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Supporting Information for

Novel Dithiano-thieno Fused Perylene Diimides: Synthesis, Characterization and Application in Organic Thin-Film Transistors (OTFTs)

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1. General information

All solvents and chemicals used were purchased from Energy Chemical and used without further purification. Compound **PDI-a** [1], **PDI-b** [2], **PDI-c** [3] were synthesized according to the reported literatures. TLC analyses were carried out by using Sorbent Technologies silica gel (200 mm) sheets. Column chromatography was performed on Sorbent silica gel 60 (40–63 mm). Solution NMR spectra were taken on a Bruker 400 MHz spectrometer in $CDCl_3$ at room temperature, both ^1H and ^{13}C NMR spectra were referenced to solvent residue peaks and the spectroscopic solvents were purchased from Cambridge Isotope Laboratories. UV−vis absorption spectra were performed with a Beijing Purkinje General Instrument Co. Ltd. TU-1901 spectrophotometer. Fluorescence spectra measurements were performed using FLS-920 Edinburgh fluorescence spectrometer. Mass spectra were measured on a Bruker Maxis UHR-TOF MS spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument TA Q50 Thermogravimetric Analyzer at a heating rate of 10 ^{o}C/min up to 700 ^{o}C.

2. Electrochemical Characterization

Electrochemical measurements were performed under nitrogen in deoxygenated 0.1 M solutions of tetra-n-butylammonium hexafluorophosphate in dry dichloromethane using a CHI 660C electrochemical workstation, a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}. The lowest unoccupied molecular orbital (LUMO) levels were estimated based on the onset reduction potential (E_{red}), and the reduction potential was calibrated using ferrocene ($E_{Fc/Fc+}$) as a reference ($E_{red} = -[E_{measured} - E_{Fc/Fc+} + 4.8]$ eV). Ferrocene as an internal standard. Under the same condition, the onset oxidation potential of ferrocene was measured to be 0.460 V versus Ag/AgCl.

3. AFM Characterization.

AFM measurements were performed by using a Scanning Probe

Microscope-Dimension 3100 in tapping mode. All films were coated on ITO glass substrates.

4. Computational Studies

The geometry was optimized by density functional theory (DFT) using the B3LYP hybrid functional with basis set 6-31G(d).[4] Quantum chemical calculation was performed with the Gaussian 09 package. The long alkyl chains were replaced with isopropyl (**PDI-aS3** and **PDI-bS3**) and isobutyl group (**PDI-cS3**) for simplification.

5. Thin Film Preparation

The substrates used here were successively cleaned with pure water, piranha solution (H_2SO_4/H_2O_2 = 7:3), pure water, pure isopropyl alcohol, and finally blown dry with high-purity nitrogen gas. Treatment of the Si/SiO_2 wafers with OTS was carried out by the vapor-deposition method. The clean wafers were dried under vacuum at 90 ^{o}C for 0.5 h in order to eliminate the influence of moisture. When the temperature decreased to 25 ^{o}C, a small drop of OTS (octadecyltrichlorosilane) was placed around the wafers. Subsequently, this system was heated to 120 ^{o}C and maintained for 135 min under vacuum. The OTS modified Si/SiO_2 substrate was cleaned with pure n-hexane, pure chloroform, and pure isopropyl alcohol. All substrates were used after OTS modification. **PDI-aS3, PDI-bS3 and PDI-cS3** were dissolved in chloroform (10 mg/mL) at room temperature. For spin coating process, 35 μL of chloroform solution was spin coated at 2200 rpm for 40 s onto the substrates (Si/SiO_2) in a nitrogen-filled glovebox, and then thermally annealed at different temperatures in air to prepare semiconductor small molecule thin films.

6. Device Fabrication

Bottom-gate/top-contact OTFTs based on the semiconductor small molecule thin film were constructed on an OTS modified Si/SiO_2 substrate using a copper grid mask technique. Au (50 nm) was used as source and drain electrodes via thermally evaporating gold (0.3 Å/s, 7×10^{-4} Pa) through a copper grid, and n-type Si wafer was used as gate.

7. Device Characterization

The as-prepared thin film were characterized by atomic force microscopy (AFM, Bruker Dimension Icon, KarlsruheCity, Germany Country), and Powder X-ray diffraction (XRD, Rigaku D/Max2500/PC, Rigaku CorporationCompany, AkishimaCity, Country Japan). The electrical characteristics of the devices were measured with a Keithley 4200 SCS semiconductor parameter analyzer (TektronixCompany, JohnstonCity, Ohio, United States Country) under ambient conditions.

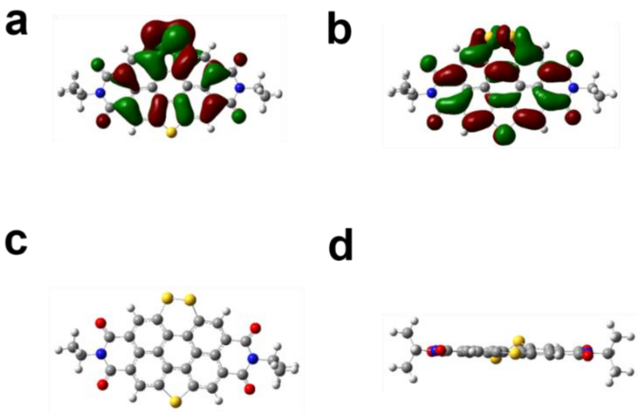


Figure S1. The calculated electron density distributions of HOMO (a) and LUMO (b) by DFT at the B3LYP/6-31G(d) level as well as top view (c) and side view (d) of optimized geometries for **PDI-aS3** or **PDI-bS3**.

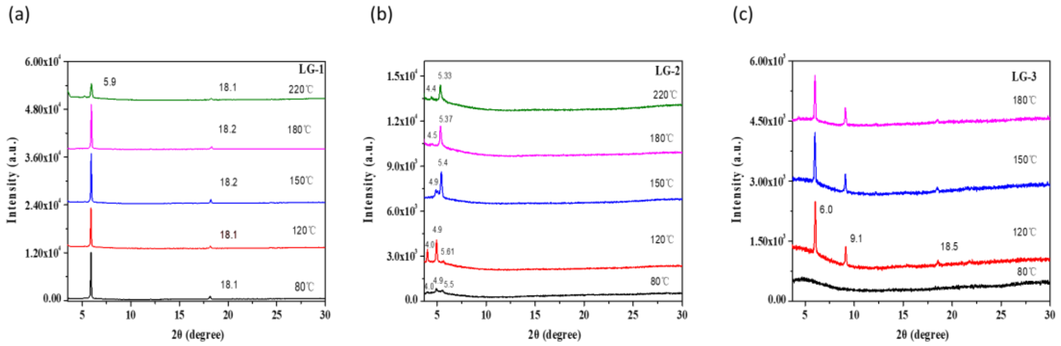


Figure S2. X-ray diffraction (XRD) patterns of (a) **PDI-aS3**, (b) **PDI-bS3** and (c) **PDI-cS3** thin films.

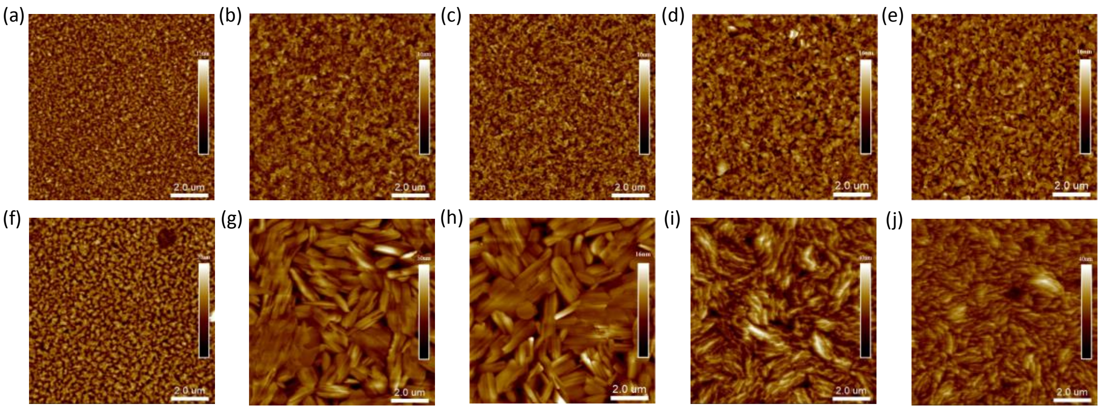


Figure S3. AFM images of (a - e) **PDI-aS3** and (f - j) **PDI-bS3** films obtained by spin-coating method after annealing at 80 °C, 120 °C, 150 °C, 180 °C and 220 °C, respectively.

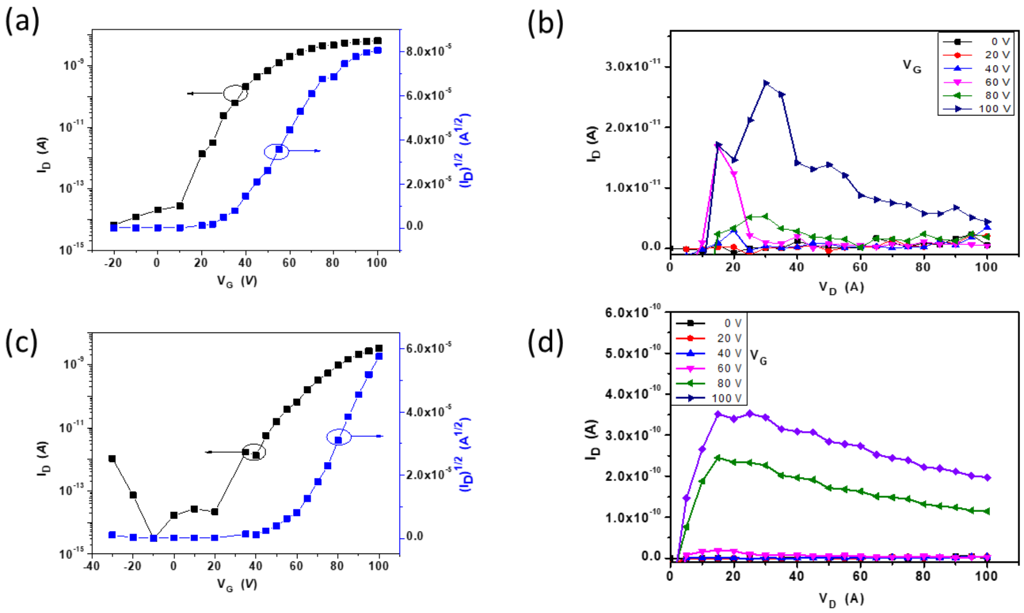


Figure S4. (a, c) transfer and (b, d) output curves of **PDI-aS3** and **PDI-bS3** thin film transistor at the optimum annealing temperature (180 °C, 150 °C). *W*/*L* = 10 and V_{DS} = 100 V.

