

Electronic Supplementary Information

Perylenediimide regioisomers with tunable physicochemical and charge-transport properties

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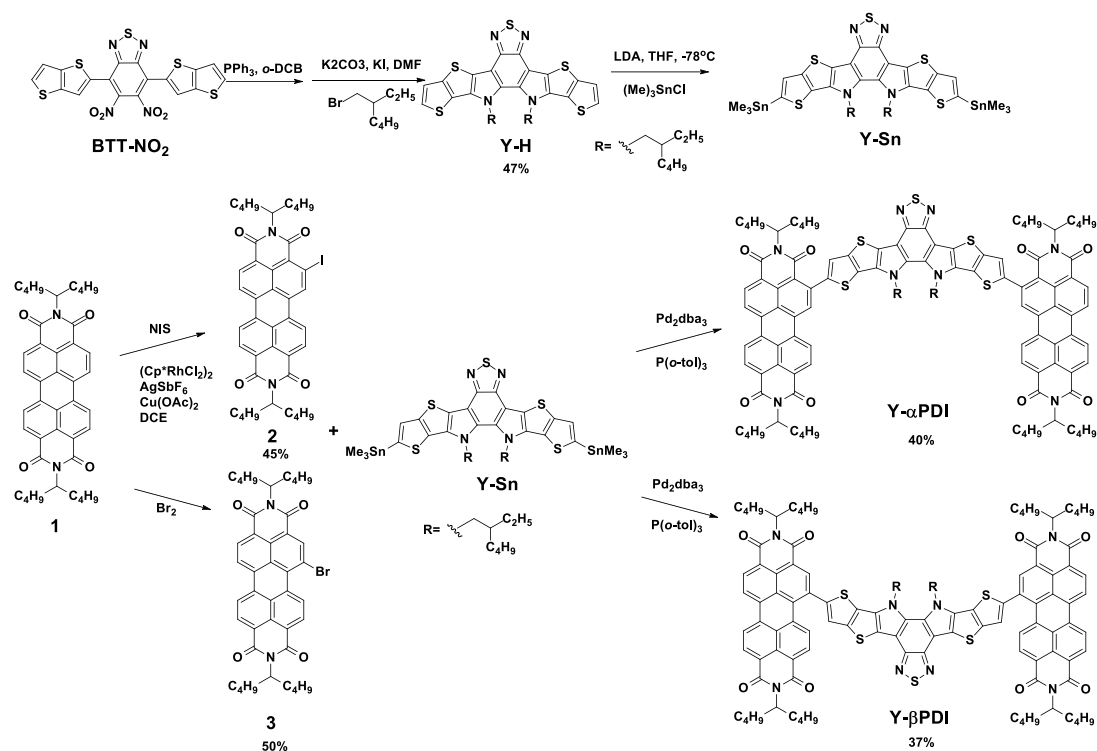
1 Instruments and Measurements

All commercially available reagents and chemicals were purchased from Aldrich, TCI, Adamas and used as received unless otherwise specified. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques. Silica gel (100-200 and 200-300 mesh) was used for column chromatography. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns were designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). Deuterated chloroform was used as the solvent. The NMR chemical shifts were reported in ppm (parts per million) relative to the residual solvent peak at 7.26 ppm (chloroform) for the ^1H NMR spectroscopy and 77.6 ppm (chloroform) for the ^{13}C NMR spectroscopy. The MALDI-TOF mass spectra were measured by a Bruker autoflex maX MALDI-TOF mass spectrometer. TGA and DSC measurements: TGA measurement was carried out on Mettler STARE (TA Instrument) with a heating (or cooling) ramp of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen flow. UV-Vis absorption spectra were acquired from Shimadzu UV3600i Plus spectrophotometer. All film samples were spin-cast on glass substrates. All the solution of small molecules were measured with a concentration of 0.02 mg/mL in chloroform. Electrochemical characterizations: Cyclic voltammetry (CV) measurements of films were performed under argon atmosphere using a CHI760E voltammetric analyzer with 0.1 M tetra-n-butylammonium hexafluorophosphate ($n\text{Bu}_4\text{NPF}_6$) in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode were

employed. The scanning rate was 0.1 V s^{-1} . Films were drop-casted from chloroform solutions of organic molecules on a Pt working electrode (2 mm in diameter). The supporting electrolyte solution was thoroughly purged with argon before all CV measurements. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured under the same conditions. It was assumed that the redox potential of Fc/Fc^+ has an absolute energy level of -4.80 eV to a vacuum. The HOMO energy levels were determined by $E_{\text{HOMO}} = - [q (E_{\text{re}} - E_{\text{ferrocene}}) + 4.8 \text{ eV}]$, while the LUMO energy levels were determined by $E_{\text{LUMO}} = - [q (E_{\text{ox}} - E_{\text{ferrocene}}) + 4.8 \text{ eV}]$. AFM: AFM measurements were performed by using Bruker's Dimension Icon[®] with true non-contact mode. All film samples were spin-cast on glass substrates according to devices fabrication conditions.

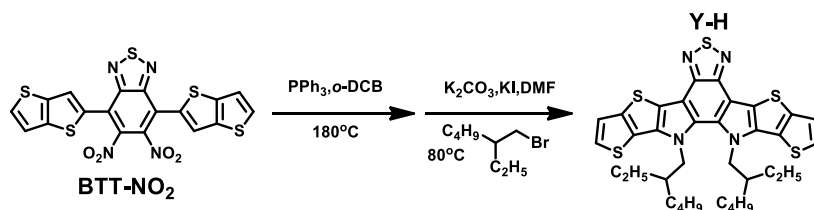
2. Materials and Synthesis

All commercially available reagents and chemicals were purchased from Aldrich, TCI, Adamas and used as received unless otherwise specified. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques. The starting compound BTT-NO₂ was synthesized by using the same procedure as reported in ref S1.



Scheme S1. The synthetic routes of **Y- α PDI** and **Y- β PDI**.

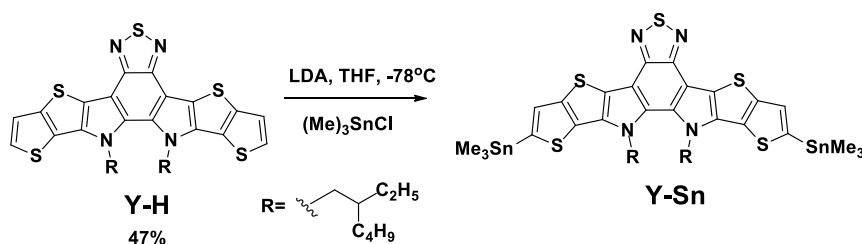
(1) Synthesis of compound **Y-H**



Compounds BTT-NO₂ (500 mg, 0.955 mmol) and PPh₃ (1565 mg, 9.95 mmol) were dissolved in 1,2-dichlorobenzene (*o*-DCB, 10 mL) under nitrogen. After being heated at 180 °C for 3 hrs, the solvent was removed to get a red crude product, which was used in the next step without further purification. The red crude product was mixed with 3-(bromomethyl) heptane (4.69 g, 23.88 mmol), potassium carbonate (2750 mg, 19.9 mmol) and potassium iodide (3960 mg, 23.88 mmol) in DMF (10 mL) under N₂. The mixture was refluxed at 80 °C overnight. After cooling down to room temperature, the

residue was poured into water and extracted with ethyl acetate 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. The residue was purified by flash column chromatography (using eluent with hexane: $\text{CH}_2\text{Cl}_2 = 5:1$, v/v) to get the product as orange oil (284 mg, 47 %). ^1H NMR (400 MHz, CDCl_3): δ 7.42 (m, 4H), 4.63 (d, $J = 7.6$ Hz, 4H), 2.06 (m, 2H), 1.26–0.84 (m, 16H), 0.63–0.59 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.86, 141.75, 136.83, 131.86, 124.92, 124.47, 123.63, 121.67, 111.72, 54.98, 40.17, 29.80, 27.86, 23.28, 22.87, 13.85, 10.15. MALDI-TOF MS ($M_w = 662.1700$): found $m/z = 662.4681$ ($[\text{M}]^+$).

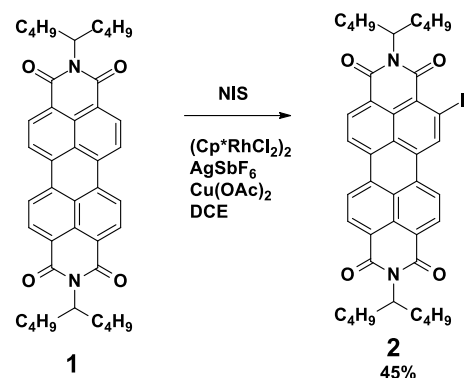
(2) Synthesis of compound Y-Sn



To a solution of compound Y-H (284 mg, 0.449 mmol) in dry THF (10 mL), lithium diisopropylamide (LDA) in hexane (2.0 M, 0.898 mL, 1.796 mmol) was added dropwise slowly at -78°C under N_2 . The mixture was stirred at -78°C for 1 h, and then $(\text{Me})_3\text{SnCl}$ (1.0 M in THF, 2.694 mL, 2.694 mmol) was added. The mixture was stirred overnight at room temperature. Brine was added and the mixture was extracted with ethyl acetate 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. The crude product was used in the next step of Stille coupling reaction

without further purification.

