Supporting Information

Phenothiazine Fused an Electroactive Bilayer Helicene: Design, Synthesis, ACQ-to-AIE Transformation and Photo-Physical Properties

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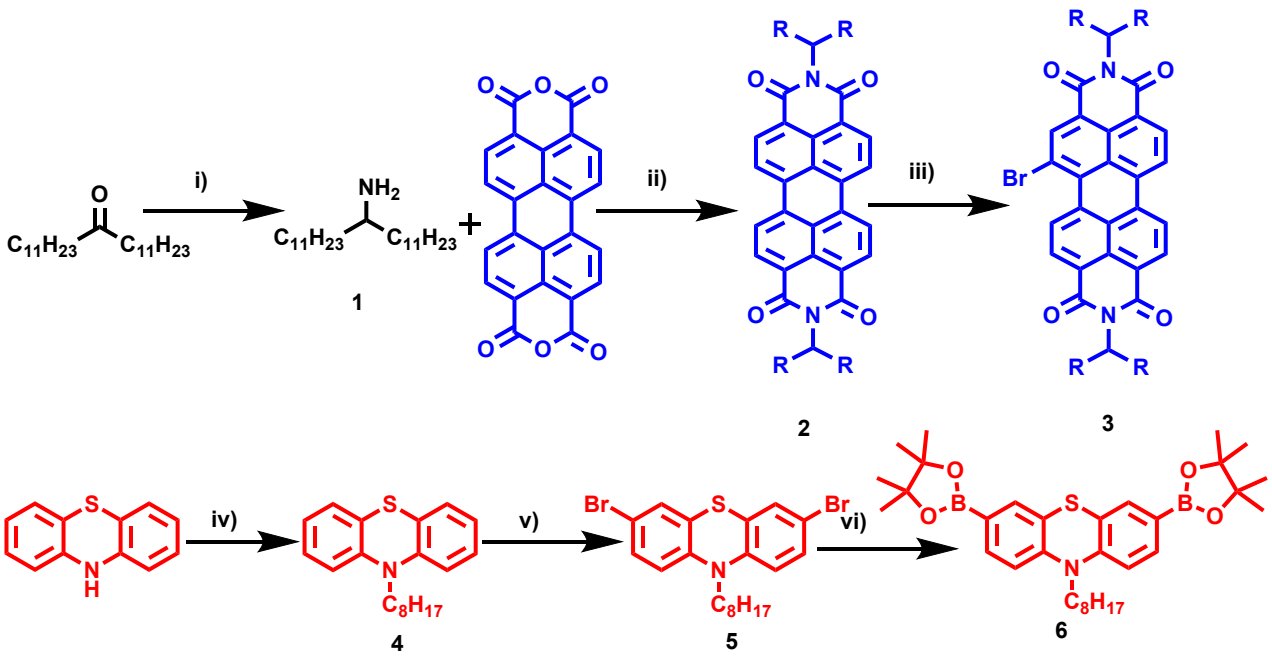
1. Materials and instrumentation

The starting materials Perylene-3,4,9,10-tetracarboxylic dianhydride phenothiazine, Sodium cyanoborohydride, [1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), Ammonium acetate, were purchased from Sigma-Aldrich, 12-Tricosanone, Imidazole purchased from TCI and bromine, potassium carbonate, Iodine, from spectrochem. Silica gel was purchased from Fluka. The solvents were purified by standard procedures and purged with nitrogen before use. All other chemicals used in this work were analytical grade and were used without further purification. All reactions were performed under an inert atmosphere. Absorption spectra were carried out on a Shimadzu UV-1800 model spectrophotometer. The photoluminescence is recorded using a Fluorolog3 spectrophotometer at their respective absorption. Electrochemical data were obtained by Cyclic Voltammetry using a conventional three-electrode cell and a BAS100 electrochemical analyzer. The working electrode was a Pt rod, the auxiliary (counter) electrode was a Pt wire, the reference electrode was Ag/AgCl, saturated KCl and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate.

Fluorescence Lifetime decay measurements were carried out by using time-correlated single-photon counting (TCSPC) setup (Fluorolog-3 Triple Illuminator, IBH Horiba JobinYvon) using a laser of 484 nm for excitation. TRMC was performed for the films prepared on a quartz substrate. The microwave frequency and its power were ~9 GHz and ~3 mW, respectively. A third harmonic generation (355 nm) of a Nd:YAG laser (Continuum Inc., Surelite II, 5−8 ns pulse duration, 10 Hz) was used for the excitation (incident photon density $I_0 = 4.6 \times 10^{15}$ photons cm^{-2} $pulse^{-1}$). The photoconductivity ($\Delta\sigma = A^{-1}\ \Delta P_r\ P_r^{-1}$ where A is the sensitivity factor, P_r is the reflected microwave power, and ΔP_r is the change in P_r upon exposure to light) was converted into the product of the quantum yield (φ) and sum of the charge carrier mobilities $\Sigma\mu$ ($= \mu_+ + \mu_-$) using the relationship $\varphi\Sigma\mu = \Delta\sigma(eI_0F_{light})^{-1}$, where e and F_{Light} are the electron charge and correction (or filling) factor, respectively. The experiments were performed at room temperature in the air. Photoelectron yield spectroscopy (PYS) was performed using a Bunko Keiki BIP-KV202GD in vacuum.^{1}H NMR, ^{13}C NMR spectra were measured with Bruker spectrometers, using TMS as internal standard. MALDI recorded on Bruker ultraflex TOF. The Circular Dichroism is performed on the JASCO J-810 spectrophotometer. The HPLC is done on a chiral column and its details are given below the spectra. Theoretical calculations were measured by Geometry optimizations in the

ground state (S0) With B3LYP 6-31G(d,p), (Alkyl chains were replaced by methyl for simplicity). TD-DFT calculations were performed with PBE/6-31g(d)



i) Na(BH$_3$)CN, MeOH, NH$_4$(OAc),RT, 24hrs ii) Imidazole, 180^{o}C, 6hrs iii) Br$_2$, DCM,RT,24hrs iv) C$_8$H$_{17}$Br, KOH, DMSO, 80^{o}C, 10hrs v) NBS, DCM, CH$_3$COOH, RT, 12hrs vi) B$_2$pin$_2$, KOAc, Pd(dppf)Cl$_2$, 1-4Dioxane, 80^{o}C, 16hrs

Scheme S1 Synthetic route for the preparation of intermediates.

Synthetic process of the Molecules

12-Aminotricosane (1)

In 5ml of diethyl ether, 12-Tricosanone (72 mg, 0.213 mmol, 1eq) was added. After complete dissolution, Ammonium acetate (164mg, 2.13 mmol,10eq) was added and the reaction mixture degassed for 10 minutes. Then Sodium cyanoborohydride (14 mg, 0.222 mmol,0.96eq) and methanol (1 ml) was added to the reaction flask and the contents were stirred at room temperature under nitrogen for 24 h. The reaction was quenched by slow addition of HCl (0.1 ml) then concentrated on a rotary evaporator to give a white solid. This was into H_2O and brought to a pH ~ 10 with solid KOH Extraction with several aliquots of chloroform, followed by evaporation of the solvent gave 12-aminotricosane as white solid (150mg,48%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.67 (m, 1H), 1.35 (m, 40H), 0.89 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 51.24, 38.17, 34.67, 31.95, 29.70, 26.22, 22.72, 14.14. HRMS (ESI/Q-TOF): m/z calcd for $C_{23}H_{49}N$ = 339.3865, found 340.3934 $(M + H)^+$.

N, N-Bis(12-aminotricosanyl) perylene-3,4:9,10-bis(dicarboximide) (2)

12-Aminotricosane (100 mg, 0.294 mmol, 2.1eq), perylene-3,4:9,10-tetracarboxydianhydride (55 mg, 0.140 mmol, 1eq), and imidazole (382 mg, 5.607 mmol, 40eq) were heated to 180 ℃ under a nitrogen atmosphere for 6 h. The reaction mixture was cooled to room temperature and 75 ml ethanol was added. This solution was poured into 2M HCl and stirred at room temperature. The red precipitate was filtered, washed with water, and dried to give compound **2** as red solid (151 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.617 (m, 8H), 5.180 (m, 2H), 2.234 (m, 4H), 1.863 (m, 4H), 1.19–1.25 (m,72H), 0.830 (t, 12H, J ¼ 6.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.58, 134.53, 131.16, 129.63, 126.48, 124.00, 122.90, 54.79, 42.86, 32.39, 31.93, 29.49, 29.27, 26.98, 23.94, 22.69, 14.12. MALDI-TOF for $C_{70}H_{102}N_2O_4$ Calculated 1034.78 found- 1033.75.

Bromoperylenebisimide(Bromo-PBI) (3)

Excess bromine (0.375ml,7.28 mmol,65 eq) was added to a solution of PBI (116 mg,0.112 mmol,1eq) in CH_2Cl_2 and the reaction mixture was stirred at room temperature for 24 h. The progress of the reaction was monitored by TLC. After the removal of excess bromine, compound was purified by silica gel column chromatography with hexane/chloroform as eluents. Further purification of second band by recrystallization yielded mono-bromo PBI as red solid **3** (220mg, 0.197mmol 57%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (d, 1H), 8.93 (d, 1H), 8.65 (ddd, 5H), 5.24 – 5.11 (m, 2H), 2.23 (m, 4H), 1.92 – 1.78 (m, 4H), 1.33 – 1.12 (m, 73H), 0.84 (t, J = 6.9 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 133.98, 131.52, 130.82, 128.98, 128.16, 127.11, 123.78, 123.00, 120.97, 55.01, 31.93, 29.56, 26.94, 22.69, 14.13. MALDI-TOF for $C_{70}H_{101}BrN_2O_4$ Calculated 1114.49 found 1114.75.

10-octyl-10H-phenothiazine (4)

In a dry flask phenothiazine (28 mg, 0.140 mmol, 1eq) and KOH (8 mg, 0.140 mmol, 1eq) was added in DMSO under nitrogen at 80 C, after 20 min, n-octyl bromide (27.13 mg, 0.140 mmol, 1eq) was slowly added by syringe the colour of the reaction mixture changed from black to yellow, and the solution was stirred at 80 C for 10 h. After completion of the reaction, the reaction mixture was diluted with H_2O and extracted with DCM by the separatory funnel. The combined organic layer was washed with brine and dried over anhydrous sodium sulfate and then the organic solvents were completely removed by rotary evaporation. The residue was purified by column chromatography using petroleum ether as eluent to give 4 (45 mg, 0.144 mmol, 95%) as a yellow

oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13(d, J=7.5, 4H), 6.86 (d, J=6.9, 4H), 3.84 (m, 2H), 1.97 – 1.71 (m, 2H), 1.33 (m, 10H), 0.86 (t,J=6.9, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.93, 134.94, 126.13, 122.03, 112.78, 104.15, 44.51, 33.89, 31.98, 29.75, 29.41, 22.74, 19.45, 14.16.

