Electronic Supplementary Information

Thienobenzene-fused perylene bisimide as non-fullerene acceptor for organic solar cells with high open-circuit voltage and power conversion efficiency

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1. Experiments

General information. The dry toluene was obtained by refluxing with the alloy of potassium/sodium under argon atmosphere. Other agents and reagents were bought from commercial sources and used without further purification. ^{1}HNMR and ^{13}CNMR spectra were obtained through a Varian Unity 300 MHz spectrometer using $CDCl_3$ as solvent. Elemental analysis of hydrogen, carbon and nitrogen was performed on a Vario EL-III microanalyzer. UV-Vis absorption spectra were measured on solutions in $CHCl_3$ and films casted onto quartz glass using a Hitachi U-3010 spectrophotometer. Cyclic voltammetric measurements were carried out on a computer-controlled EG&G Potentiostat/Galvanostat model 283 using tetrabutyl-ammonium hexafluorophosphate (0.1 M) as supporting electrolyte in CH_3CN. A conventional three-electrode cell with a Pt work electrode, a platinum-wire counter electrode and a Ag/AgCl reference electrode was employed. The film was deposited on the Pt work electrode for

measurement. Computation for the molecule was carried out by DFT (B3LYP/6-31G(d)) method, in which the alkyl chains were replaced by methyl groups.

Fabrication and characterization of solar cells. Solar cells were based on the architecture of ITO/PEDOT:PSS/PDBT-T1:SdiPBI-BT/Ca/Al. ITO glass was cleaned with detergent, ultrasonicated in deionized water, acetone and isopropanol, subsequently treated by UV-Ozone for 20 min before using. PEDOT:PSS (Heraeus Clevios P VP A 4083) was spin-coated onto the ITO with the thickness about 40 nm, and then dried at 140 °C for 10 min in air. PDBT-T1 and SdiPBI-BT was co-dissolved in dichlorobenzene with different mass ratios and DIO concentrations (the concentration of PDBT-T1 was fixed at 6mg/mL). The blend solution was spin-coated at 1200 r/min for 40s onto the PEDOT: PSS layer. Then the substrate was annealed at 100 °C for 5 min in a glove box filled with N_2 (O_2 concentration < 1ppm and H_2O concentration < 1 ppm). A thin Ca layer (10 nm) and Al layer (100 nm) were evaporated through a shadow mask in sequence under vacuum of 5×10^{-6} Pa. The active area was 4.50 mm^2. During the measurement, an aperture with the area of 3.14 mm^2 was used. Current density-voltage (*J–V*) characteristics were obtained using a Keithley 2400 sourcemeter in the glove box. Solar cell performance was measured on an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW/cm^{-2}. IPCE spectra were obtained through a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.). Electron mobility was measured by space charge limit current (SCLC) method. The electron mobility was measured with the device structure of ITO/Al/PDBT-T1: Acceptor (0.5% DIO)/Al. The mobility was extractedby using the equation: $J = 9\varepsilon_0\varepsilon_r\mu^2V^2/8d^3$, where J is the current density, d is the film thickness of theactive layer, μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0V here). The carrier mobility is extracted from the slope of the $J^{1/2} \sim$ V curves.

2. Cyclic voltammetry curves of SdiPBI-BT and diPBI-BT

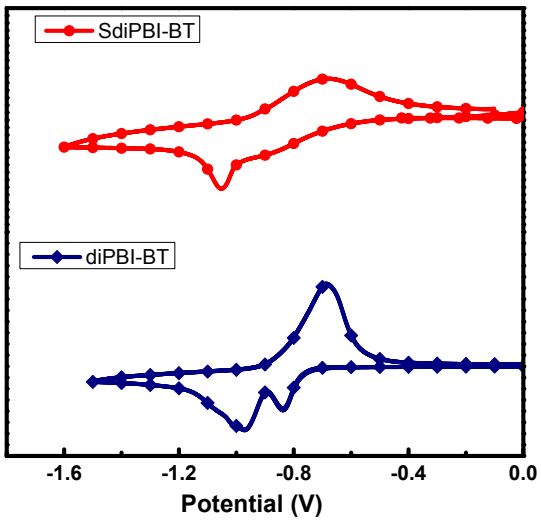


Figure S1 Cyclic voltammograms of **SdiPBI-BT** and **diPBI-BT** in CH_3CN solution (vs. Ag/Ag^+).

