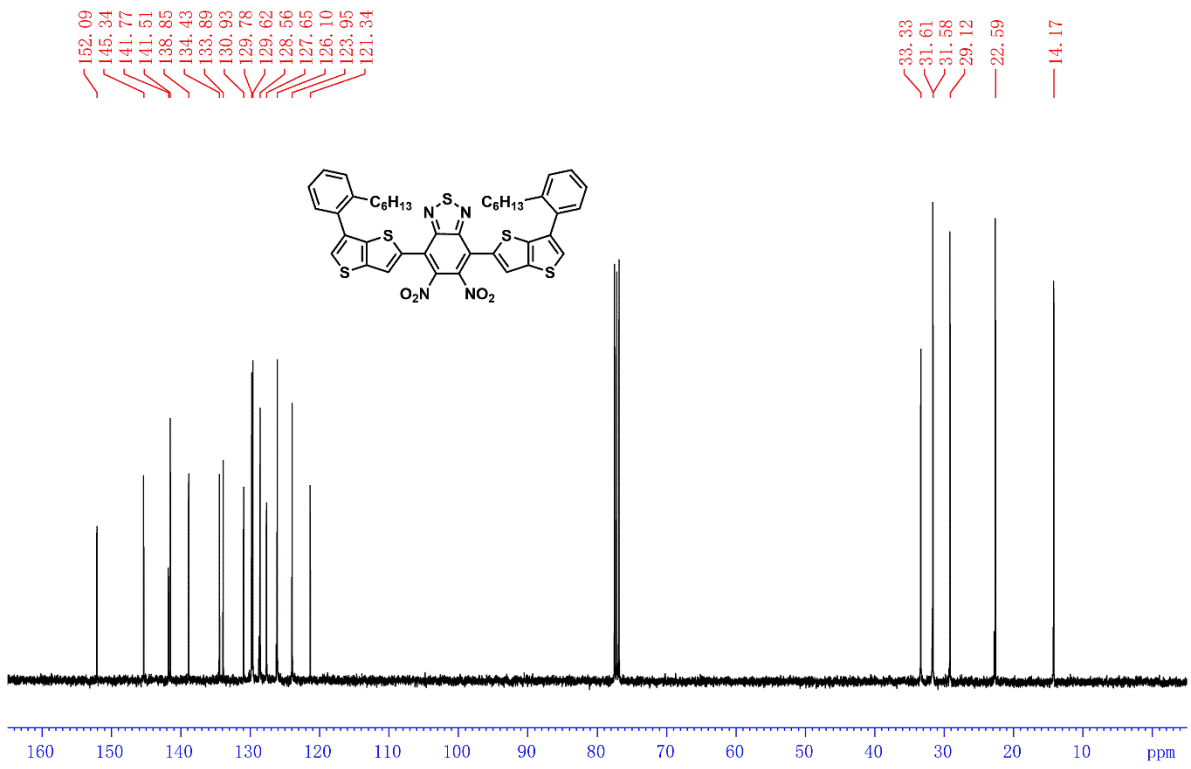


Fig. S15 ^{13}C NMR spectrum of compound *o*-4.

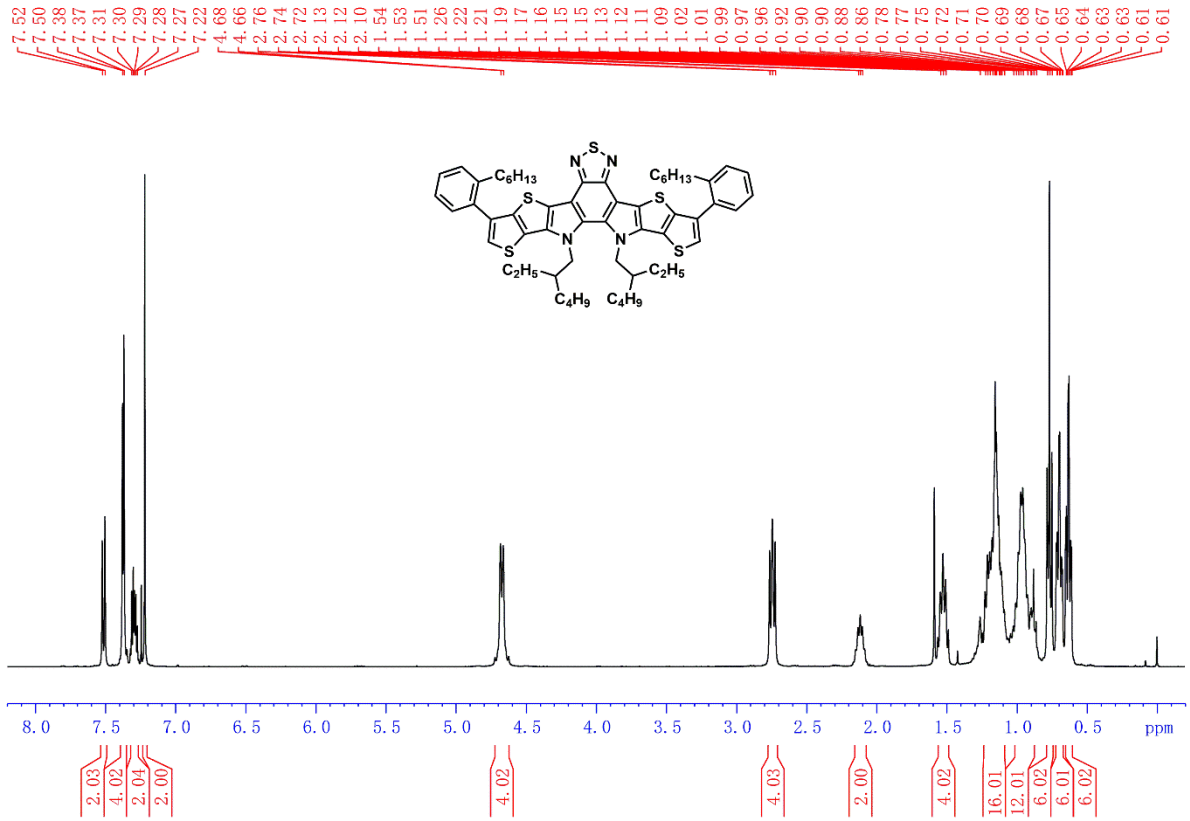


Fig. S16 ^{1}H NMR spectrum of compound *o*-5.

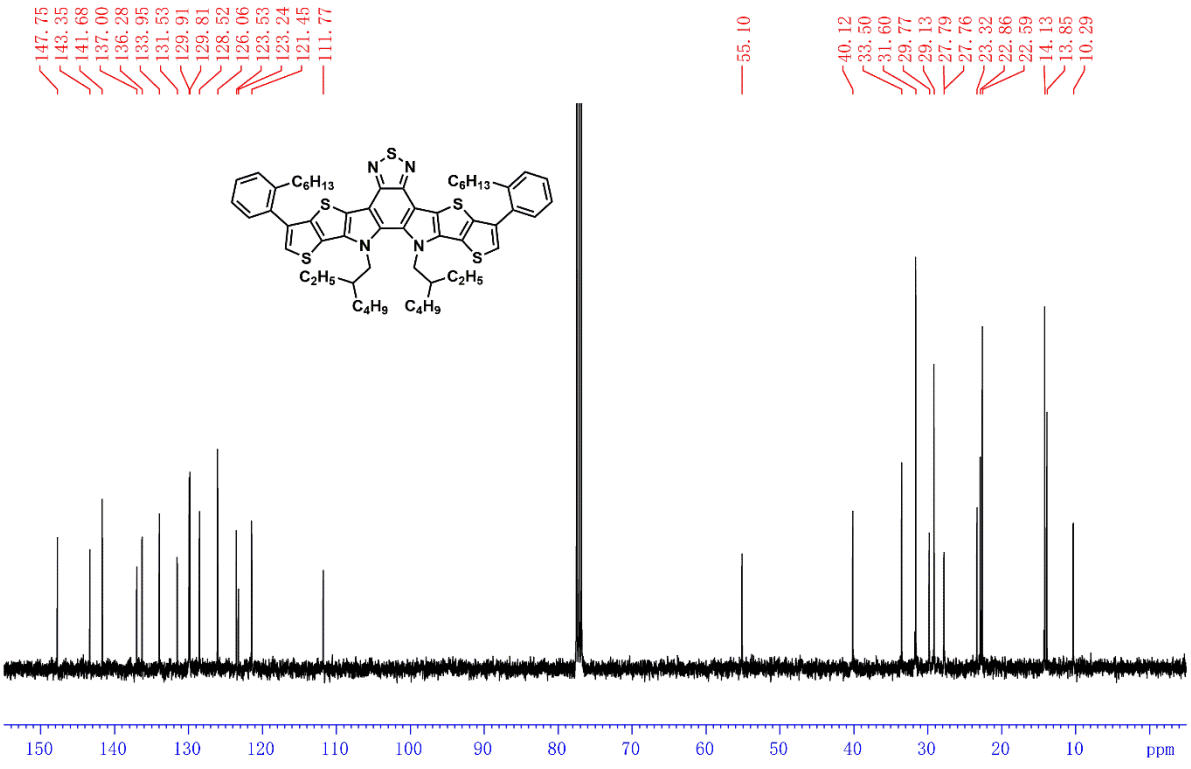


Fig. S17 ^{13}C NMR spectrum of compound *o*-5.

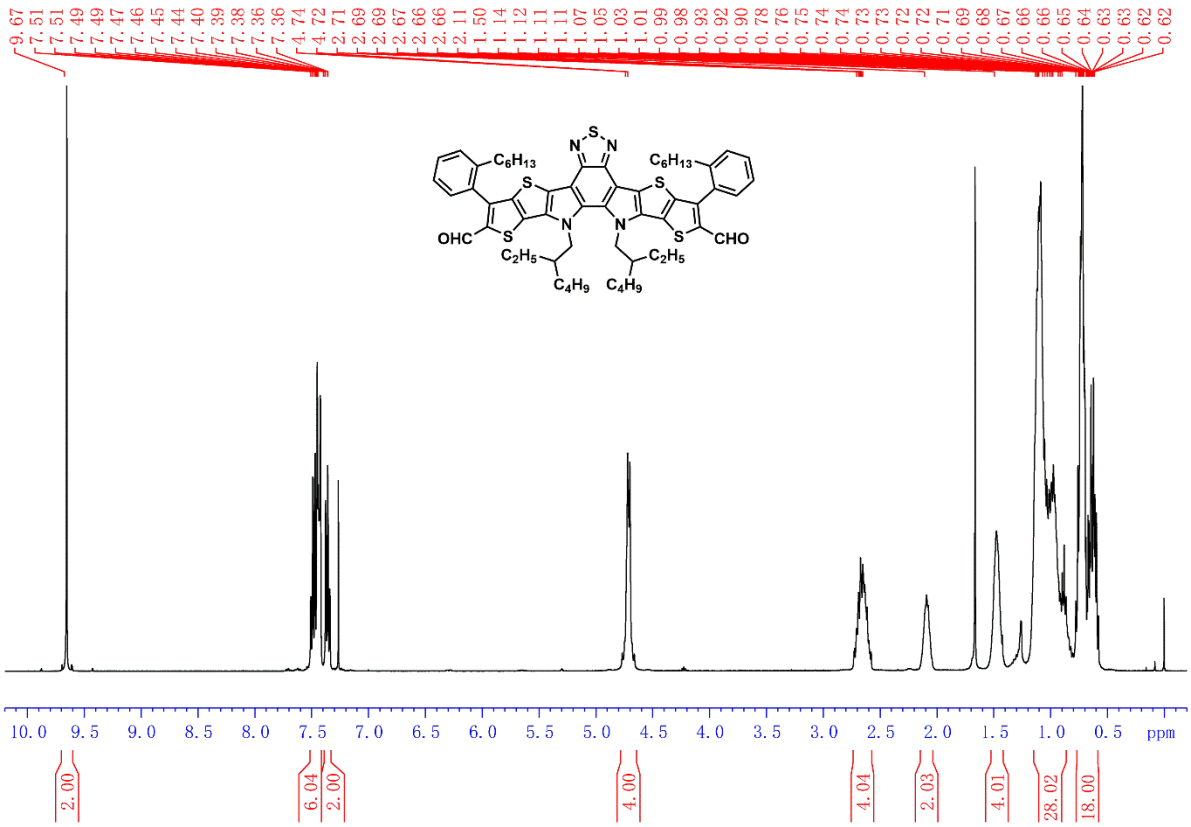


Fig. S18 ^{1}H NMR spectrum of compound *o*-6.

