

Supporting Information for

**High performance three-dimensional thiophene-annulated
perylene dye as acceptor for organic solar cells**

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Materials and Methods:

^1H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker AVANCE 400 NMR Spectrometer and a Bruker AVIII 500WB NMR Spectrometer. ^1H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer. Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammetry (CV) was performed with a Zahner IM6e electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) dissolved in CH_2Cl_2 was employed as the supporting electrolyte. The plot includes the signal of the ferrocene as an internal potential marker. CH_2Cl_2 was freshly distilled prior to use. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were carried out in a Xenocs-SAXS/WAXS system with X-ray wavelength of 1.5418 Å. The samples were irradiated at a fixed angle of 0.2. The films were made on Si wafer substrates under the same preparation conditions for solar cells.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified.

1. Synthesis and characterization of compounds 2, 3, tetra-PBI and tetra-PBI-S.

The starting materials 1-nitroperylene bisimide **1**, tetra-PBI, and tetrakis[4-(4',4',5',5'-tetramethyl-1',3',2',-dioxaborolanophenyl)]methane were synthesized according to literature procedures.^[1,2]

Compound 2

A mixture of Sulfur (1.72 g, 53.78 mmol) and 1-nitroperylene bisimide **1** (4 g, 5.38 mmol) were heated in *N*-methylpyrrolidone (NMP, 100 mL) at 190°C under an argon atmosphere for 1 h. Next, the cooled mixture was poured into 2M HCl (1 L) and stirred for 5 min. Then the precipitate was filtered, washed with water, dried, and

purified by silica gel column chromatography (petroleum ether: CH₂Cl₂, 3:1) to isolate **2** as a bright yellow solid (3.33 g, 85%).

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 9.30-9.26 (d, *J* = 16.0 Hz, 2H), 8.91-8.88 (m, 4H), 5.30 (m, 2H), 2.37-2.28 (m, 4H), 1.97-1.90 (m, 4H), 1.43-1.25 (m, 24H), 0.85-0.82 (m, 12H); ¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 164.63, 163.92, 138.05, 132.93, 131.19, 129.92, 129.27, 127.74, 127.07, 126.11, 123.30, 122.93, 122.32, 55.05, 32.46, 31.79, 26.75, 22.59, 14.02; HRMS (MALDI (N), 100%): calcd (%) for C₄₆H₅₂N₂O₄S: 728.3648; found, 728.3653. M p: 254-257°C.

Compound 3

In a closed round-bottom flask, bromine (32.8 g, 0.205 mol) was added in one portion to a solution of Compound **2** (3g, 4.11 mmol) in 50 mL of dichloromethane with vigorous stirring for 5h. Then the excess of bromine was quenched with saturated sodium sulfite solution. The organic layer was separated, dried over MgSO₄, and purified by silica gel column chromatography (petroleum ether : CH₂Cl₂, 4:1) to give **3** as an orange solid (3.05 g, 92%).

¹H NMR (400 MHz, 298 K, CDCl₃): δ = 9.81-9.73 (m, 1H), 9.01 (s, 2H), 8.80 (s, 1H), 8.64 (s, 1H), 5.34-5.28 (m, 2H), 2.39-2.35 (m, 4H), 2.00-1.97 (m, 4H) , 1.48-1.33 (m, 24H) , 0.90-0.87 (m, 12H); ¹³C NMR (100 MHz, 298 K, CDCl₃): δ = 164.37, 163.25, 162.19, 137.59, 136.97, 131.76, 129.90, 129.71, 129.33, 129.12, 128.50, 126.84, 125.29, 124.45, 124.37, 122.69, 121.04, 55.32, 55.15, 32.44, 32.38, 31.83, 31.82, 26.88, 22.68, 14.09; HRMS (MALDI (N), 100%): calcd (%) for C₄₆H₅₁BrN₂O₄S: 806.2753; found, 806.2758. M p: 236-239°C.

Compound of tetra-PBI:

The general procedure was according to the corresponding literature.^[1] Compound **3** (100 mg, 0.1213 mmol), 1-bromoperylene bisimide (316 mg, 0.522 mmol) and Pd(PPh₃)₄ (16 mg, 0.0146 mmol) were added into a glass pressure vessel under nitrogen atmosphere. Then THF (6 ml) and potassium carbonate (835 mg, 2M) were added by injection in sequence. The reaction mixture was stirred at 87 °C for 2 days.

After cooling down, the mixture was poured into methanol, filtered. The residue was purified by silica gel chromatography (dichloromethane: petroleum ether =1:1) to afford compound **tetra-PBI** (294 mg, 78%) as a red solid.