Table S1. Optical and electrochemical properties of **PDI-aS3, PDI-bS3** and **PDI-cS3**.

Samples	λ^{max}_{abs}	$\varepsilon(M^{-1}cm^{-1})$	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{cv}	E_g^{opt}
PDI-aS3	600	14300	− 5.71	− 3.66	1.81	1.81
PDI-bS3	600	10000	− 5.67	− 3.63	1.81	1.80
PDI-cS3	600	10600	− 5.67	− 3.65	1.81	1.80
PDI-a			− 6.12	− 3.82	-	2.30
PDI-b			− 6.09	− 3.79	-	2.30
PDI-c			− 6.14	− 3.84	-	2.30

Table S2. Calculated HOMO and LUMO energy level of compounds **PDI-aS3**, **PDI-bS3** and **PDI-cS3.**

Molecules	**HOMO (eV)**	**LUMO (eV)**
PDI-aS3	− 6.20	− 3.86
PDI-bS3	− 6.20	− 3.86
PDI-cS3	− 6.02	− 3.68

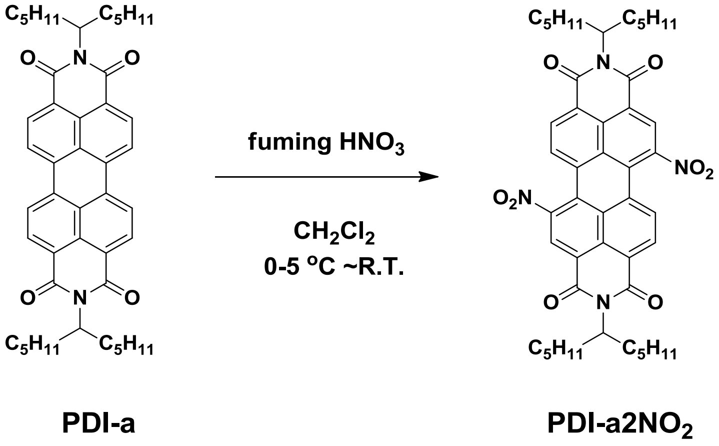
Table S3. OTFT Performance of compounds **PDI-aS3**, **PDI-bS3** and **PDI-cS3.**

Molecules	T_a [^{o}C]	$\mu_{e,max}$ [cm^2 V^{-1} s^{-1}]	$\mu_{e,avg}$ [cm^2 V^{-1} s^{-1}]	V_{th}	I_{on}/I_{off}
PDI-aS3	80	6.3×10^{-6}	3.8×10^{-6}	49.40	1.5×10^{4}
	120	7.6×10^{-6}	4.9×10^{-6}	52.05	1.7×10^{4}
	150	1.6×10^{-5}	8.5×10^{-6}	50.87	4.6×10^{4}
	180	6.2×10^{-5}	4.5×10^{-5}	51.10	5.3×10^{6}
	220	3.4×10^{-5}	2.9×10^{-5}	34.12	1.1×10^{6}
PDI-bS3	80	9.2×10^{-6}	7.1×10^{-6}	59.01	5.6×10^{4}
	120	1.2×10^{-5}	1.2×10^{-5}	45.43	8.6×10^{4}
	150	1.1×10^{-4}	7.3×10^{-5}	28.37	3.0×10^{6}
	180	6.4×10^{-5}	5.6×10^{-5}	32.16	7.9×10^{5}
	220	2.8×10^{-5}	1.9×10^{-5}	21.83	4.5×10^{5}
PDI-cS3	80	1.3×10^{-5}	7.1×10^{-6}	35.89	4.6×10^{5}
	120	2.7×10^{-3}	2.3×10^{-3}	64.05	4.0×10^{7}
	150	$\mathbf{8.0 \times 10^{-3}}$	$\mathbf{5.4 \times 10^{-3}}$	**40.88**	$\mathbf{2.2 \times 10^{7}}$
	180	7.1×10^{-4}	5.3×10^{-4}	32.49	4.6×10^{6}

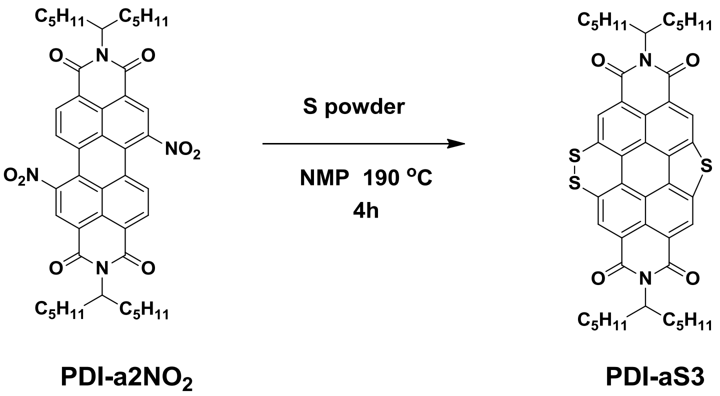
Table S4. Optimization of Reaction Conditions

Entry	PDI-a2NO$_2$ (mmol)	S (mmol)	S: PDI-a2NO$_2$	NMP (mL)	Temperature (°C)	PDI-aS3 (mg)	Yield (%)
1	**0.38**	**3.80**	**10**	**18**	**190**	**256**	**85**
2	0.38	3.03	8	15	190	160	53
3	0.38	2.28	6	11	190	145	48
4	0.38	1.53	4	8	190	95	32
5	0.38	0.75	2	4	190	55	18

8. Synthesis and Characterization

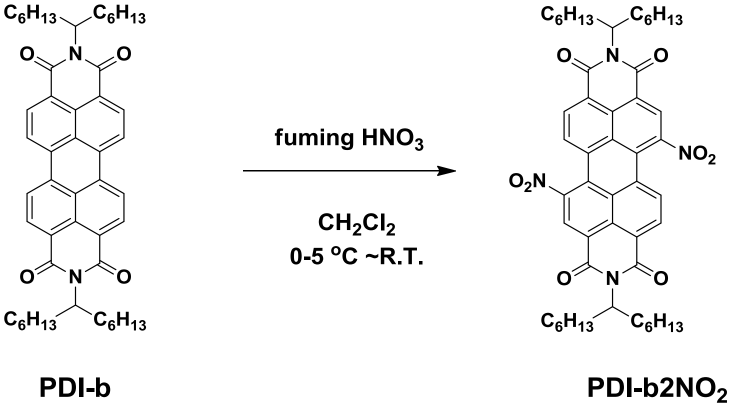


Synthesis of **PDI-a2NO$_2$**: Compound **PDI-a** (0.46 g, 0.66 mmol) and dichloroethane (20 mL) was mixed in 100 mL round-bottom flask and cooled to 0-5 °C for 15 minutes. Then fuming nitric acid (1.5 mL) was added dropwise to the above mixture (about 20 mins) and stirred for 20 mins at 0-5 °C, then heated to room temperature for 12 h. The reaction process was monitored using thin-layer chromatography. Next, CH_2Cl_2 (100 mL) and water (100 mL) were added into the resulting solution, extracted with CH_2Cl_2, washed with saturate brine and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatography (SiO_2, CH_2Cl_2: petroleum ether, 1:1) to give target product as a dark-red solid (0.45 g, 86% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, 2H), 8.69 (m, 2H), 8.31 (t, 2H), 5.16 (m, 2H), 2.22 (m, 4H), 1.82 (m, 4H), 1.28 (m, 24H) 0.84 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.33, 162.53, 161.56, 133.07, 132.37, 131.54, 130.86, 130.26, 129.59, 129.25, 128.91, 128.90, 128.77, 128.55, 128.25, 127.74, 127.55, 126.83, 126.43, 126.18, 125.48, 55.79, 55.48, 55.19, 32.24, 32.14, 32.05, 31.69, 31.65, 31.62, 26.57, 26.54, 22.53, 14.03. MAIDI-TOF: $(M+H)^+$, $C_{46}H_{53}N_4O_8$, calcd, 789.3785; found, 789.3818.