3, 7-dibromo-10-octyl-10H-phenothiazine (5)

NBS (43 mg, 0.24 mmol, 2.5eq) was added to a solution of 10-octyl-10H-(30 mg, 0.096 mmol, 1eq) in DCM (20 mL) and acetic acid (70 mL). The reaction mixture was stirred for 12 hours at room temperature in the absence of light. Water was added to stop the reaction, and the mixture was extracted with ethyl acetate three times. The organic phase was combined and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography using dichloromethane/hexane (v/v 1: 3) as the eluent to result in 3,7-dibromo-10-octyl-10H-phenothiazine as a viscous oil (50 mg, 0.106 mmol, 90 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24 – 7.18 (m, 7H), 6.67 (d, *J* = 8.6 Hz, 2H), 3.74 (t, 2H), 1.77 – 1.69 (m, 2H), 1.42 – 1.33 (m, 2H), 1.26 (8H), 0.86 (t, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.16, 129.72, 126.47, 116.68, 114.76, 47.64, 31.75, 29.17, 26.67,22.65, 14.14.

10-Octyl-3,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- phenothiazine. **(6)**

3,7-Dibromo-10-octylphenothiazine (45 mg ,0.095 mmol, 1eq), B_2Pin_2 (119 mg, 0.21 mmol, 2.2eq), KOAc (56 mg, 0.575 mmol, 6eq) and $Pd(PPh_3)_2Cl_2$ (6.0 mg, 0.005 mmol) were added under inert atmosphere in 1,4-Dioxane and then kept at 80 C for 16 hrs to afford compound (60 mg, 0.106 mmol, 90%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, 1H), 7.51 (d, 1H), 6.80 (d, 1H), 3.84 (t, 1H), 1.77 (m, 2H), 1.43 – 1.37 (m, 2H), 1.32 (s, 24H), 1.28 – 1.18 (m, 8H), 0.89 – 0.83 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.19, 134.32, 123.97, 114.76, 83.71, 47.59, 31.76, 29.20, 24.86, 22.82, 14.13. MALDI-TOF for $C_{32}H_{47}NSO_4B_2[M^+]$: calculated 563.3412 Found 563.3440.

Synthesis of PY-PT-Un (7)

In a 25-mL Round flask, the 10-octyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (50 mg, 0.088 mmol, 1 eq), 1-Bromo Perylenebisimide (207 mg, 0.186 mmol, 2.1 eq), dry potassium carbonate (300mg, 2.16 mmol, 24.6 eq), and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (5.5 mg, 0.074 mmol, 8.5 mol%) were dissolved in 10 mL of an nitrogen-sparged, 2:1 (v/v) mixture of THF and water, respectively. The mixture was heated by an oil bath with stirring at 77 °C for 18 h. The resultant mixture was diluted with ethyl acetate, washed with brine in a separatory funnel, dried over magnesium sulphate, and

filtered. The solvents were removed under reduced pressure. Purification by column chromatography on silica gel (hexanes/ ethyl acetate) yielded as a reddish solid (171 mg, 0.0712 mmol, 82%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 – 8.50 (m, 10H), 8.38 – 8.13 (m, 4H), 7.40 (s, 2H), 7.25 (dd, *J* = 8.4, 1.4 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 5.27 – 5.08 (m, 4H), 3.98 (s, 2H), 2.25 (s, 8H), 2.03 – 1.92 (m, 2H), 1.84 (d, *J* = 3.8 Hz, 8H), 1.68 (s, 2H), 1.41 – 1.07 (m, 152H), 0.93 – 0.76 (m, 27H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 164.82,163.74,144.96, 140.55, 137.00,134.78, 132.22, 131.61, 131.30, 131.24,128.81, 129.27, 129.27, 128.51, 128.00, 127.37, 126.16, 123.85, 122.86, 122.19, 121.15, 116.90, 54.73, 48.06, 32.37, 31.92, 29.75, 29.48, 26.98, 22.69, 14.13. -Anal. Calcd for $C_{160}H_{225}N_5O_8S$: C,80.79; H,9.53; N,2.94; O,5.38; S,1.35. Found: C,80.52; H,9.90; N,2.82; S,1.33. MALDI-TOF for $C_{160}H_{225}N_5O_8S[M^+]$: calculated 2378.647 Found 2378.664.

Synthesis of SPS-PY-PT (8)

In a photochemical reaction vessel equipped with a stir bar and quartz double-walled immersion well, compound **7** (100 mg, 0.042 mmol, 1 eq) and iodine (27 mg, 0.212 mmol, 5.05 eq) were dissolved in 50 mL of toluene. The solution was sealed to air and irradiated with UV light from a 450 W mercury lamp for 6 h. A reaction temperature of ~25 °C was maintained by flowing chilled water continuously through the immersion well. The benzene was removed under reduced pressure. The crude solid was sonicated in DCM and loaded onto a silica plug, the plug was flushed with DCM, which was collected and evaporated to dryness under reduced pressure to yield **SPS-PY-PT** as Red solid (91 mg, 0.038 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.08 (d, J = 78.9 Hz, 1H), 9.41 (d, J = 95.7 Hz, 1H), 9.03 (dd, J = 57.3, 42.1 Hz, 2H), 8.81 – 8.52 (m, 6H), 8.41 – 7.99 (m, 3H), 7.90 –7.43 (m, 3H), 5.35 (s, 1H), 5.18 (s, 3H), 4.75 (s, 1H), 4.37 (s, 1H), 2.45 – 2.14 (m, 8H), 1.85 (s, 8H), 1.58 – 0.95 (m, 156H), 0.94 – 0.72 (m, 27H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 164.82, 163.66, 139.43, 138.87, 137.90, 136.65, 134.79, 134.50, 133.62, 132.42, 131.69, 130.91, 129.85, 129.31, 127.58, 123.82, 123.06, 122.81, 118.06, 117.70,54.91,32.39,31.92, 29.49, 26.96, 22.69, 14.13. Anal. Calcd for $C_{160}H_{221}N_5O_8S$: C,80.93; H,9.38; N,2.95; O,5.39; S,1.35 Found: C,80.45; H,9.28; N,2.16; S,1.06 MALDI-TOF for $C_{160}H_{221}N_5O_8S[M^+]$: calculated 2374.67 Found 2374.97.

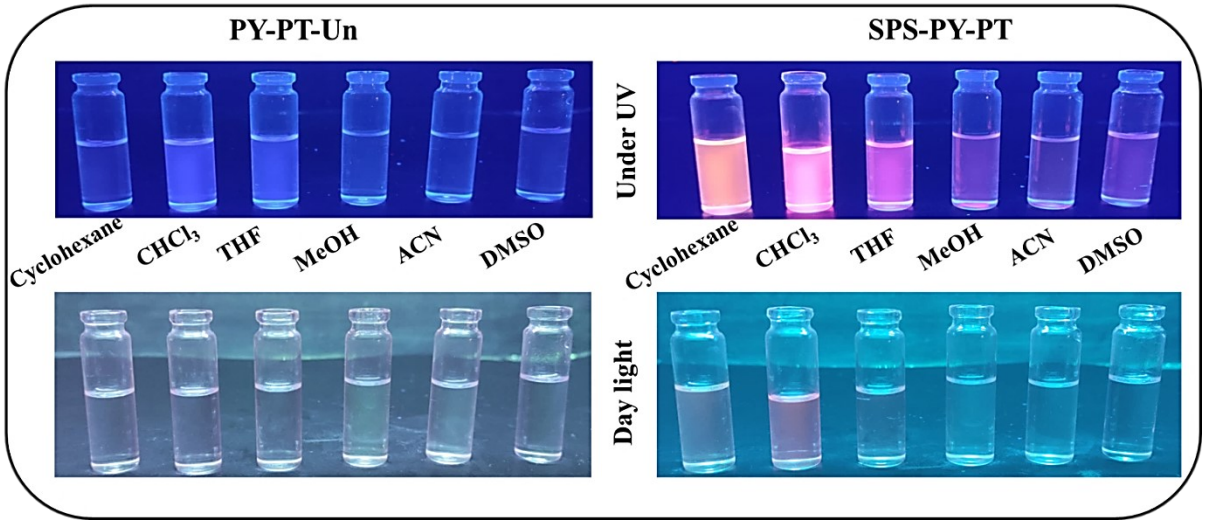


Fig. S1 Solution phase images under UV light of PY-PT-Un and SPS-PY-PT.

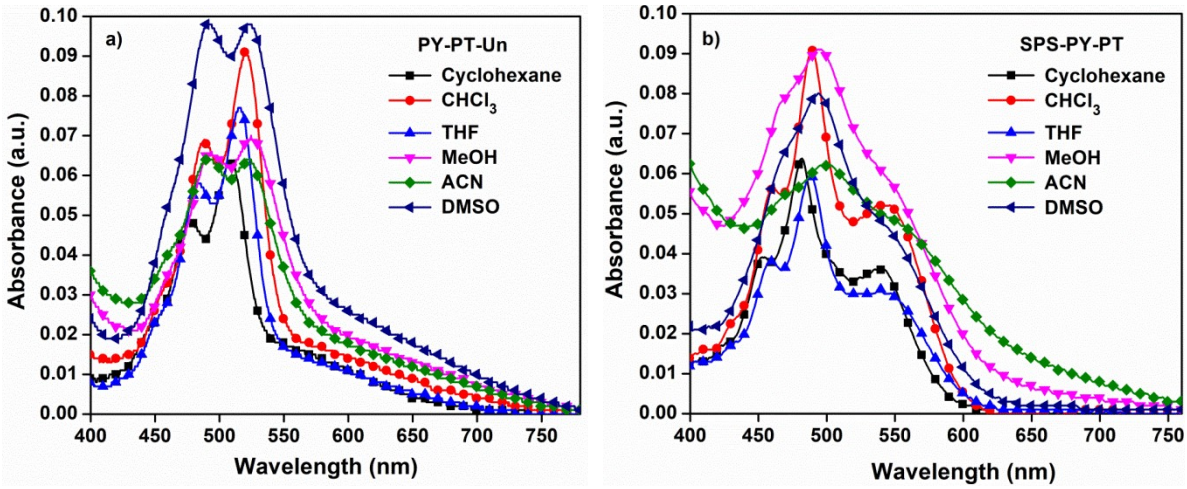


Fig. S2 The UV absorption spectra with their intensity ratio in different solvents of a) PY-PT-Un and b) SPS-PY-PT.

