

A Three-Dimensional Thiophene-Annulated Perylene Bisimide as Fullerene-Free Acceptor for High Performance Polymer Solar Cell with the Highest PCE of 8.28% and V_{OC} over 1.0 V

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Materials and Measurements

All solvents and reagents were used as received from commercial sources and used without further purification unless otherwise specified. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a MERCURYVX300 spectrometers. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-2700 recording spectrophotometer. Cyclic voltammetry (CV) measurements were carried out on a CHI voltammetric analyzer at room temperature. Tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆, 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode with a 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl wire reference electrode. Cyclic voltammograms were obtained at a scan rate of 100 mV/s. PL spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. The film morphology was measured using an atomic force microscope (AFM, Bruker-ICON2-SYS) using the tapping mode. The RMS values of the surface AFM images are averaged based on five times testing on different areas for each sample. DFT

calculations were performed by using Gaussian at the B3LYP/6-31G* level, and the long alkyl chain was simplified as methyl. TEM images were performed on a JEOL JEM-1400 transmission electron microscope.

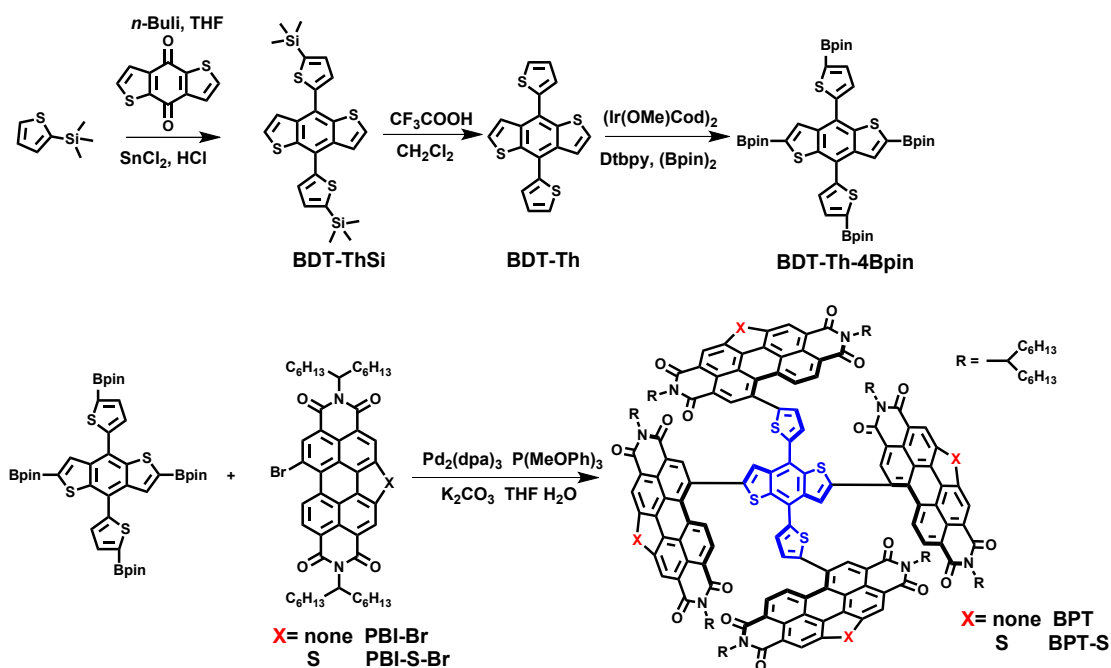
Device fabrication and characterization

The PSCs were fabricated with a structure of ITO/PEDOT: PSS (40 nm)/active layers/ZrAcAc/Al. A thin layer of PEDOT: PSS was deposited through spin-coating on precleaned ITO-coated glass from a PEDOT: PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 4000 rpm and dried subsequently at 150 °C for 15min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer of PDBT-T1 polymer and BPT (or BPT-S) was spin-coated from its *o*-DCB solution onto the PEDOT: PSS layer under a spin-coating rate of 1600 rpm. After spin-coating, the active layers were annealed at 100 °C for 2min for the devices with thermal annealing treatment. The thickness of the active layers is ca. 100 nm. Then methanol solution of ZrAcAc at a concentration of 1.0 mg mL⁻¹ was deposited atop the active layer at 3500 rpm for 30 s to afford a ZrAcAc cathode buffer layer. Finally, an aluminum layer (100 nm) at the vacuum condition of 5×10⁻⁵ Pa was deposited by thermal evaporation method. All film thickness was measured by the Alpha-Step D-500 surface profilometer. The current density–voltage (*J–V*) characteristics of the PSCs were measured in glovebox on a computer-controlled Keithley 2450 Source-Measure Unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450 W xenon lamp and an air mass (AM) 1.5 filter was used as the light source. The light intensity was calibrated to 100 Mw cm⁻² by a Newport Oriel 91150V reference cell. The input photon to converted current efficiency (IPCE) was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd.,

Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. Optical microscope (Olympus BX51) was used to defined the active area (4.5 mm²) of the device. Masks made using laser beam cutting technology to have a well-defined area of 3.14 mm² were attached to define the effective area for accurate measurement. All the masked and unmasked tests gave consistent results with relative errors within 0.5%. All the device measurements were undertaken in a nitrogen glovebox.

Mobility Measurements

Hole and electron mobility were measured using the space charge limited current (SCLC) method. Device structures are ITO/MoO_x/PDBT-T1: BPT or BPT-S (1:1, w/w)/MoO_x/Al for hole-only devices and ITO/Al/PDBT-T1: BPT or BPT-S (1: 1, w/w)/Al for electron-only devices. The SCLC mobilities were calculated by MOTT-Gurney equation: $J = (9/8)\epsilon_r\epsilon_0\mu_h(\mu_e)(V^2/L^3)$, where J is the current density, ϵ_0 is the vacuum permittivity, ϵ_r is the dielectric permittivity of the active layer, L is the thickness of the active layer, μ_h is the hole mobility, μ_e is the electron mobility. $V=V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here). The mobility can be calculated from the slope of the $J^{0.5} \sim V$ curves.



Scheme S1. Synthesis of BPT, BPT-S.

Synthesis

General Information:

The solvents were dried using standard procedures. All other reagents were used as received from commercial sources unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Advanced II (400 MHz) spectrometers. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. EI-MS spectra were recorded on VJ-ZAB-3F-Mass spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2501 recording spectrophotometer. Cyclic voltammetry (CV) measurements were carried out on a CHI voltammetric analyzer at room temperature. Tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$, 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode

with a 2 mm diameter, a platinum wire counter electrode, and an Ag/AgCl wire reference electrode. Cyclic voltammograms were obtained at a scan rate of 100 mV/s.

BDT-ThSi: 2-TriMethylsilylthiophene (1.56 g, 10 mmol) in anhydrous THF (30 mL) was added to a three-necked, round-bottomed flask equipped with a condenser. When the solution was cooled to 0 °C under an argon atmosphere, n-butyllithium (4.4 mL, 11 mmol, 2.5M in hexane) was added dropwise. The reactant solution was then heated to 50 °C and kept at the same temperature for 2 h. Then, 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-dione (0.88 g, 4.0 mmol) in anhydrous THF (30 mL) was added dropwise. The mixture was stirred at 50 °C overnight, and then cooled to ambient temperature. SnCl₂·H₂O (4.5 g, 20 mmol) in HCl (8 mL; 10%) was added, and the mixture was stirred for another 2 h. Then ice water was added and extracted with dichloromethane. The combined extracts were dried over anhydrous MgSO₄ and evaporated. The crude product was purified by column chromatography (SiO₂, hexane) to give **BDT-ThSi** as a light-yellow powder (1.59 g, 80%). ¹H NMR (CDCl₃, 400 MHz): δ [ppm]: 8.65 (d, *J* = 4.0 Hz, 2H), 8.57 (d, *J* = 4.0 Hz, 2H), 8.47 (d, *J* = 4.0 Hz, 2H), 8.38 (d, *J* = 4.0 Hz, 2H), 0.41 (s, 18H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm]: 144.84, 141.64, 138.84, 136.42, 134.22, 129.22, 127.54, 123.90, 123.34, 0. EI-MS (m/z, [M+1]): 498.95. Elemental anal. calcd for C₂₄H₂₆S₄Si₄: C, 57.78; H, 5.25. Found: C, 57.80; H, 5.39.