^1H NMR (500 MHz, 373 K, $\text{CDCl}_2\text{CDCl}_2$, ppm) δ = 8.71-8.69 (d, J = 10 Hz, 8H), 8.65-8.59 (m, 12H), 8.11-8.07 (m, 8H), 7.77-7.69 (m, 16H), 5.19-5.13 (m, 4H), 4.88 (s, 4H), 2.27-2.19 (m, 8H), 1.93-1.87 (m, 16H) , 1.65 (s, 8H) , 1.31-1.29 (m, 44H), 1.09-1.08(m, 44H), 0.85-0.83 (m, 24H), 0.69-0.66 (m, 24H) ; ^{13}C NMR (125 MHz, 373 K, $\text{CDCl}_2\text{CDCl}_2$): δ = 163.94, 146.48, 141.69, 141.18, 135.94, 134.97, 134.88, 134.51, 133.14, 132.70, 131.04, 129.79, 129.65, 129.33, 128.77, 128.52, 128.20, 127.76, 123.78, 123.42, 123.01, 122.84, 122.62, 55.00, 54.62, 32.54, 32.33, 31.68, 31.49, 26.61, 26.42, 22.39, 22.24, 13.83, 13.67; HRMS (MALDI (N), 100%) m/z calcd for $\text{C}_{209}\text{H}_{228}\text{N}_8\text{NaO}_{16}$ (M^+) = 3128.7166 , found 3128.7159

Compound of tetra-PBI-S:

Compound **3** (100 mg, 0.1213 mmol), Compound **6** (332 mg, 0.522 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 0.0146 mmol) were added into a glass pressure vessel under nitrogen atmosphere. Then THF (6 ml) and potassium carbonate (835 mg, 2M) were added by injection in sequence. The reaction mixture was stirred at 87 °C for 2 days. After cooling down, the mixture was poured into methanol, filtered. The residue was purified by silica gel chromatography (dichloromethane: petroleum ether =1:1) to afford compound **tetra-PBI-S** (317 mg, 81%) as an orange solid.

^1H NMR (500 MHz, 373 K, $\text{CDCl}_2\text{CDCl}_2$, ppm) δ = 9.41(s, 4H), 9.33 (s, 4H), 8.93 (s, 4H), 8.50-8.44 (m, 8H), 8.06-8.05 (d, J = 5 Hz, 8H), 7.96-7.94 (d, J = 10 Hz, 8H), 5.31-5.25 (m, 4H), 5.02 (s, 4H), 2.33-2.27 (m, 8H), 2.02-1.91 (m, 16H) , 1.73 (s, 8H) , 1.35-1.15 (m, 88H), 0.86-0.83 (m, 24H), 0.73-0.70 (m, 24H) ; ^{13}C NMR (125 MHz, 373 K, $\text{CDCl}_2\text{CDCl}_2$): δ = 164.24, 147.07, 142.04, 141.01, 138.58, 137.90, 134.25, 133.87, 133.19, 132.06, 131.93, 130.95, 128.88, 128.57, 128.34, 127.25, 126.38, 125.93, 124.88, 124.63, 123.30, 122.33, 55.32, 54.97, 32.66, 32.40, 31.71, 31.53, 26.66, 26.48, 22.41, 22.27, 13.83, 13.69; HRMS (MALDI (N), 100%) m/z calcd for $\text{C}_{209}\text{H}_{220}\text{N}_8\text{NaO}_{16}\text{S}_4$ (M^+) = 3248.5422 , found 3248.5412.