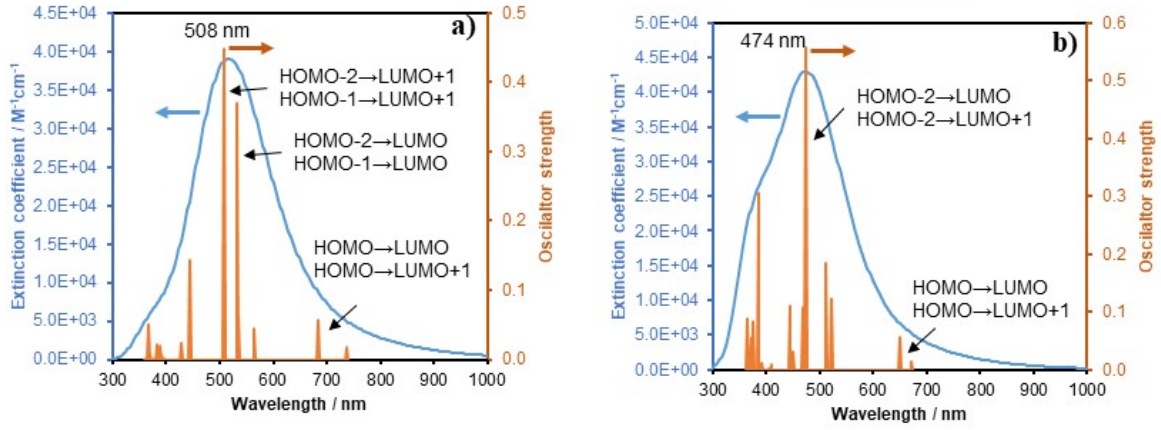


Fig. S3 The UV-absorption spectra of the a) PY-PT-Un and b) SPS-PY-PT calculated from the TD-DFT analysis and its respective HOMO-LUMO Oscillator strength.

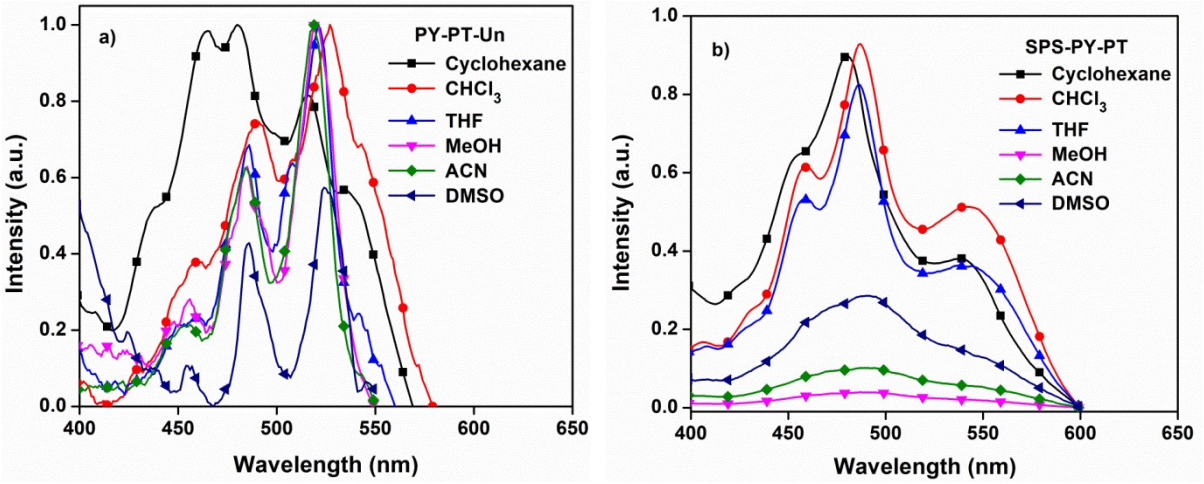


Fig. S4 PL excitation spectra of a) PY-PT-Un and b) SPS-PY-PT.

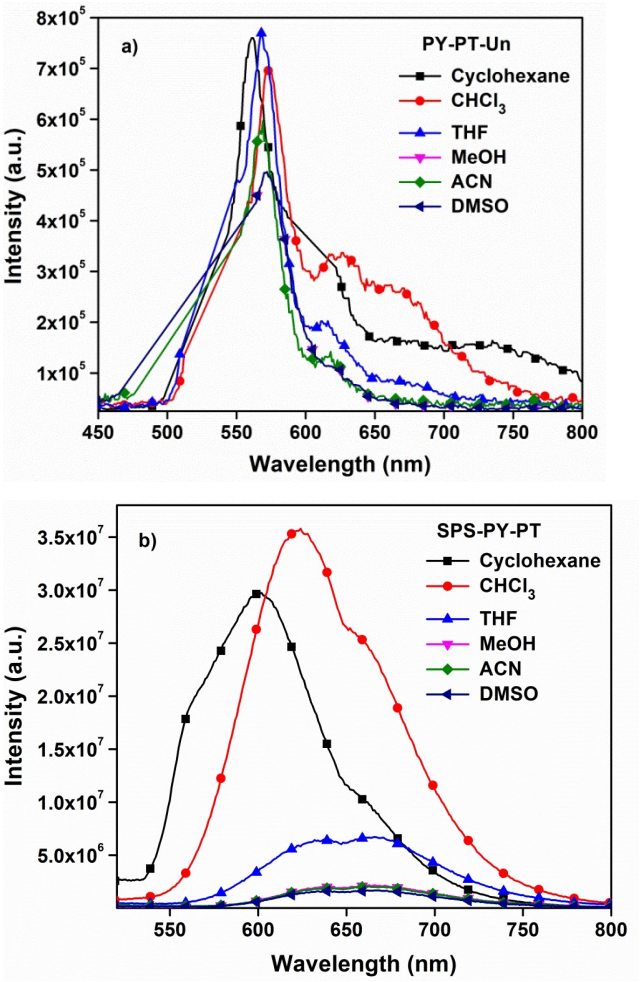


Fig. S5 PL emission spectra of a) PY-PT-Un and b) SPS-PY-PT without normalization.

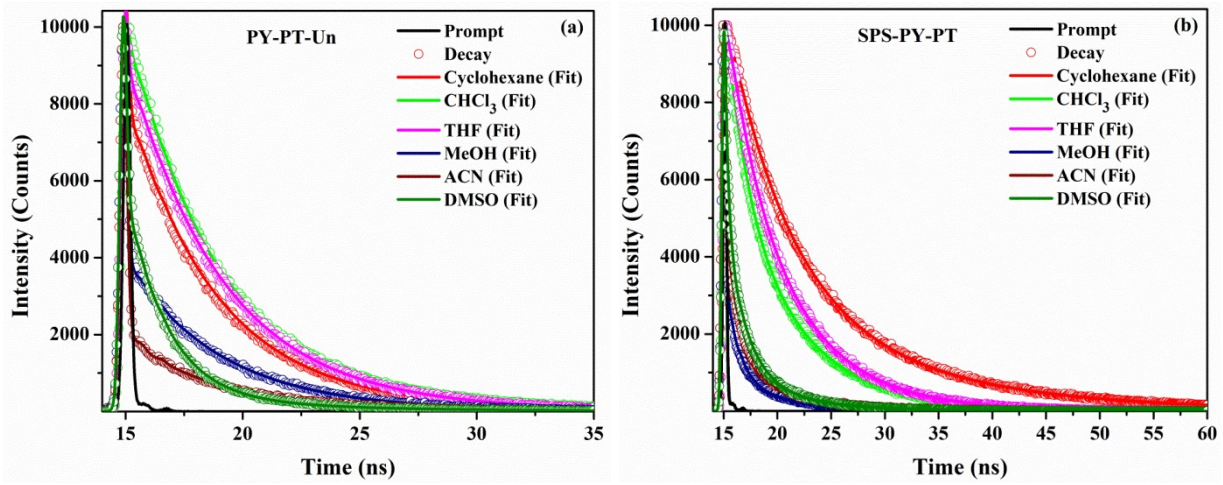


Fig. S6 Linear arrangement of Lifetime of a) PY-PT-Un and b) SPS-PY-PT in different solvents.

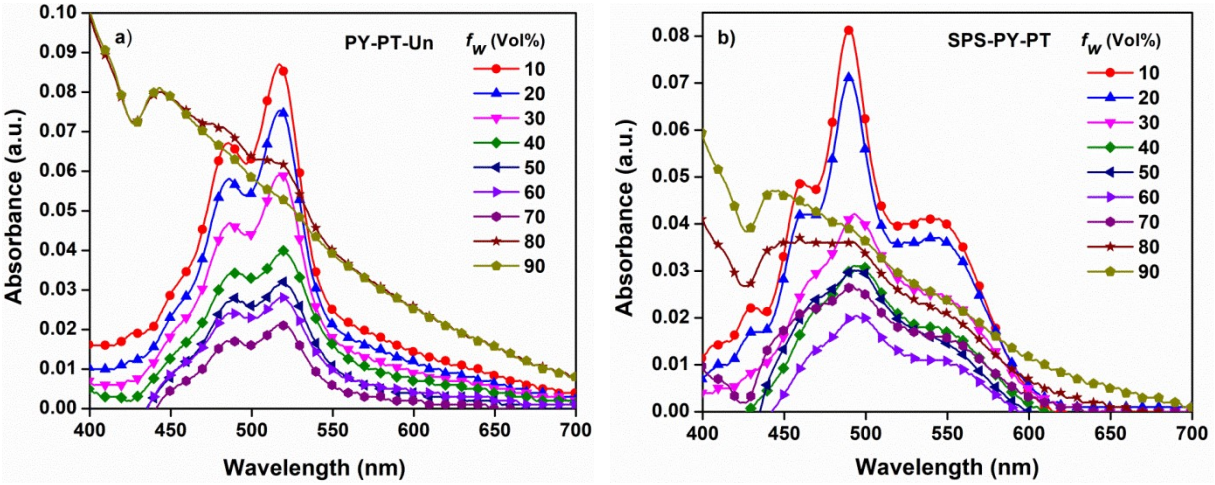


Fig. S7 UV absorption spectra of aggregation of a) PY-PT-Un and b) SPS-PY-PT in different water fractions.

Table S1. QY of the PY-PT-Un and SPS-PY-PT in THF+Water ratio.