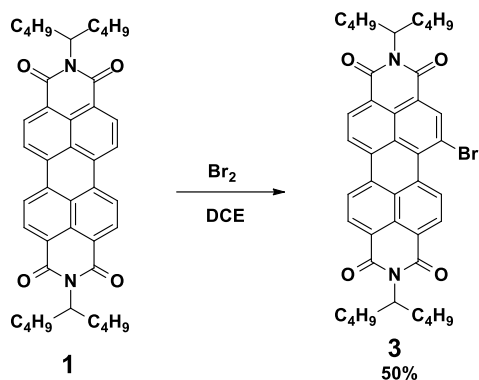
(3) Synthesis of compound **2**



To a solution of compound **1** (500 mg, 0.778 mmol), NIS (210 mg, 0.933 mmol), AgSbF_6 (93.5 mg, 0.272 mmol) and $\text{Cu}(\text{OAc})_2$ (77.6 mg, 0.389 mmol) in dry dichloroethane (10 mL) was added $(\text{Cp}^*\text{RhCl}_2)_2$ (24 mg, 0.039 mmol) under N_2 . The mixture was refluxed for 16 hours and then allowed to cool to room temperature. Brine was added and the mixture was extracted with CH_2Cl_2 for three times. The combined organic phase was washed with water three times. Then the solution was dried over Na_2SO_4 and concentrated under reduced pressure. After removing the solvent, the residue was purified using column chromatography on silica gel (using eluent with hexane: CH_2Cl_2 = 2:1, v/v), yielding the title compound as a red solid (268 mg, 45%). ^1H NMR (400 MHz, CDCl_3): δ 9.20 (s, 1H), 8.73–8.60 (m, 6H), 5.19–5.11 (m, 2H), 2.24–2.16 (m, 4H), 2.24–2.16 (m, 4H), 1.90–1.83 (m, 4H), 1.32–1.23 (m, 16H), 0.85 (td, J = 6.0, 4.0 Hz, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 137.87, 134.61, 134.08, 133.61, 132.85, 130.78, 129.47, 126.25, 126.15, 123.43, 123.27, 123.03, 55.60, 54.98, 32.29, 32.15, 29.42, 29.39, 22.85, 14.29. MALDI-TOF MS (M_w = 768.2424): found

$m/z = 767.5503$ ($[M]^+$).

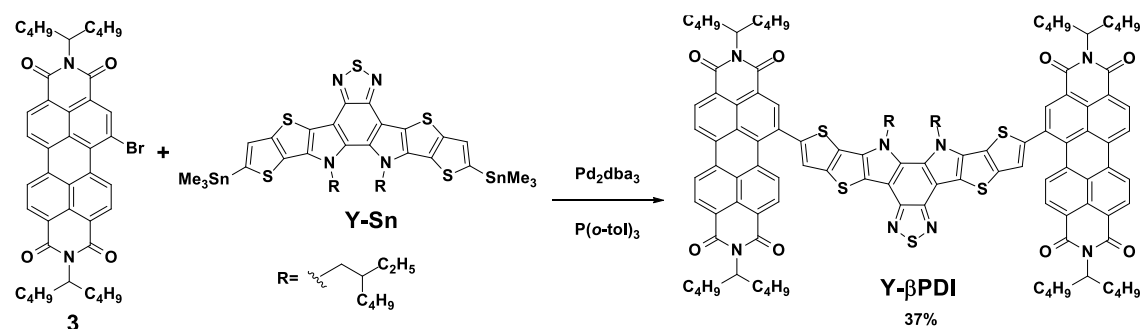
(4) Synthesis of compound **3**



To a solution of compound **1** (500 mg, 0.778 mmol) in dry dichloroethane (10 mL) was added Br_2 (1244.8 mg, 7.78 mmol) under N_2 . The mixture was refluxed for 16 hours and then allowed to cool to room temperature. Brine was added and the mixture was extracted with CH_2Cl_2 for three times. The combined organic phase was washed with water three times. Then the solution was dried over Na_2SO_4 and concentrated under reduced pressure. After removing the solvent, the residue was purified using column chromatography on silica gel (using eluent with hexane: $\text{CH}_2\text{Cl}_2 = 1:1$, v/v), yielding the title compound as a yellow solid (307 mg, 40%). ^1H NMR (400 MHz, CDCl_3): δ 9.80 (d, $J = 8.0$ Hz 1H), 8.92 (s, 1H), 8.69–8.62 (m, 5H), 5.20–5.14 (m, 2H), 2.26–2.22 (m, 4H), 1.92–1.82 (m, 4H), 1.36–1.22 (m, 16H), 0.85 (td, $J = 6.0, 4.0$ Hz, 12H)

(5) Synthesis of compound **Y- α PDI**

(6) Synthesis of compound **Y-βPDI**



To a solution of compound **3** (307 mg, 0.311 mmol) and **Y-Sn** (449.4 mg, 0.622 mmol) in dry toluene (10 mL) was added Pd_2dba_3 (14.6 mg, 0.016 mmol) and $\text{P}(o\text{-tol})_3$ (37.8 mg, 0.124 mmol) under N_2 . The mixture was refluxed for 16 hours and then allowed to cool to room temperature. After the evaporation of the toluene, brine was added and the mixture was extracted with CH_2Cl_2 for three times. The combined organic phase was washed with water three times. Then the solution was dried over Na_2SO_4 and concentrated under reduced pressure. After removing the solvent, the residue was purified using column chromatography on silica gel (using eluent with hexane: $\text{CH}_2\text{Cl}_2 = 4:1$, v/v), yielding the target product as a dark red solid (223.8 mg, 37%). ^1H NMR (400 MHz, CDCl_3): δ 8.66 (s, 2H), 8.64–8.24 (m, 12H), 7.73 (s, 2H), 5.22–5.14 (m, 4H), 4.58–4.52 (m, 4H), 2.29–2.20 (m, 8H), 2.00 (s, 2H), 1.89–1.83 (m, 8H), 1.35–1.22 (m, 40H), 1.11–0.78 (m, 24H), 0.70–0.58 (m, 6H); 0.52–0.46 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.80, 143.40, 142.51, 137.12, 135.10, 134.43, 134.34, 133.73, 133.46, 129.96, 129.38, 129.18, 128.35, 127.75, 125.73, 124.82, 124.02, 123.12, 121.72, 112.25, 109.90, 55.17, 55.12, 55.02, 54.84, 40.39, 40.37, 32.28, 32.24, 29.95, 29.91, 29.33, 29.31, 28.04, 27.88, 23.54, 22.91, 22.85, 22.82, 14.28, 14.23, 13.89, 10.61,

10.50. MALDI-TOF MS ($M_w = 1942.83022$): found $m/z = 1943.80768$ ($[M+H]^+$).

3. Fabrication of Thin-Film Transistors

The bottom-gate bottom contact OFET devices based on the thin films of **Y- α PDI** and **Y- β PDI** were fabricated. A Si/SiO₂ wafer with patterned Au electrode was used as the substrate. The substrate was firstly cleaned with a solution of volume ratio H₂SO₄:H₂O₂ = 2:1, and followed by sonication in deionized water and ethanol, respectively. After that, the octadecyltrichlorosilane was deposited on the substrate with 120°C for 3 hours to modify the surface and followed by sonication in *n*-hexane, isopropanol and chloroform respectively. The organic semiconductor layer was obtained by using chlorobenzene solution of **Y- α PDI** and **Y- β PDI** (5 mg/mL), which were spin-cast on the substrate to form thin films. The obtained device was thermal annealing at 60 °C for 10 min and then go to measurement. The field-effect transistors were measured in a N₂-filled glove box with Keithley S4200 SCS semiconductor characterization system. The saturation field effect mobility (μ) was calculated from the average slope of the sqrt of the drain current $|I_{SD}|^{1/2}$ vs V_g plot according to the following equation:

$$I_{SD} = (W/2L)C_i\mu(V_g - V_{th})^2$$

where I_{SD} is the drain current in the saturated regime, W (1400 μ m) and L (50 μ m) are the semiconductor channel width and length, respectively, C_i (SiO₂) = 11.5 nF·cm⁻² in this work according to our measurement is the capacitance per unit area of the dielectric layer, and V_g and V_{th} are the gate voltage and threshold voltage, respectively.

4. Supporting Tables

Table S1 Optical properties of the PDI derivatives

Molecules	$\lambda_{\max}^{\text{sol}}$	$\lambda_{\max}^{\text{film}}$	$\lambda_{\text{onset}}^{\text{film}}$	E_g^{a}	$E_{\text{LUMO}}^{\text{b}}$	$E_{\text{HOMO}}^{\text{b}}$
	(nm)	(nm)	(nm)	(eV)	(eV)	(eV)
Y- α PDI	492, 529	498, 535	578	2.15	-3.59	-5.26
Y- β PDI	492, 529	498, 535	613	2.02	-3.76	-5.58

^a Optical band gap estimated from the onset wavelength of films. ^b Calculated After calibration using ferrocene (Fc/Fc⁺) as the external standard, the corresponding energy levels were calculated using $E_{\text{LUMO}} = -(E_{\text{re}} + 4.46)$ eV; $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.46)$ eV.