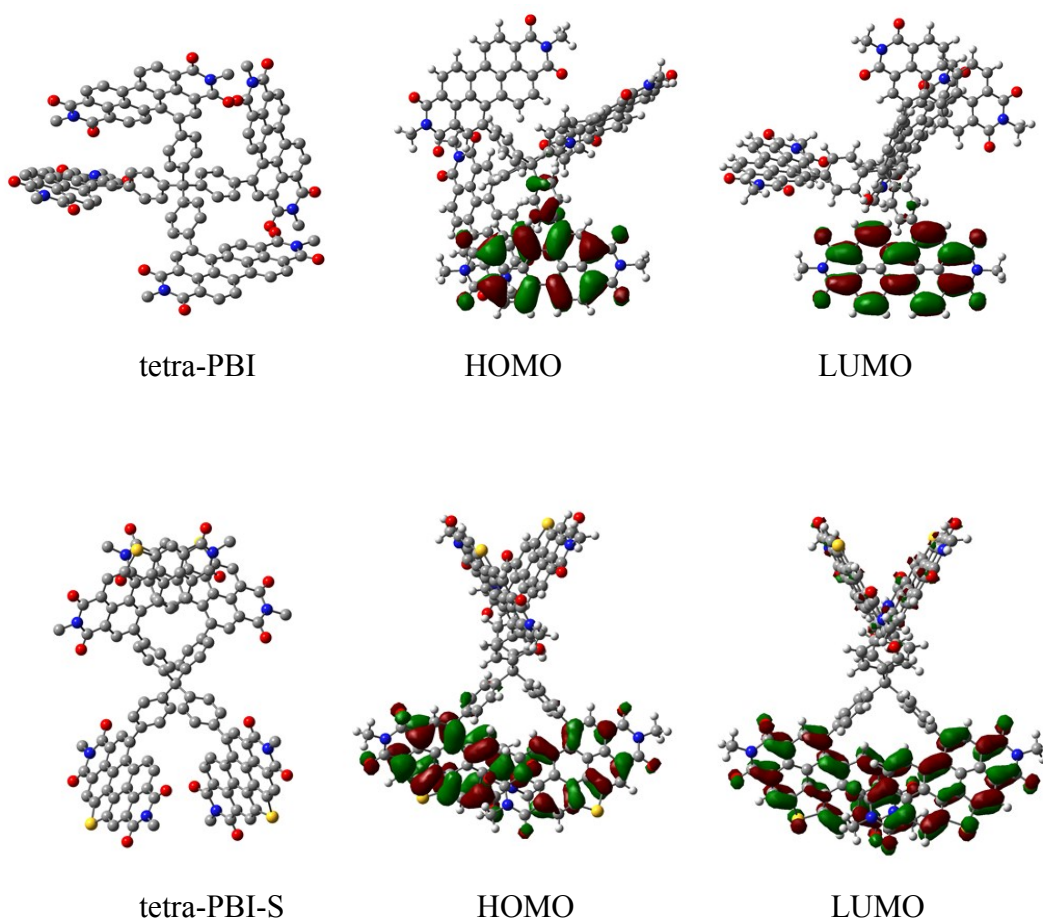


Figure S1. Molecular geometry and frontier molecular orbitals of tetra-PBI and tetra-PBI-S calculated at the DFT-B3LYP/6-31G(d,p) level.

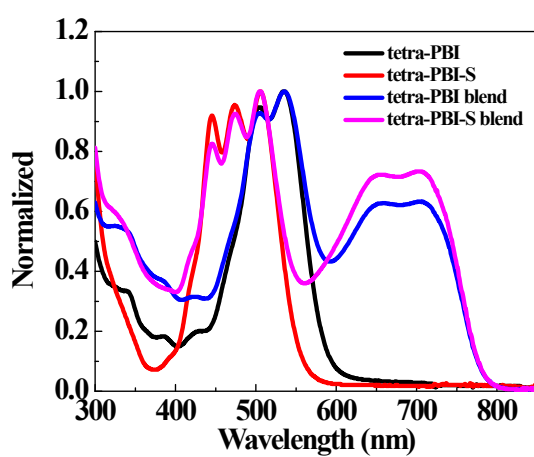


Figure S2. Absorption spectra of tetra-PBI, tetra-PBI-S, tetra-PBI blend and tetra-PBI-S blend in film.

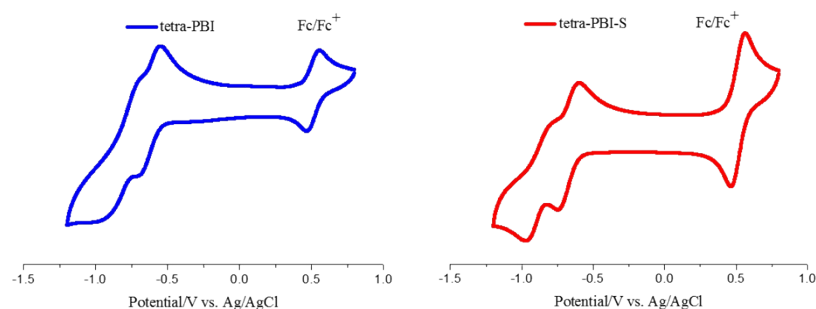


Figure S3. Reductive cyclic voltammeteries of **tetra-PBI** and **tetra-PBI-S** in CH_2Cl_2 solution.

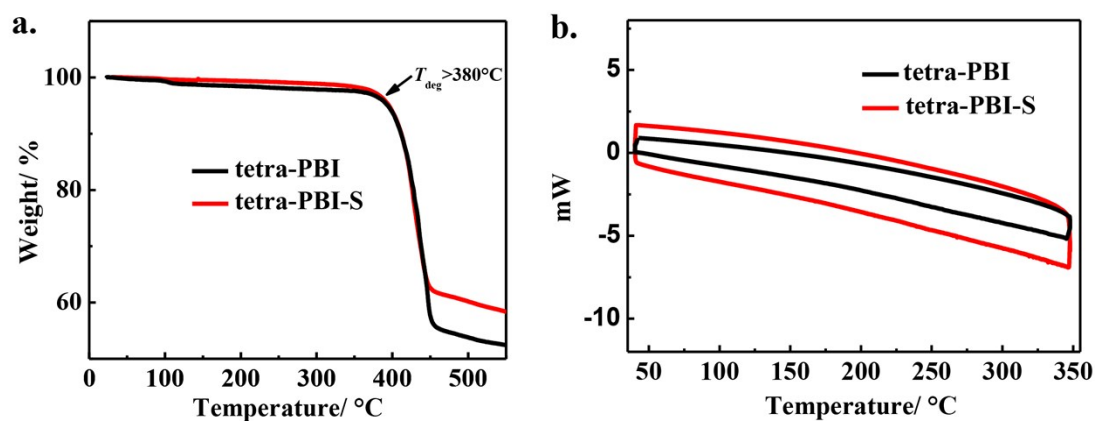


Figure S4. TGA curves of compounds **tetra-PBI** and **tetra-PBI-S** under nitrogen flow. DSC curves of compounds **tetra-PBI** and **tetra-PBI-S**.