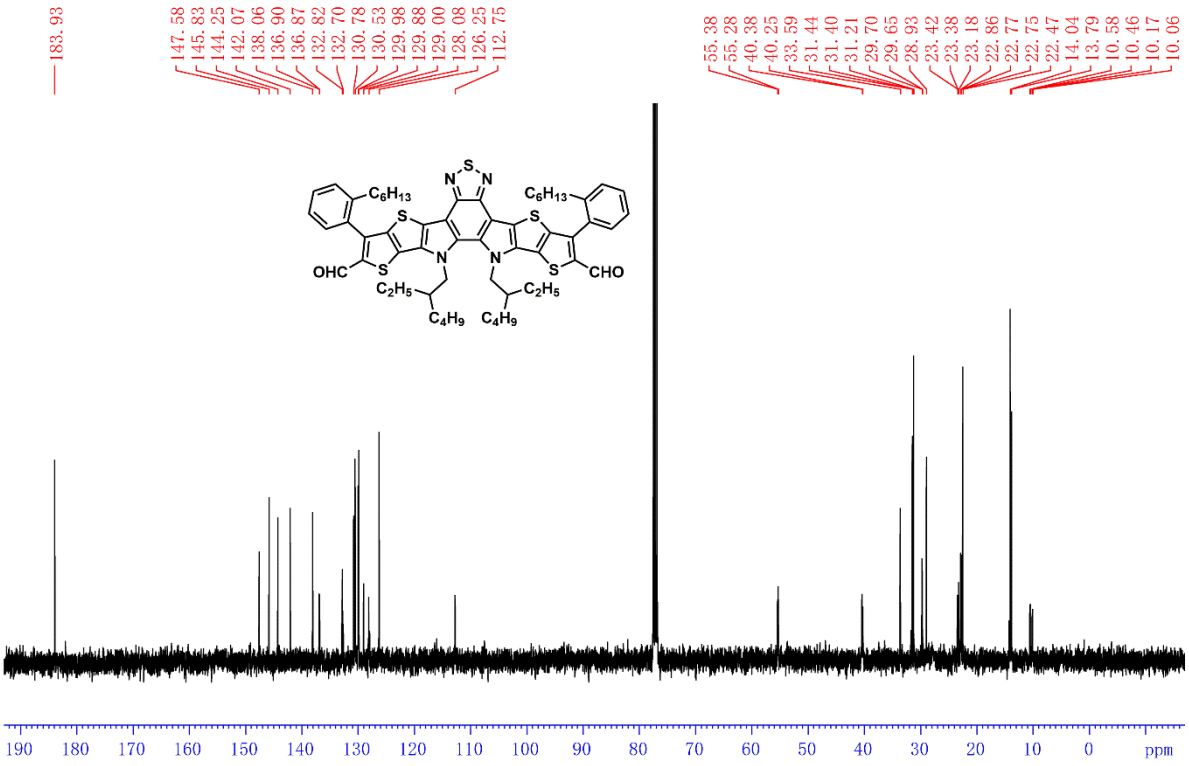


Fig. S19 ^{13}C NMR spectrum of compound *o*-6.

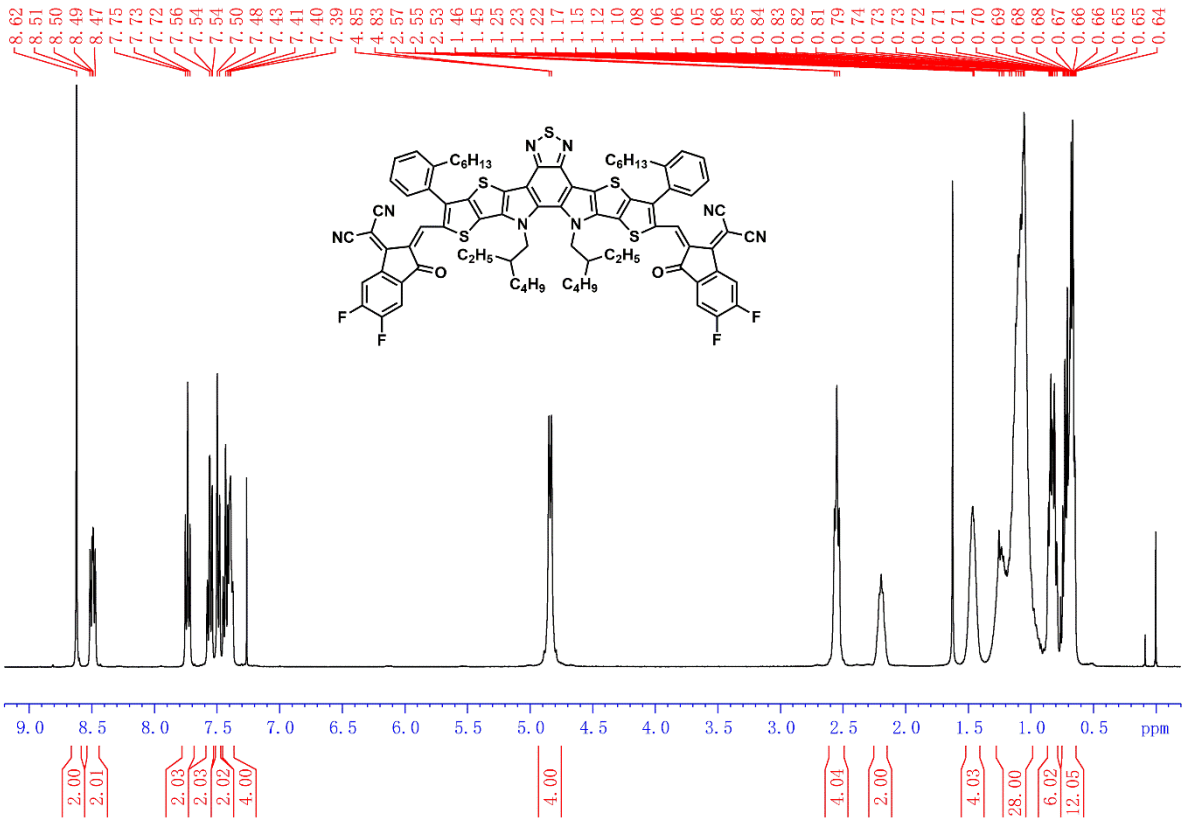


Fig. S20 ^{1}H NMR spectrum of compound *o*-BTP-PhC6.

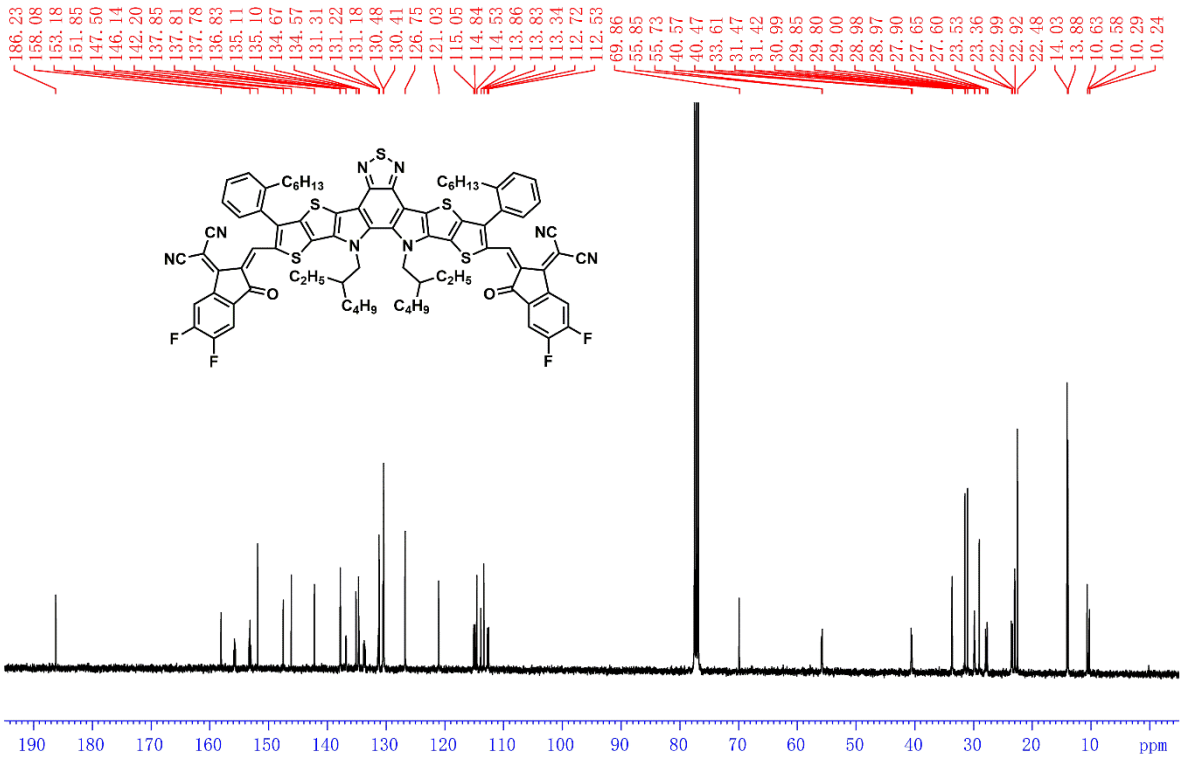


Fig. S21 ^{13}C NMR spectrum of compound *o*-BTP-PhC6.