Table S2 Organic transistor parameters based on the PDI derivatives

Molecules	$\mu_{\text{h,max}}^{\text{a}}$	$V_{\text{h,onset}}$	$I_{\text{on}}/I_{\text{off}}$	$\mu_{\text{e,max}}^{\text{a}}$	$V_{\text{e,onset}}$	$I_{\text{on}}/I_{\text{off}}$
	(cm ² V ⁻¹ s ⁻¹)	(V)		(cm ² V ⁻¹ s ⁻¹)	(V)	
Y-αPDI	4.5×10 ⁻⁵ (3.6×10 ⁻⁵)	0 to 5	10~10 ²	2.2×10 ⁻⁴ (1.4×10 ⁻⁴)	60 to 75	10~10 ²
Y-βPDI	2.3×10 ⁻⁴ (1.1×10 ⁻⁴)	5 to 10	10~10 ²	1.4×10 ⁻³ (1.2×10 ⁻³)	45 to 55	10 ² ~10 ³

^a Maximum values of the hole/electron mobilities. Mobilities are measured in the glovebox under N₂. The average values are in parentheses (from 15 devices).

5. Supporting Figures

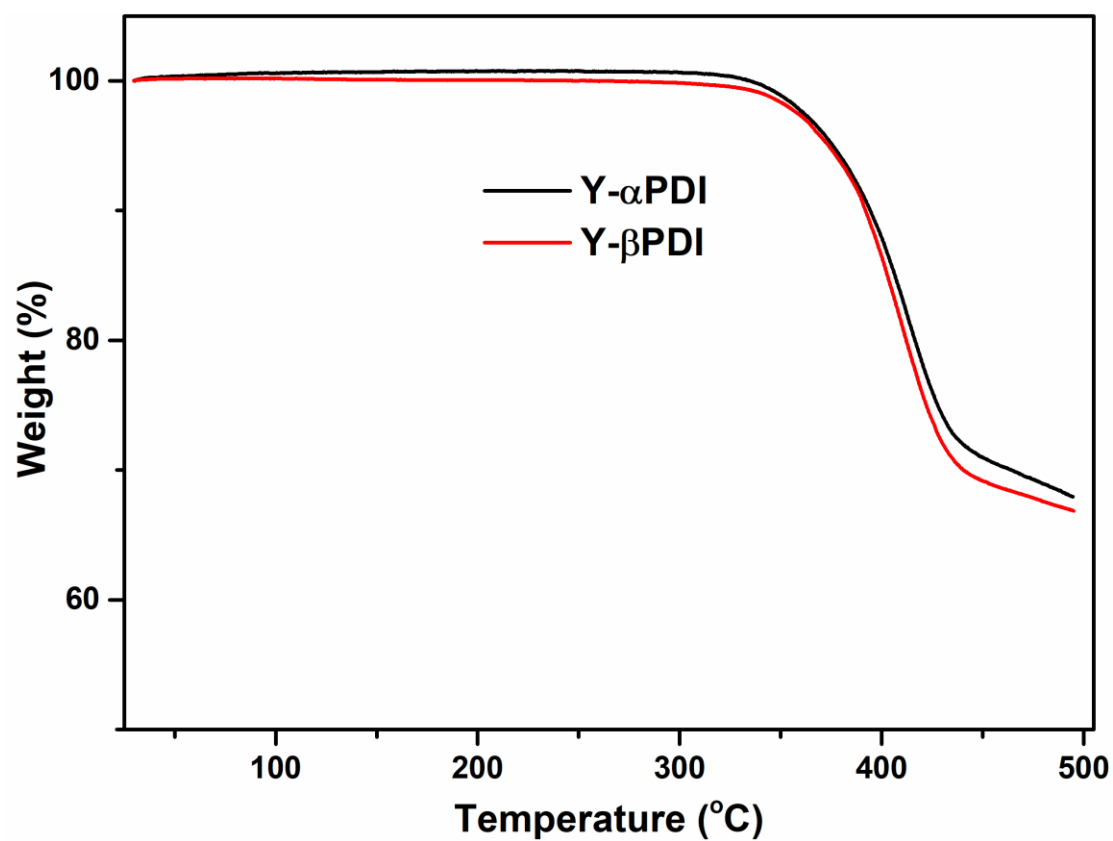


Fig. S1 Thermogravimetric analysis (TGA) curves. The 5% weight loss temperature of Y-αPDI is 376 °C while it is 374 °C for Y-βPDI.

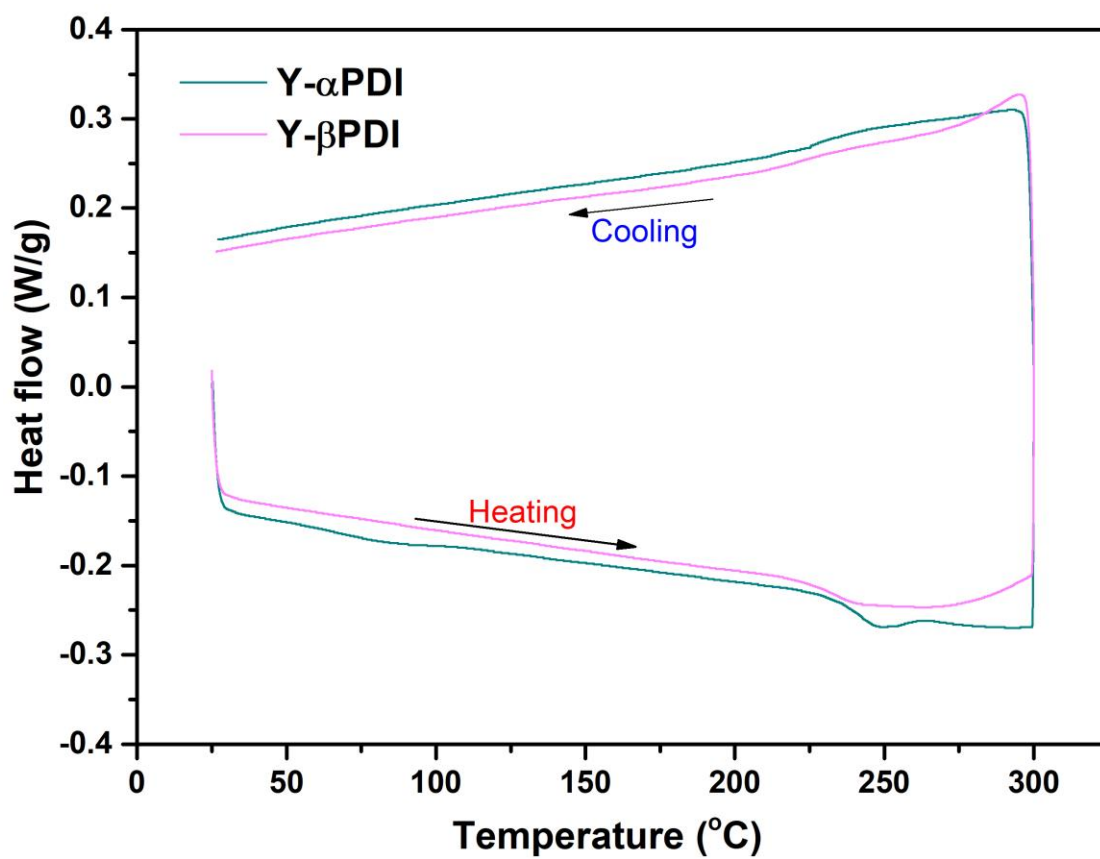


Fig. S2 The differential scanning calorimetry (DSC) plots of Y- α PDI and Y- β PDI.

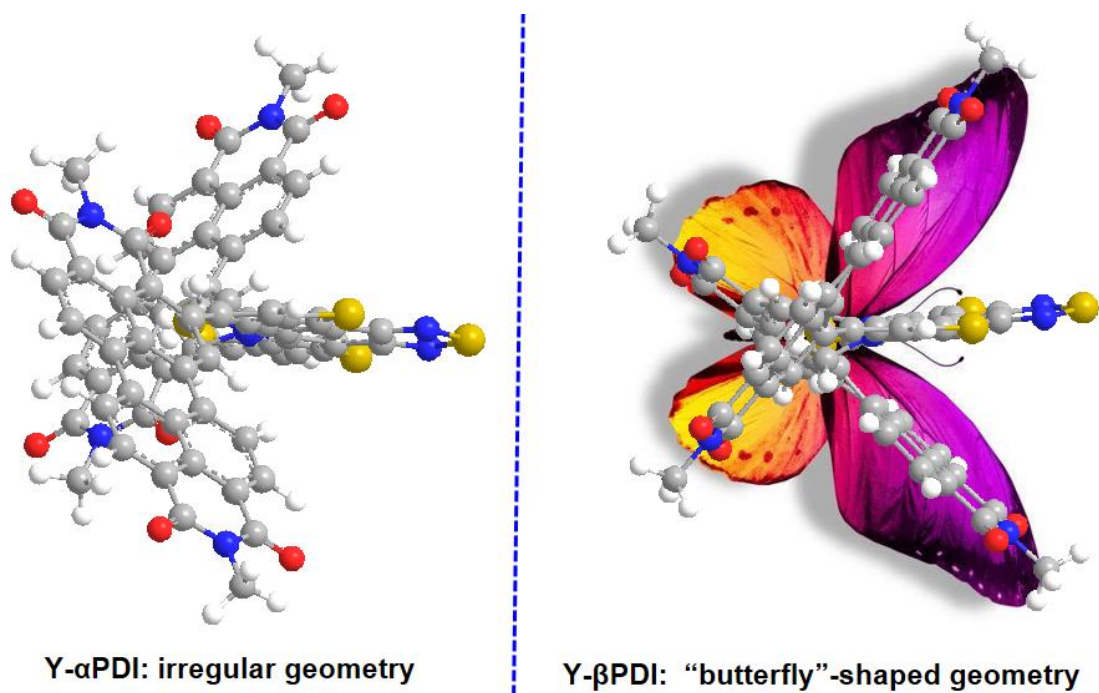


Fig. S3 The DFT optimized molecular geometry of Y- α PDI and Y- β PDI (the long alkyl chains are shortened to methyl for clarity).