The two molecules **tetra-PBI** and **tetra-PBI-S** were not observed obvious melting point and recrystallization peaks due to their noncrystalline in nature by the DSC measurement.

Y. M. Sun , J. H. Seo , C. J. Takacs , J. Seifter , A. J. Heeger , Adv. Mater. 2011 , 23 , 1679 .

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2. OPV Device Fabrication and Characterization

The ZnO solution used to make the cathode buffer layers was synthesized according to the previous literature.^[3] ITO(15 Ω /sq) was cleaned ultrasonically with detergent, deionized (DI) water, acetone and isopropanol, respectively. The dried ITO-glass treated with UV-ozone for 20 minutes was spin-coated the ZnO solution on the surface with 4000 rpm for 30 seconds. Then the PBDT-TS1:acceptor blend liquid was spin-coated on the ZnO layer to get a film with 120 nm thickness. Finally, MoO₃ and Al layers were evaporated on top of the active layer. The device area, the overlap section between the ITO and Al electrodes, was about 4 mm².

Table S1. Device performance parameters of PSCs based on PBDT-TS1:tetra-PBI-S BHJ at different donor/acceptor ratios under AM 1.5G illumination at 100 mW/cm².

PBDT-TS1:tetra-PBI-S [wt/wt]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
2:1	0.920	9.24	42.03	3.58
1.5:1	0.941	10.97	43.47	4.41
1:1	0.960	11.70	43.80	4.92
1:1.5	0.965	11.97	43.32	5.00
1:2	0.970	10.77	41.88	4.37

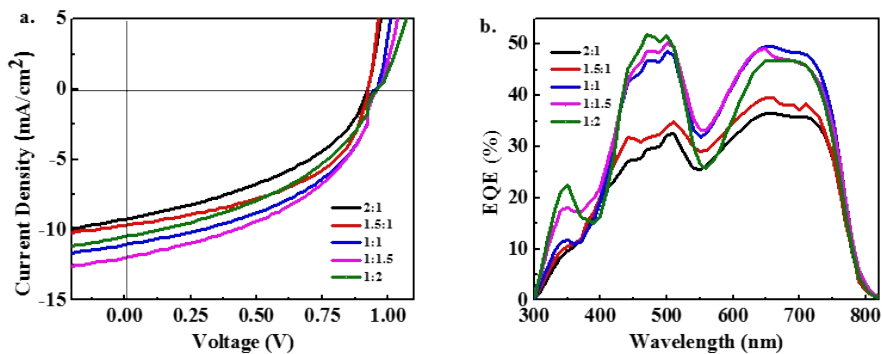


Figure S5. (a) J - V characteristic and (b) EQE characteristic of PSCs based on PBDT-TS1:tetra-PBI-S BHJ at different donor/acceptor ratios.

Table S2. Device performance parameters of PSCs based on PBDT-TS1:tetra-PBI-S BHJ with different DPE amount under AM 1.5G illumination at 100 mW/cm².

DPE [by volume, %]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.966	11.95	43.32	5.00
1	0.962	12.40	44.42	5.32
3	0.947	13.02	50.00	6.17
5	0.927	11.80	49.29	5.39

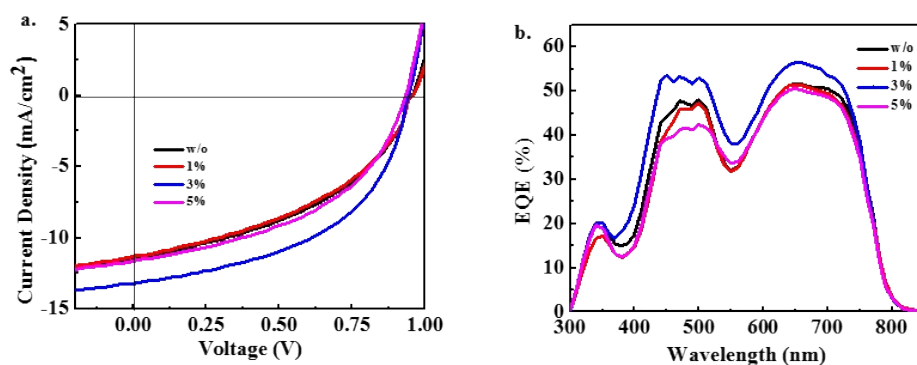


Figure S6. (a) J - V characteristic and (b) EQE characteristic of PSCs based on PBDT-TS1:tetra-PBI-S BHJ with different DPE amount.