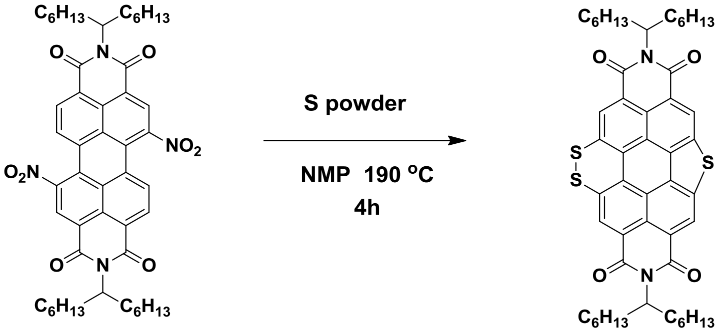


Synthesis of **PDI-aS3**: Under an argon atmosphere, a mixture of sulfur (131 mg, 4.1 mmol) was dissolved in N-methylpyrrolidone (NMP, 35 mL) at 70°C for 30 minutes and compound **PDI-a2NO$_2$** (323 mg, 0.41 mmol) was added and heated to 190°C with vigorous stirring for 3 h monitored by TLC. Next, the cooled mixture was poured into 2 M HCl (1 L) and stirred for 5 min. The resulting precipitate was filtered, washed with water, dried, and purified by silica gel column chromatography (petroleum ether: CH_2Cl_2, 1:1) to isolate target product as a green solid (0.27 g, 85% yield). ^1H NMR (400 MHz, *$CDCl_3$*, ppm): δ 9.18 (d, 2H), 8.56 (d, 2H), 5.27 (s, 2H), 2.29 (m, 4H), 1.90 (m, 4H), 1.30 (m, 24H), 0.84 (t, 12H). ^{13}C NMR (100 MHz, *$CDCl_3$*, ppm): δ 164.78, 163.91, 162.80, 139.16, 131.95, 130.59, 129.95, 128.50, 127.84, 126.89, 125.36, 123.51, 123.02, 55.23, 32.37, 31.76, 26.68, 22.60, 14.06. FT-IR (KBr):

3349, 3064, 2954, 2926, 2856, 1814, 1700, 1662, 1617, 1588, 1544, 1463, 1429, 1357, 1276, 1246, 1174, 1112, 806. MAIDI-TOF: $C_{46}H_{51}N_2O_4S_3$ $(M+H)^+$, calcd, 791.3011, found, 791.3000.

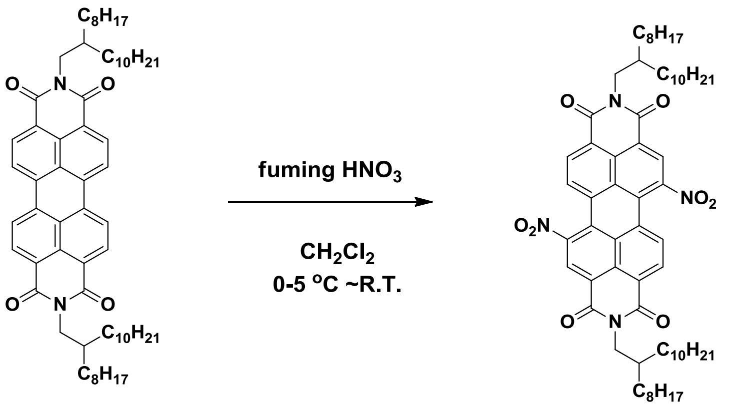


Synthesis of **PDI-b2NO$_2$**: Compound **PDI-b** (0.5 g, 0.66 mmol) and dichloroethane (20 mL) was mixed in 100 mL round-bottom flask and cooled to 0-5 ^{o}C for 15 minutes. Then fuming nitric acid (1.5 mL) was added dropwise to the above mixture (about 20 mins) and stirred for 20 mins at 0-5 ^{o}C, then heated to room temperature for 12 h. The reaction process was monitored using thin-layer chromatography. Next, CH_2Cl_2 (100 mL) and water (100 mL) were added into the resulting solution, extracted with CH_2Cl_2, washed with saturate brine and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatography (SiO_2, CH_2Cl_2: petroleum ether, 1:1) to give compound **PDI-b2NO$_2$** as a dark-red solid (0.48 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (d, 2H), 8.68 (m, 2H), 8.32 (q, 2H), 5.16 (m, 2H), 2.22 (m, 4H), 1.85 (m, 4H), 1.28 (m, 24H) 0.83 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.74, 163.31, 162.51, 162.09, 161.51, 148.70, 148.34, 133.09, 132.39, 131.54, 130.84, 130.25, 129.58, 129.25, 128.91, 128.89, 128.76, 128.55, 128.25, 127.74, 127.55, 126.83, 126.43, 126.17, 125.48, 124.28, 55.80, 55.49, 55.20, 32.29, 32.19, 32.10, 31.72, 29.18, 29.14, 29.12, 26.87, 26.84, 22.57, 14.05, 13.93. MAIDI-TOF: $(M+H)^+$, $C_{50}H_{61}N_4O_8$ calcd, 845.4411, found, 845.4441.



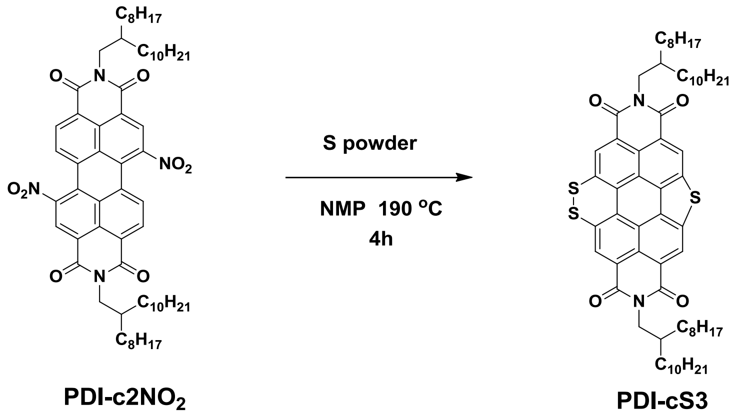
PDI-b2NO$_2$ **PDI-bS3**

Synthesis of **PDI-bS3**: Under an argon atmosphere, a mixture of sulfur (131 mg, 4.1 mmol) was dissolved in N-methylpyrrolidone (NMP, 35 mL) at 70°C for 30 minutes and compound **PDI-b2NO$_2$** (350 mg, 0.41 mmol) was added and heated to 190°C with vigorous stirring for 3 h monitored by TLC. Next, the cooled mixture was poured into 2 M HCl (1 L) and stirred for 5 min. The resulting precipitate was filtered, washed with water, dried, and purified by silica gel column chromatography (petroleum ether: CH_2Cl_2, 1:1) to isolate target product as a green solid (0.29 g, 82% yield). ^{1}H NMR (400 MHz, *$CDCl_3$*, ppm): δ 9.23 (d, 2H), 8.60 (d, 2H), 5.26 (s, 2H), 2.30 (m, 4H), 1.88 (m, 4H), 1.27 (m, 32H), 0.83 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 164.73, 163.88, 163.52, 162.72, 139.09, 131.87, 130.49, 129.85, 128.49, 127.81, 127.57, 126.81, 125.30, 124.36, 123.62, 123.45, 122.92, 122.72, 55.21, 53.44, 32.39, 31.79, 29.25, 26.99, 22.60, 14.07. FT-IR (KBr): 3064, 2954, 2925, 2855, 1700, 1662, 1617, 1587, 1543, 1463, 1429, 1356, 1276, 1243, 1170, 1113, 807. MAIDI-TOF: $(M-H)^+$, $C_{50}H_{57}N_2O_4S_3$, calcd, 845.3559; found, 845.4441.



PDI-c **PDI-c2NO$_2$**

Synthesis of **PDI-c2NO$_2$**: Compound **PDI-c** (0.62 g, 0.66 mmol) and dichloroethane (20 mL) was mixed in 100 mL round-bottom flask and cooled to 0-5 °C for 15 minutes. Then fuming nitric acid (1.5 mL) was added dropwise to the above mixture (about 20 mins) and stirred for 20 mins at 0-5 °C, then heated to room temperature for 12 h. The reaction process was monitored using thin-layer chromatography. Next, CH_2Cl_2 (100 mL) and water (100 mL) were added into the resulting solution, extracted with CH_2Cl_2, washed with saturate brine and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by chromatography (SiO_2, CH_2Cl_2: petroleum ether, 1:1) to give compound **PDI-c2NO$_2$** as a dark-red solid (0.56 g, 80% yield). ^{1}H NMR (400 MHz, *CDCl$_3$*, ppm): δ 8.85 (s, 2H), 8.71 (m, 2H), 8.33 (m, 2H), 4.14 (m, 4H), 1.98 (m, 2H), 1.23 (m, 64H), 0.86 (t, 12H). ^{13}C NMR (100 MHz, *CDCl$_3$*, ppm): δ 162.81, 162.36, 161.86, 161.45, 148.68, 148.31, 132.70, 131.17, 130.36, 129.67, 129.06, 128.98, 128.80, 128.73, 128.38, 127.86, 127.64, 127.58, 126.45, 125.61, 125.51, 124.51, 124.42, 123.54, 45.30, 45.11, 44.95, 36.70, 36.63, 36.58, 31.91, 31.89, 31.60, 30.05, 30.02, 30.00, 29.65, 29.63, 29.58, 29.35, 29.30, 26.41, 22.68, 22.67, 14.12. MAIDI-TOF: $(M+H)^+$, $C_{64}H_{89}N_4O_8$, calcd,1041.6602; found,1041.6622.



Synthesis of **PDI-cS3**: Under an argon atmosphere, a mixture of sulfur (307 mg, 9.6 mmol) was dissolved in N-methylpyrrolidone (NMP, 60 mL) at 70°C for 30 minutes and compound **PDI-c2NO$_2$** (1.0 g, 0.96 mmol) was added and heated to 190°C with vigorous stirring for 3 h monitored by TLC. Next, the cooled mixture was poured into 2 M HCl (1 L) and stirred for 5 min. The resulting precipitate was filtered, washed with water, dried, and purified by silica gel column chromatography (petroleum ether: CH_2Cl_2, 1:1) to isolate target product as a green solid (0.86 g, 86% yield). ^{1}H NMR (400 MHz, *CDCl$_3$*, ppm): δ 8.96 (s, 2H), 8.39 (s, 2H), 4.10 (d, 4H), 1.97 (m, 2H), 1.21 (m, 64H), 0.83 (t, 12H). ^{13}C NMR (100 MHz, *CDCl$_3$*, ppm): δ 163.43, 162.61, 138.98, 131.88, 130.31, 129.54, 128.11, 127.00, 124.74, 123.47, 122.50, 45.00, 36.66, 31.91, 31.65, 30.07, 29.68, 29.65, 29.61, 29.36, 26.47, 22.68, 14.12. FT-IR (KBr): 3094, 2923, 2852, 1698, 1657, 1614, 1587, 1544, 1464, 1434, 1403, 1355, 1285, 1240,1162, 1115, 907. MAIDI-TOF: (M-H)$^+$, $C_{64}H_{85}N_2O_4S_3$, calcd, 1041.5750; found,1041.6622.