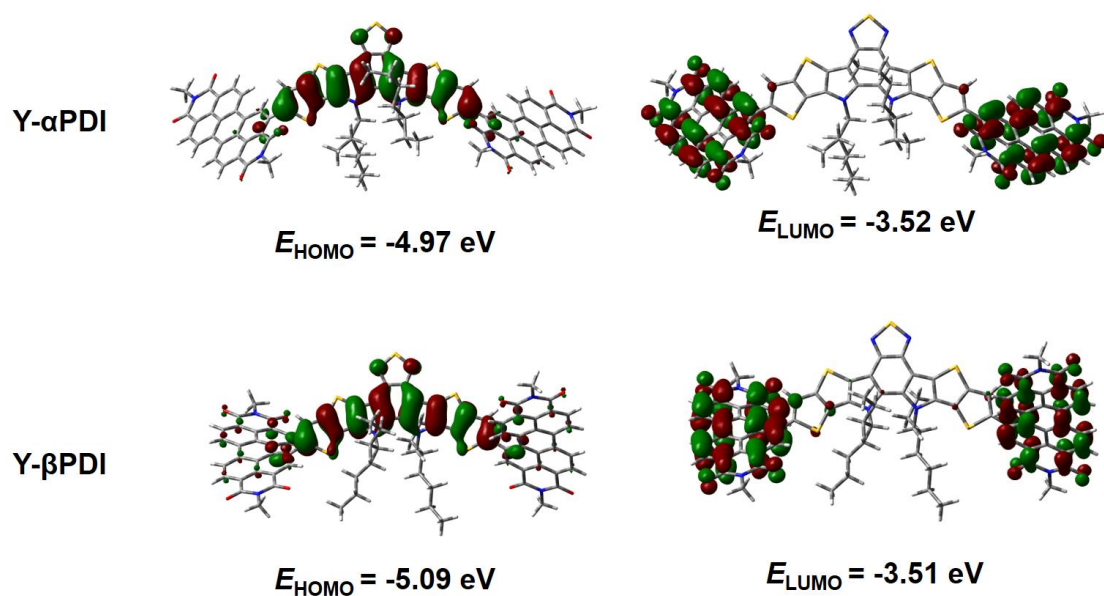


Fig. S4 The DFT calculated HOMO/LUMO energy levels of Y- α PDI and Y- β PDI.

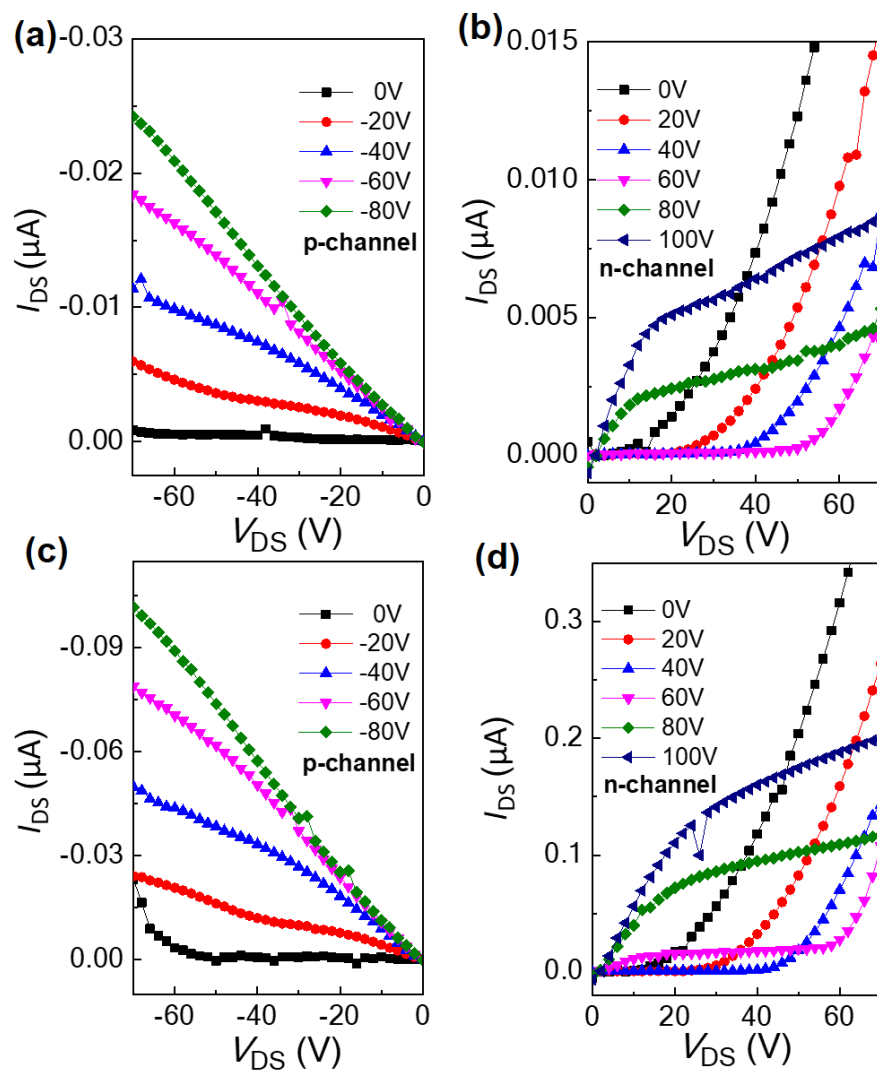


Fig. S5 The output characteristics of the organic transistors based on Y- α PDI (a and b) and Y- β PDI (c and d).

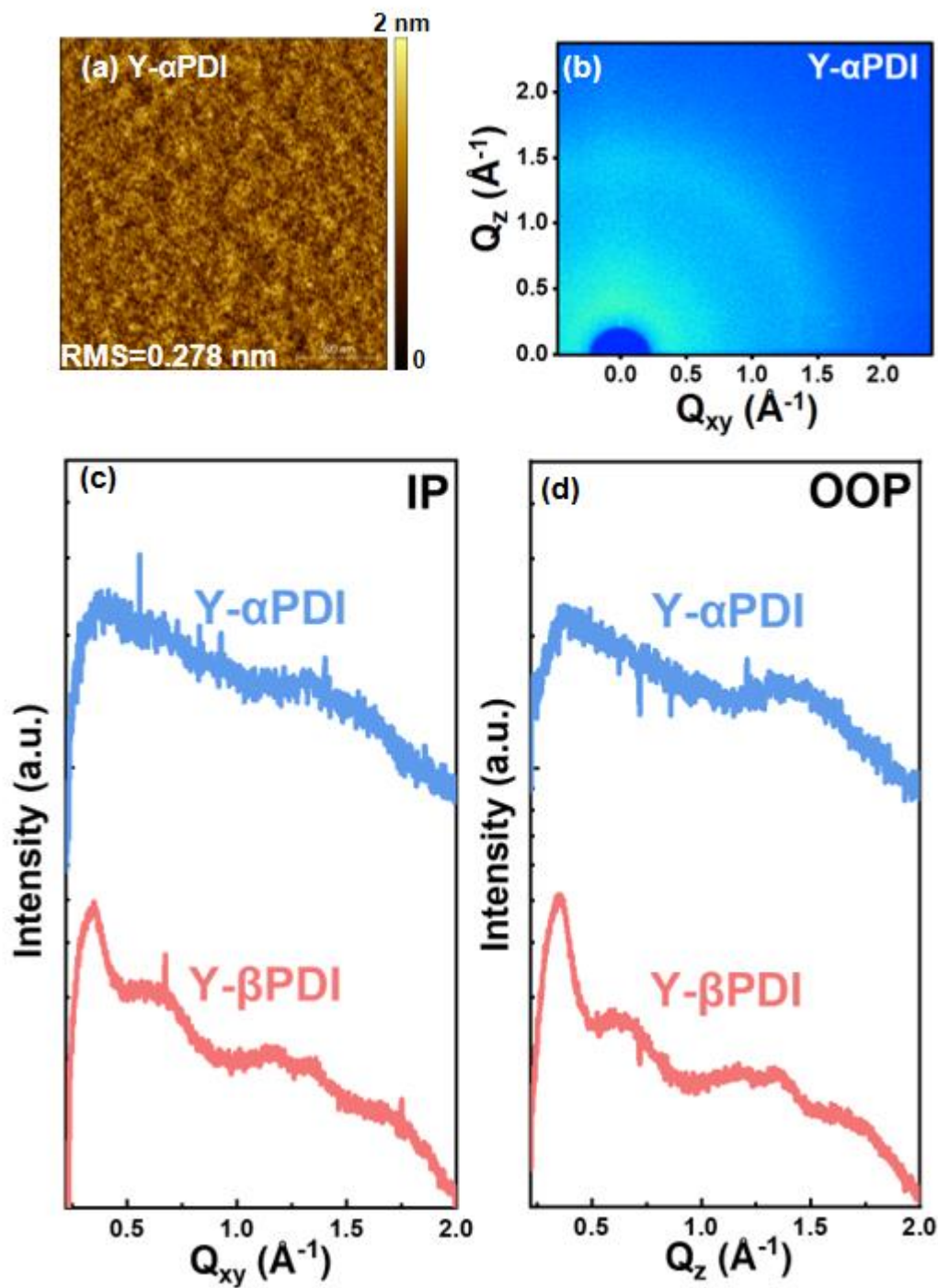


Fig. S6 (a) The AFM height images of **Y- α PDI**; (b) GIWAXS patterns of **Y- α PDI** ; (c) the in-plane 1D profile and (d) the out-of-plane 1D profile of **Y- α PDI** and **Y- β PDI**.