3. Calculated HOMO and LUMO distributions of SdiPBI-BT

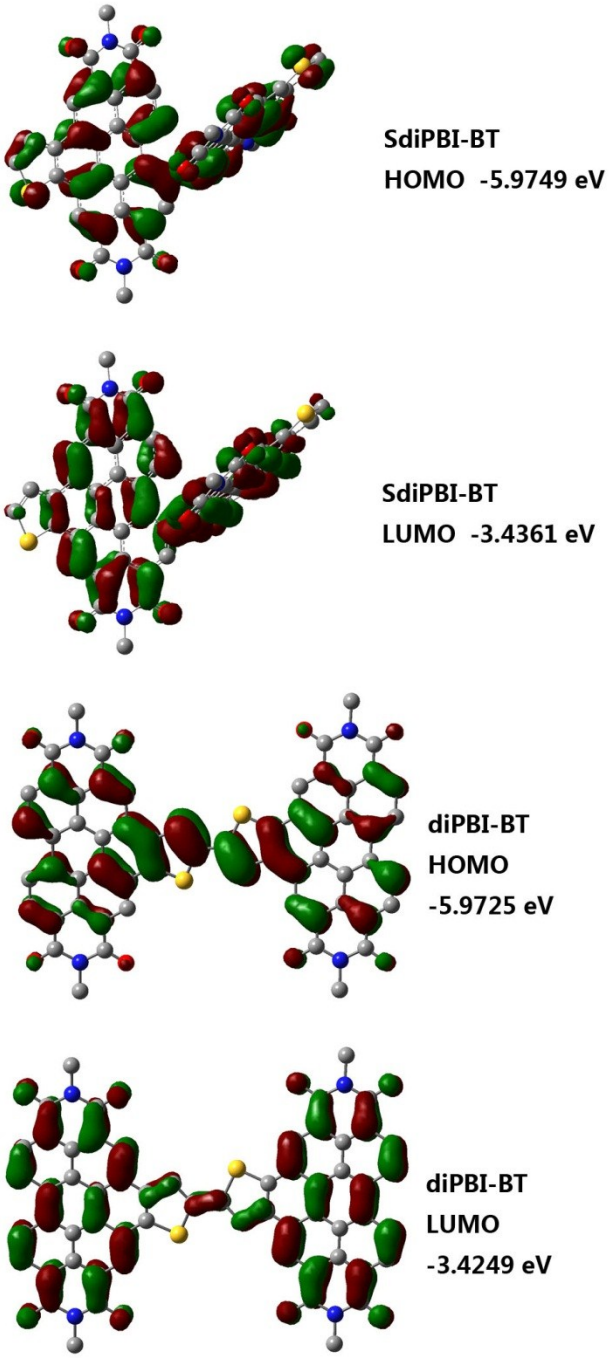


Figure S2 HOMO and LUMO distributions of **SdiPBI-BT** and **diPBI-BT** obtained from theory calculations.