S.No.	f_W (Vol%)	PY-PT-Un (QY)	SPS-PY-PT (QY)
1.	10	0.000122	0.004242587
2.	20	0.000525	0.003492098
3.	30	0.000505	0.009196753
4.	40	0.000876	0.013228668
5.	50	0.001301	0.014105453
6.	60	0.000318	0.022169006
7.	70	0.000201	0.019802695
8.	80	5.78E-06	0.003442246
9.	90	5.76E-05	0.001020381

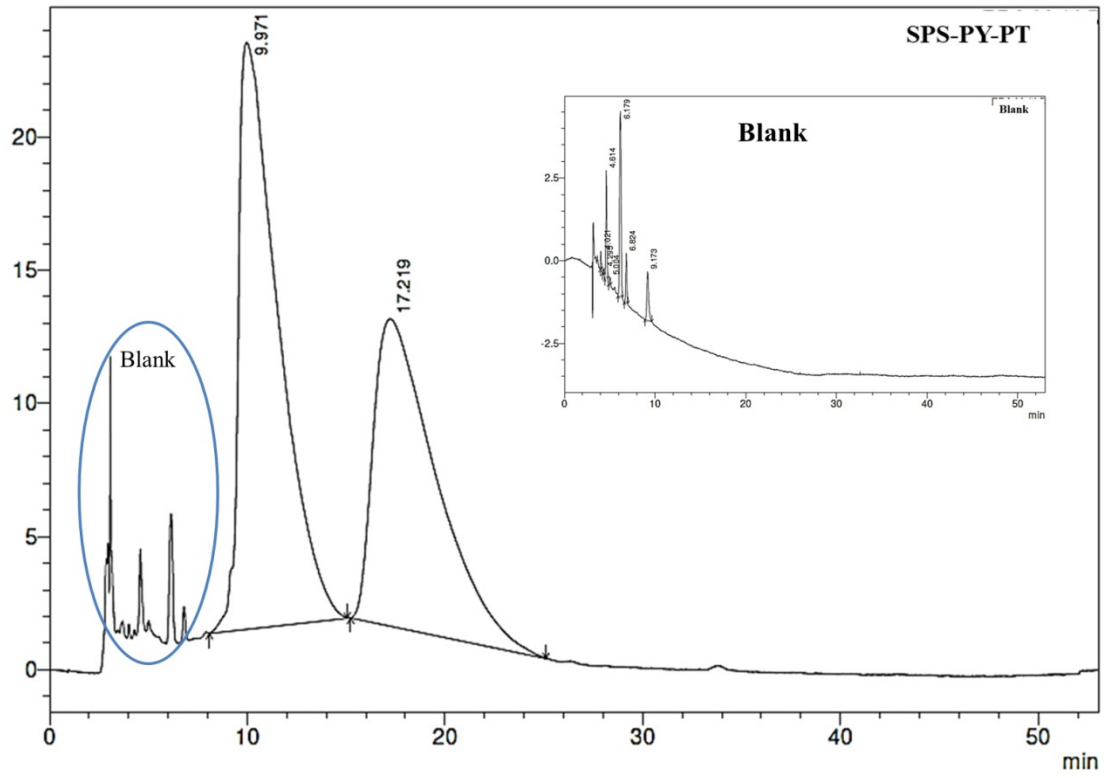


Fig. S8 HPLC spectra of the SPS-PY-PT and inset with its blank sample.

[Resolution of the enantiomers of SPS-PY-PT by analytical HPLC. The enantiomers of SPS-PY-PT (i.e. M and P-isomer) were resolved from a racemic mixture dissolved in 20% Isopropyl alcohol/hexane. This solution was injected in 50-µL onto a CHIRALPAK IA (4.6mm X 250mm,5 µm) with 20% Isopropyl alcohol/hexane eluent flowing at 1ml/min at room temperature].

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.973	2894982	21299	54.208	64.955
2	17.218	2445477	11492	45.792	35.045
Total		5340459	32791	100.000	100.000

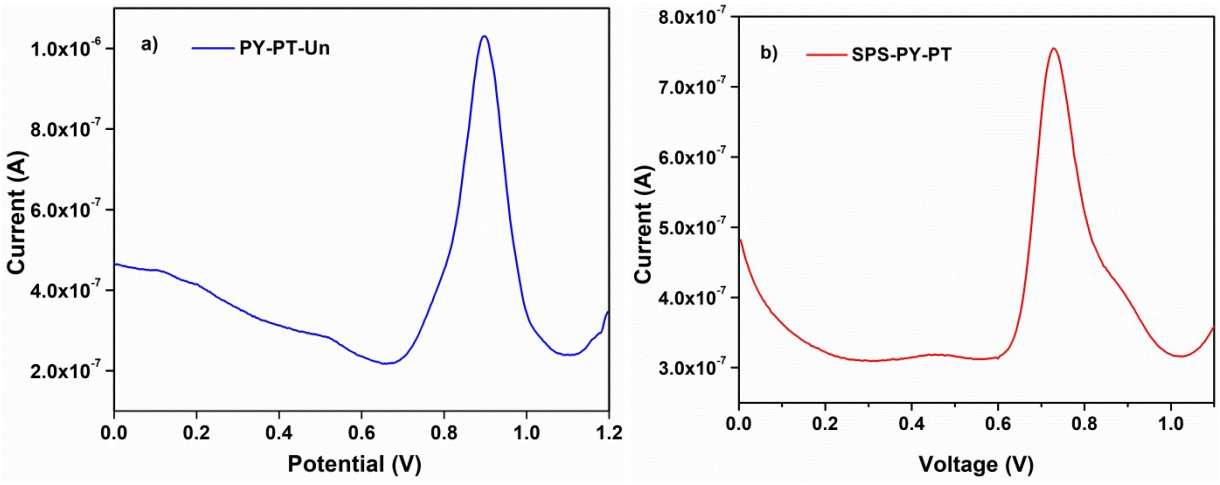


Fig. S9 DPV images of a) PY-PT-Un and b) SPS-PY-PT.

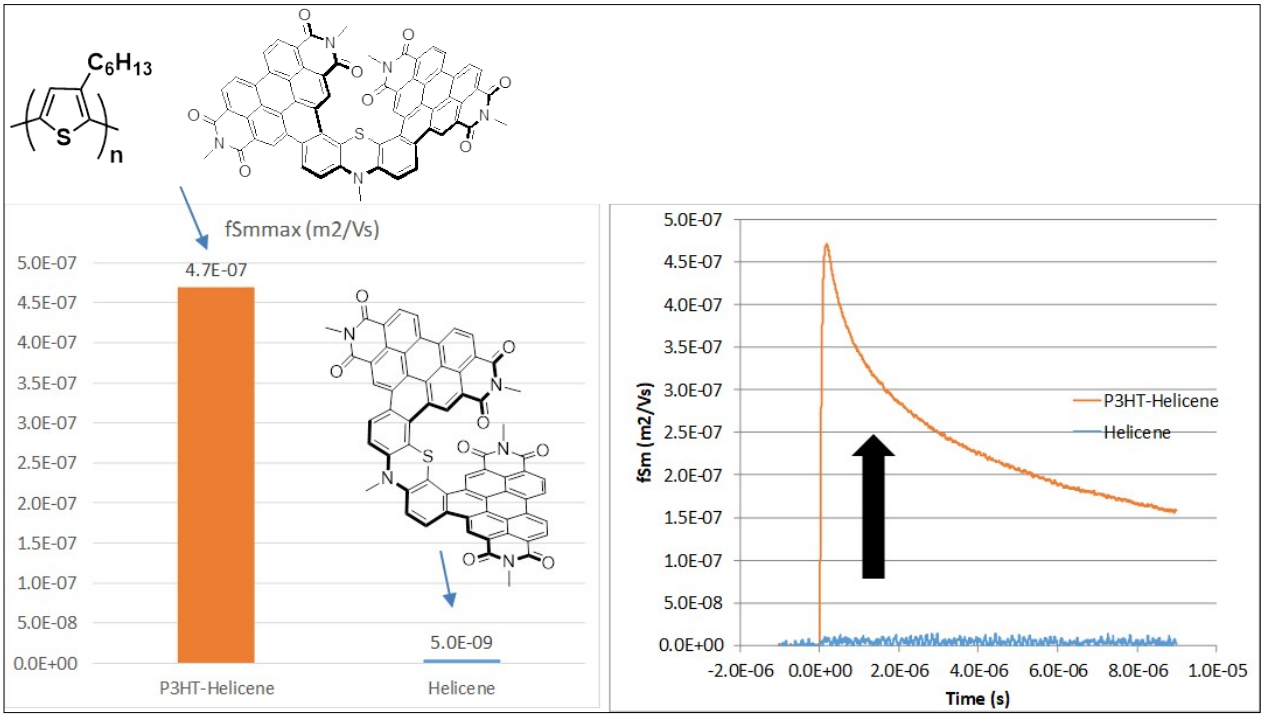


Fig. S10 TRMC signal (fSm = fSm) shows a great increase by mixing with P3HT (P3HT:helicene=1:1), indicating an efficient electron transfer from P3HT to helicene. [TRMC (ex 355nm, I0=4.6x10^{15} photons/cm^2)]

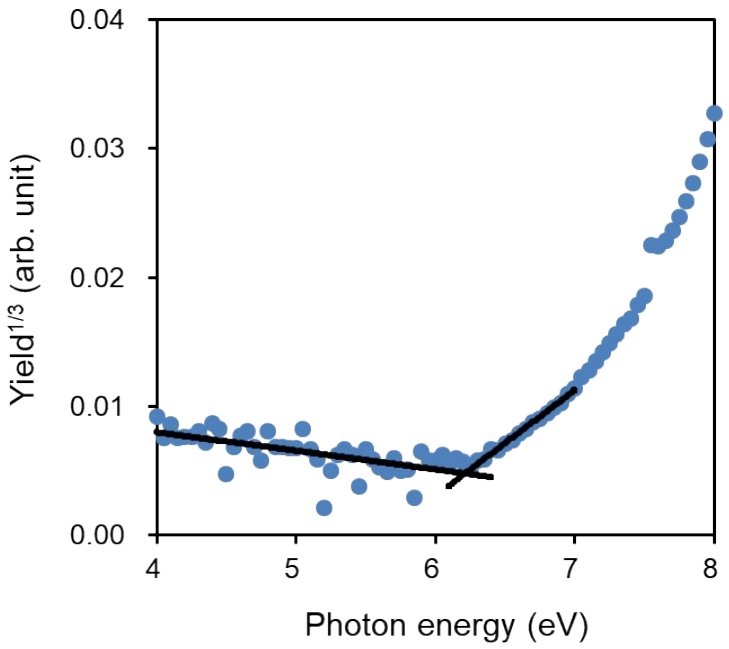


Fig. S11 PYS spectrum of SPS-PY-PT film. The black lines are the interpolated curves to calculate the HOMO energy level from the vacuum.

[PYS (photoelectron yield spectroscopy) result shows a very deep HOMO level of -6.21 eV in the film state. If we suppose the bandgap energy of 2.0 eV, the LUMO level is calculated to be -4.21 eV, which is enough deep to facilitate electron transfer from P3HT (HOMO=-4.92eV, LUMO=-2.98 eV)].