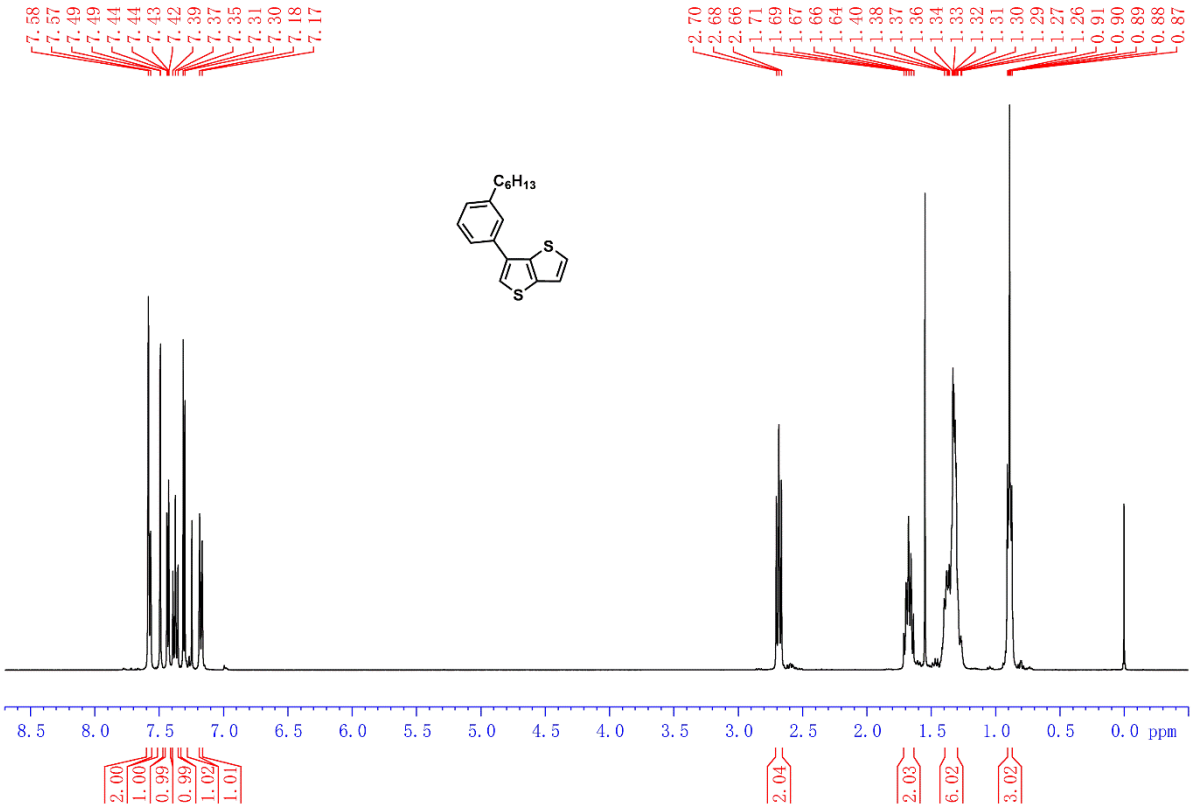


Fig. S22 ^{1}H NMR spectrum of compound *m*-2.

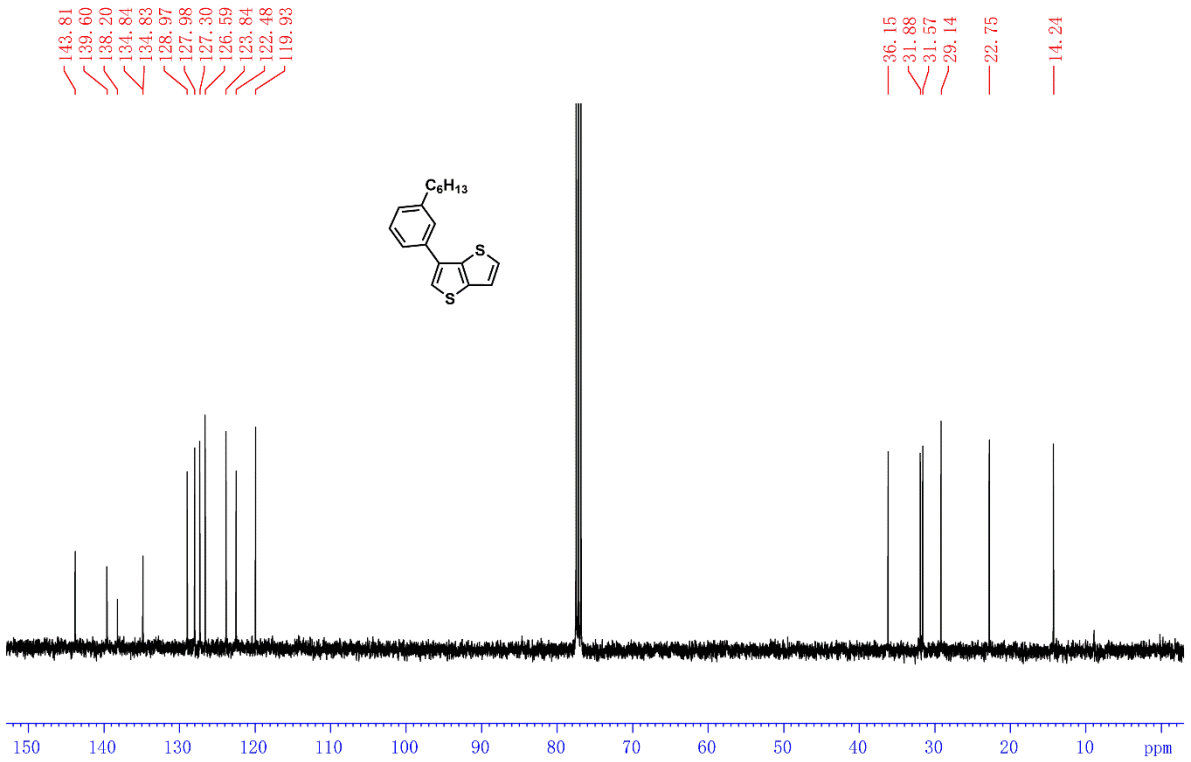


Fig. S23 ^{13}C NMR spectrum of compound *m*-2.

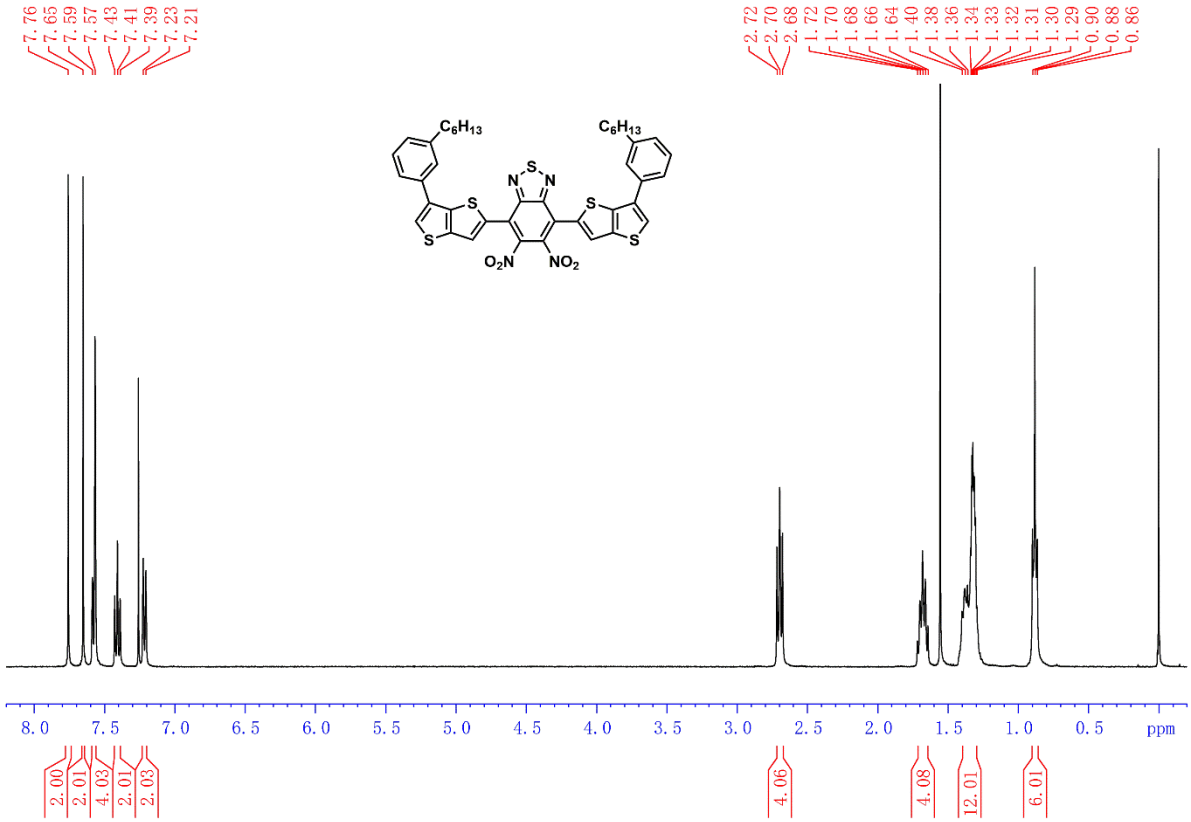


Fig. S24 ^{1}H NMR spectrum of compound *m*-4.

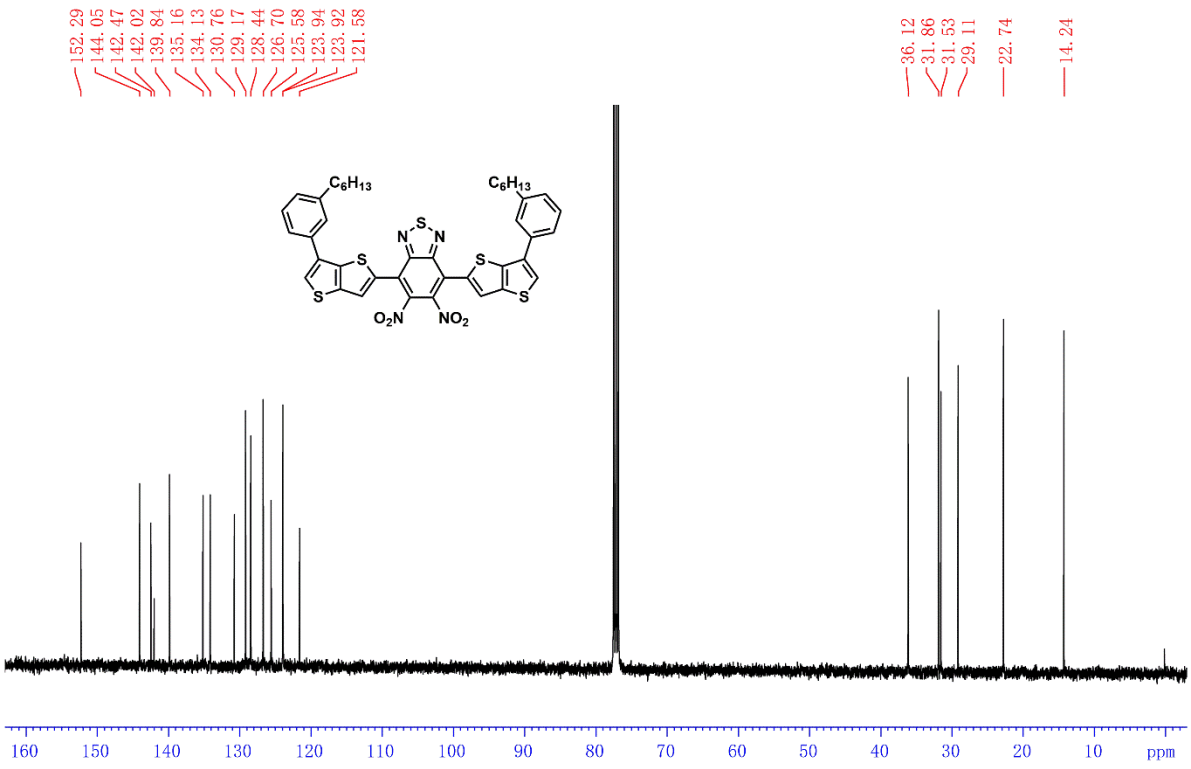


Fig. S25 ^{13}C NMR spectrum of compound *m*-4.