4. OPV device characterization

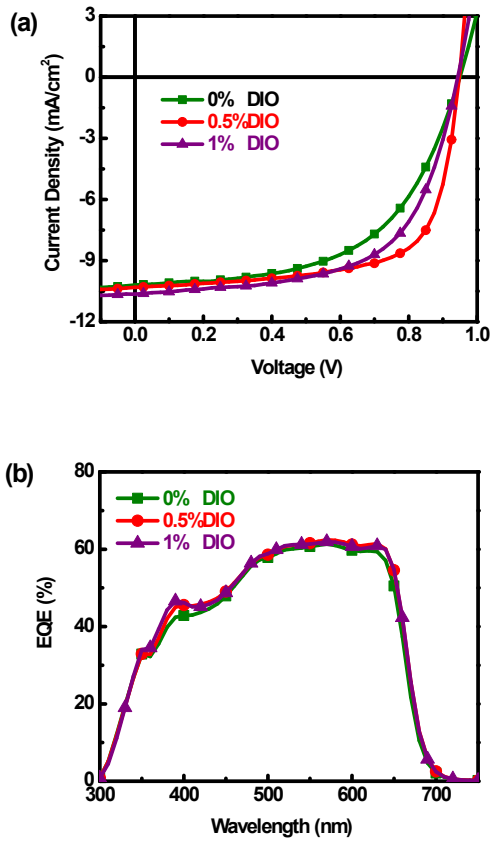


Figure S3 *J-V* characteristics (a) and IPCE spectra (b) of PDBT-T1: SdiPBI-BT (1:1) solar cells with different DIO concentrations.

Table S1. Summary of device parameters of **PDBT-T1:SdiPBI-BT** (1: 1) solar cells with different DIO concentrations under the illumination of AM1.5G, 100 mW/cm^2.

DIO (%)	V_{oc} (V)	J_{sc} (mA/cm^2)[a]	FF (%)	PCE (%)
0	0.95	10.20 (9.92)	55.9	5.41
0.5	0.95	10.31(10.26)	68.7	6.71
1	0.94	10.65(10.34)	60.7	6.10

[a] The values in the parentheses are the integrated current density calculated from the IPCE spectrum

5. AFM phase images

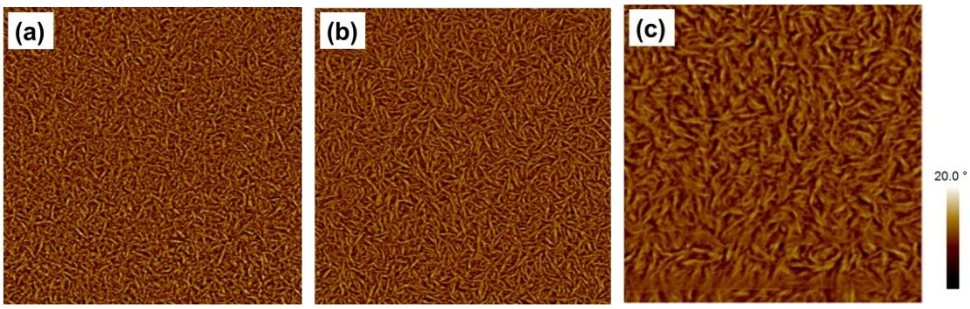


Figure S4 AFM phase images (2 μm × 2 μm) of **PDBT-T1**: **SdiPBI-BT** (1: 1) films without (a) and with (b) 0.5% DIO; AFM phase images (2 μm × 2 μm) of **PDBT-T1**: **diPBI-BT** (1: 1, 0.5%DIO) blend films (c).