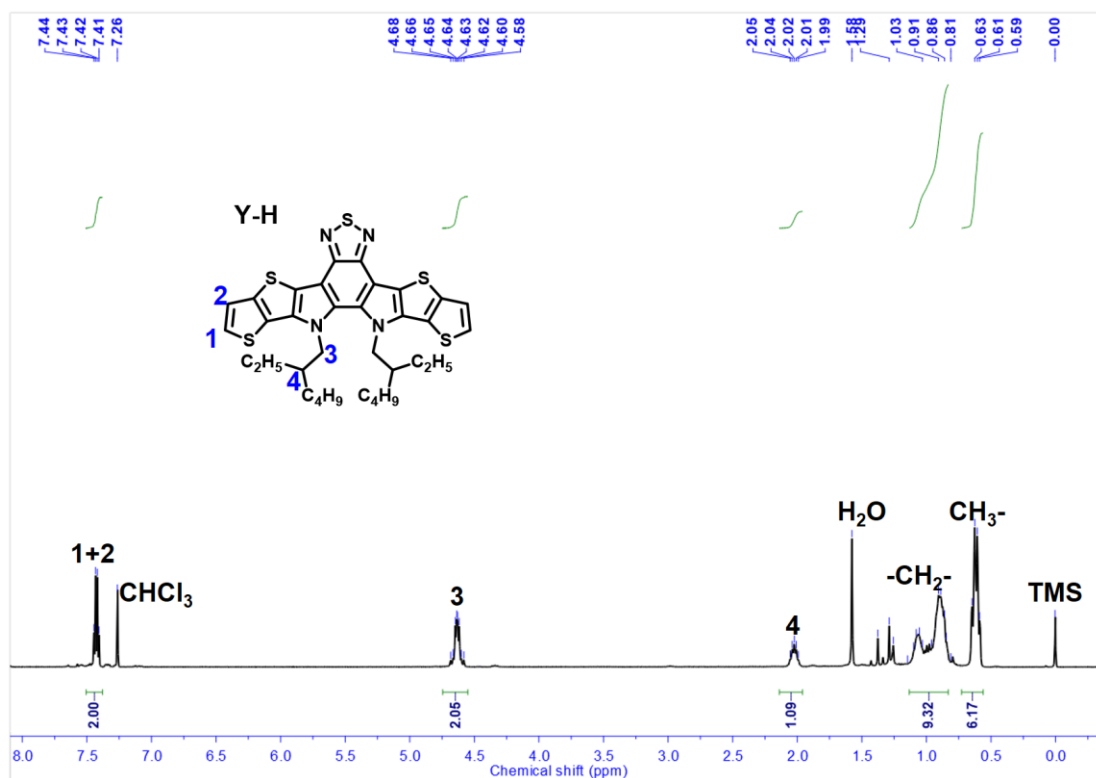


Fig. S7 ^1H NMR spectrum of compound Y-H.

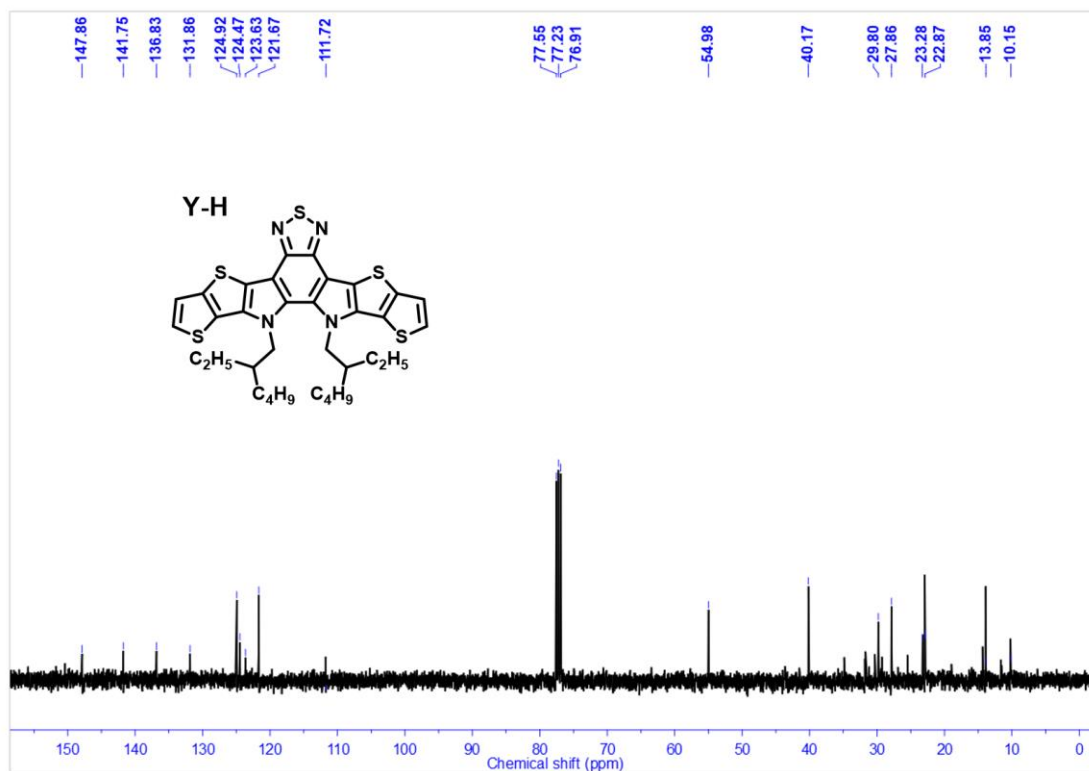


Fig. S8 ^{13}C NMR spectrum of compound Y-H.

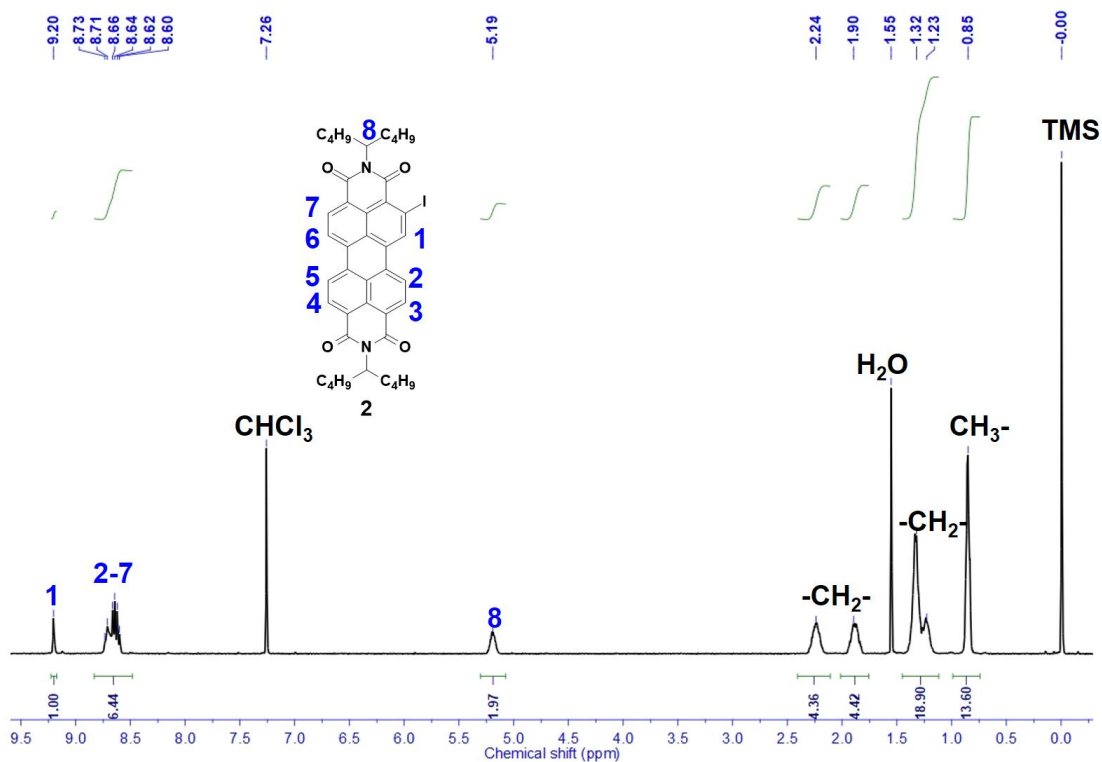


Fig. S9 ^1H NMR spectrum of compound 2.