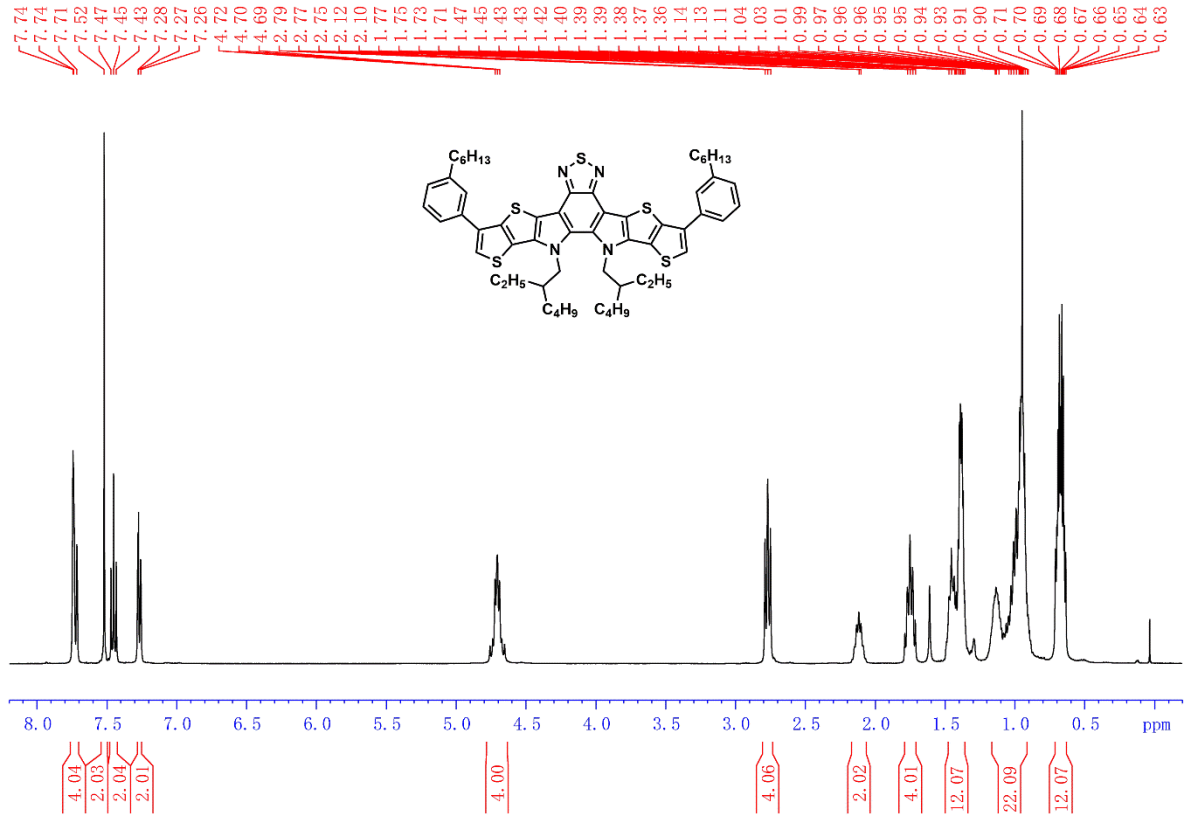


Fig. S26 ^{13}C NMR spectrum of compound *m*-5.

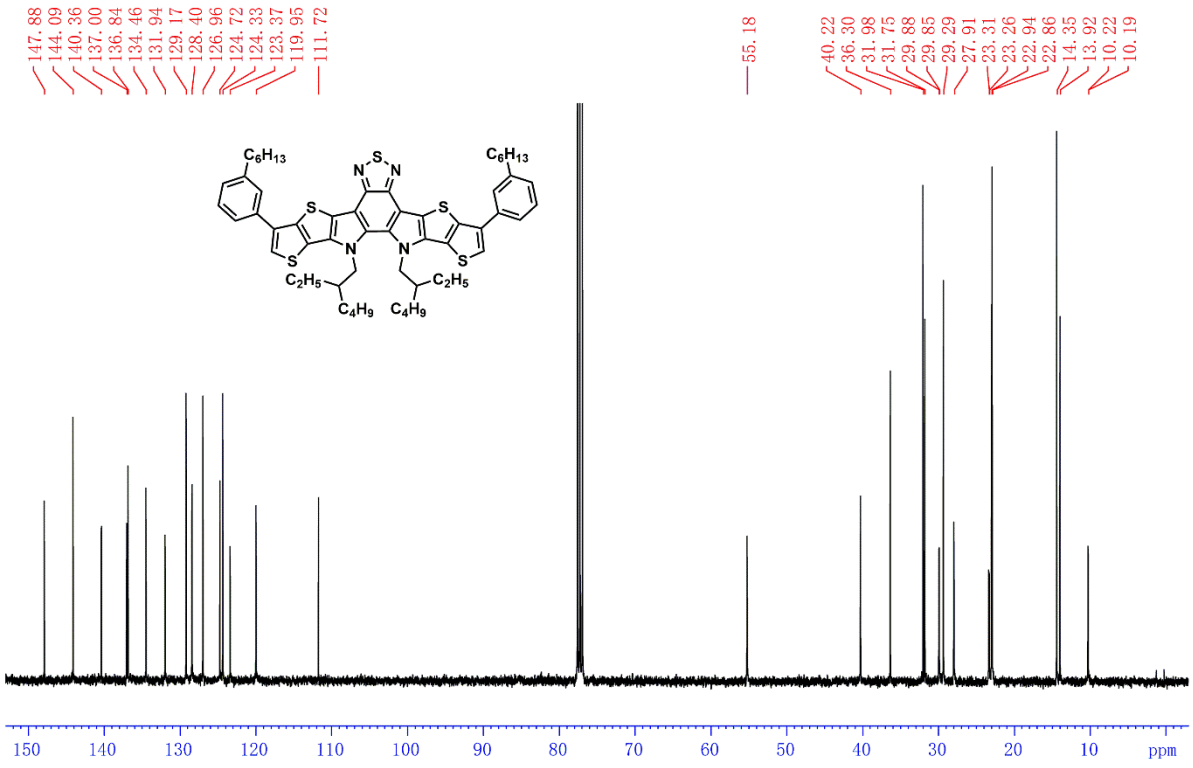


Fig. S27 ^{13}C NMR spectrum of compound *m*-5.

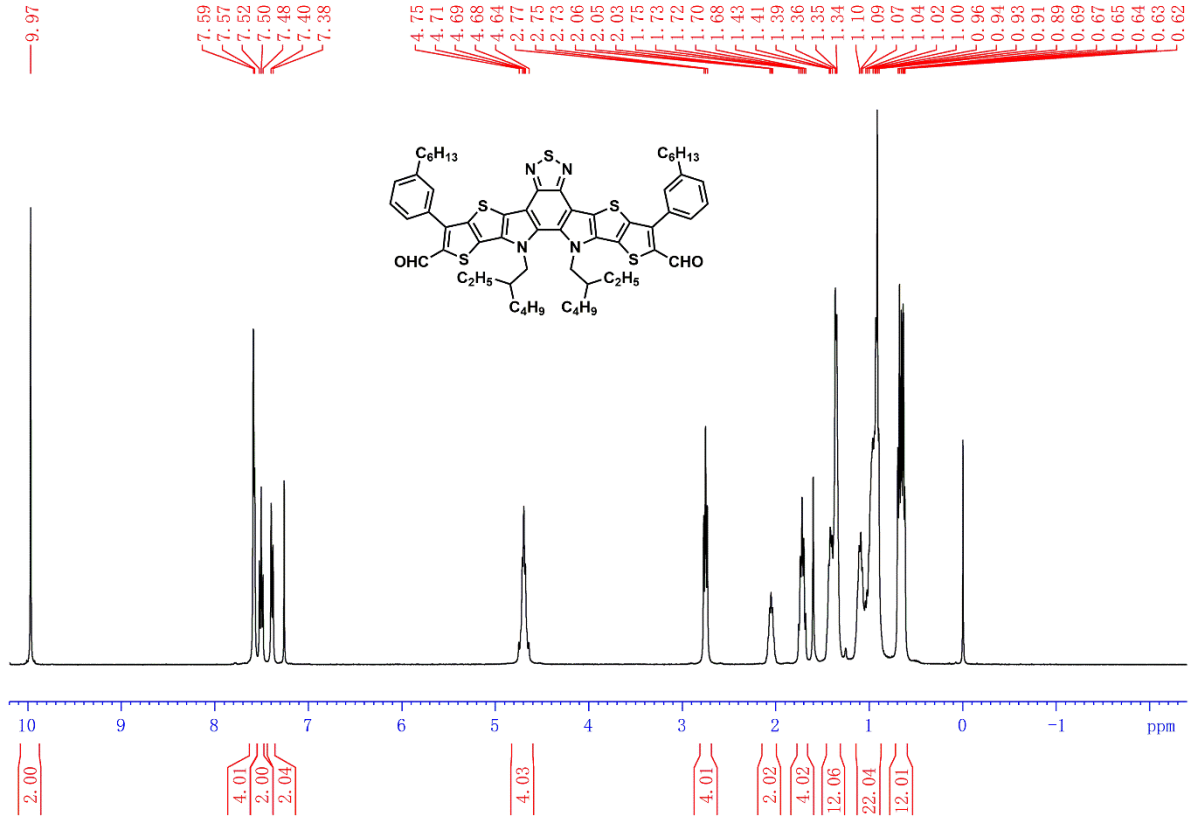


Fig. S28 ^{1}H NMR spectrum of compound *m*-6.