BDT-Th: Trifluoroacetic acid (6.0 mL) was added to a solution of **BDT-ThSi** (500 mg,

1 mmol) in CH_2Cl_2 (100 mL) under a N_2 atmosphere. The solution was stirred for 16 h in the absence of light. After addition of ethanol (200 mL), the precipitate was collected on a fritted funnel. The yellow solid was washed with ethanol and hexane to give 2 (336mg, 95%). Compound **BDT-Th** was used without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ [ppm]: 7.60 (d, $J = 4.0$ Hz, 2H), 7.55-7.53 (m, 2H), 7.50-7.46 (m, 4H), 7.27-7.25 (m, 2H).

BDT-Th-4Bin: To a mixture of **BDT-Th** (0.445g, 1.25 mmol), $(\text{BPin})_2$ (1.91 g, 7.52 mmol), 4,4'-ditert-butyl-2,2'-dipyridyl (91 mg, 0.34 mmol) and $\{\text{Ir}(\text{OMe})\text{Cod}\}$ (45 mg, 0.068 mmol) in 50 mL sealed tube, 20 ml anhydrous hexane were added under Ar atmosphere. After reacting at 120 °C for 24 hours, the solvent was removed under reduced pressure. 0.96 g of pure compound BDT-Th-4Bpin (90 %) was obtained by recrystallization in hexane and methanol. ^1H NMR (CDCl_3 , 400 MHz): δ [ppm]: 8.10 (s, 2H), 7.75 (d, $J = 12$ Hz, 2H), 7.54 (d, $J = 24$ Hz, 2H), 1.42 (s, 24H), 1.33(s, 24H).