6. SCLC Measurements.

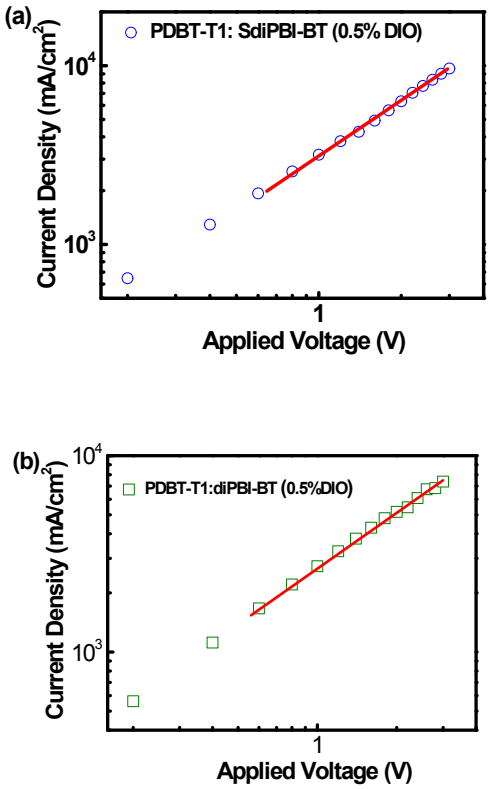
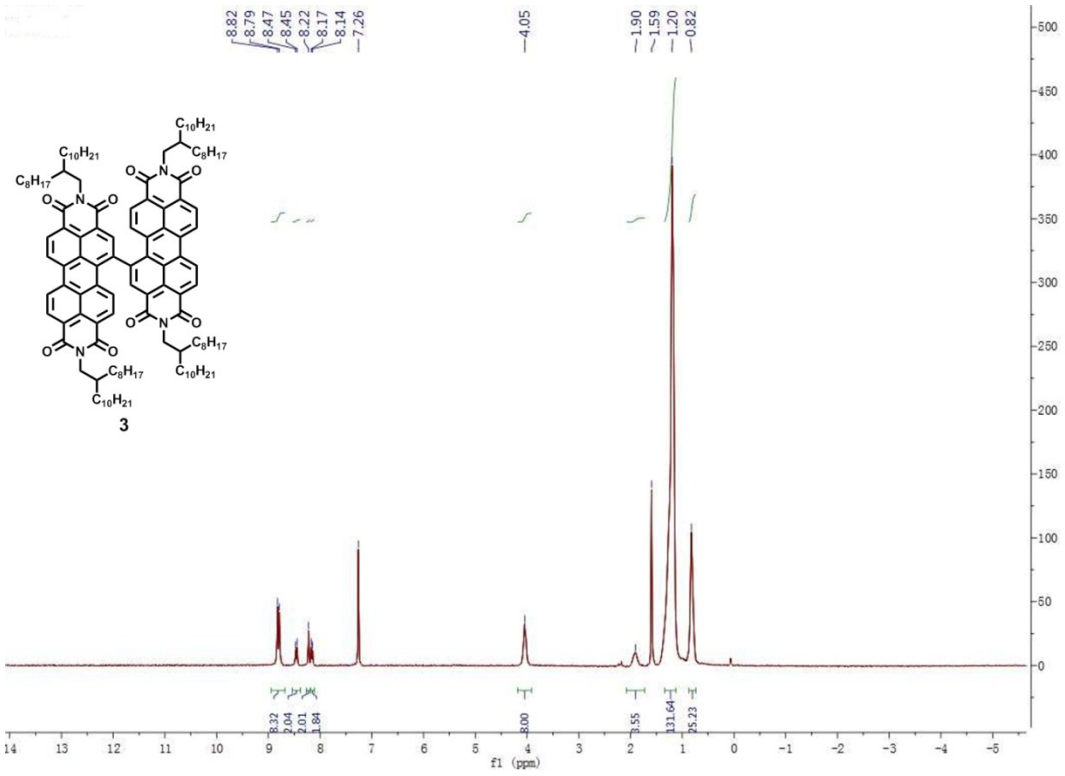
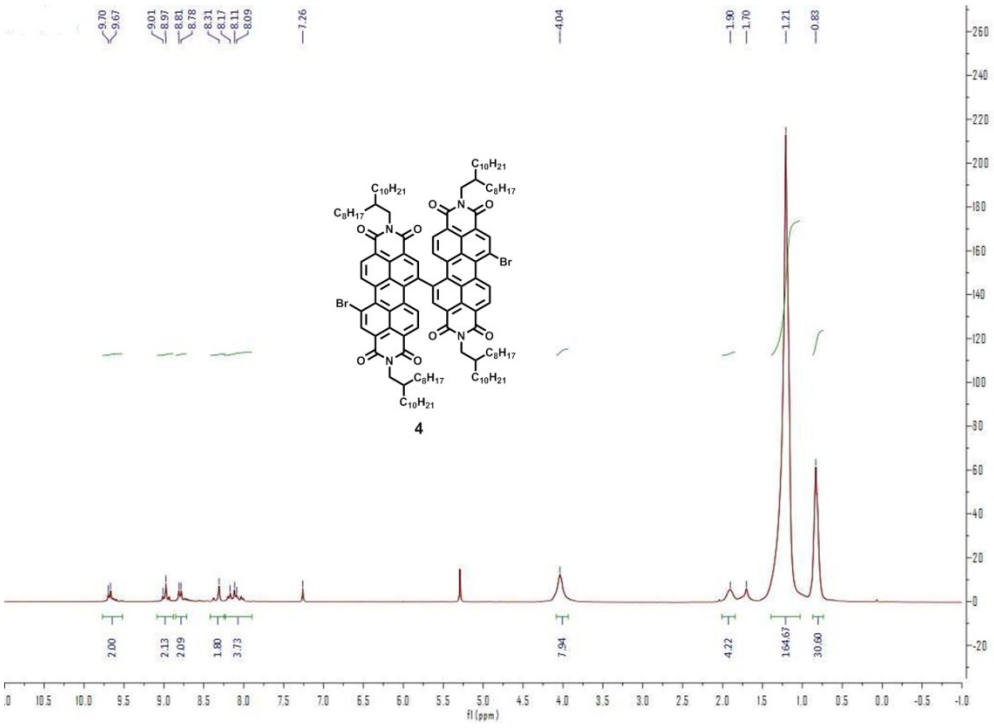