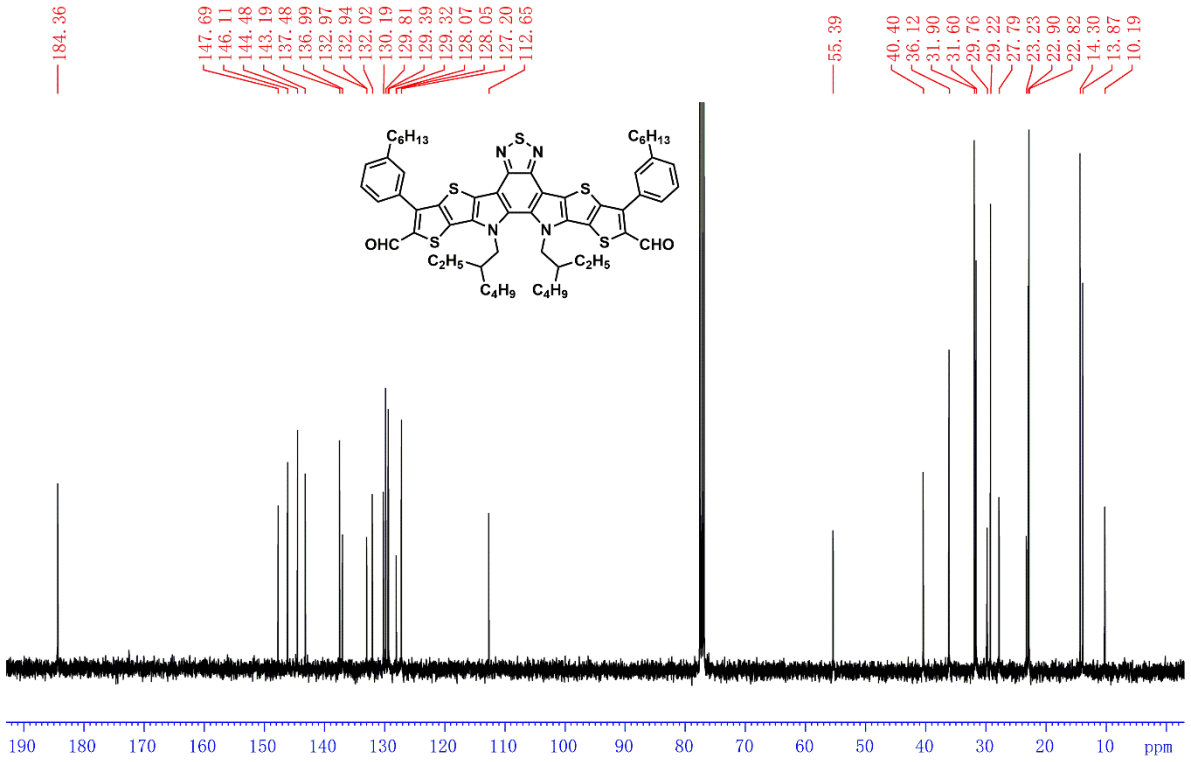


Fig. S29 ^{13}C NMR spectrum of compound *m*-6.

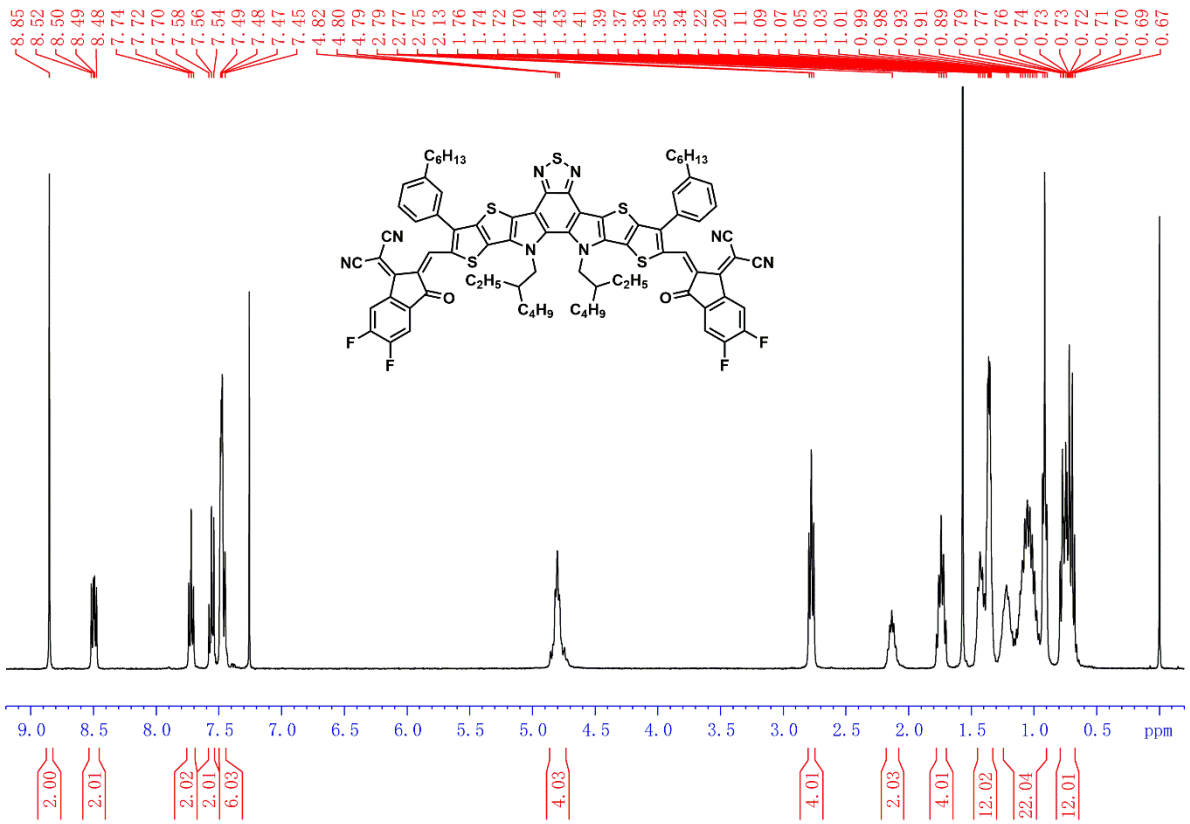


Fig. S30 ^{1}H NMR spectrum of compound *m*-BTP-PhC6.

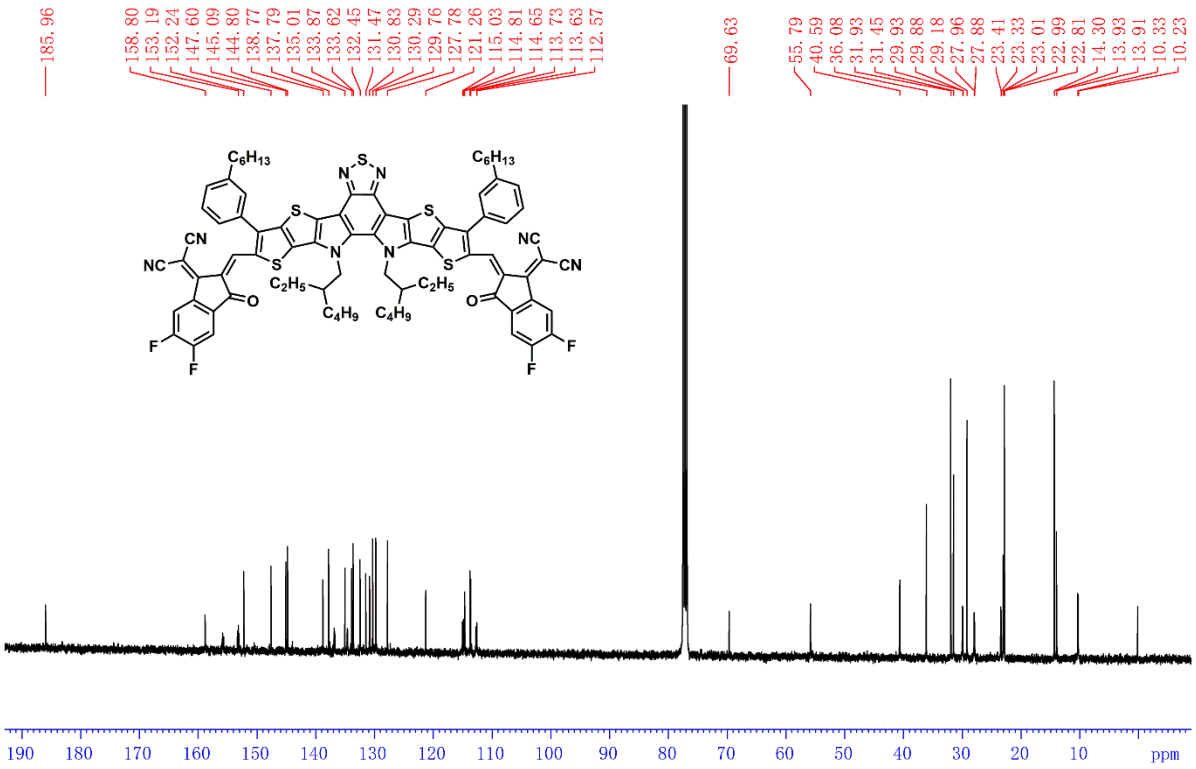


Fig. S31 ^{13}C NMR spectrum of compound *m*-BTP-PhC6.

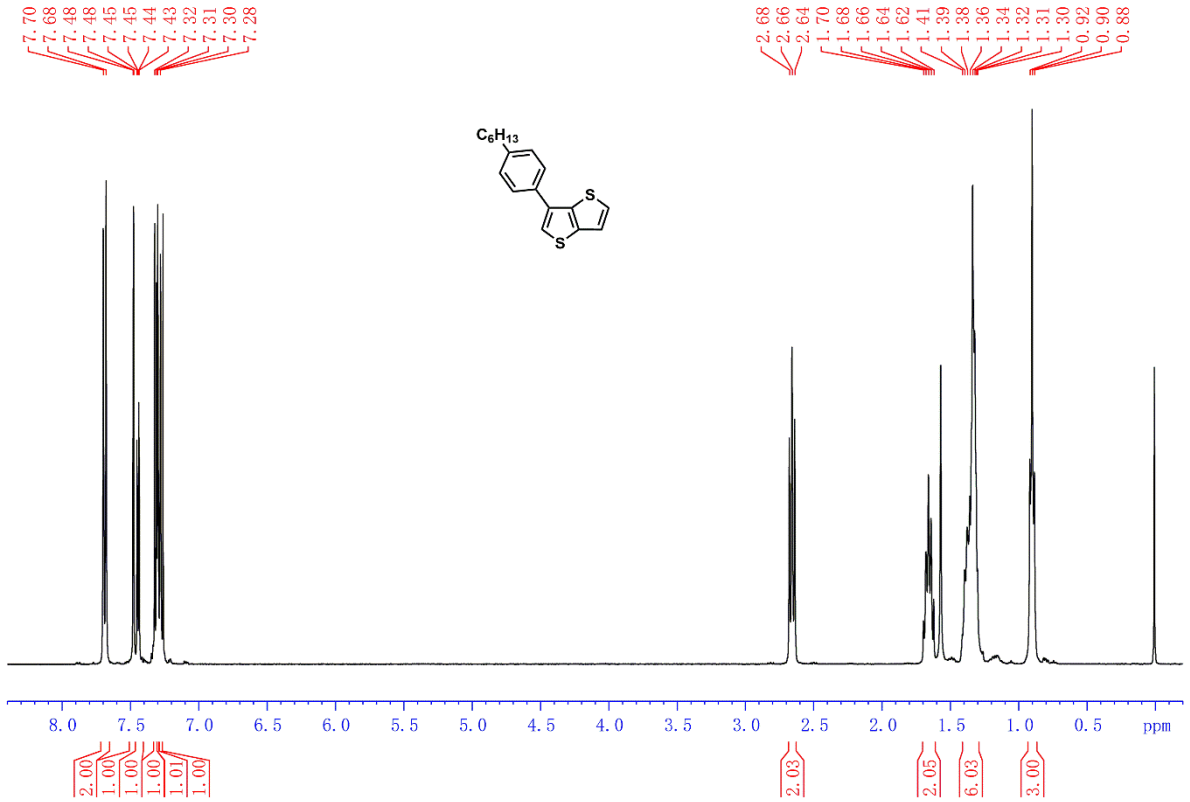


Fig. S32 ^{1}H NMR spectrum of compound *p*-2.