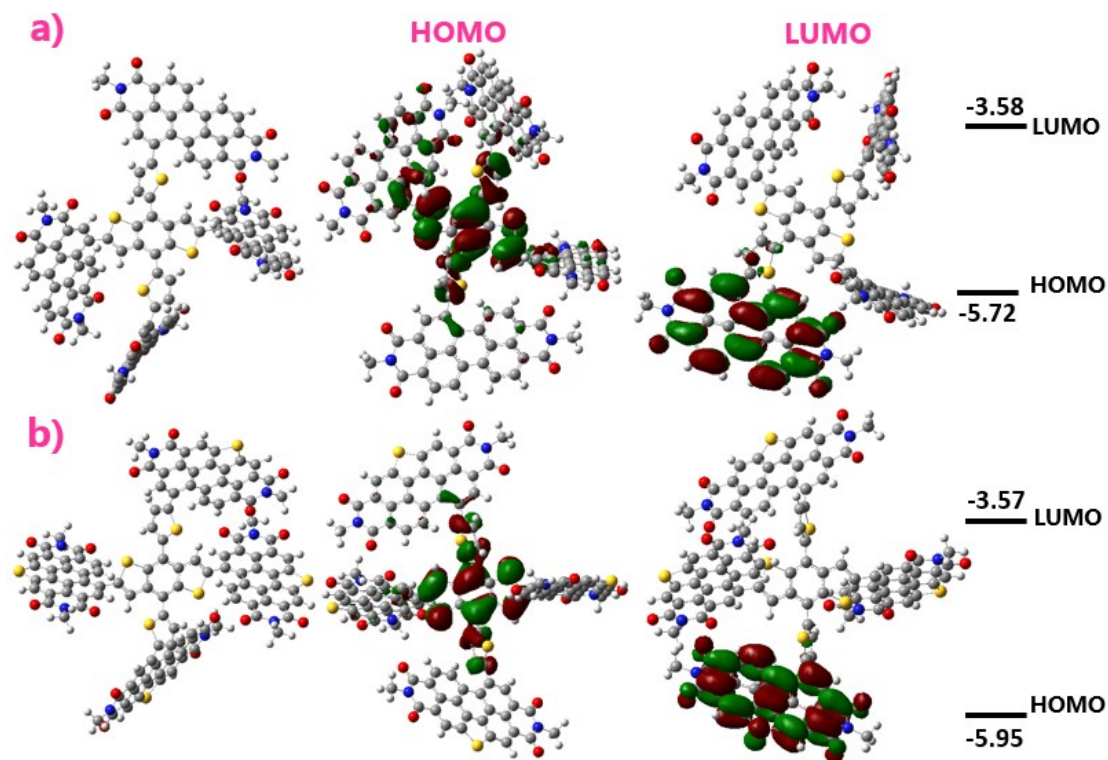


Figure S1. Optimized geometries of a) BPT, and b) BPT-S by DFT at the B3LYP/6-31G(d) level.

Table S1. The summary of PCEs over 7% in high-performance fullerene-free solar cells based on PDIs as acceptors.

| Acceptor | Donor | PCE _{max} (%) | FF | V_{oc} (V) | J_{sc} (mA cm ⁻¹) | Ref |
|---------------------|----------------|------------------------|--------------|--------------|---------------------------------|------------------|
| BPT | PDBT-T1 | 7.16 | 0.639 | 1.00 | 11.25 | This work |
| BPT-S | PDBT-T1 | 8.28 | 0.681 | 1.02 | 11.94 | This work |
| SdiPBI-S | PBDTS-Se | 8.22 | 0.700 | 0.91 | 12.90 | 1 |
| SdiPBI-Se | PDBT-T1 | 8.42 | 0.702 | 0.96 | 12.49 | 2 |
| TPB | PTB7-Th | 8.47 | 0.58 | 0.80 | 18.25 | 3 |
| TPH-Se | PDBT-T1 | 9.28 | 0.715 | 1.00 | 12.99 | 4 |
| β TPB6-C | PTB7-T1 | 7.69 | 0.56 | 0.92 | 14.9 | 5 |
| 7b | P3TEA | 7.55 | 0.61 | 1.13 | 11.03 | 6 |
| Ta-PDI | PTB7-Th | 9.15 | 0.685 | 0.78 | 17.10 | 7 |
| H-tri-PDI | PBDT-TS1 | 7.25 | 0.60 | 0.732 | 16.52 | 8 |
| FITP | PTB7-Th | 7.33 | 0.56 | 0.99 | 13.24 | 9 |
| SF-PDI ₂ | P3TEA | 9.50 | 0.643 | 1.11 | 13.27 | 10 |
| PBI-Por | PBDB-T | 7.40 | 0.66 | 0.78 | 14.5 | 11 |

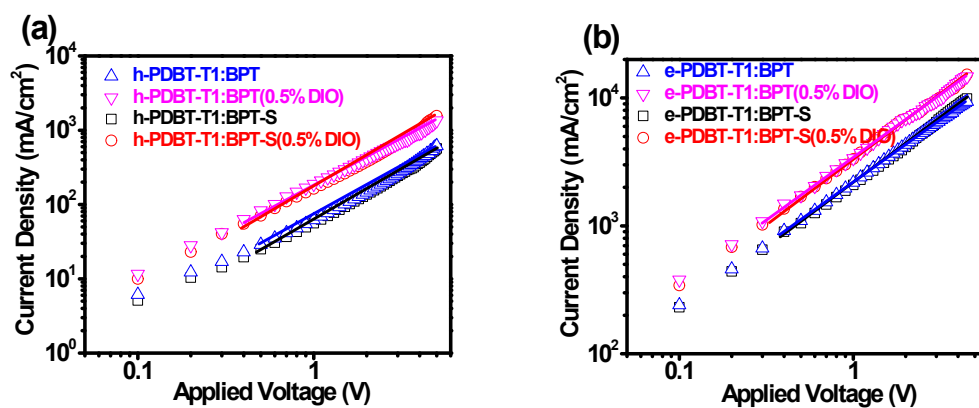


Figure S2. Space-charge-limited (SCLC) J - V characteristics of PDBT-T1/acceptors under dark condition, a) Electron-Only and b) Hole-Only.