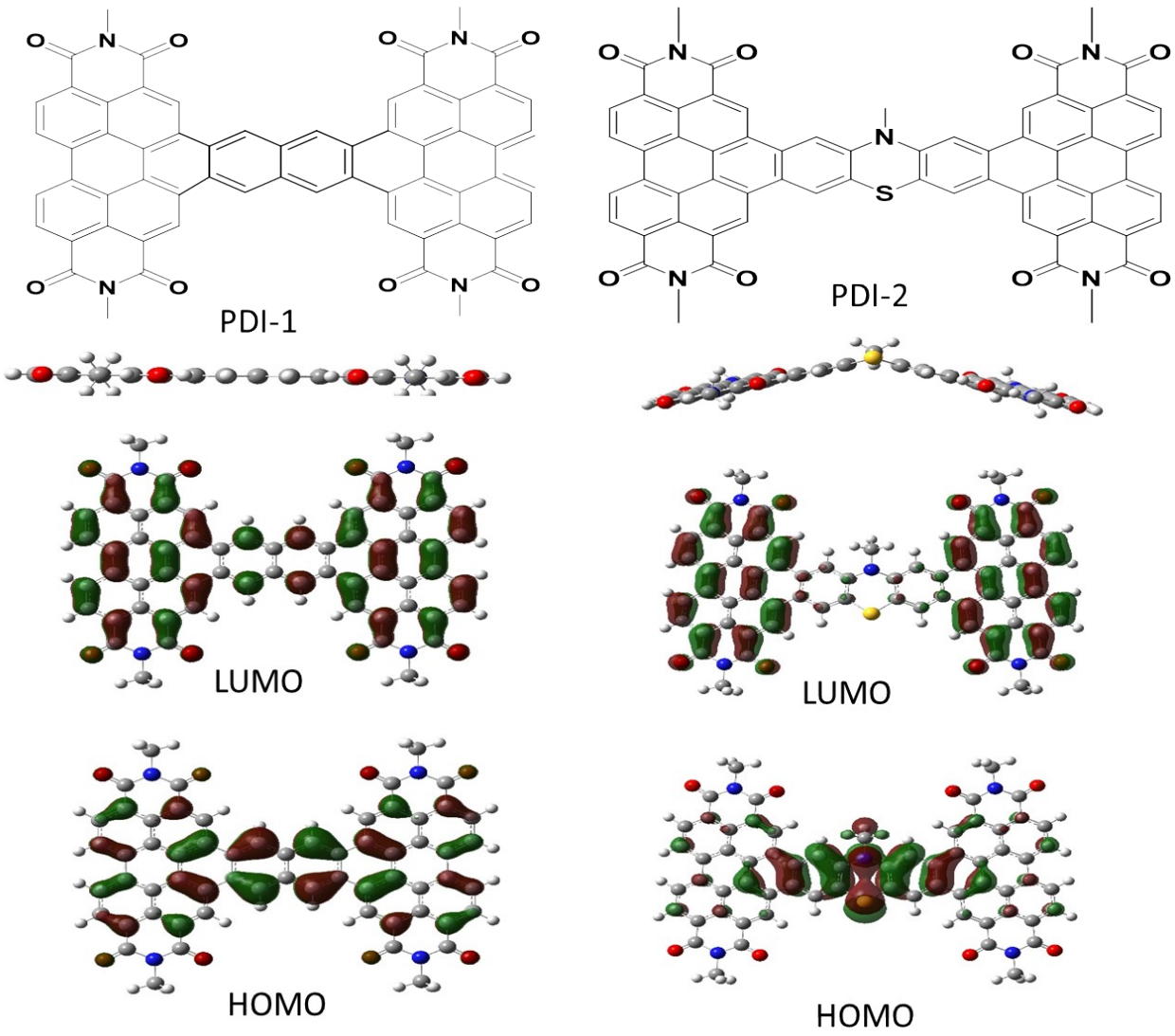


Fig. S12 PDI -1 and PDI-2 molecules and their Optimization, HOMO-LUMO orbitals (B3LYP 6-31G(d,p) Alkyl chains were replaced by methyl for simplicity).

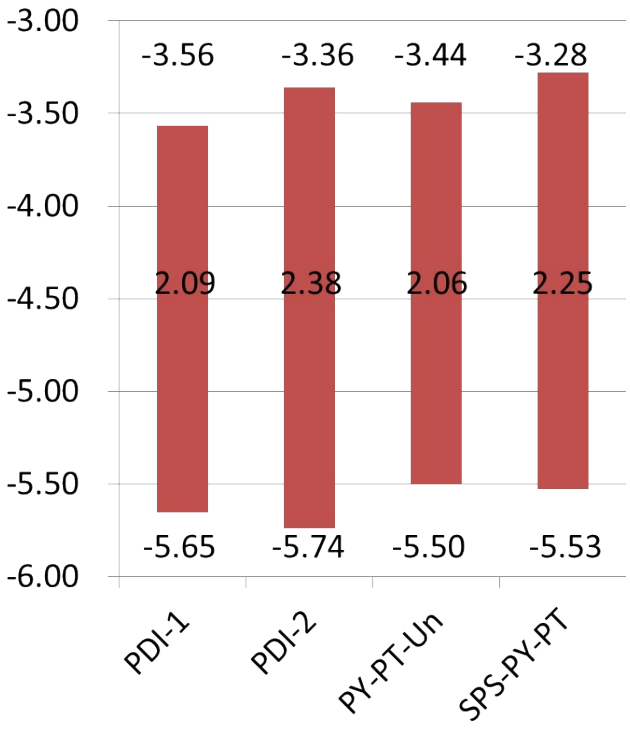
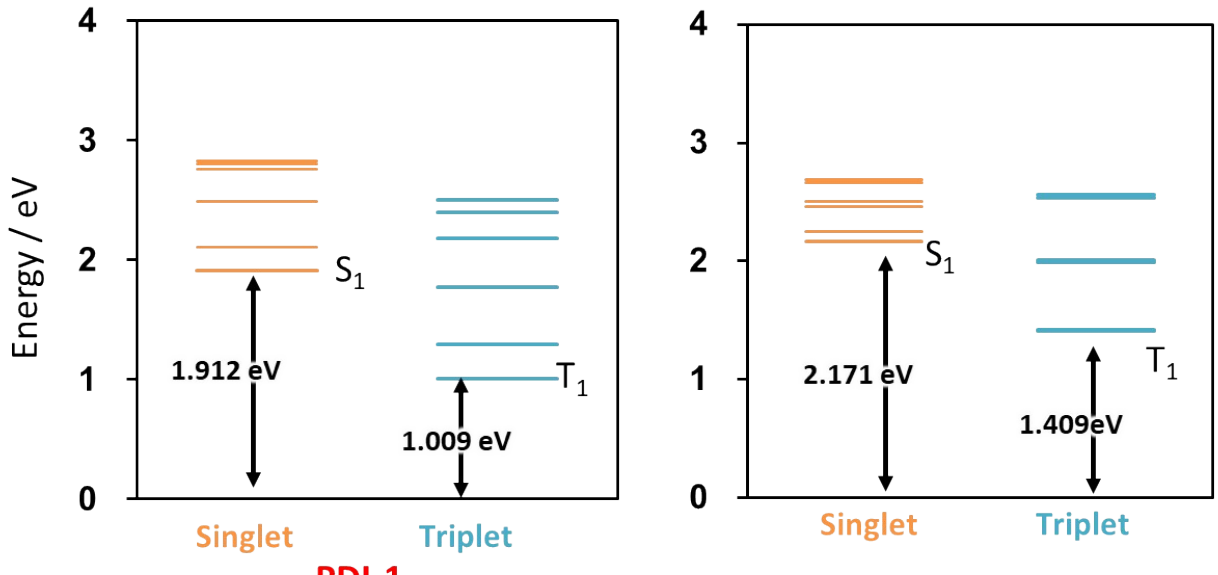


Fig. S13 Comparative statement of HOMO-LUMO.



PDI-1

ΔE_{ST} (eV)	0.9030