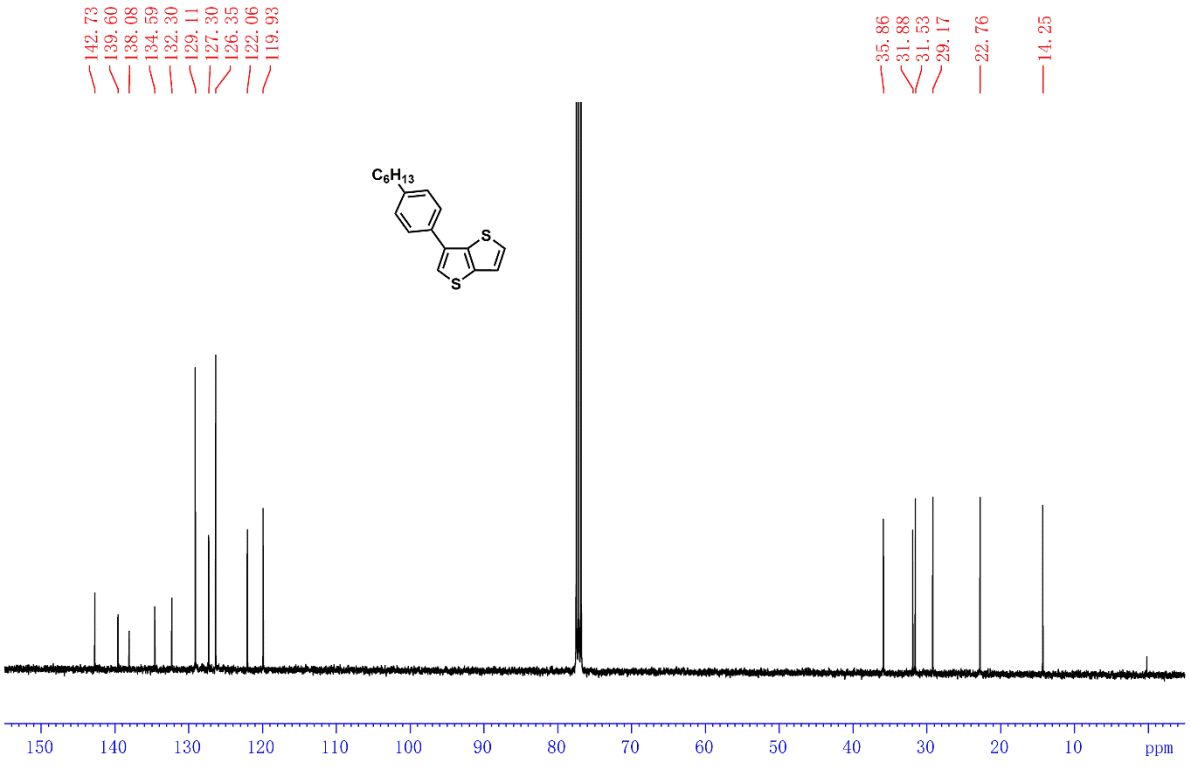


Fig. S33 ^{13}C NMR spectrum of compound *p*-2.

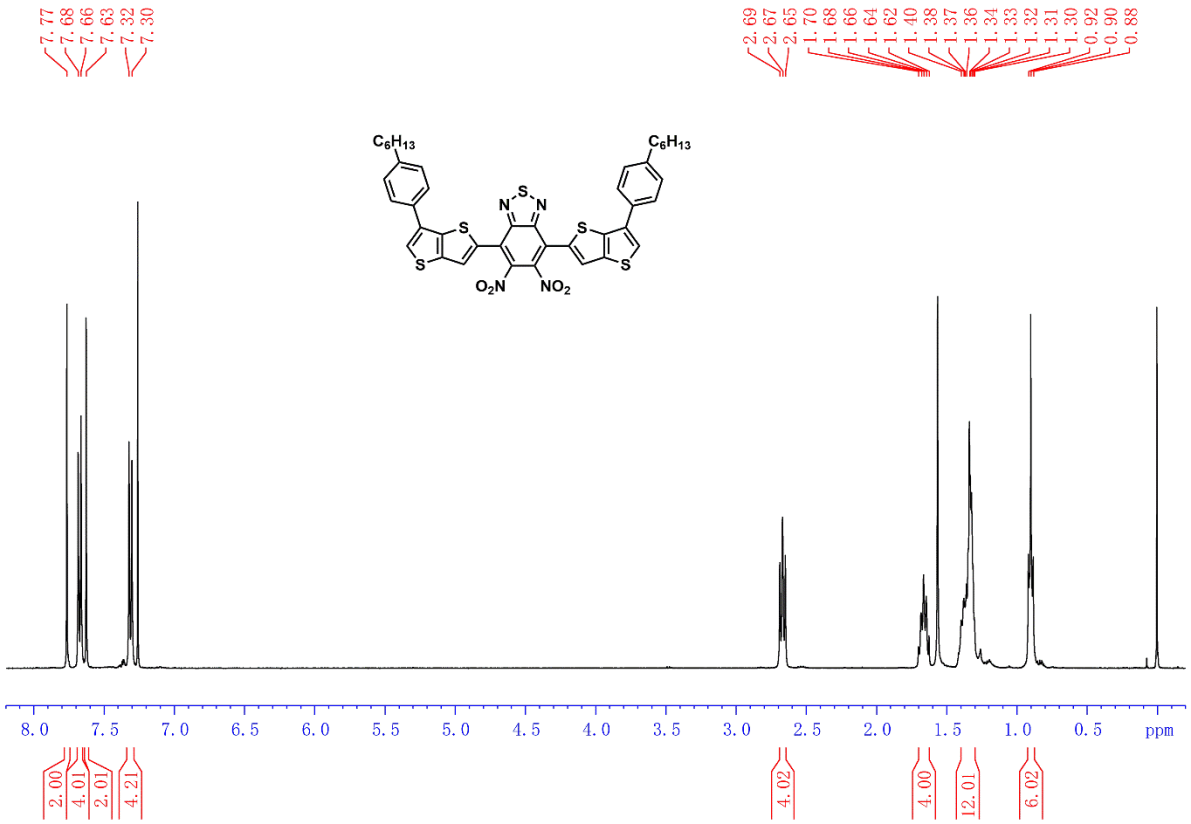


Fig. S34 ^{1}H NMR spectrum of compound *p*-4.

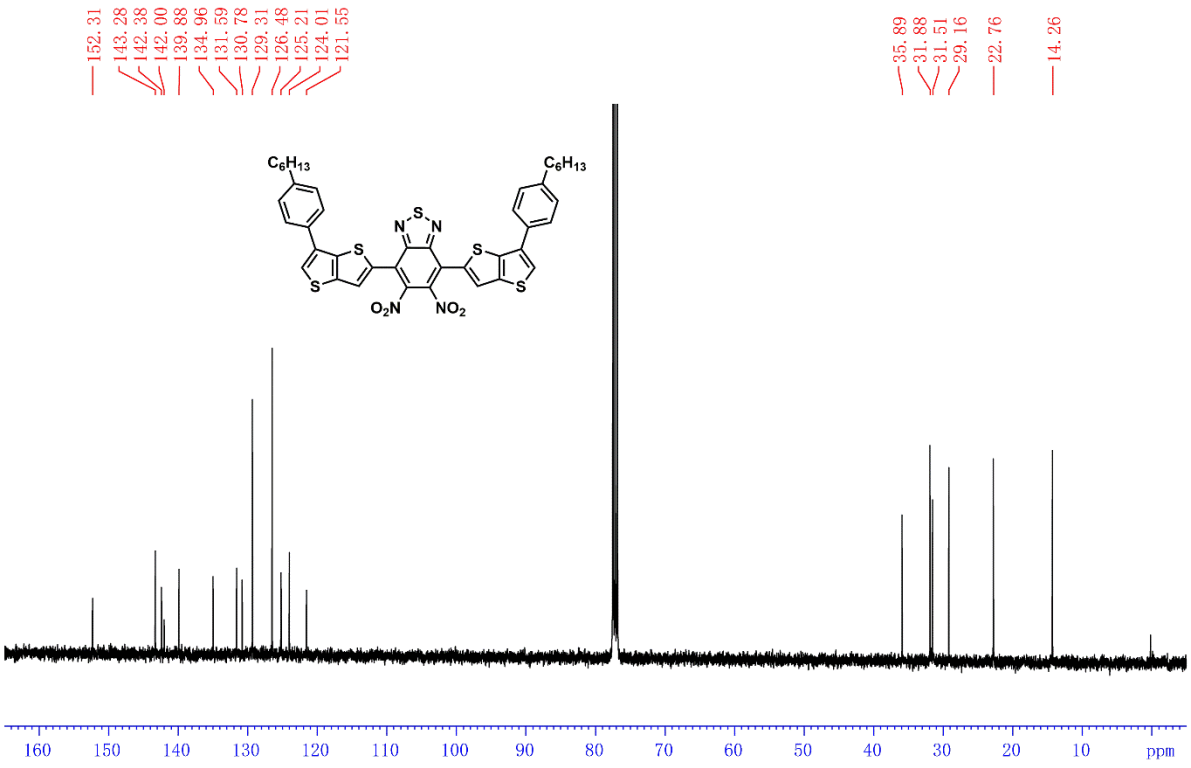


Fig. S35 ^{13}C NMR spectrum of compound *p*-4.