9. Characterization data

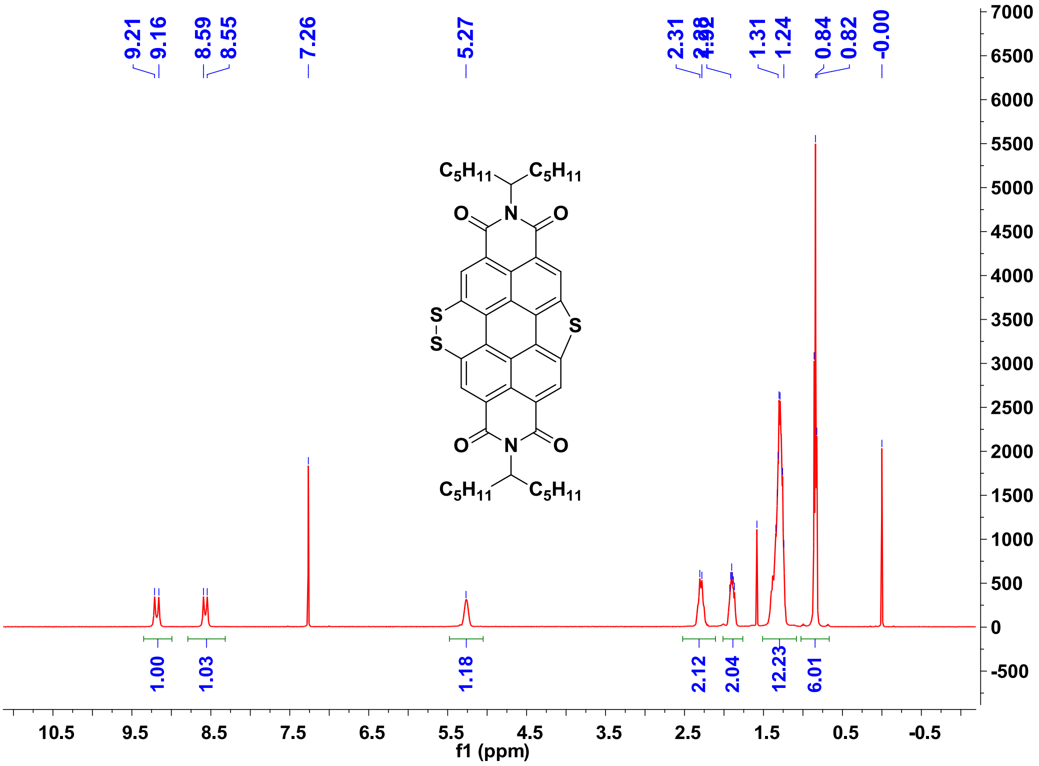


Figure S5. ^{1}H NMR spectrum of compound **PDI-aS3**.

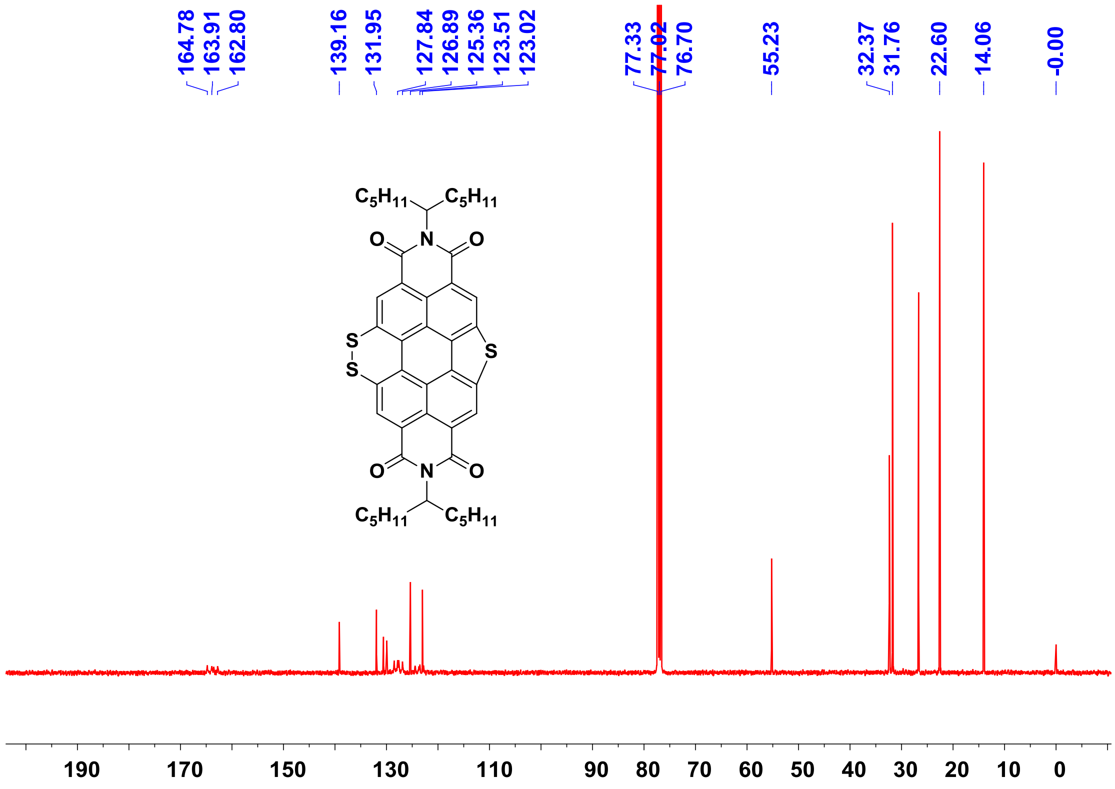


Figure S6. ^{13}C NMR spectrum of compound **PDI-aS3**.

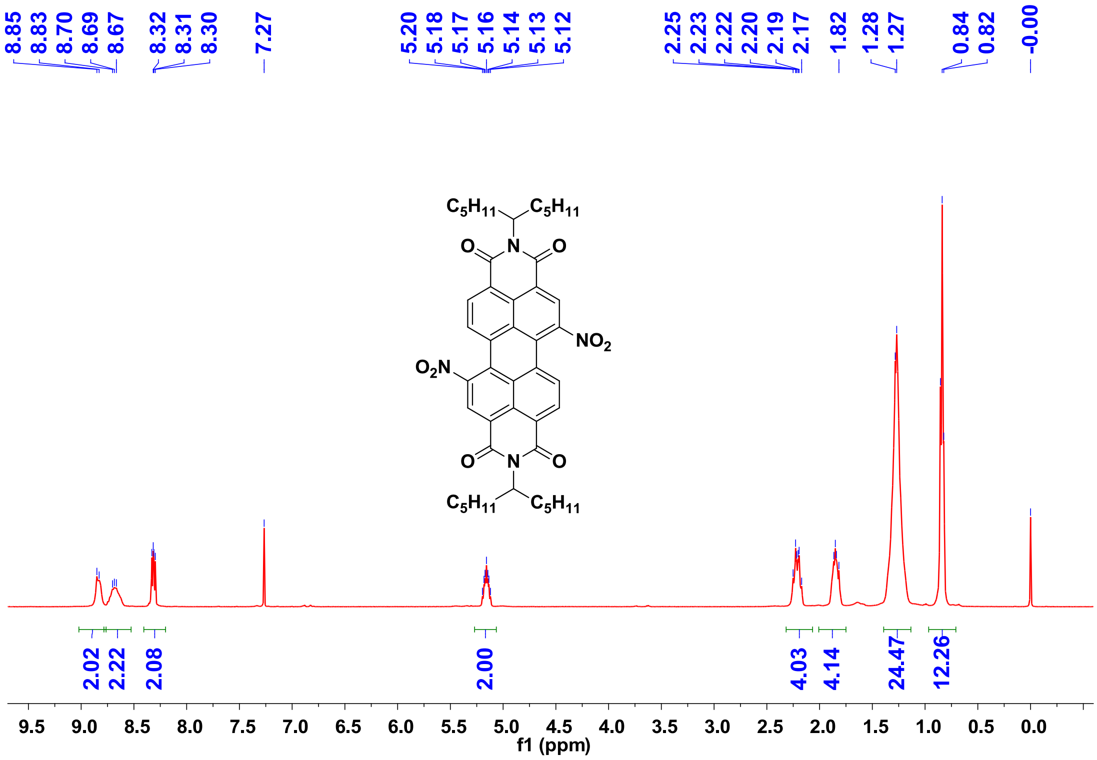


Figure S7. ^{1}H NMR spectrum of compound **PDI-a2NO$_2$**.