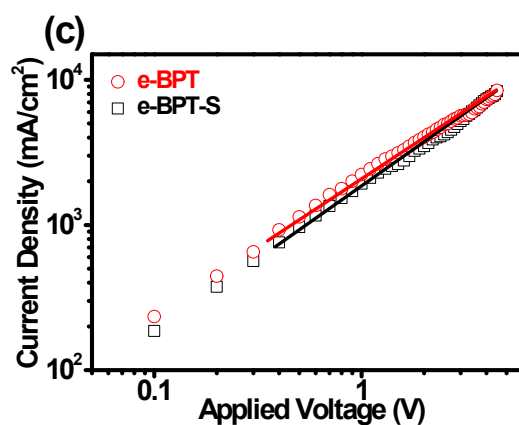


Figure S3. Space-charge-limited (SCLC) J - V characteristics of neat acceptor films.

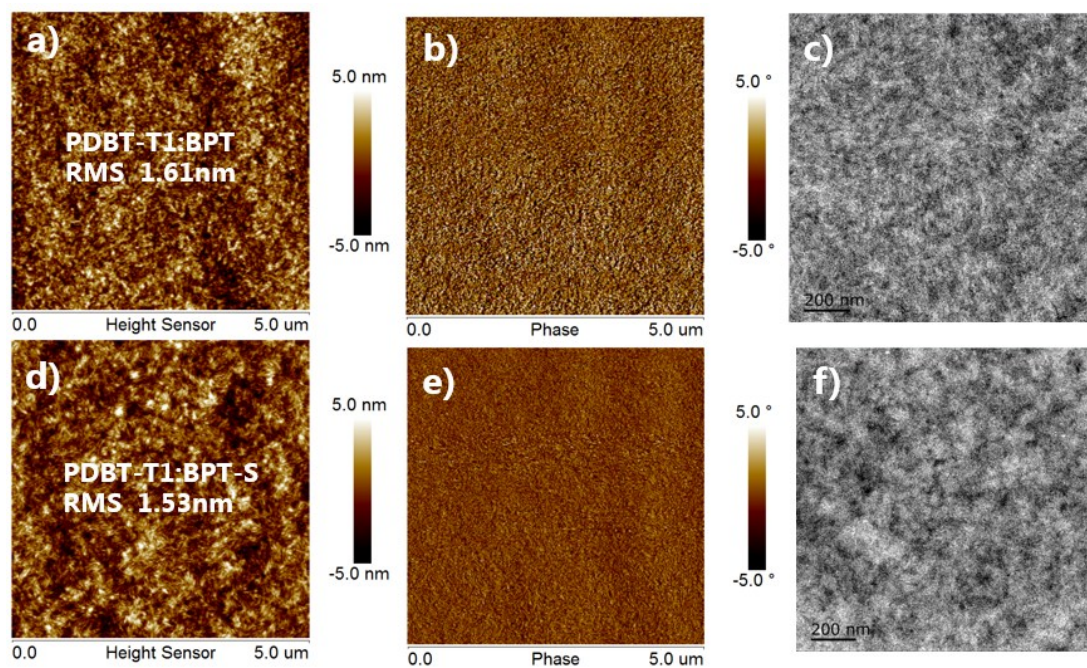


Figure S4. Morphology images of the as cast blend films: a) AFM height, b) AFM phase, and c) TEM images of the PDBT-T1:BPT (1:1, w/w) blend film; d) AFM height, e) AFM phase, and f) TEM images of the PDBT-T1:BPT-S (1:1, w/w) blend film.

Figure S5. ^1H NMR spectrum of BDT-ThSi.