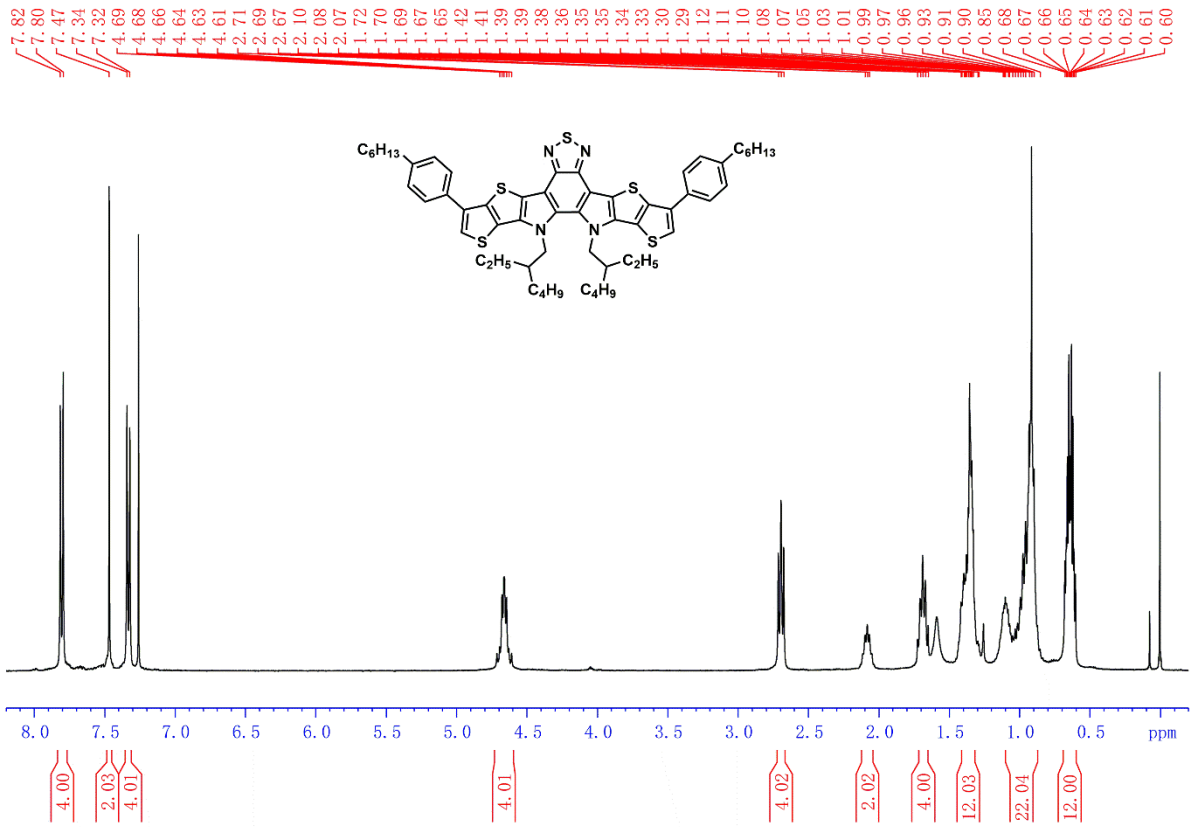


Fig. S36 ^{1}H NMR spectrum of compound *p*-5.

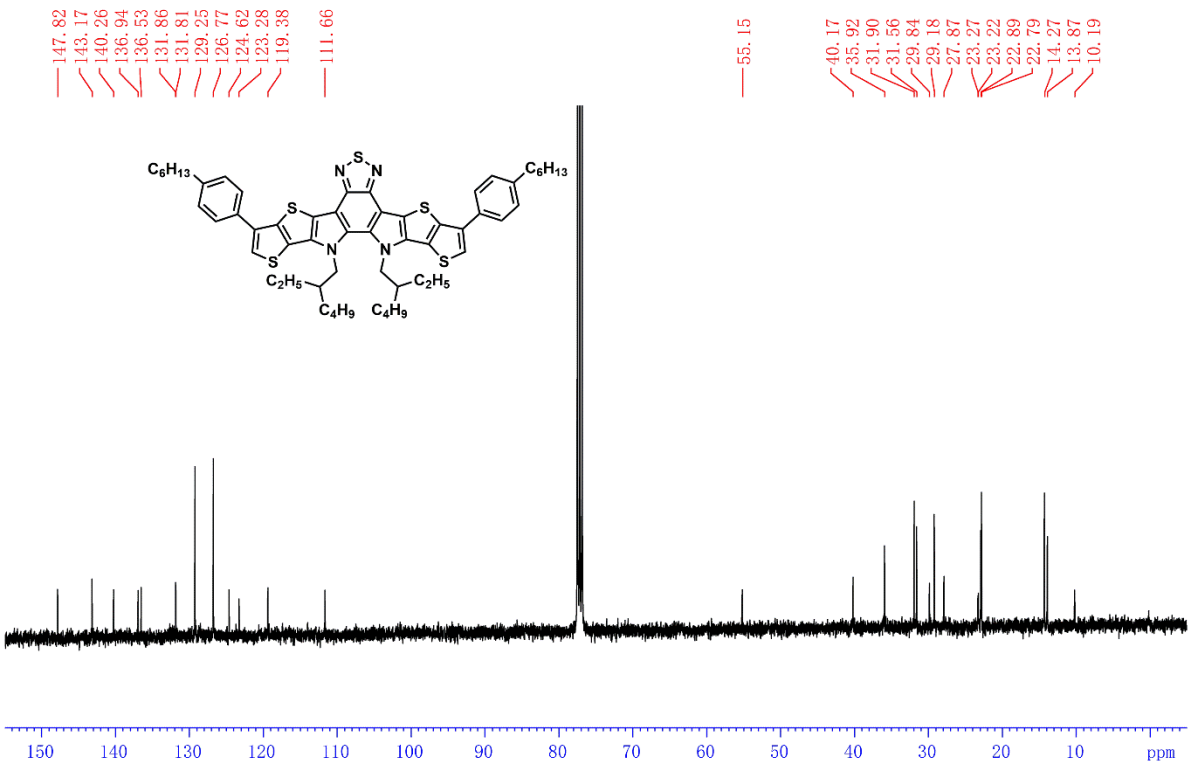


Fig. S37 ^{13}C NMR spectrum of compound *p*-5.

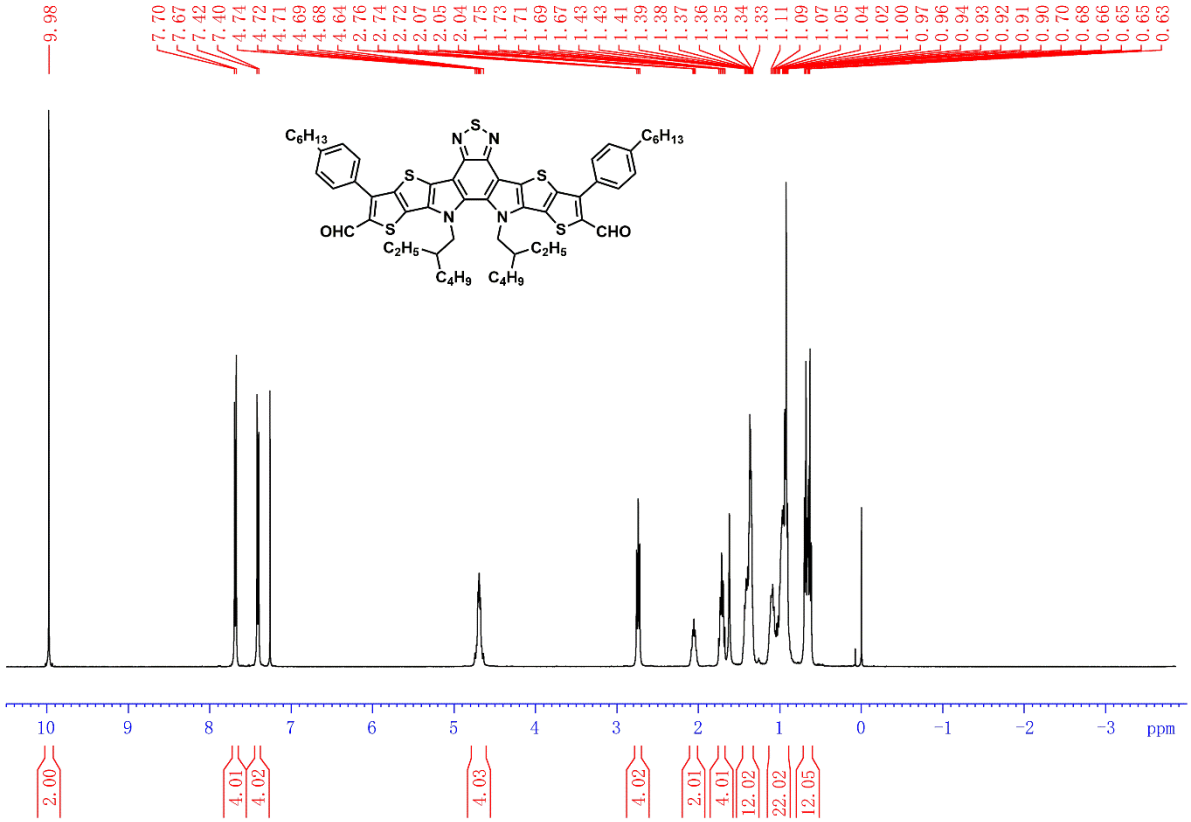


Fig. S38 ^{1}H NMR spectrum of compound *p*-6.

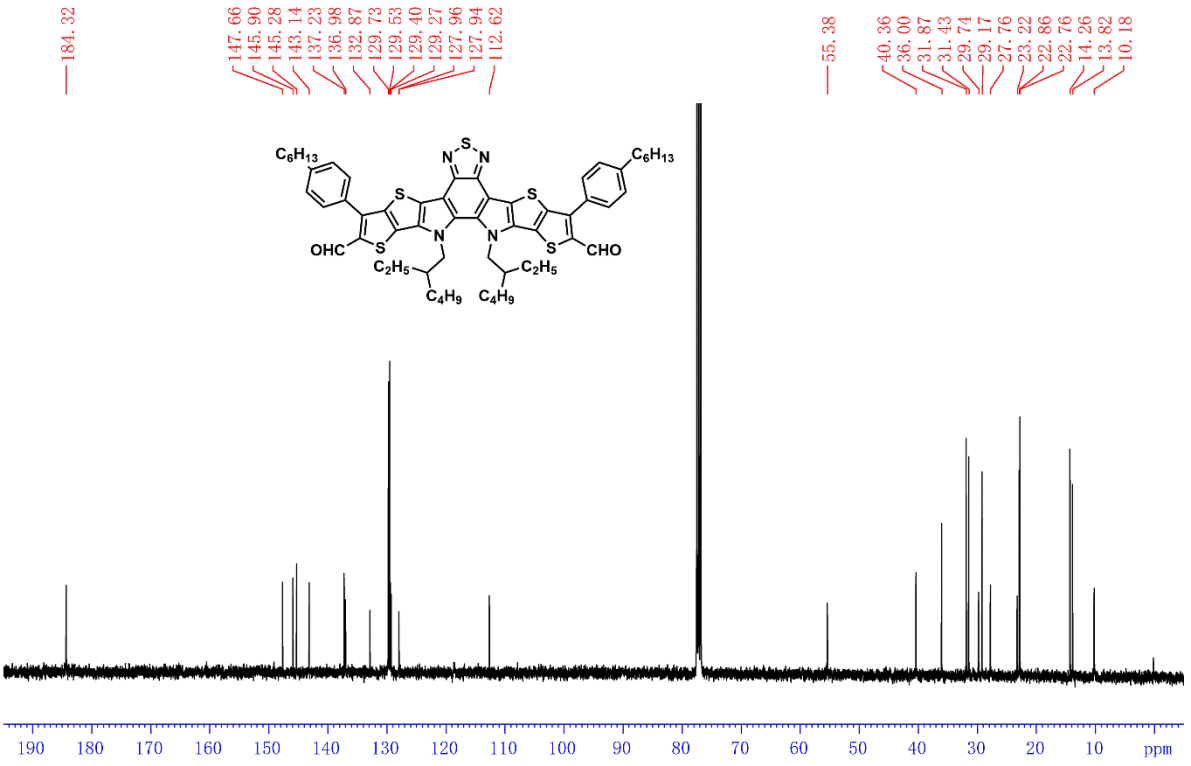


Fig. S39 ^{13}C NMR spectrum of compound *p*-6.