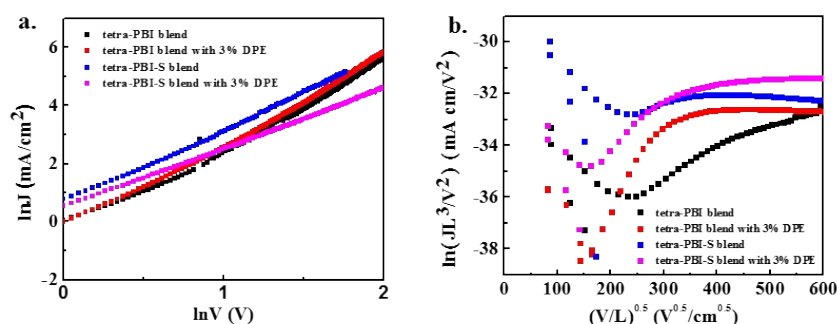


Figure S7. (a) Plots of $\ln J$ vs $\ln V$ obtained from the electron-only devices for the solar cell devices and (b) Plots of $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$ obtained from the hole-only devices.

Table S3. Charge transport parameters of the SCLC devices of PBDT-TS1:tetra-PBI blend and PBDT-TS1:tetra-PBI-S blend.

blend	μ_h [cm ² v ⁻¹ s ⁻¹]	μ_e [cm ² v ⁻¹ s ⁻¹]	μ_h/μ_e
tetra-PBI blend	6.5×10^{-7}	1.0×10^{-6}	0.65
tetra-PBI blend with 3% DPE	2.7×10^{-5}	1.0×10^{-6}	27
tetra-PBI-S blend	6.4×10^{-5}	3.8×10^{-6}	17
tetra-PBI-S blend with 3% DPE	5.8×10^{-5}	9.6×10^{-6}	6

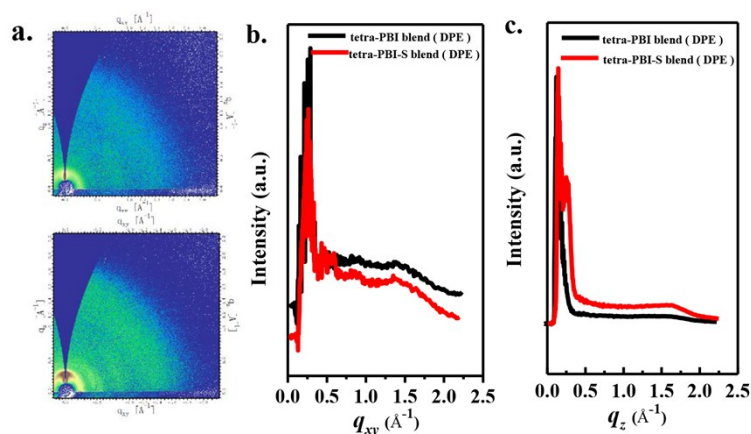


Figure S8. (a) Two-dimensional GIWAXS patterns and scattering profiles (b) in-plane and (c) out-of-plane for tetra-PBI blend film with 3% DPE and tetra-PBI-S blend film with 3% DPE.

References:

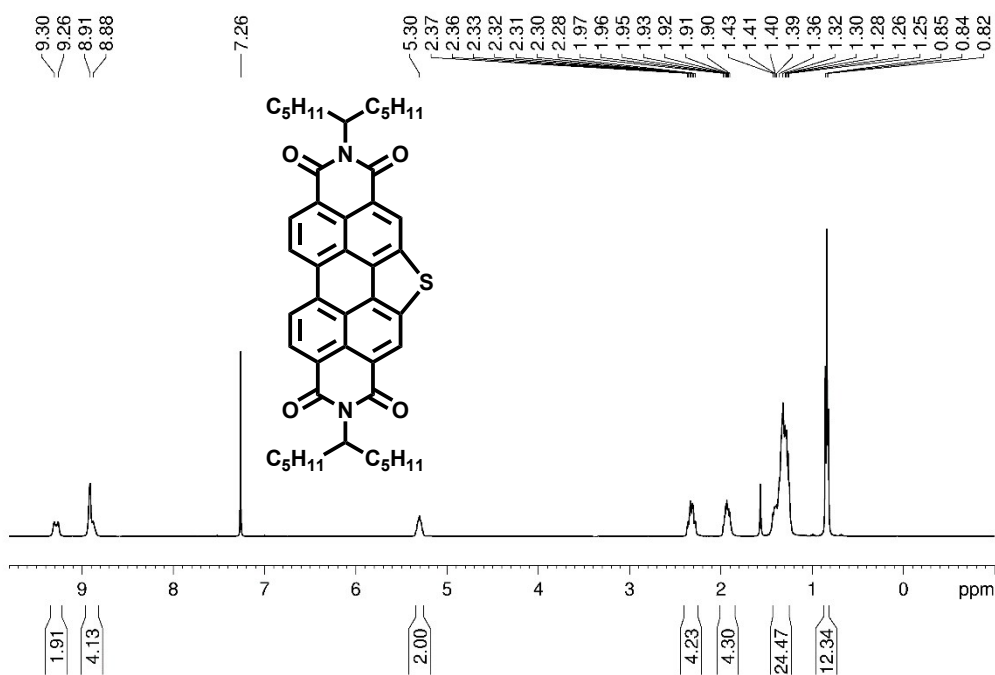
- (1). Y. Liu, J. Y. L. Lai, S. Chen, Y. Li, K. Jiang, J. Zhao, Z. Li, H. Hu, T. Ma, H. Lin, J. Liu, J. Zhang, F. Huang, D. Yu and H. Yan, *J. Mater. Chem. A*, 2015, **3**,

13632.