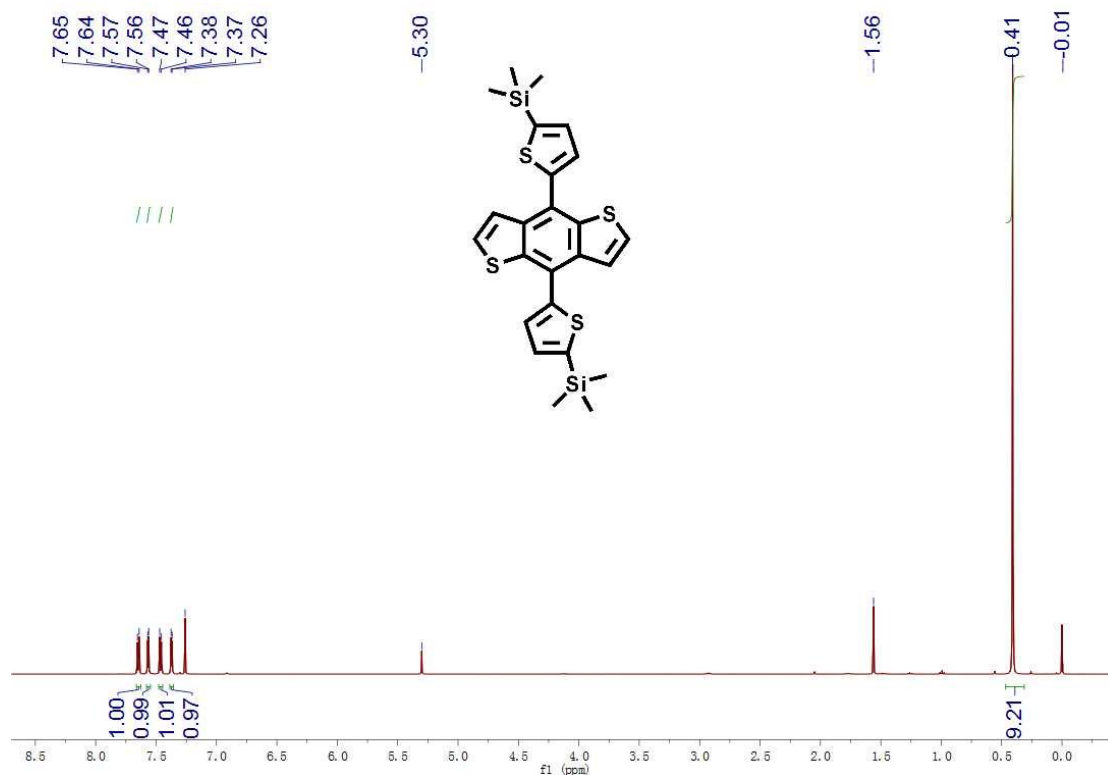


Figure S6. ^1H NMR spectrum of BPT-S.