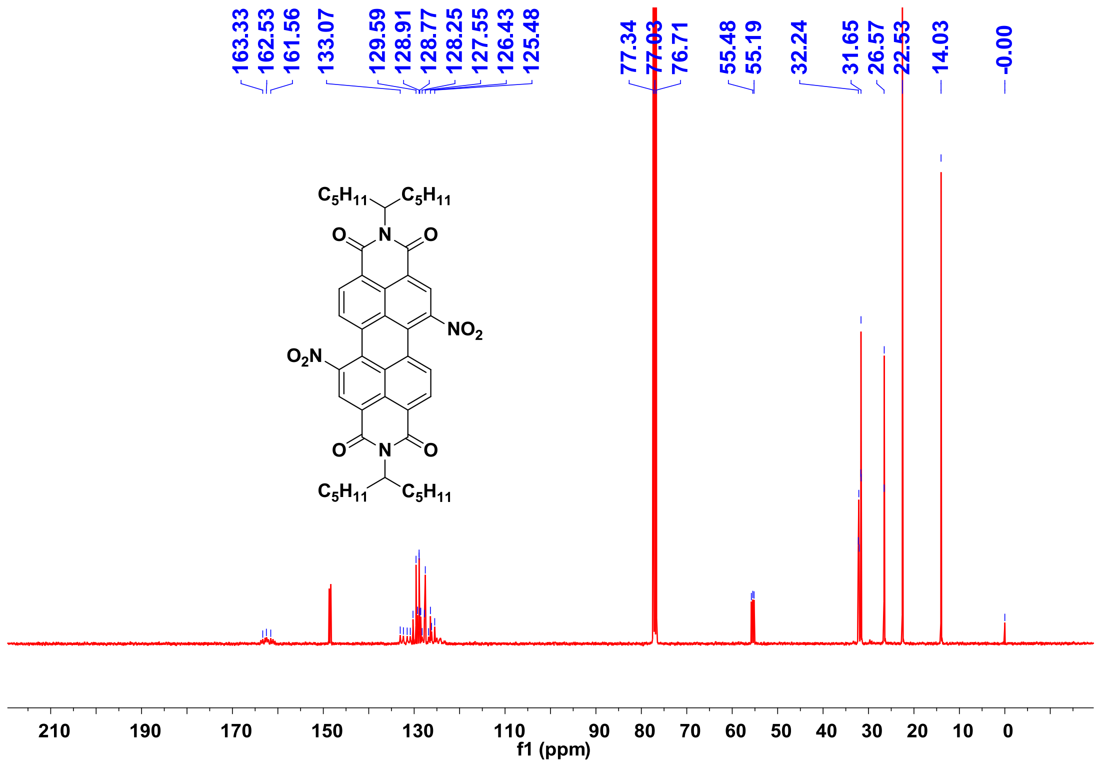


Figure S8. ^{13}C NMR spectrum of compound **PDI-a2NO$_2$**.

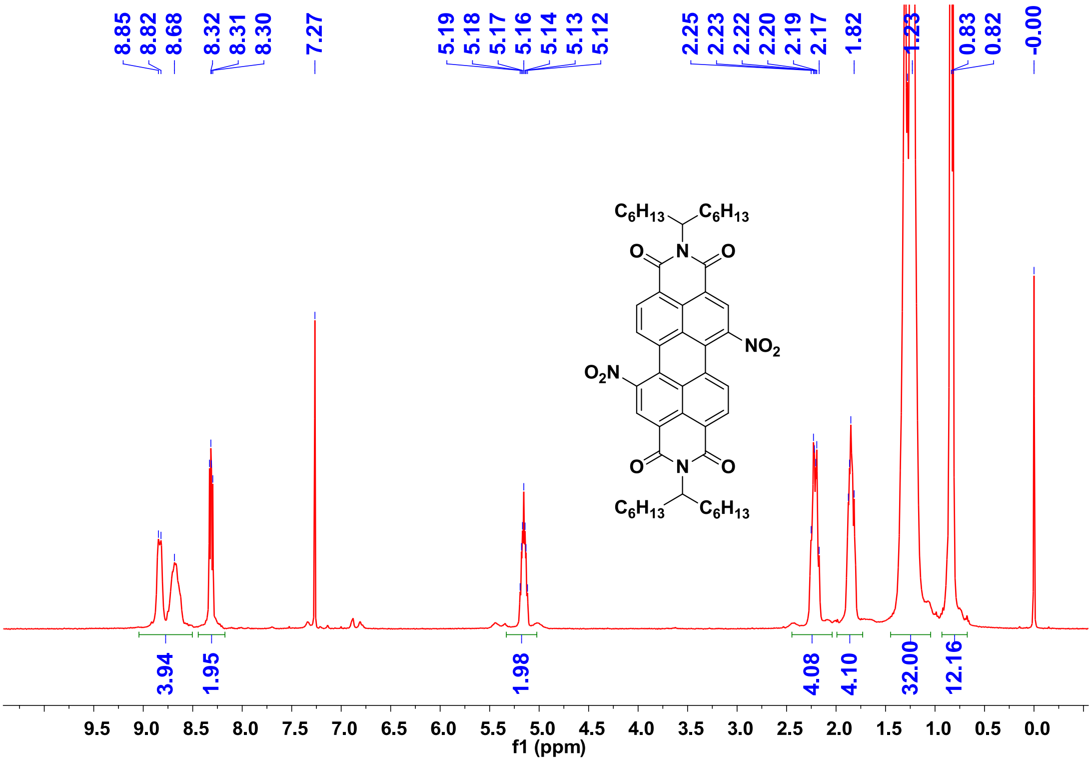


Figure S9. ^{1}H NMR spectrum of compound **PDI-b2NO$_2$**.

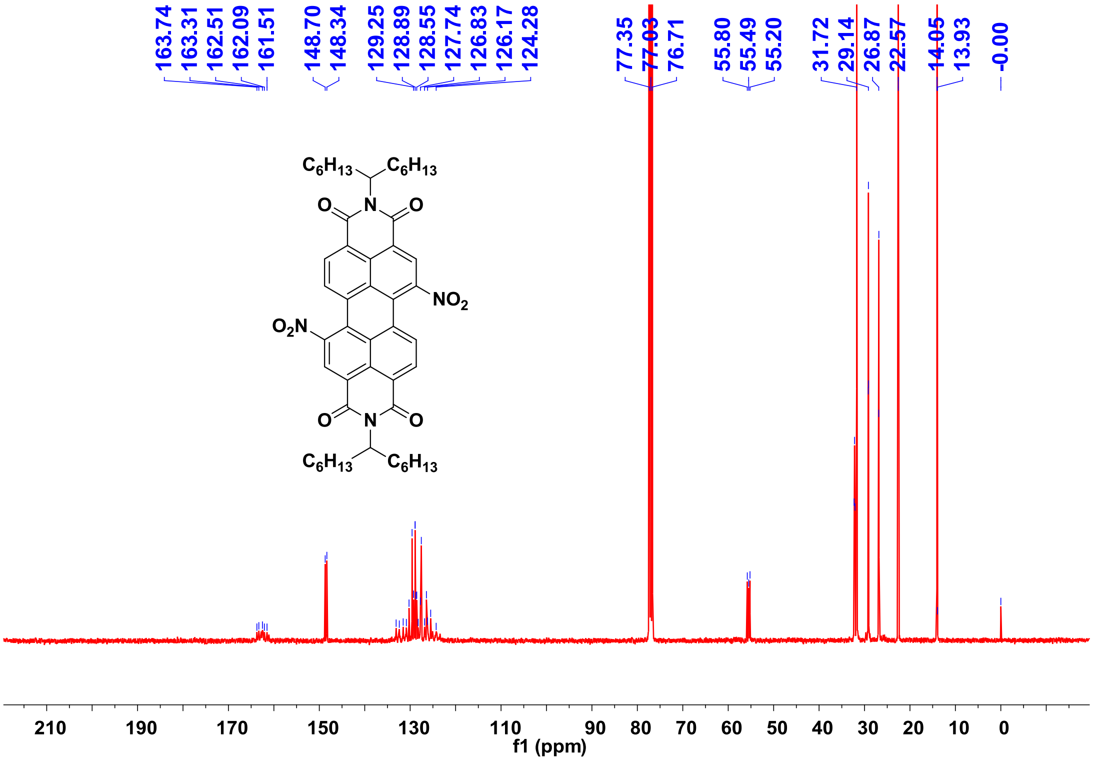


Figure S10. ^{13}C NMR spectrum of compound **PDI-b2NO$_2$**.

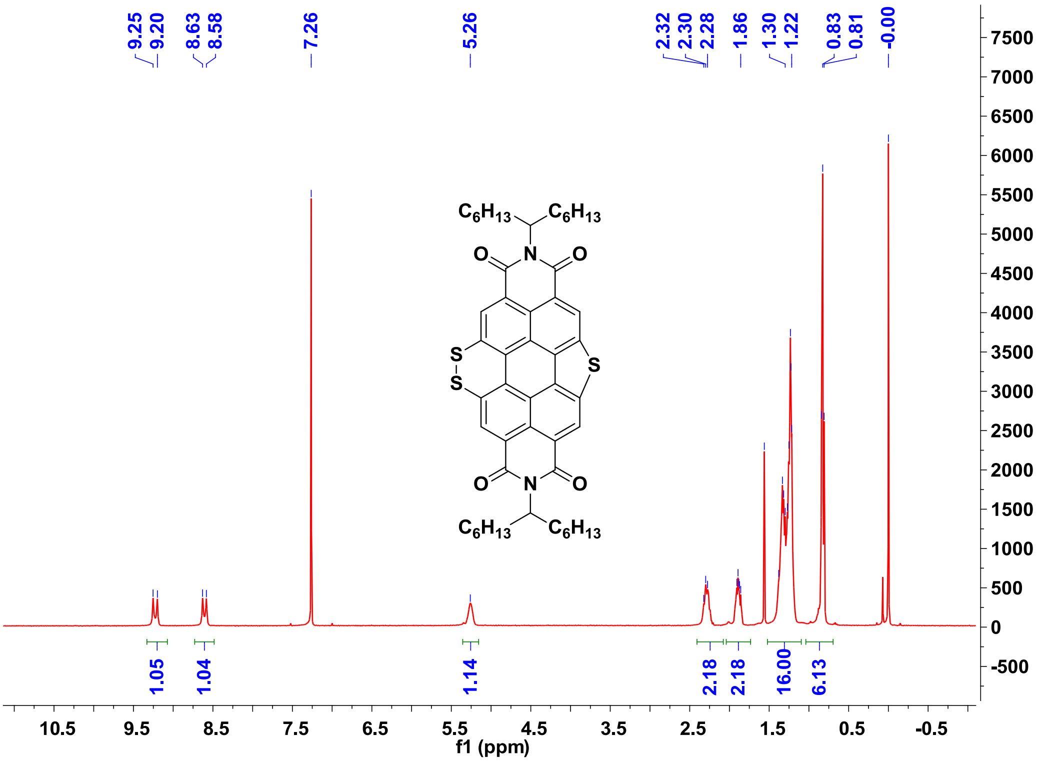


Figure S11. ^{1}H NMR spectrum of compound **PDI-bS3**.