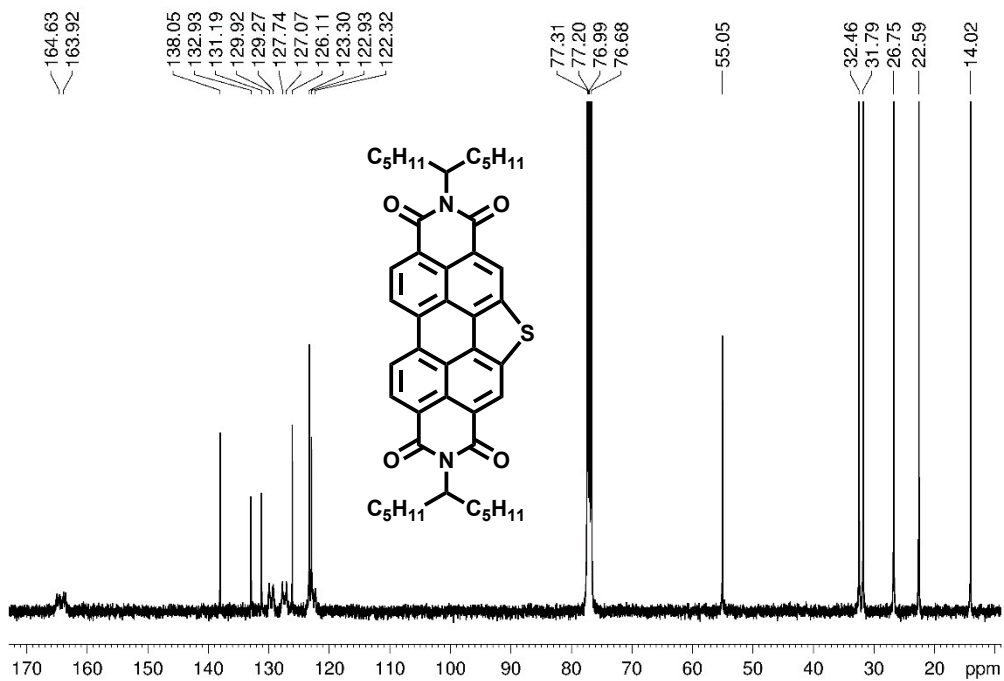
(2). D. Sun, D. Meng, Y. Cai, B. Fan, Y. Li, W. Jiang, L. Huo, Y. Sun and Z. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 11156.

(3). Y. M. Sun , J. H. Seo , C. J. Takacs , J. Seiffter , A. J. Heeger , *Adv. Mater.* **2011**, 23, 1679