f(S_0-S_1)	0.1948
$\Delta E(S_0\text{-}S_1)$ (eV)	1.9122
$\Delta E(S_0\text{-}T_1)$ (eV)	1.0092

PDI-2

ΔE_{ST} (eV)	0.7621
f(S_0-S_1)	0.3918
$\Delta E(S_0\text{-}S_1)$ (eV)	2.1707
$\Delta E(S_0\text{-}T_1)$ (eV)	1.4086

Fig. S14 Singlet and triplet energy levels of PDI-1 and 2.

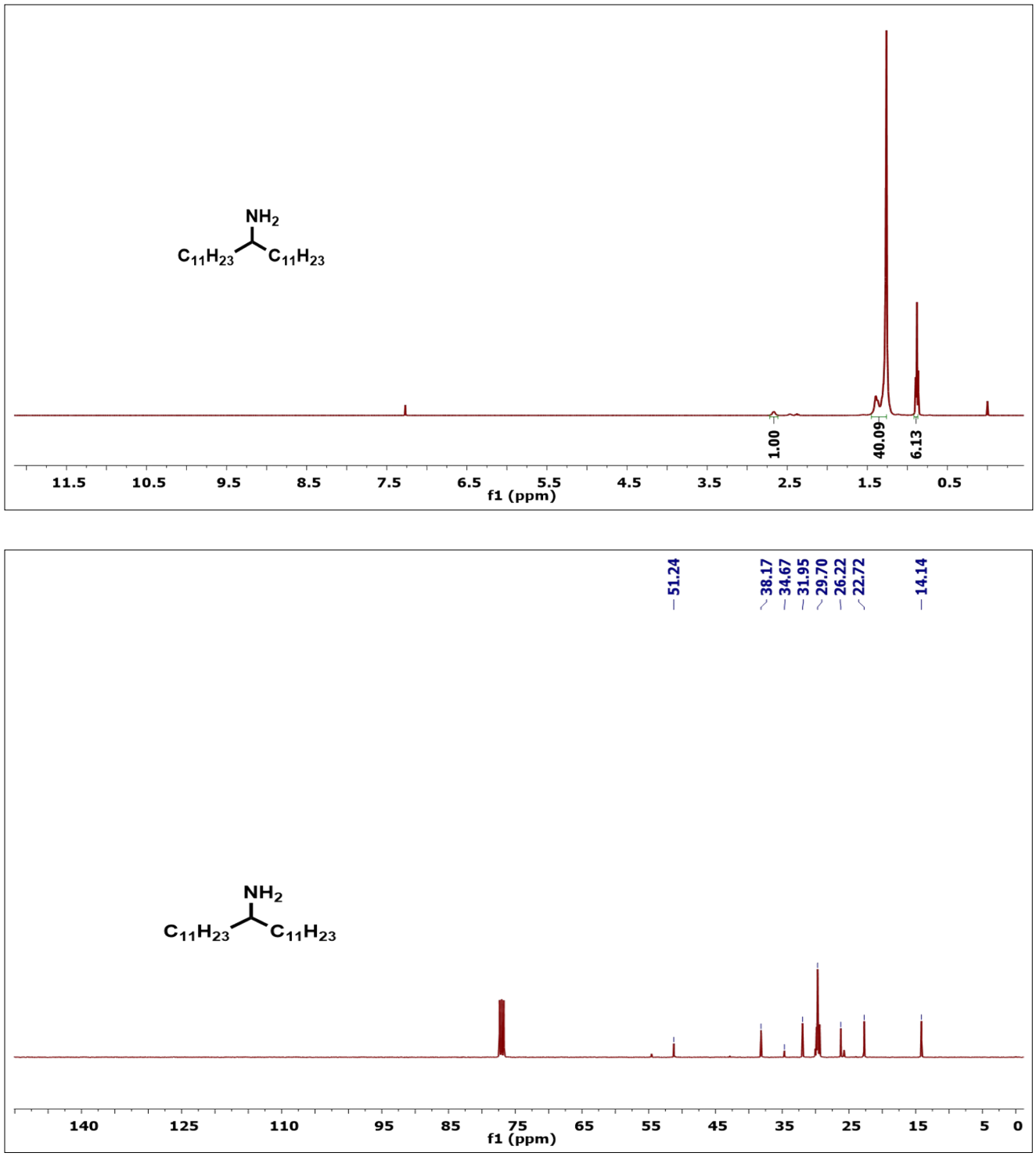
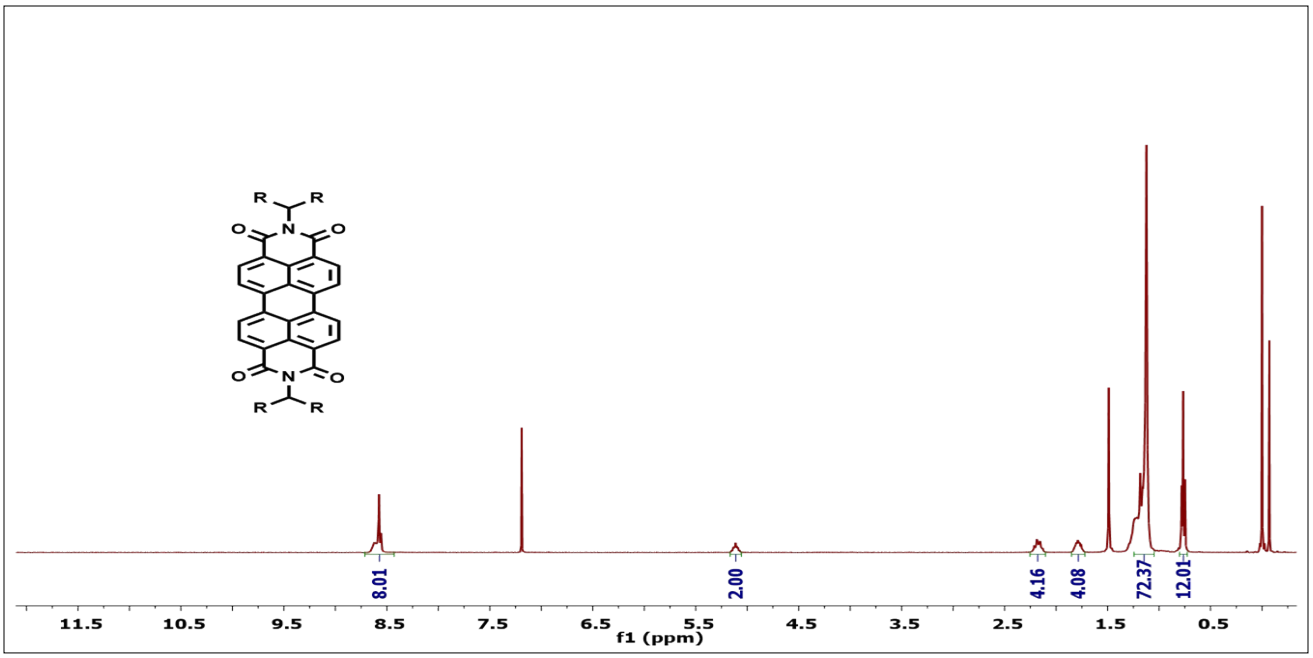