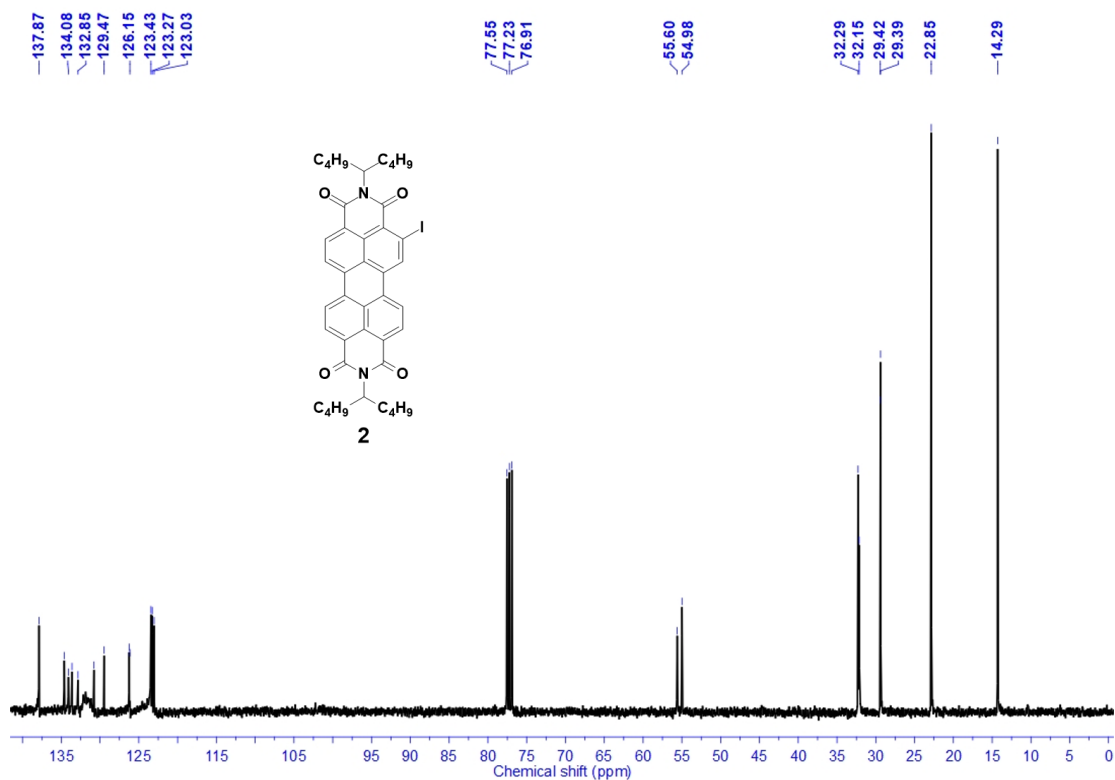


Fig. S10 ^{13}C NMR spectrum of compound 2.

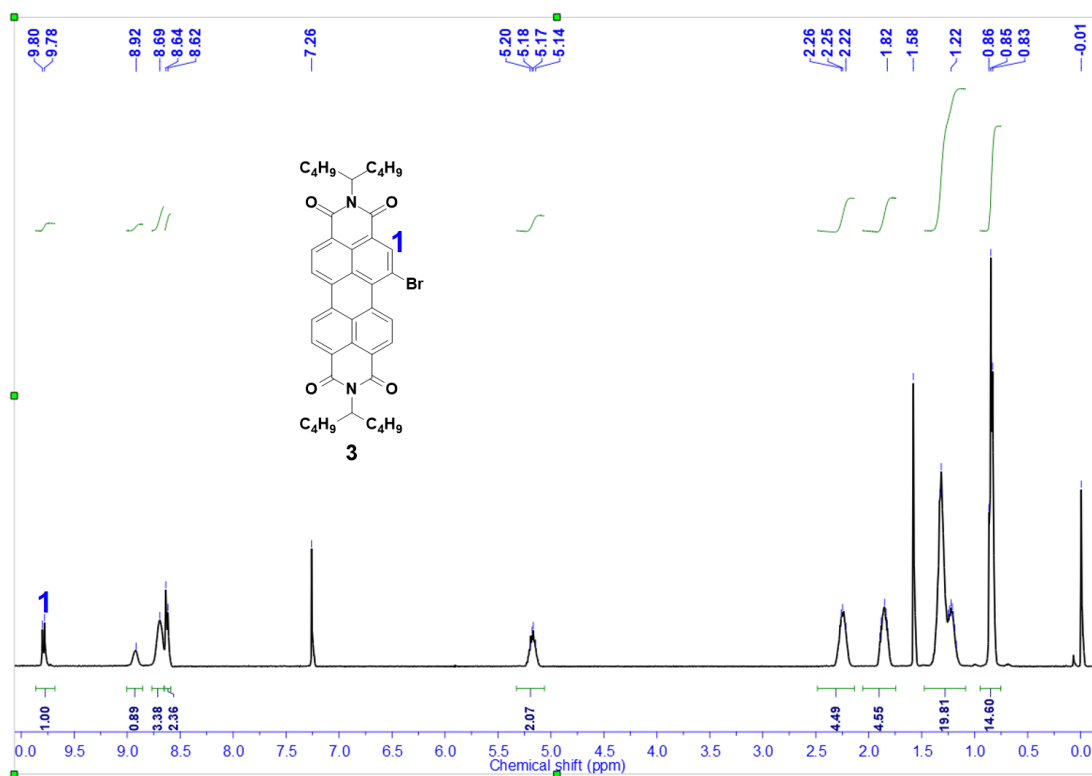


Fig. S11 ^1H NMR spectrum of compound 3.

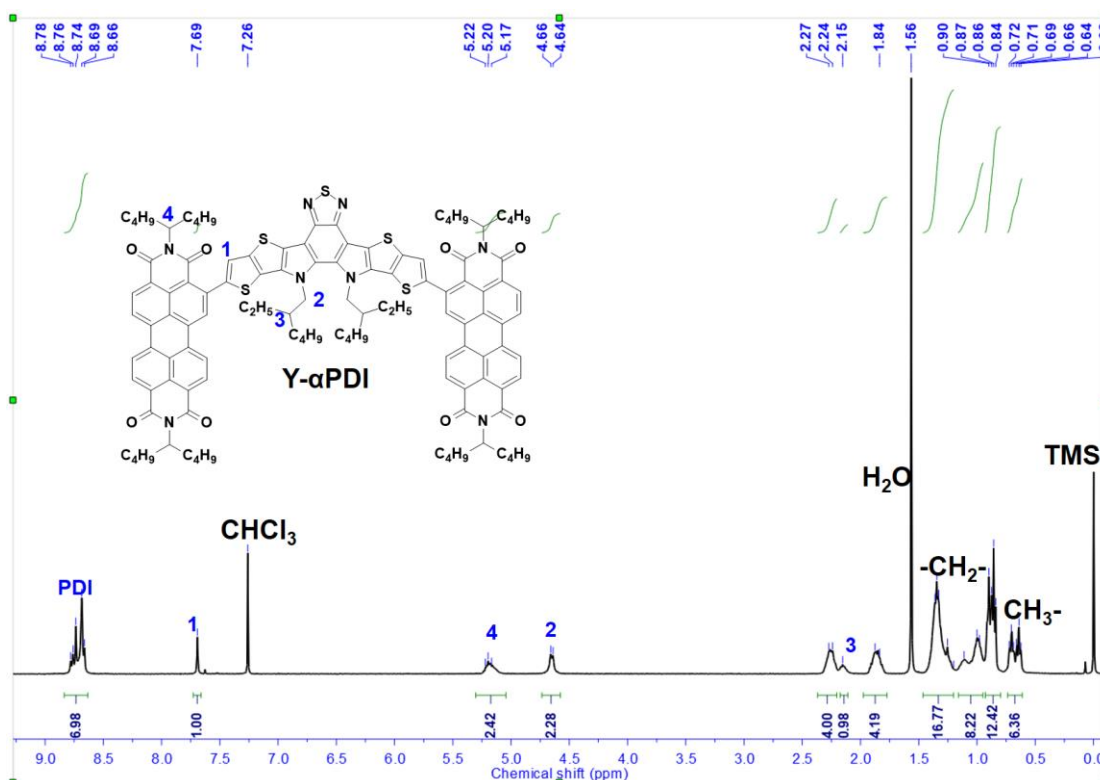


Fig. S12 ^1H NMR spectrum of compound Y- α PDI.