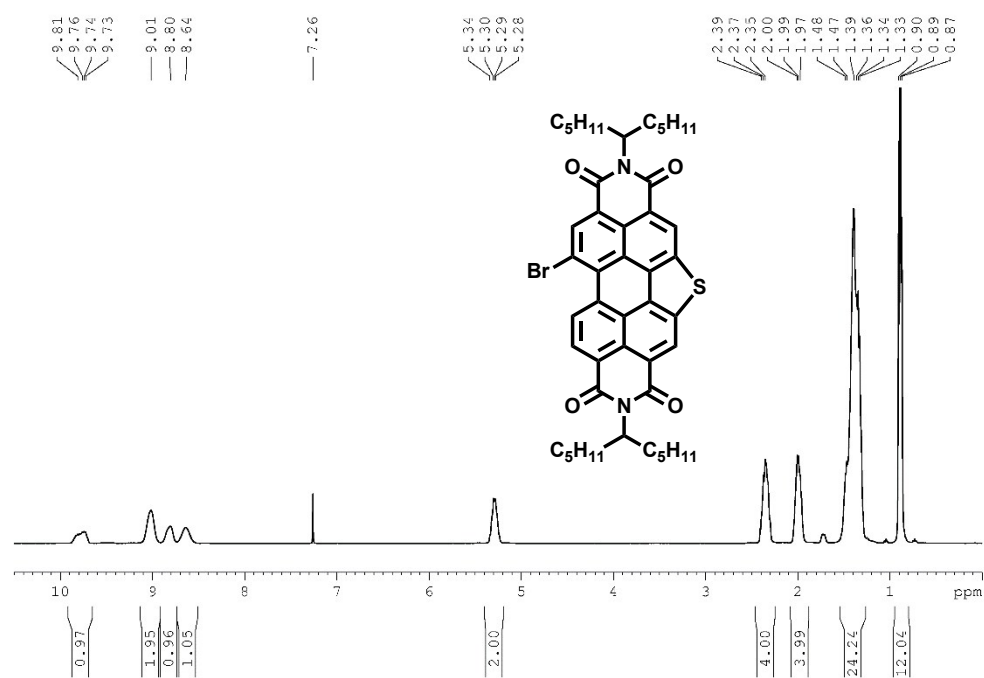
^1H NMR spectrum of **2** in CDCl_3



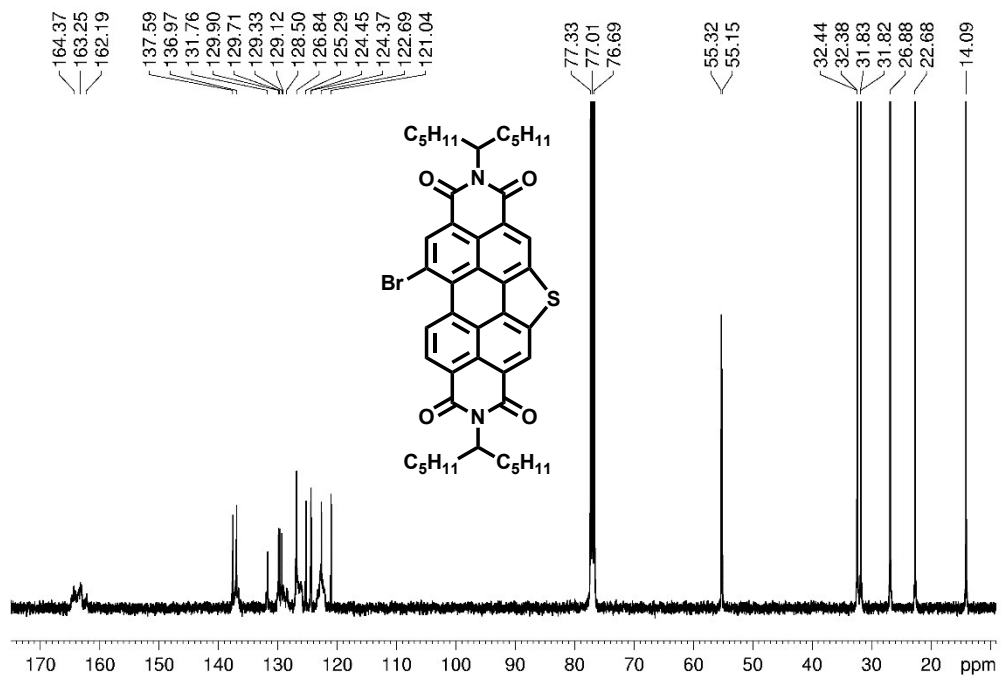
^{13}C NMR spectrum of **2** in CDCl_3



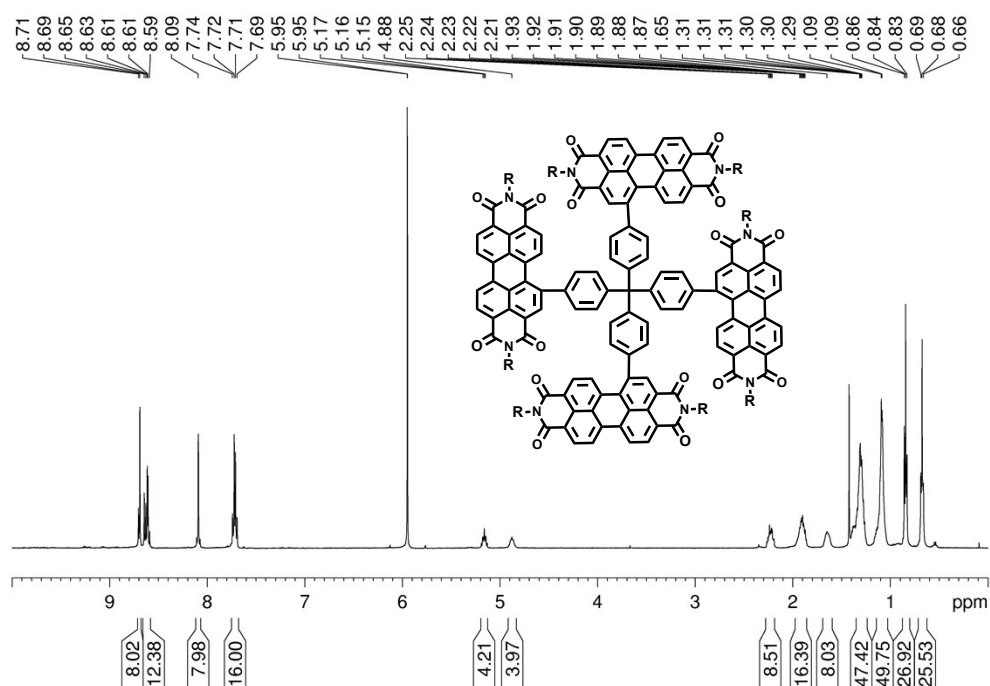
^1H NMR spectrum of **3** in CDCl_3



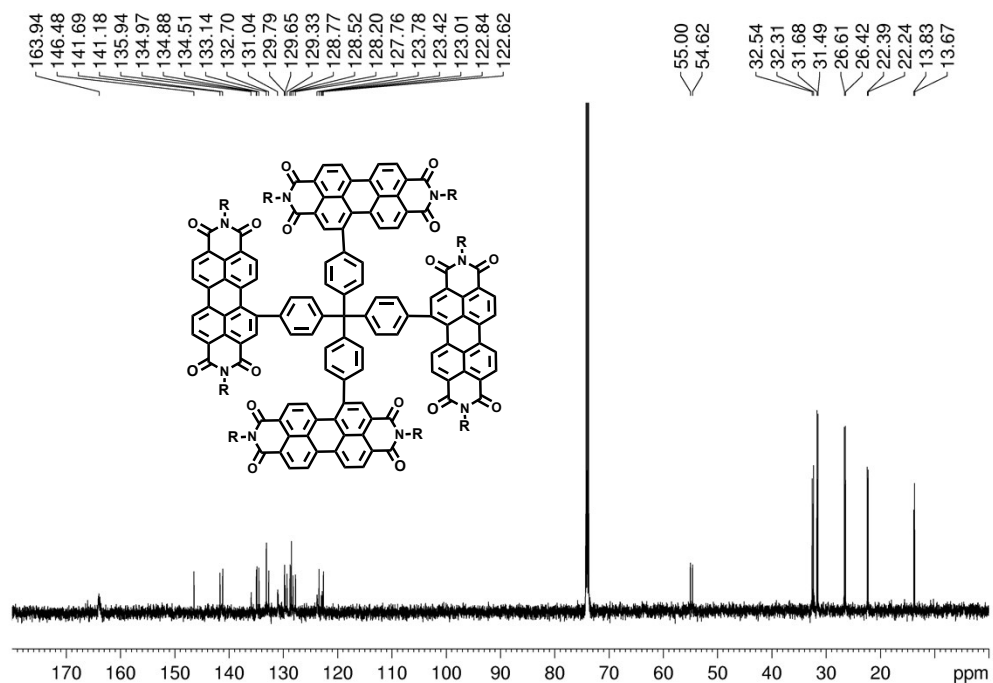
^{13}C NMR spectrum of **3** in CDCl_3