Fig. S15 ^{1}H AND ^{13}C NMR spectra of **1.**



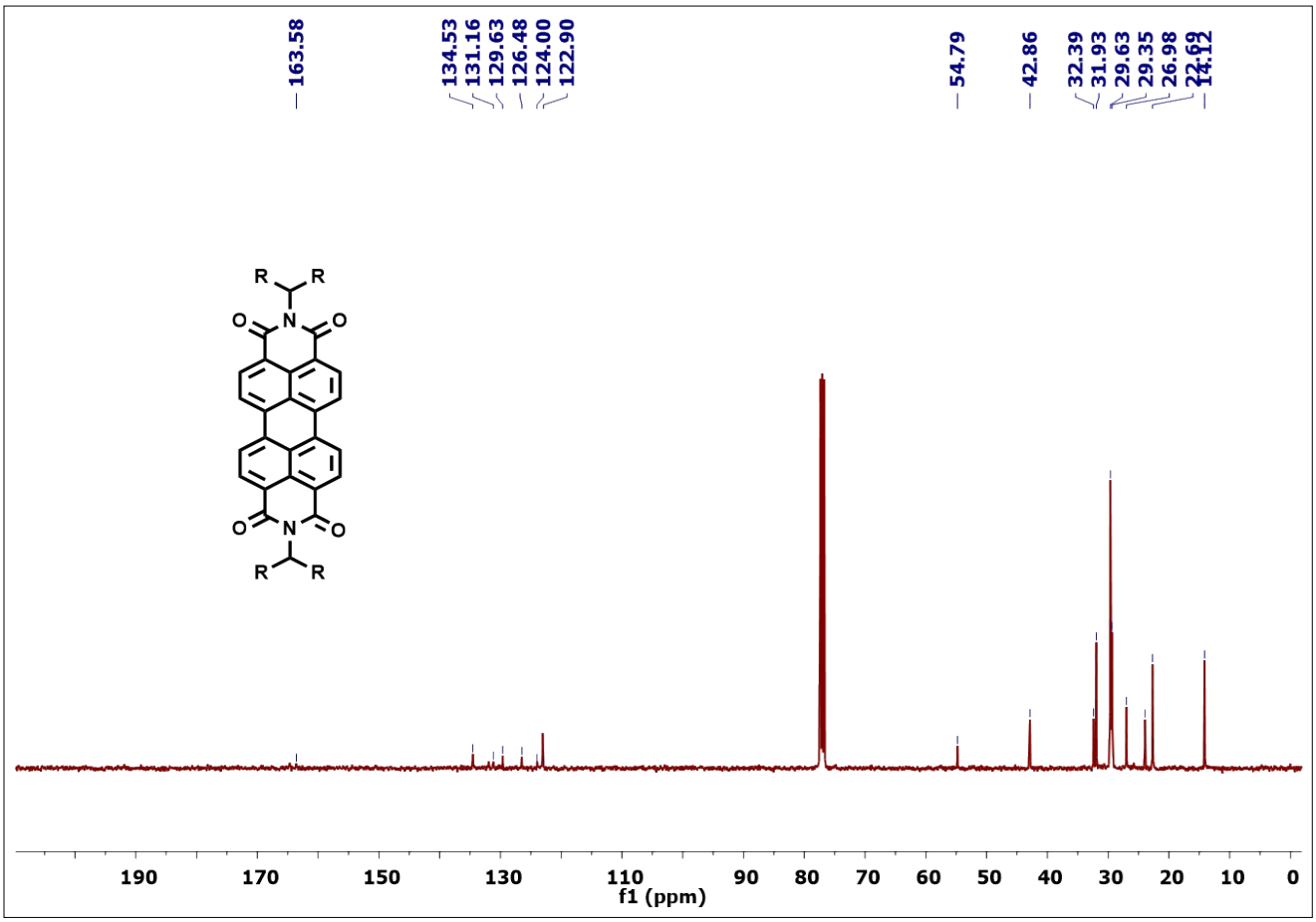


Fig. S16 ^{1}H AND ^{13}C NMR spectra of **2.**

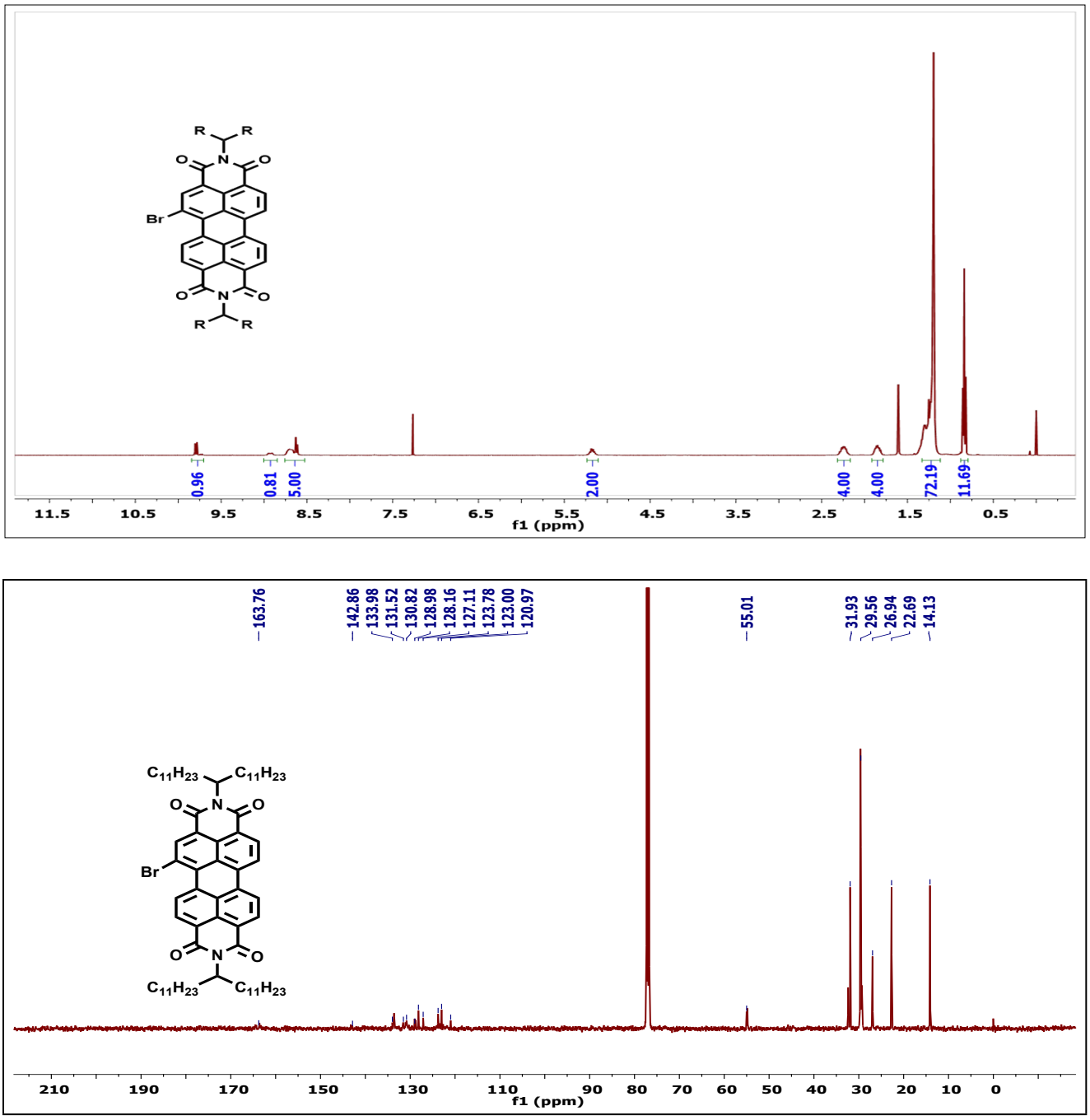


Fig. S17 ^{1}H And ^{13}C NMR spectra of **3.**

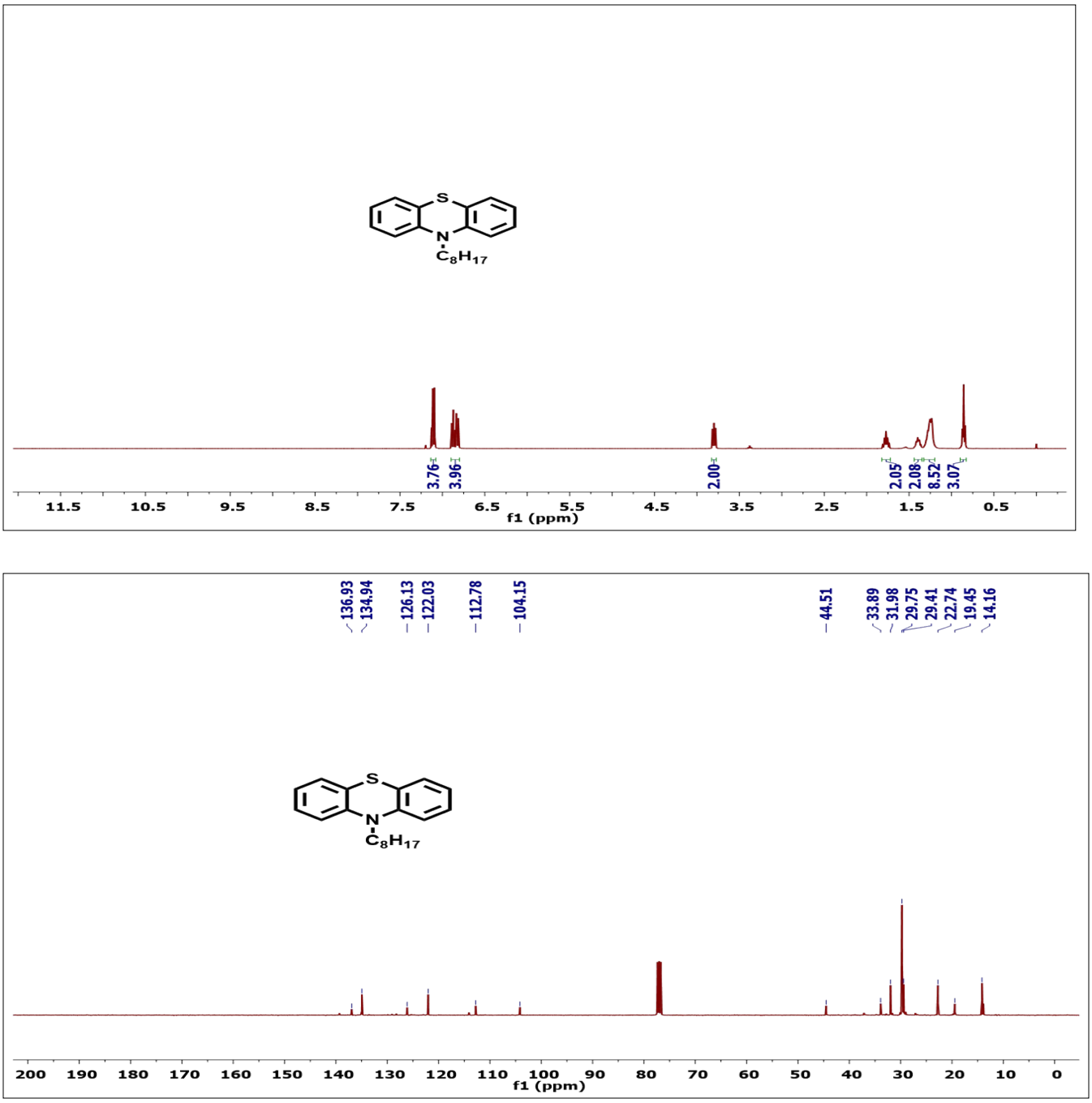
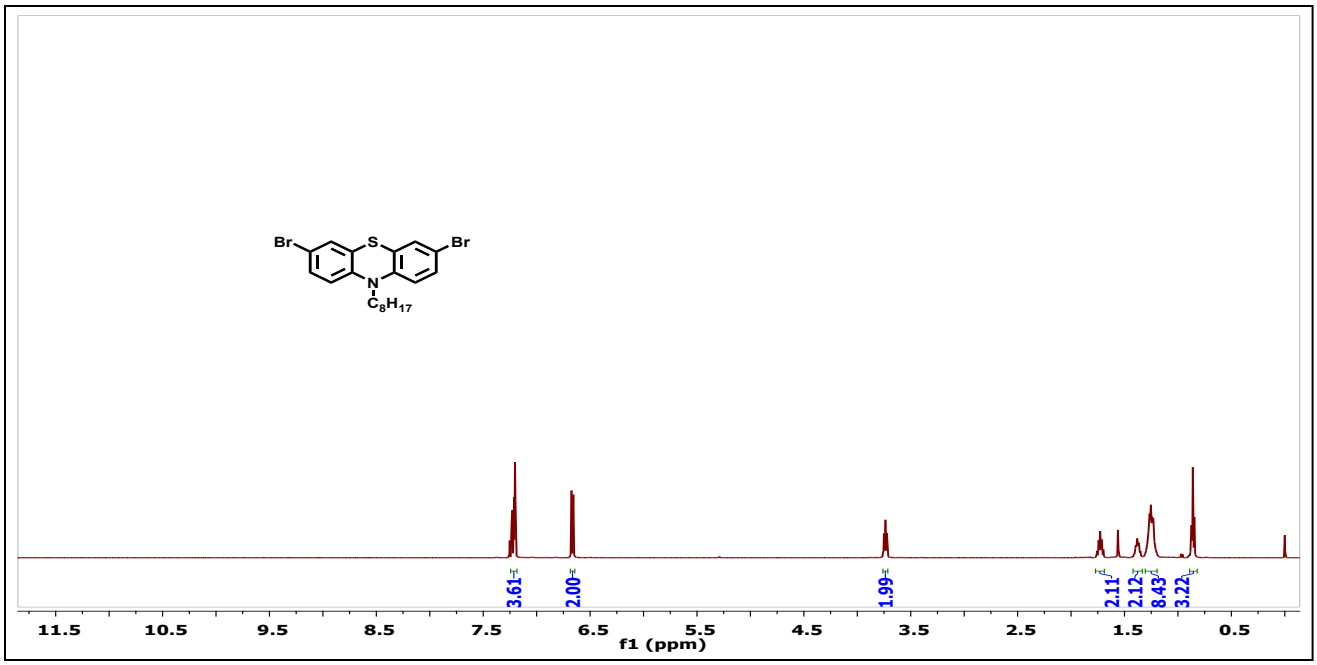