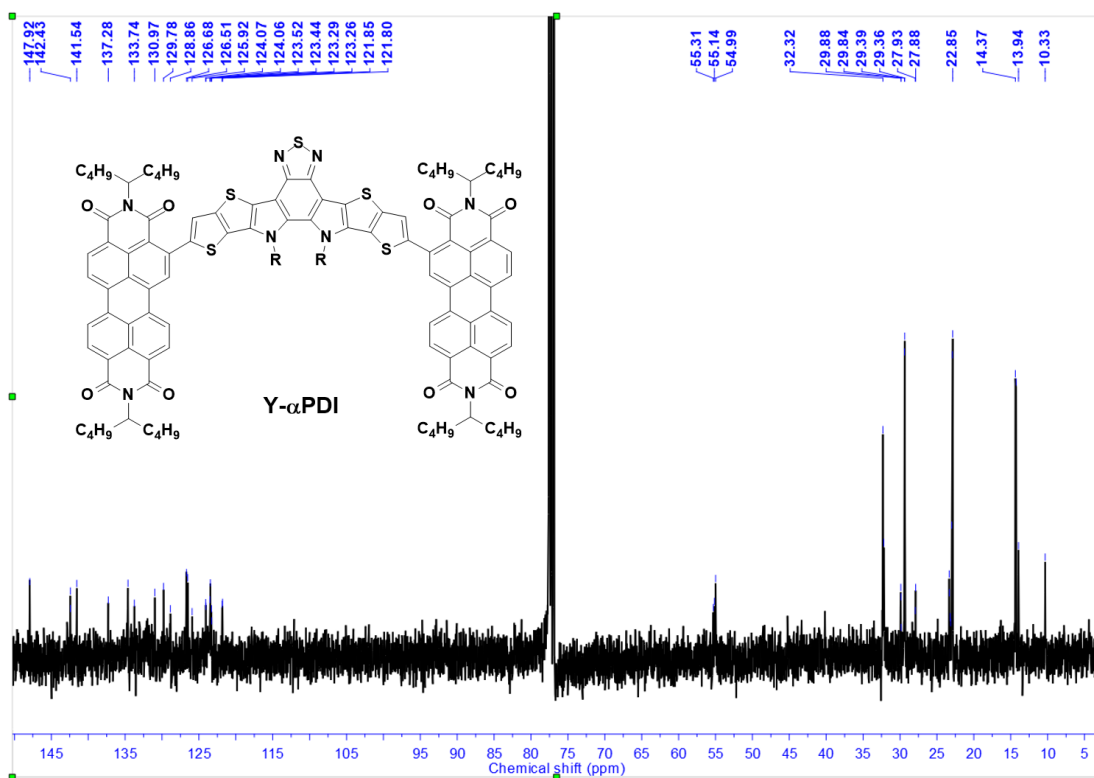


Fig. S13 ^{13}C NMR spectrum of compound **Y- α PDI**.

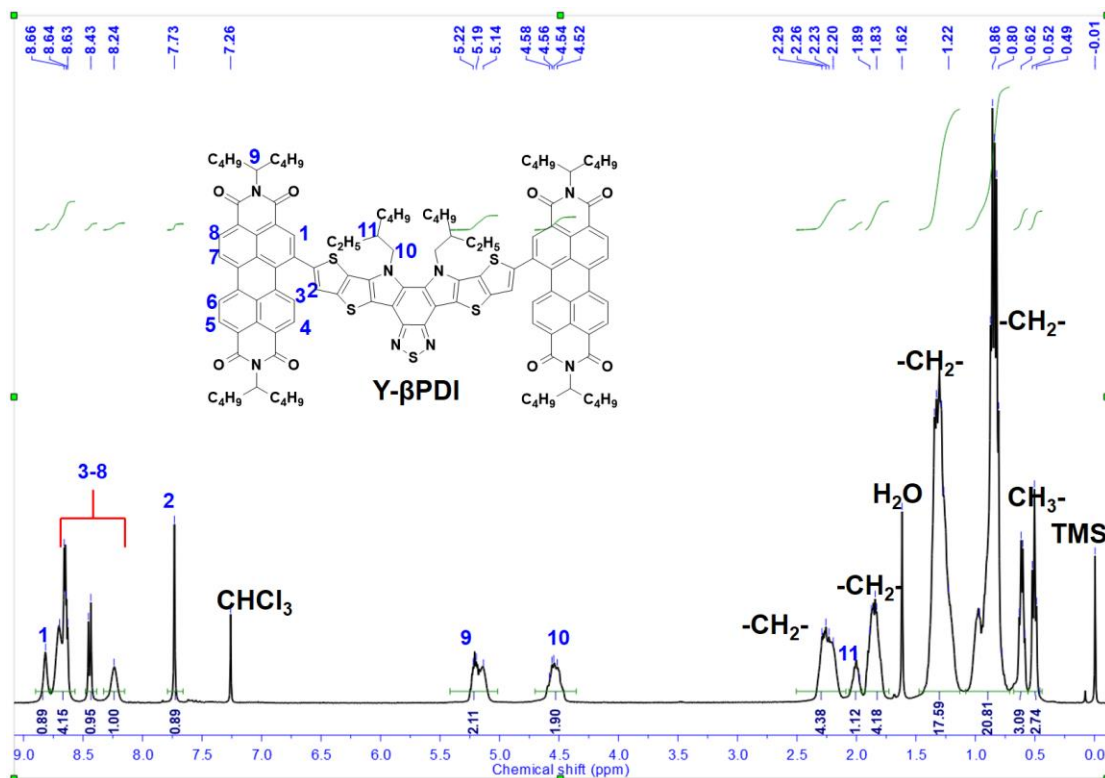


Fig. S14 ^1H NMR spectrum of compound **Y- β PDI**.

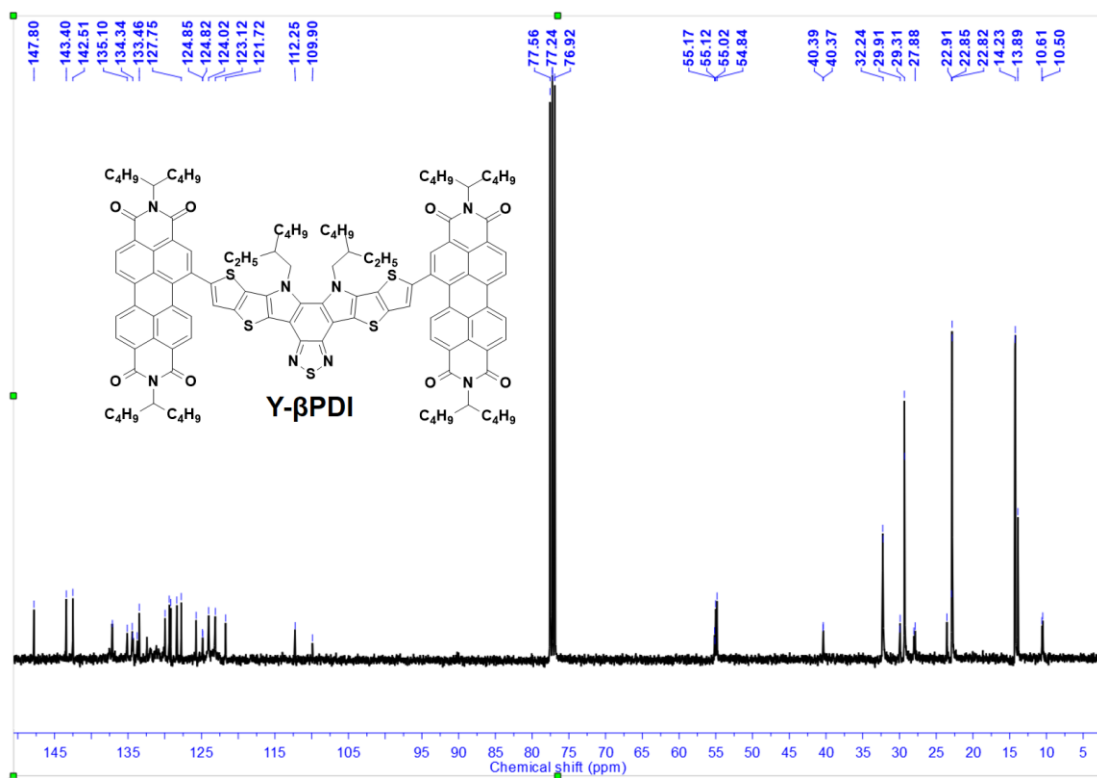


Fig. S15 ^{13}C NMR spectrum of compound Y-βPDI.

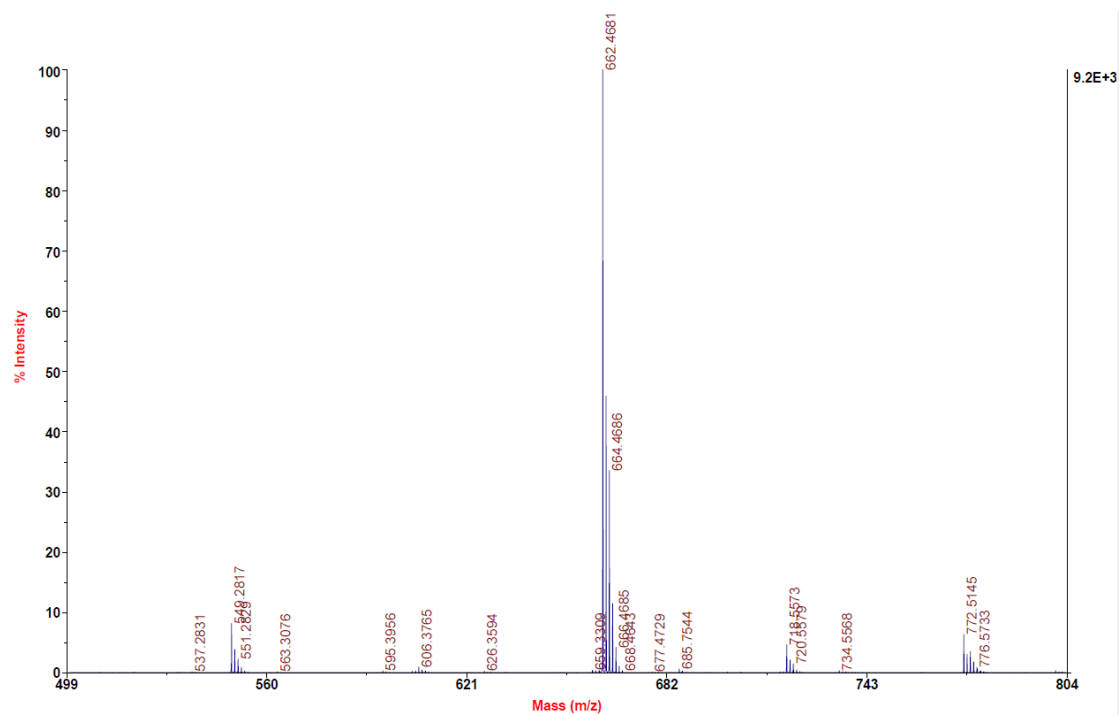


Fig. S16 MALDI-TOF-MS spectrum of compound Y-H.