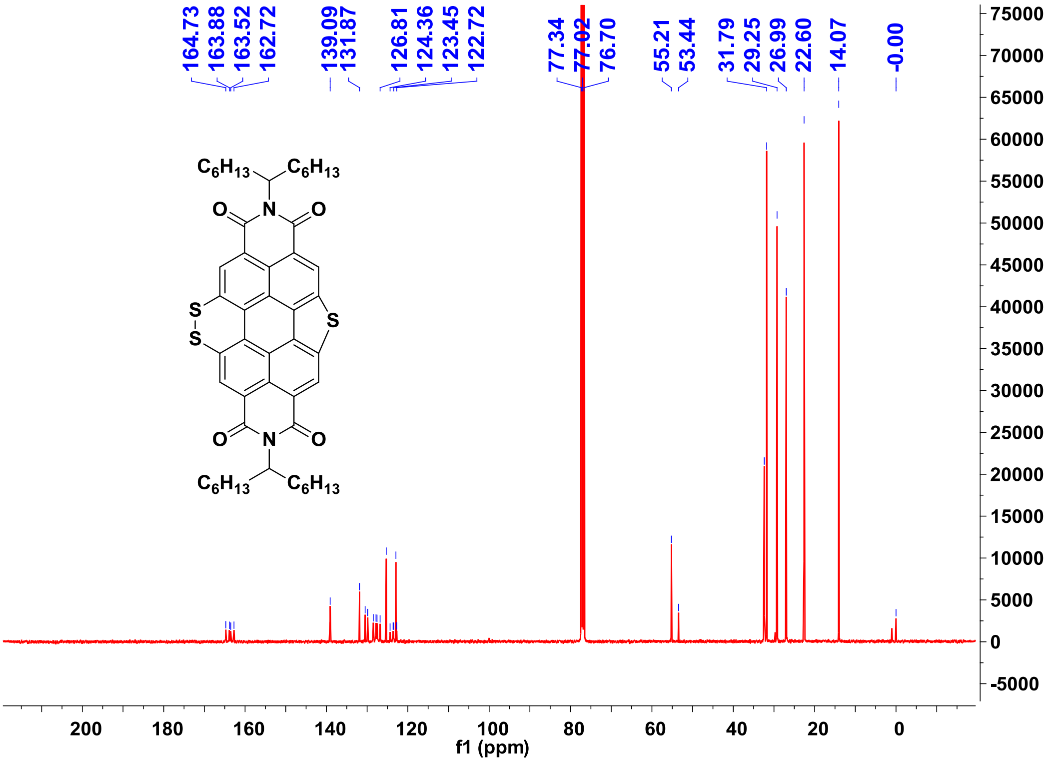


Figure S12. ^{13}C NMR spectrum of compound **PDI-bS3**.

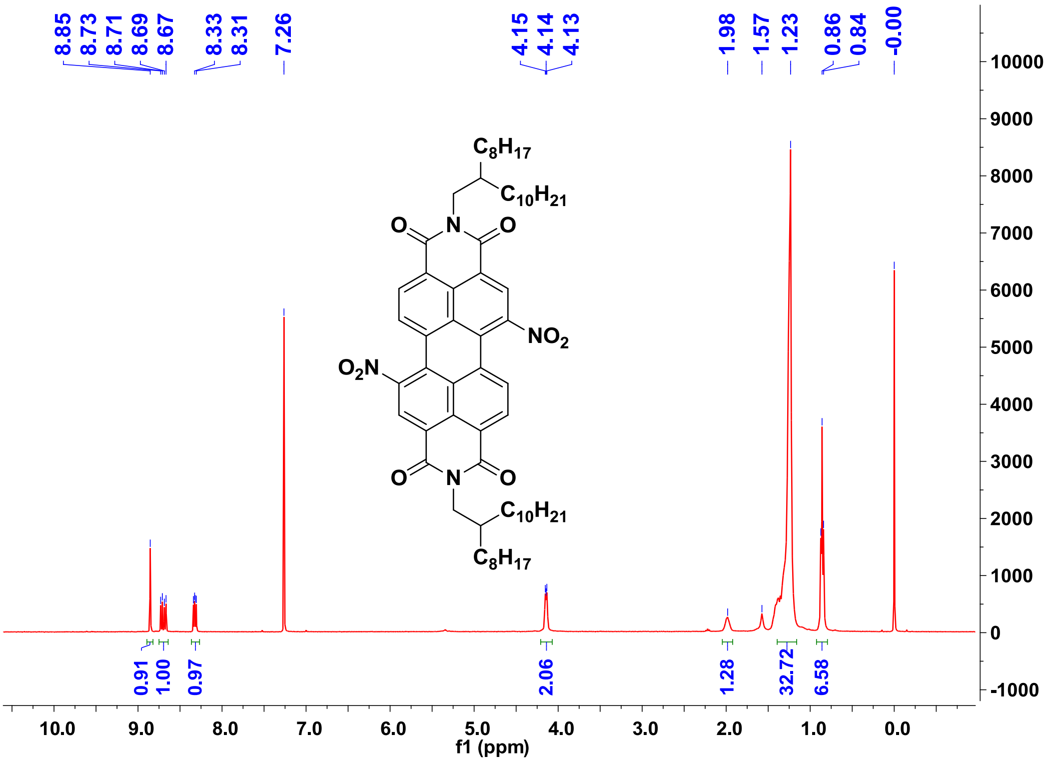


Figure S13. ^{1}H NMR spectrum of compound **PDI-c2NO$_2$**.

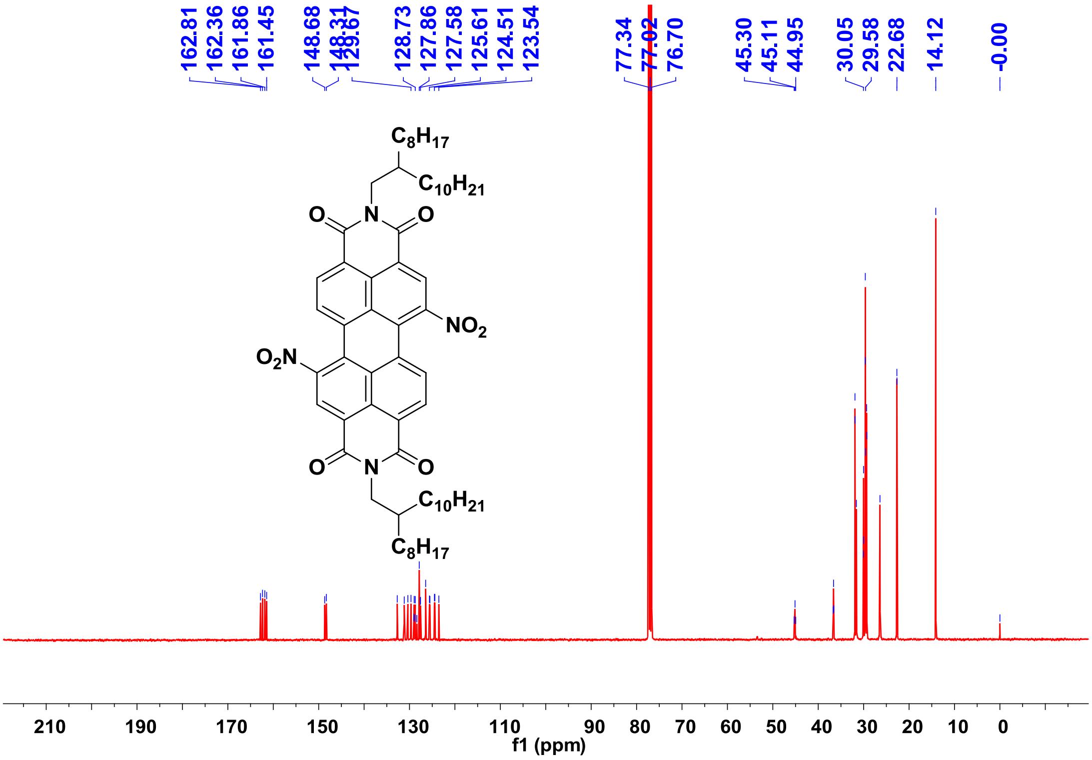


Figure S14. ^{13}C NMR spectrum of compound **PDI-c2NO$_2$**.