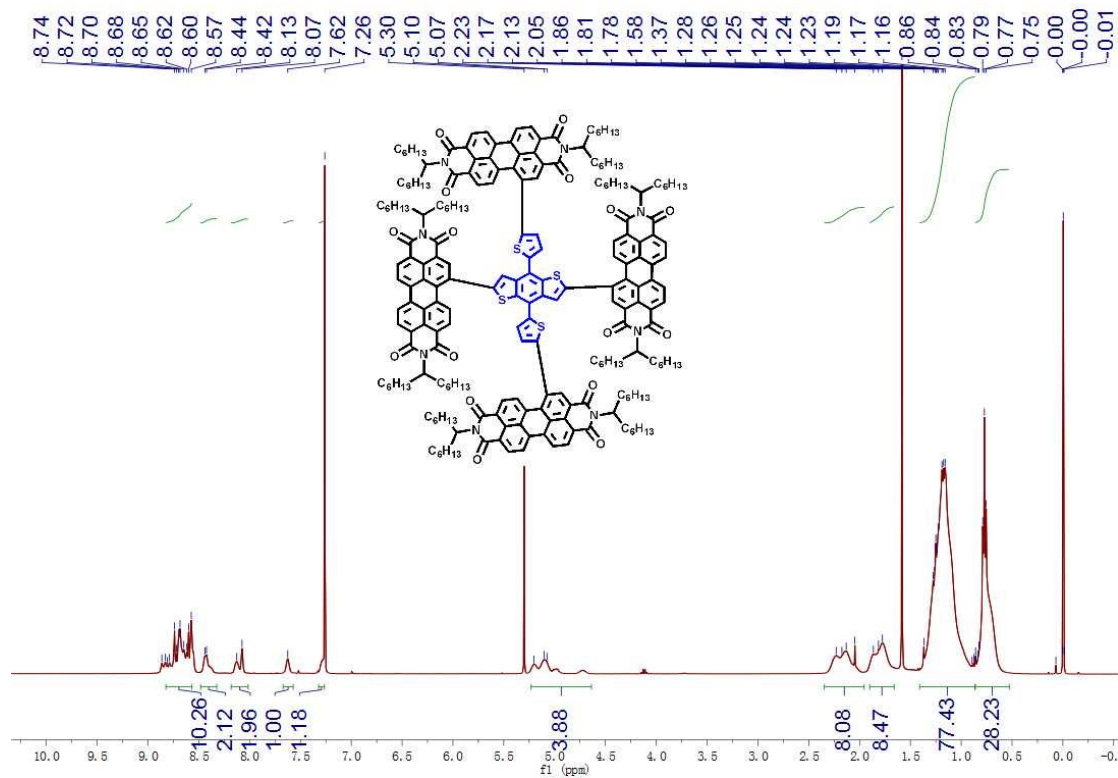
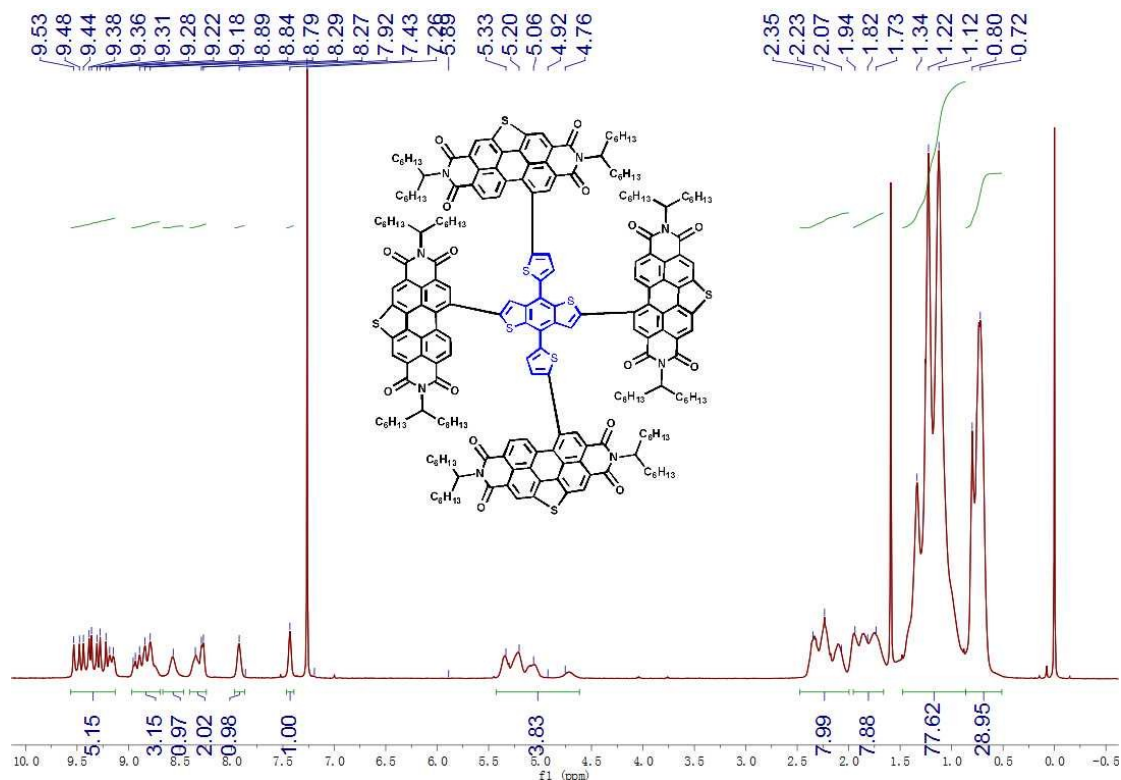


Figure S7. ^1H NMR spectrum of BPT-S.



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