Figure S5 The experimental current density-applied voltage (*J-V*) characteristics for the electron-only devices of PDBT-T1: SdiPBI-BT (0.5% DIO) (a) and PDBT-T1: diPBI-BT (0.5% DIO) (b).

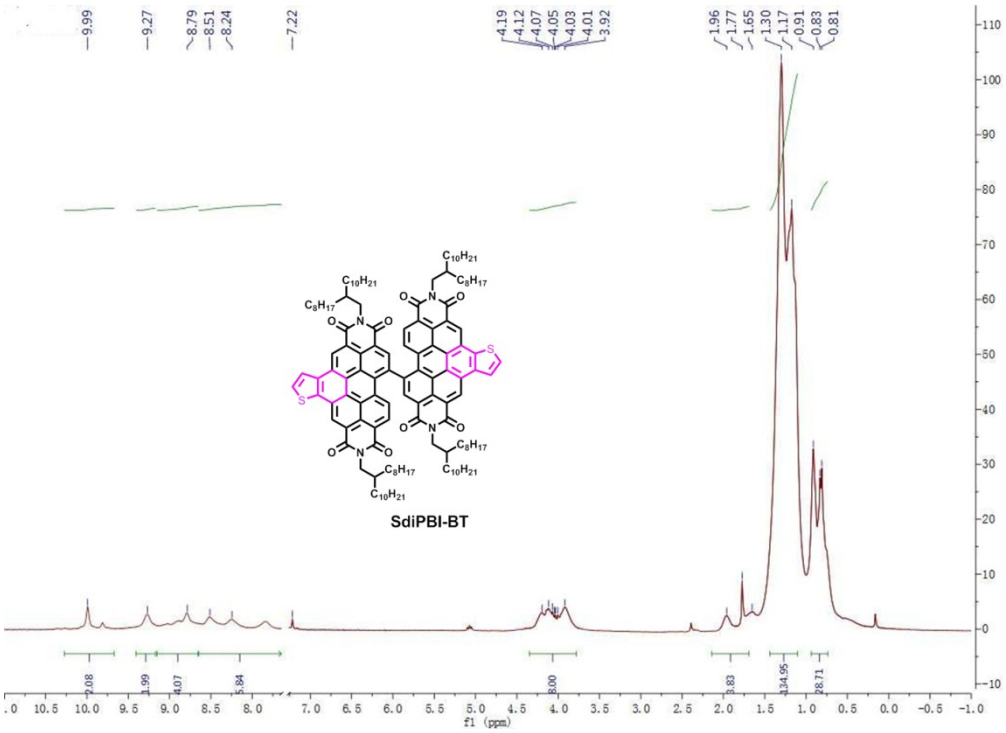
7. NMR spectra



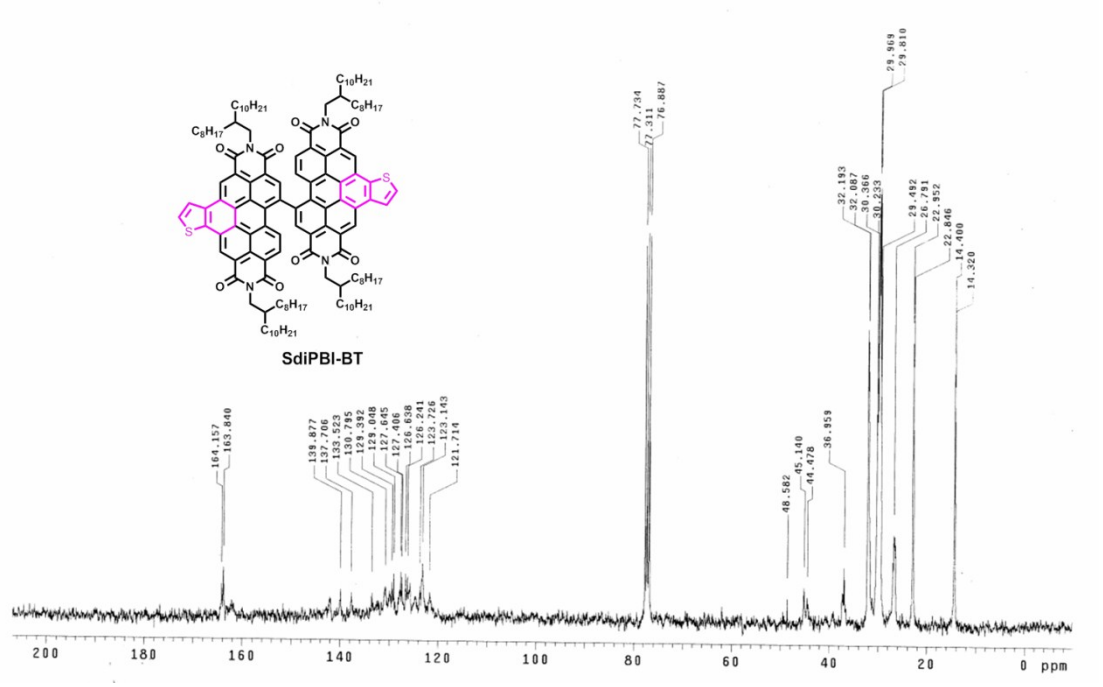
^{1}H NMR spectrum of compound 3



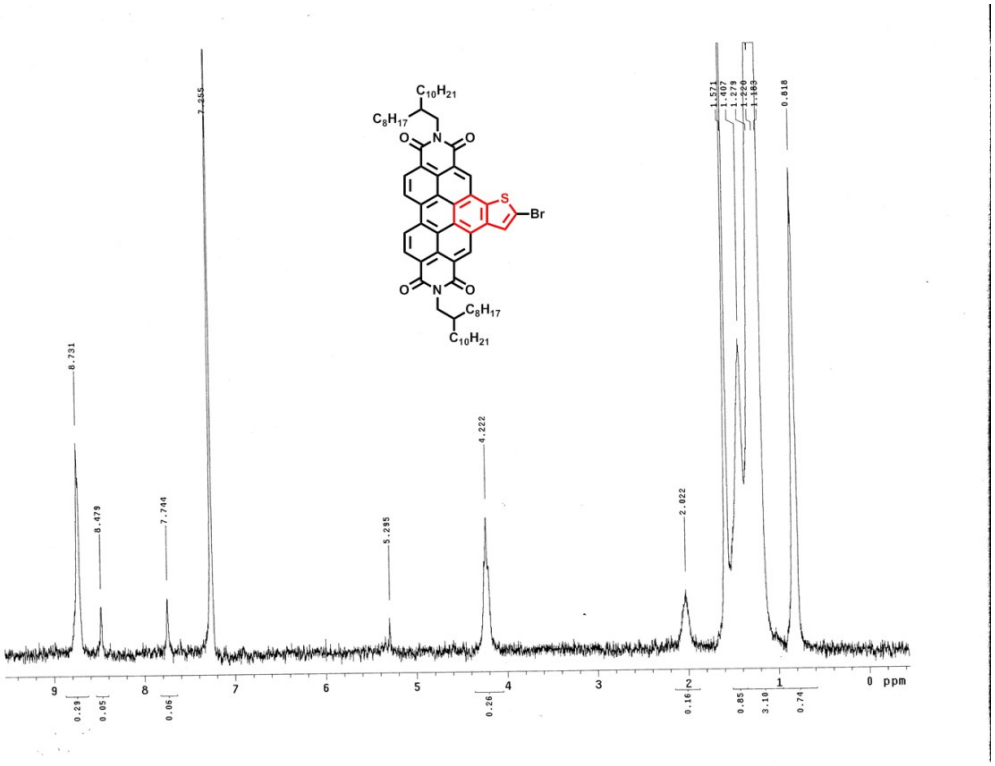