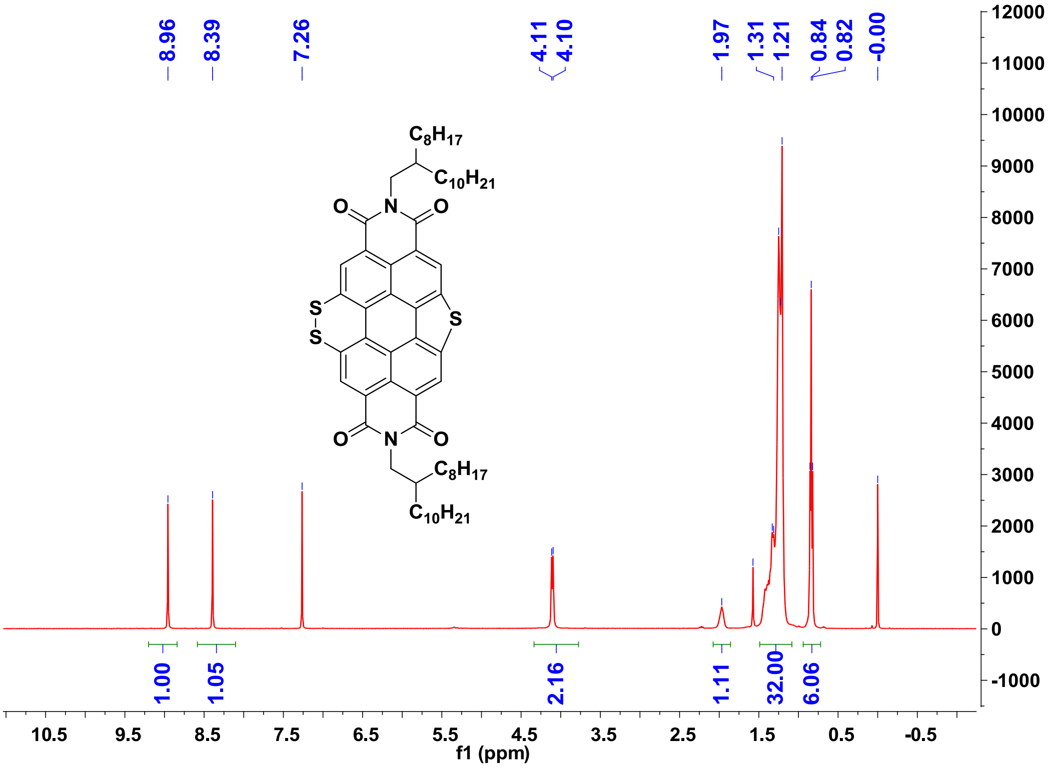


Figure S15. ^{1}H NMR spectrum of compound **PDI-cS3**.

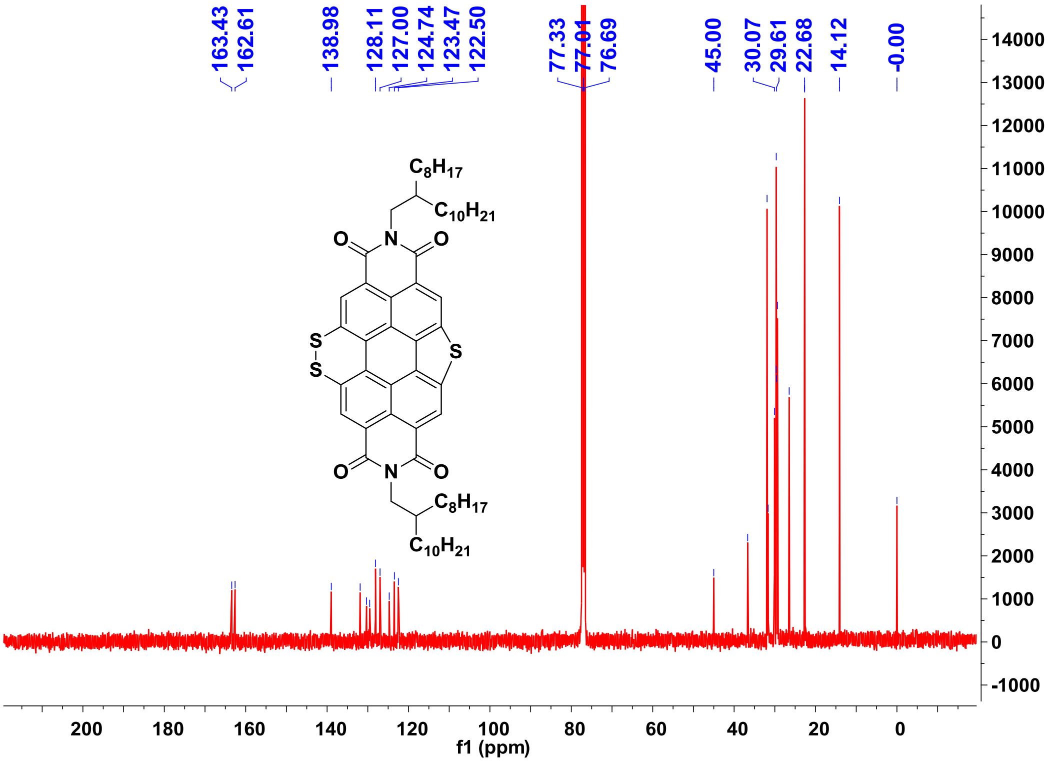


Figure S16. ^{13}C NMR spectrum of compound **PDI-cS3**.

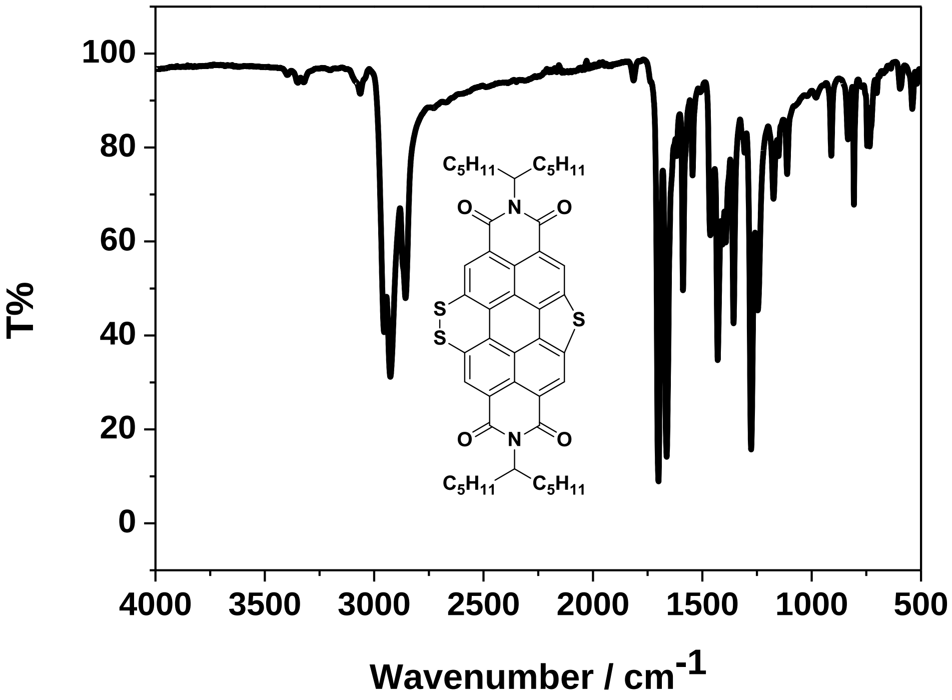


Figure S17. FT-IR spectrum of compound **PDI-aS3**.

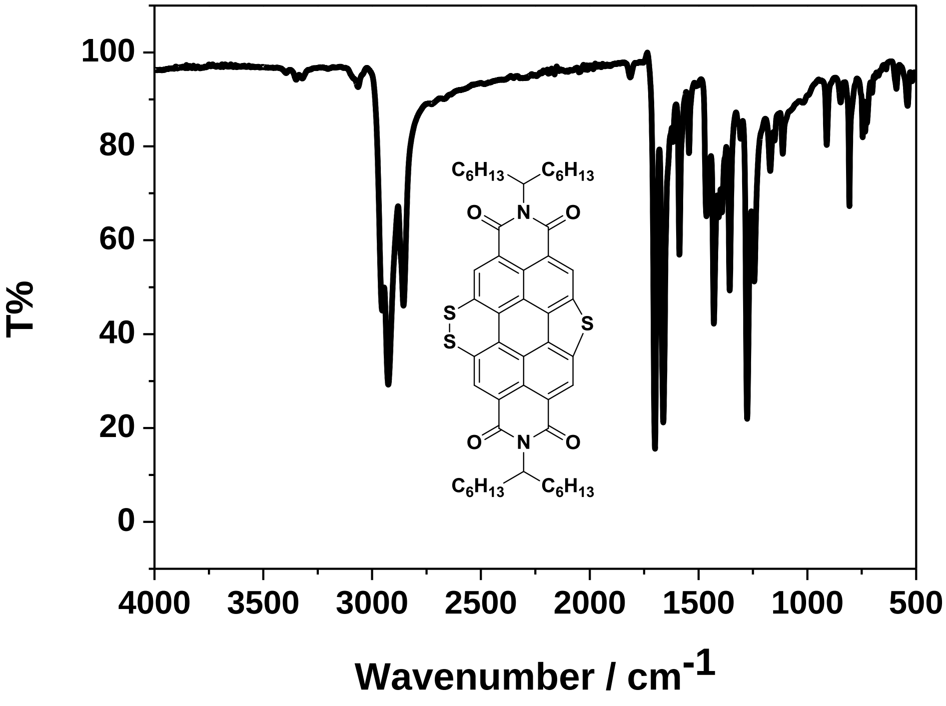


Figure S18. FT-IR spectrum of compound **PDI-bS3**.

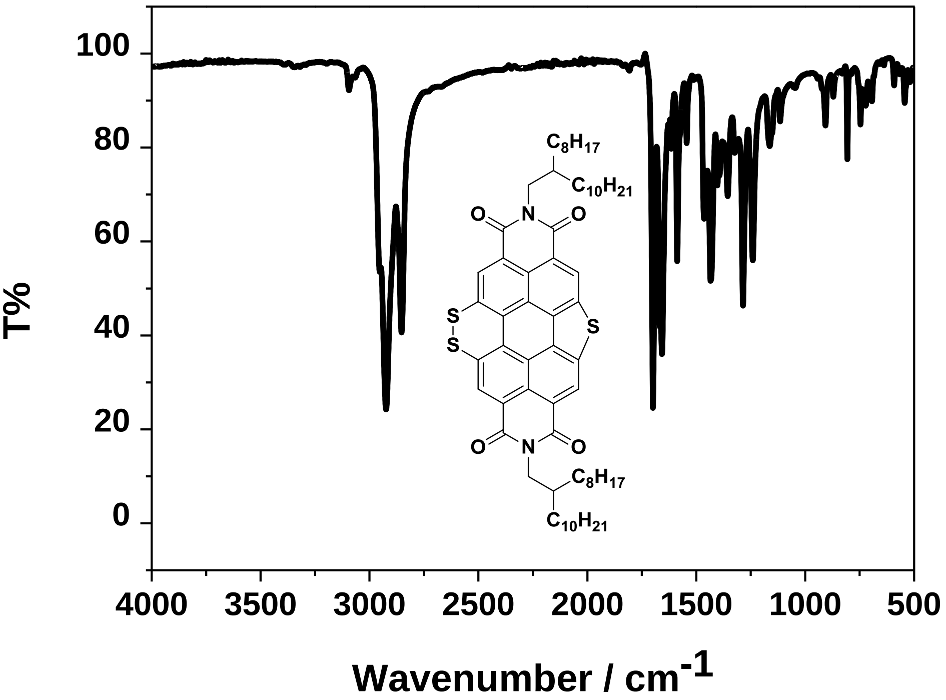


Figure S19. FT-IR spectrum of compound **PDI-cS3**.