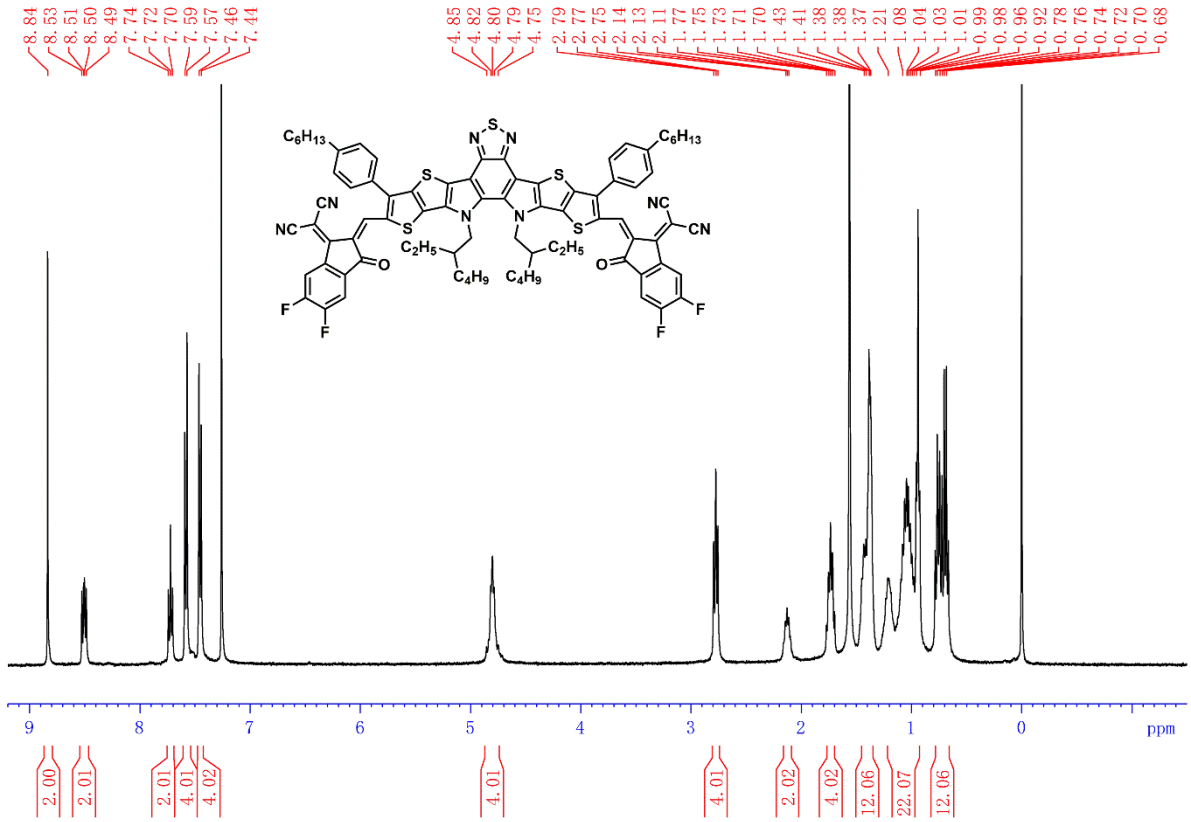


Fig. S40 ^{1}H NMR spectrum of compound *p*-BTP-PhC6.

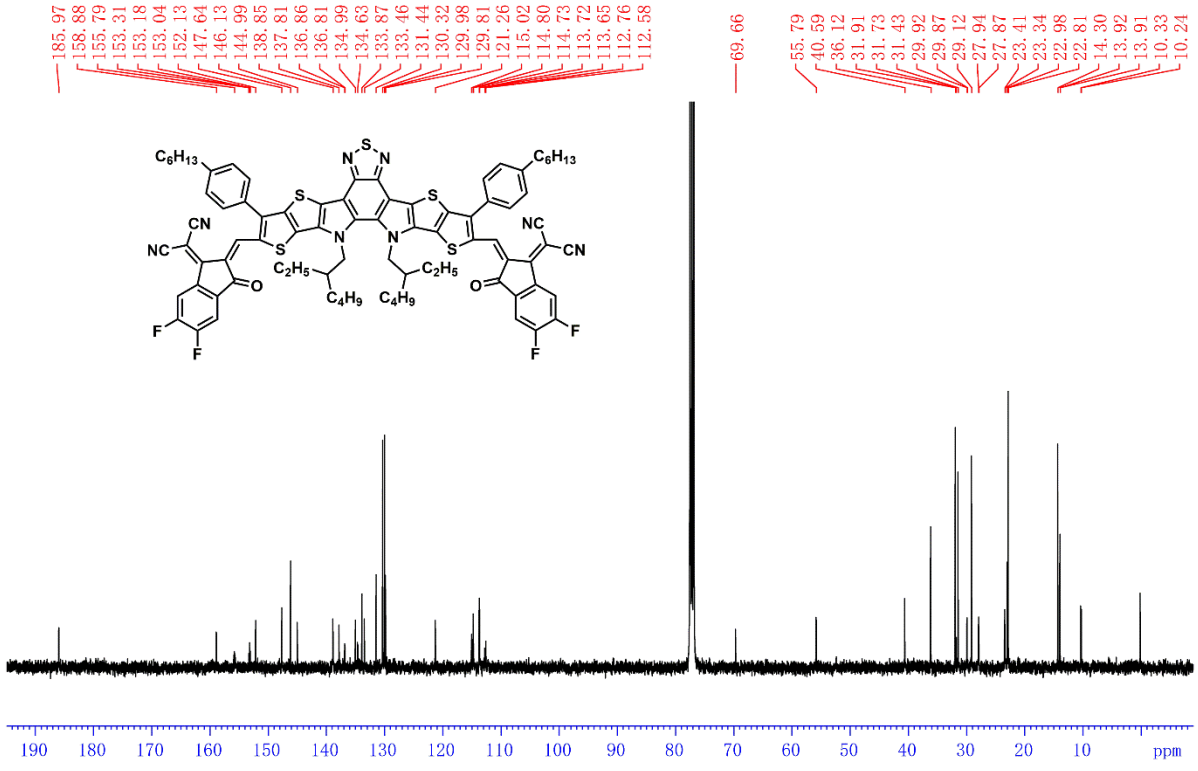


Fig. S41 ^{13}C NMR spectrum of compound *p*-BTP-PhC6.

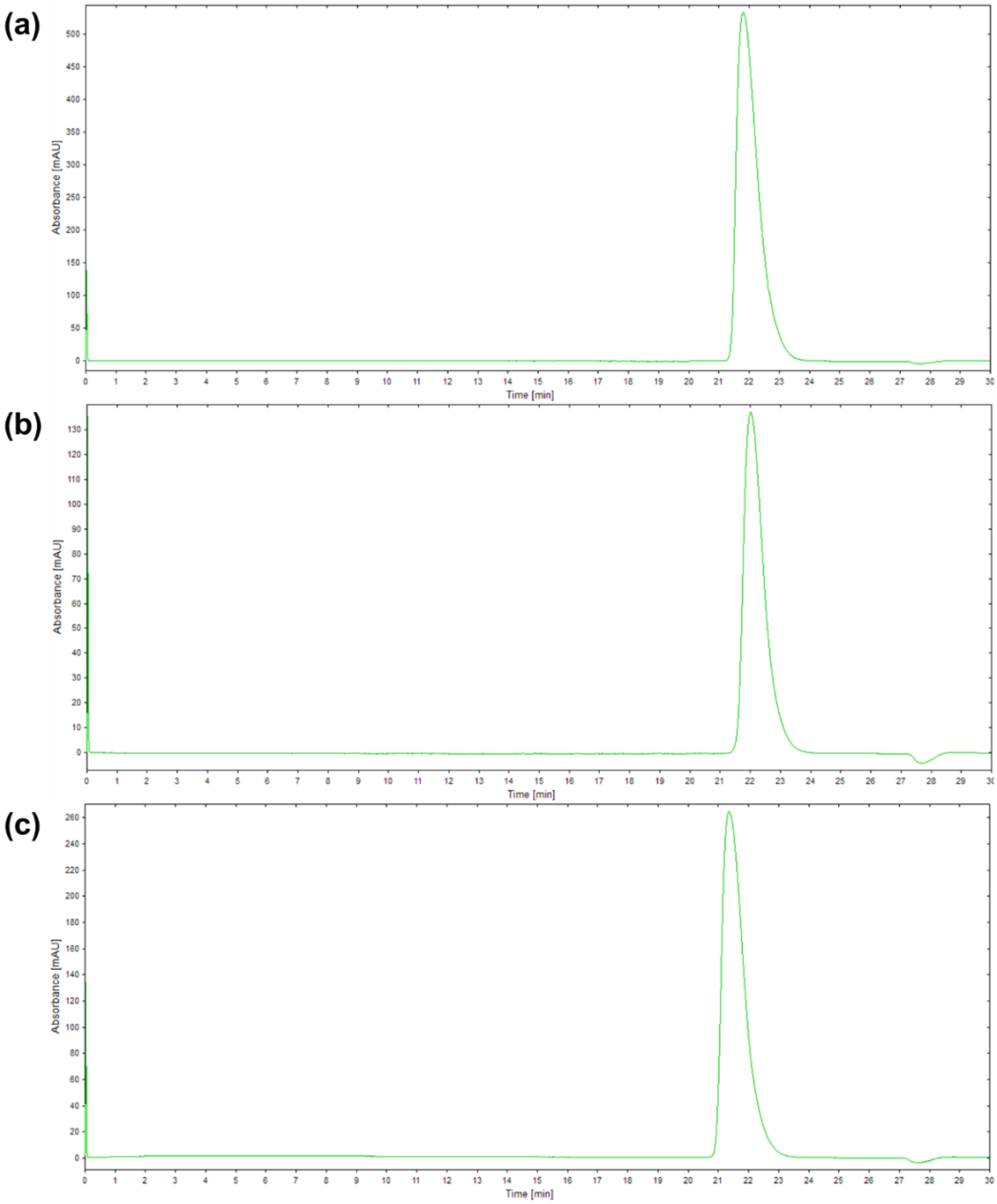


Fig. S42 High-performance gel permeation chromatography results of the final acceptors: (a) *o*-BTP-PhC6, (b) *m*-BTP-PhC6, and (c) *p*-BTP-PhC6.

References

1. Y. Wu, Y. Zheng, H. Yang, C. Sun, Y. Dong, C. Cui, H. Yan and Y. Li, *Sci. China: Chem.*, 2019, **63**, 265-271.
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