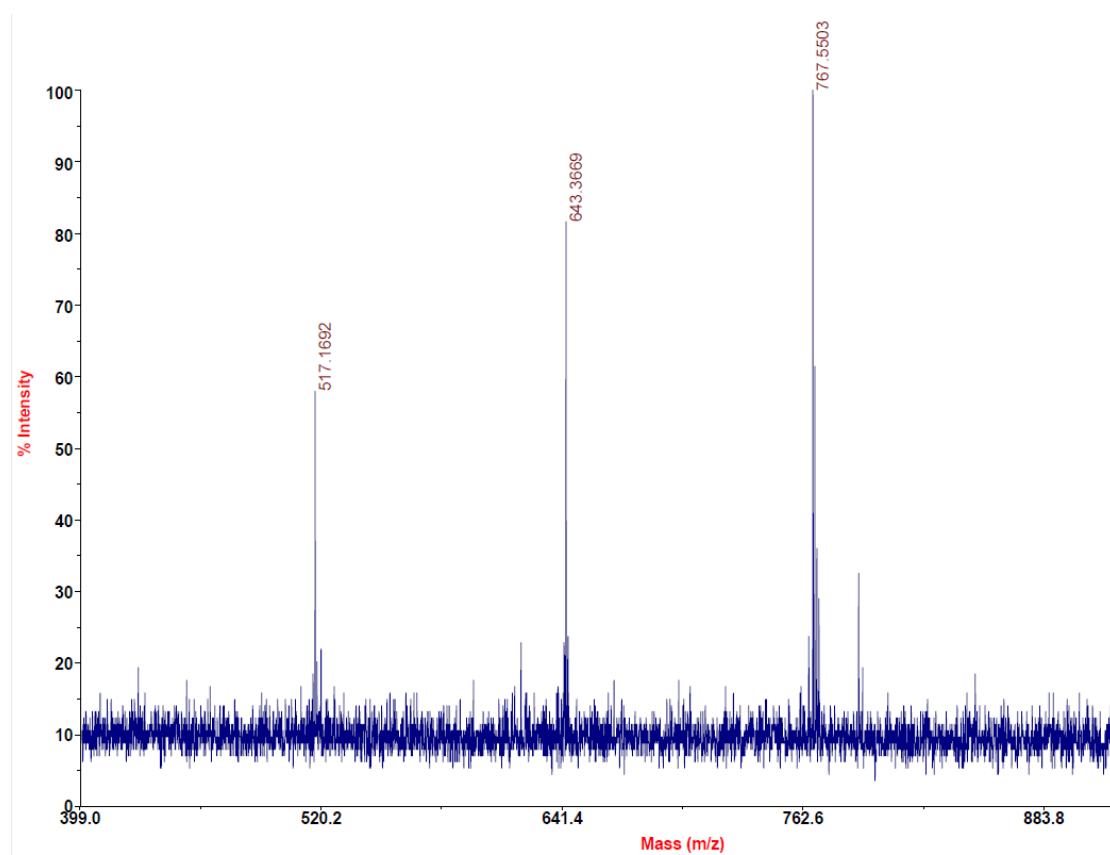


Fig. S17 MALDI-TOF-MS spectrum of compound **2**.

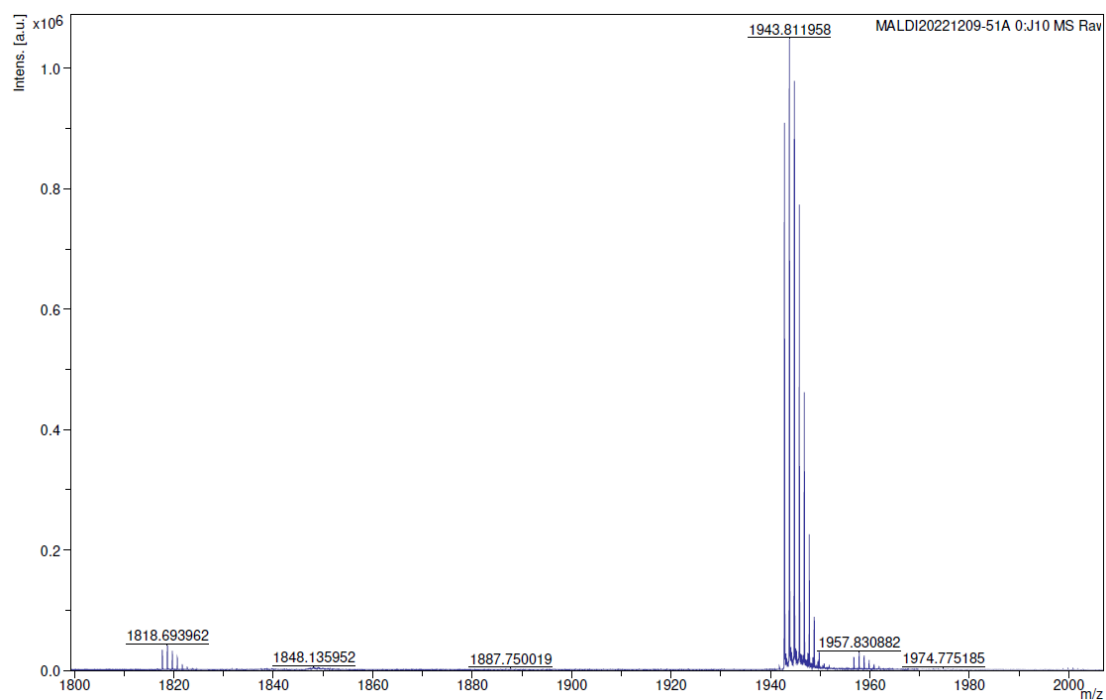


Fig. S18 MALDI-TOF-MS spectrum of compound **Y- α PDI**.

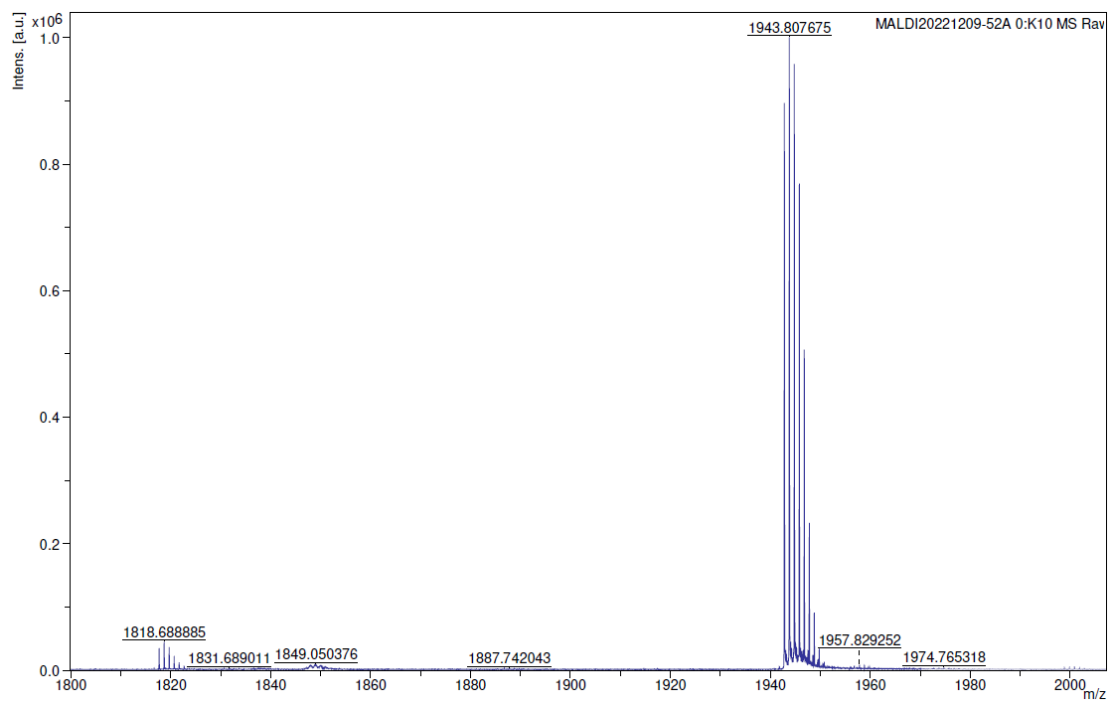


Fig. S19 MALDI-TOF-MS spectrum of compound **Y-βPDI**.

Reference

[S1] W. Liu, S. Xu, H. Lai, W. Liu, F. He and X. Zhu, *CCS Chem.*, 2023, **5**, 654.