^{1}H NMR spectrum of compound 4



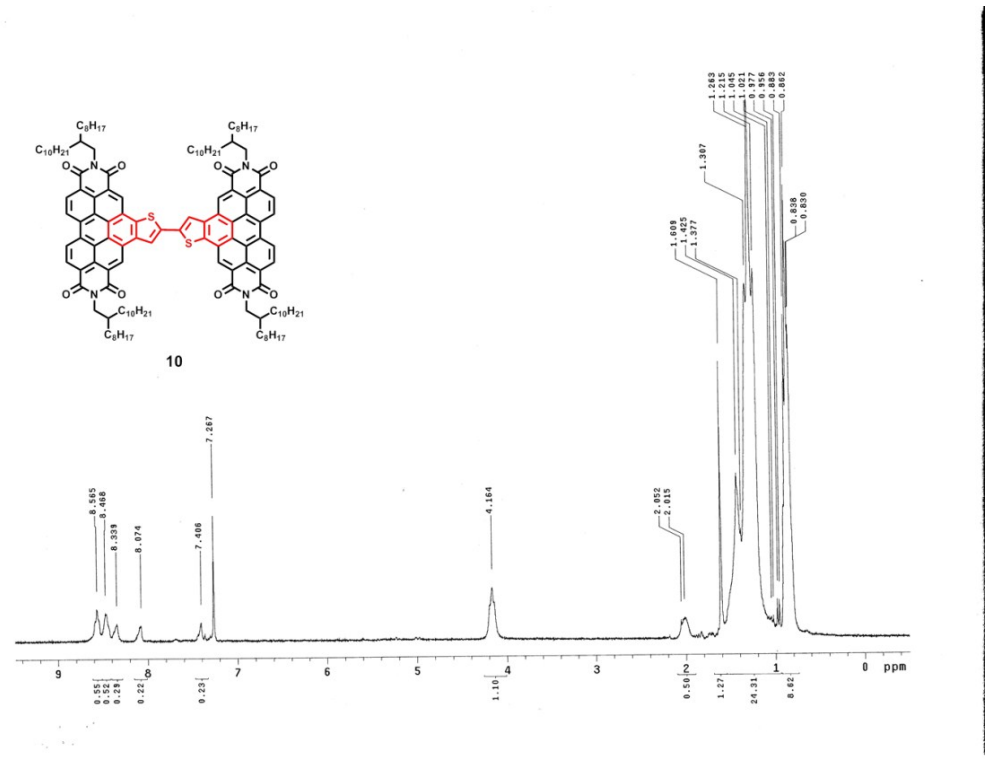
^{1}H NMR spectrum of SdiPBI-BT



^{13}C NMR spectrum of SdiPBI-BT



^{1}H NMR spectrum of 9



^{1}H NMR spectrum of diPBI-BT