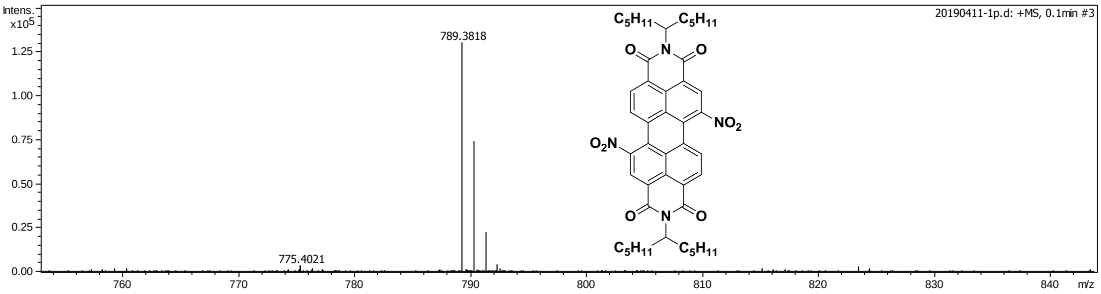


Figure S20. HRMS profile of compound **PDI-a2NO2**.

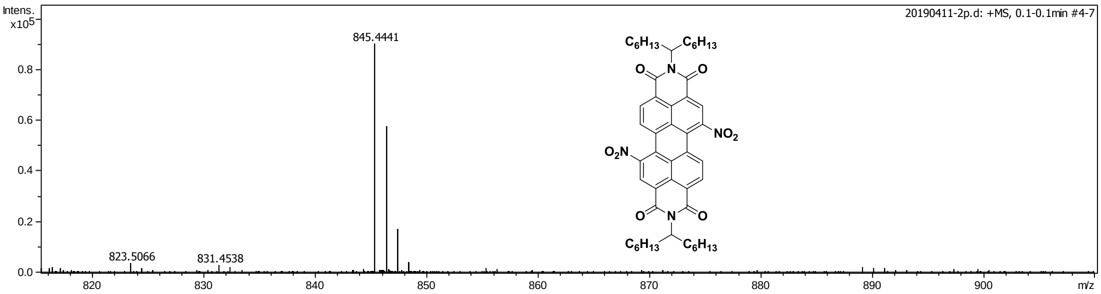


Figure S21. HRMS profile of compound **PDI-a2NO2**.

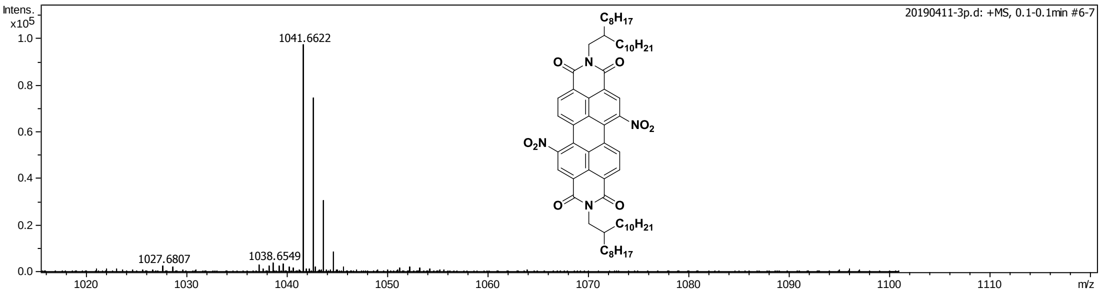


Figure S22. HRMS profile of compound **PDI-a2NO$_2$**.

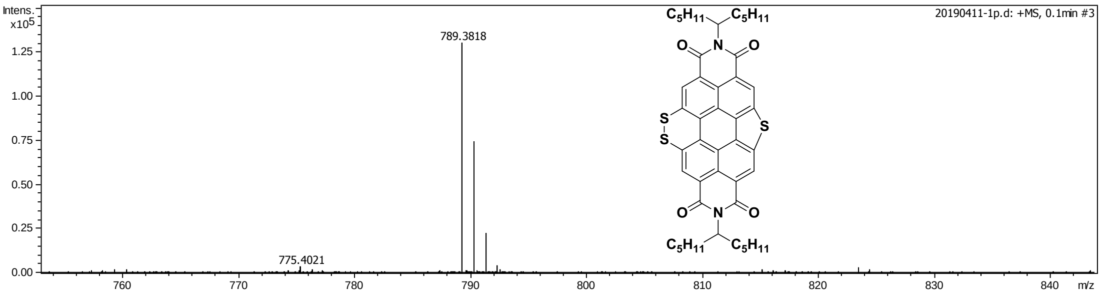


Figure S23. HRMS profile of compound **PDI-aS3**.

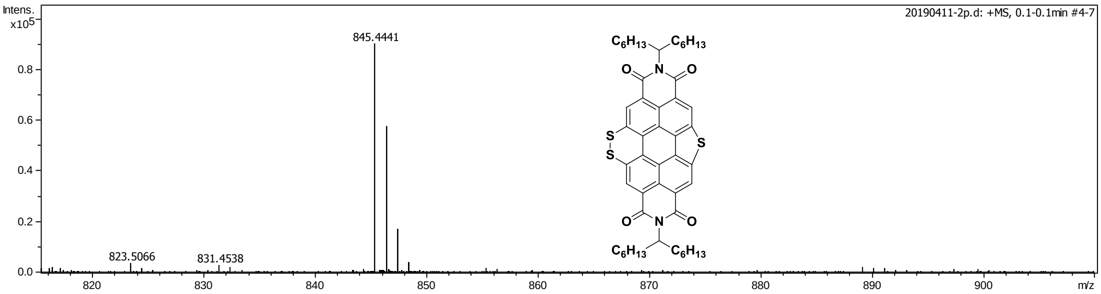


Figure S24. HRMS profile of compound **PDI-bS3**.

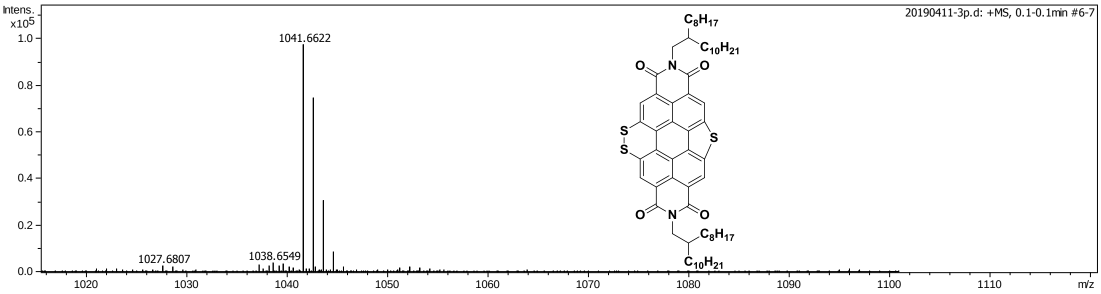


Figure S25. HRMS profile of compound **PDI-cS3**.

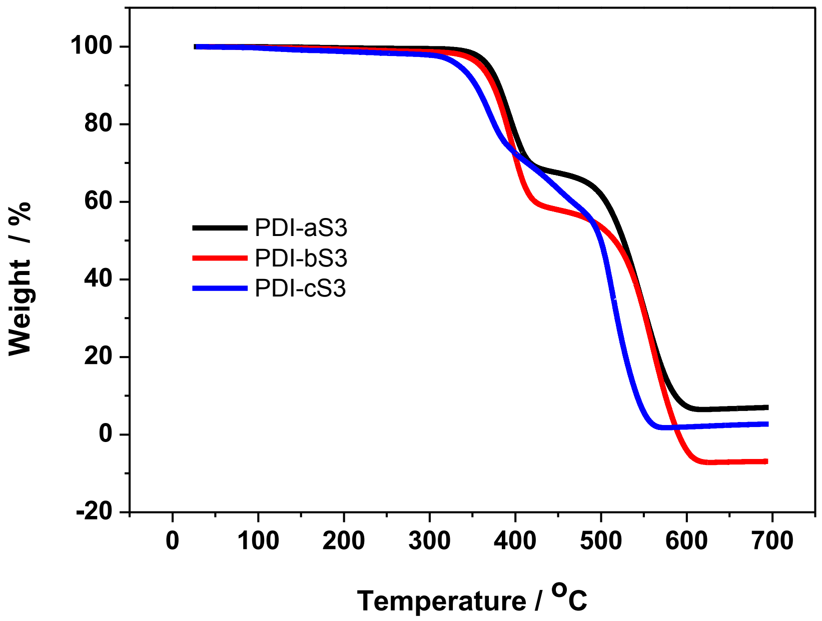


Figure S26. TGA profile of compound **PDI-aS3**, **PDI-bS3** and **PDI-cS3**.

10. Reference

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