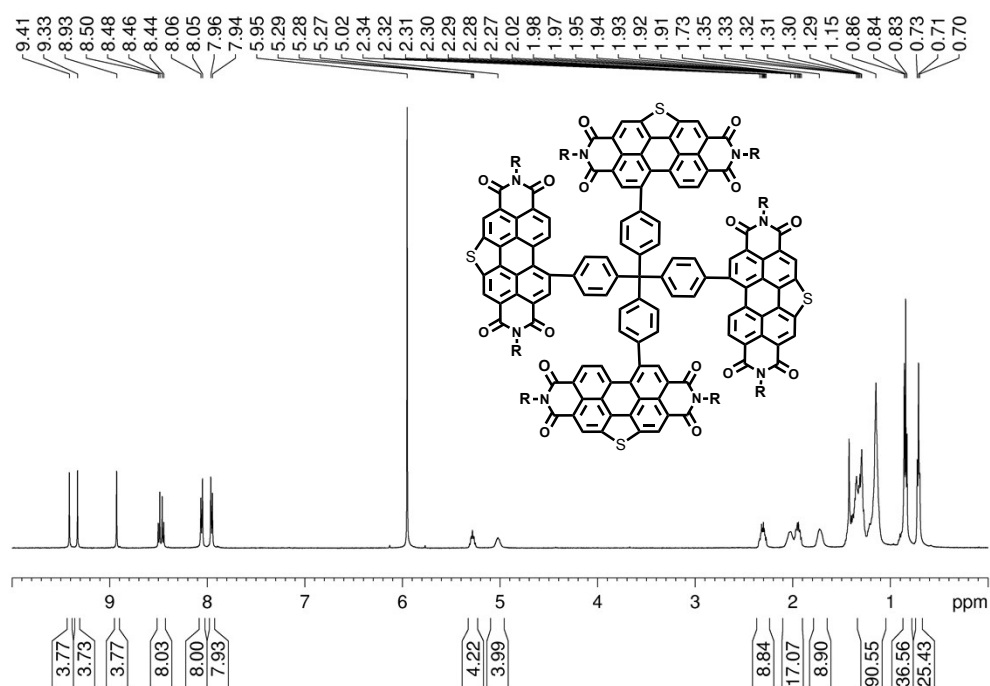
^1H NMR spectrum of **tetra-PBI** in $\text{CDCl}_2\text{CDCl}_2$



^{13}C NMR spectrum of **tetra-PBI** in $\text{CDCl}_2\text{CDCl}_2$



^1H NMR spectrum of **tetra-PBI-S** in $\text{CDCl}_2\text{CDCl}_2$



^{13}C NMR spectrum of **tetra-PBI-S** in $\text{CDCl}_2\text{CDCl}_2$