Fig. S18 ^{1}H And ^{13}C NMR spectra of **4.**



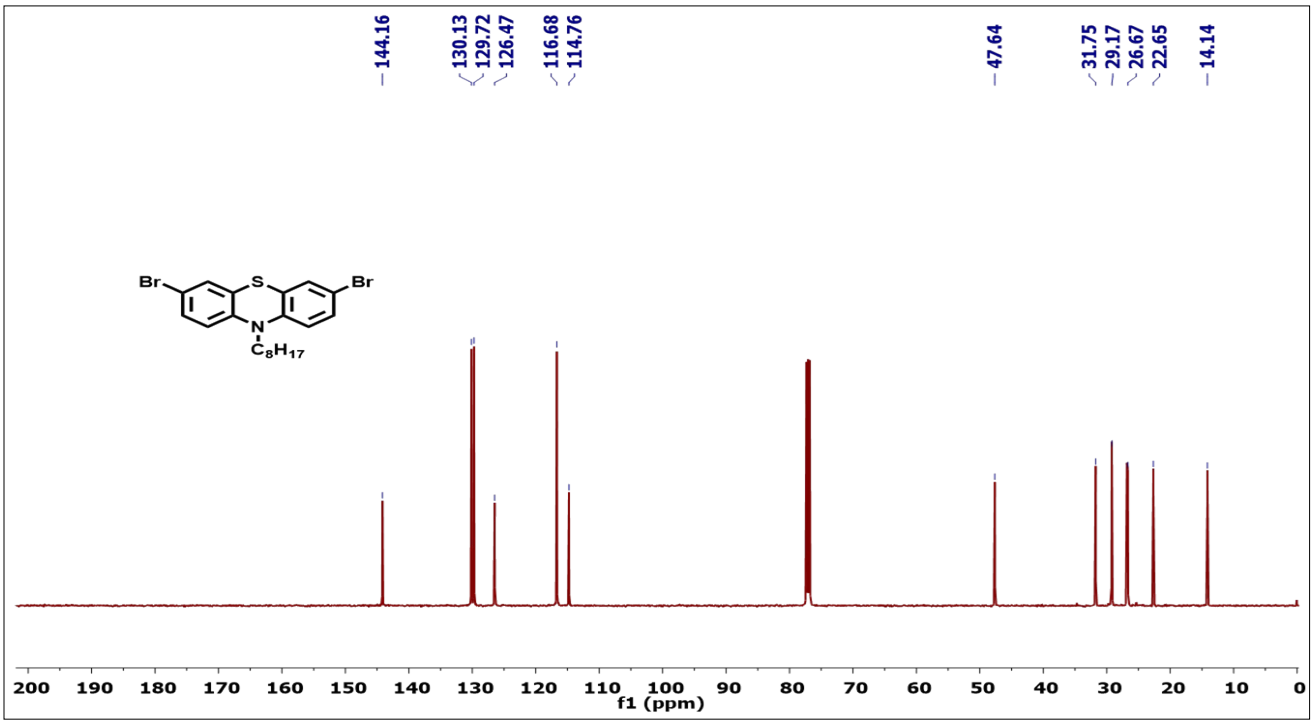


Fig. S19 ^{1}H AND ^{13}C NMR spectra of **5.**

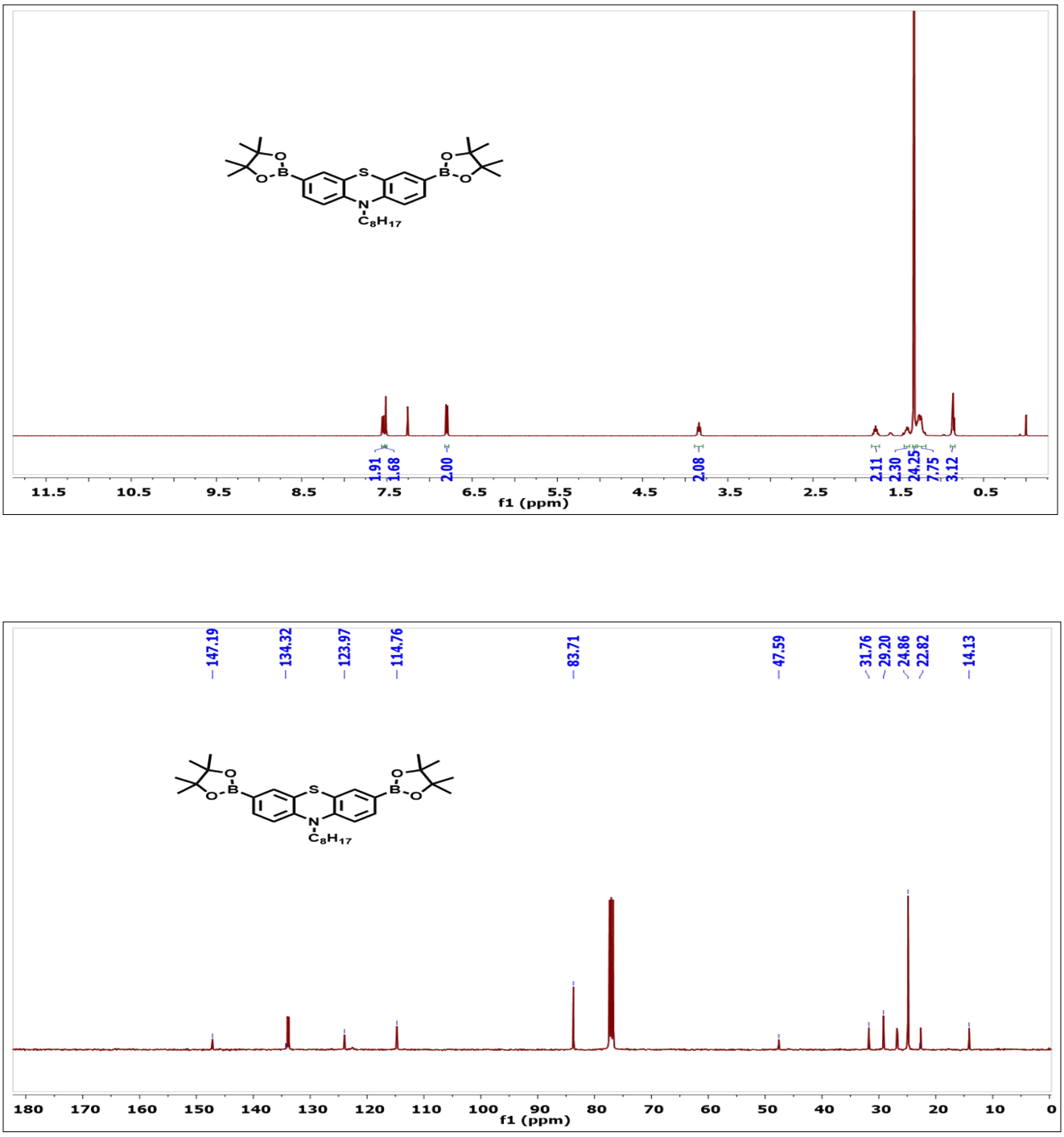


Fig. S20 ^{1}H AND ^{13}C NMR spectra of **6.**

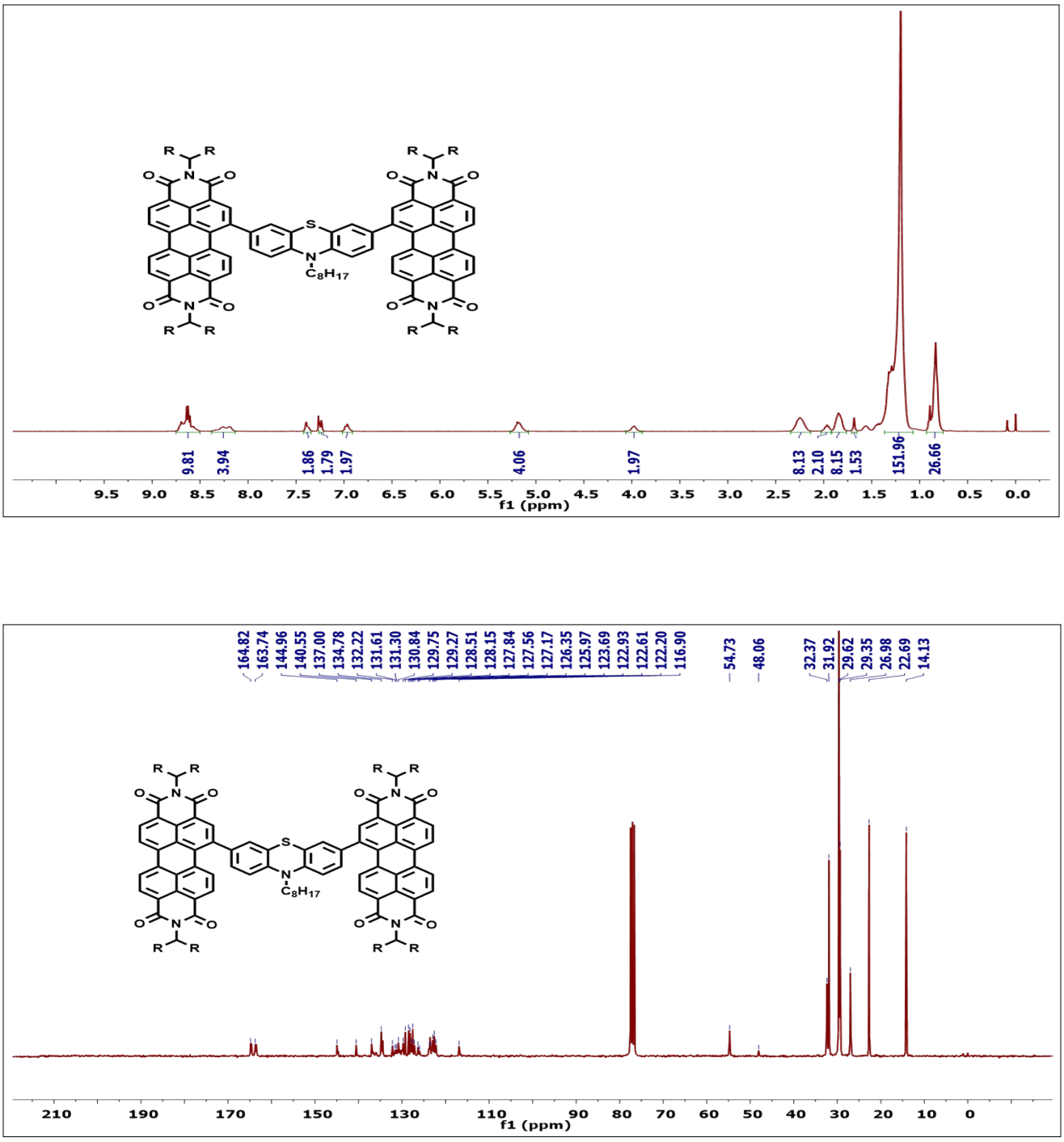


Fig. S21 ^{1}H AND ^{13}C NMR spectra of **PY-PT-Un.**

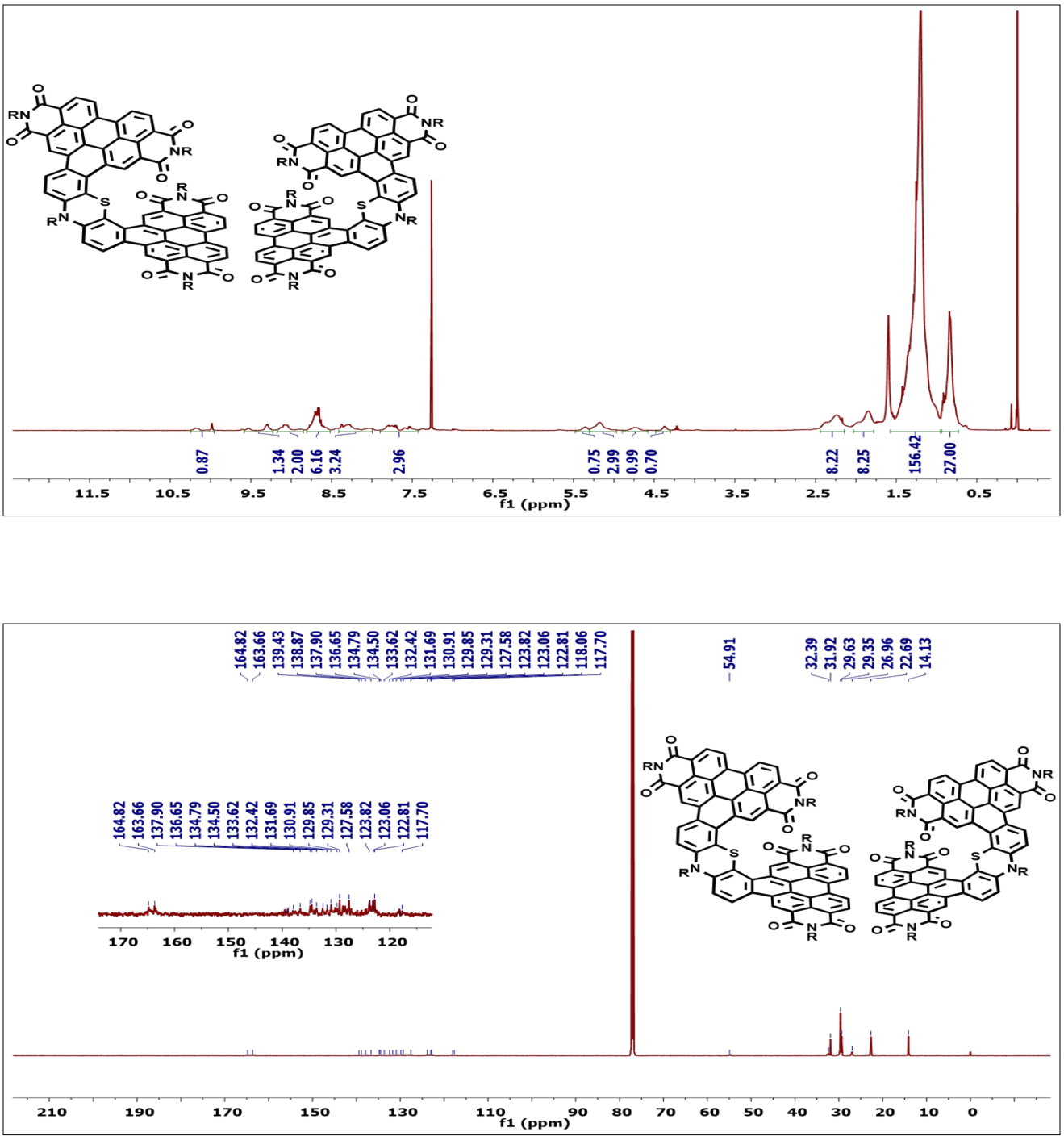


Fig. S22 ^{1}H AND ^{13}C NMR spectra of **SPS-PY-PT.**

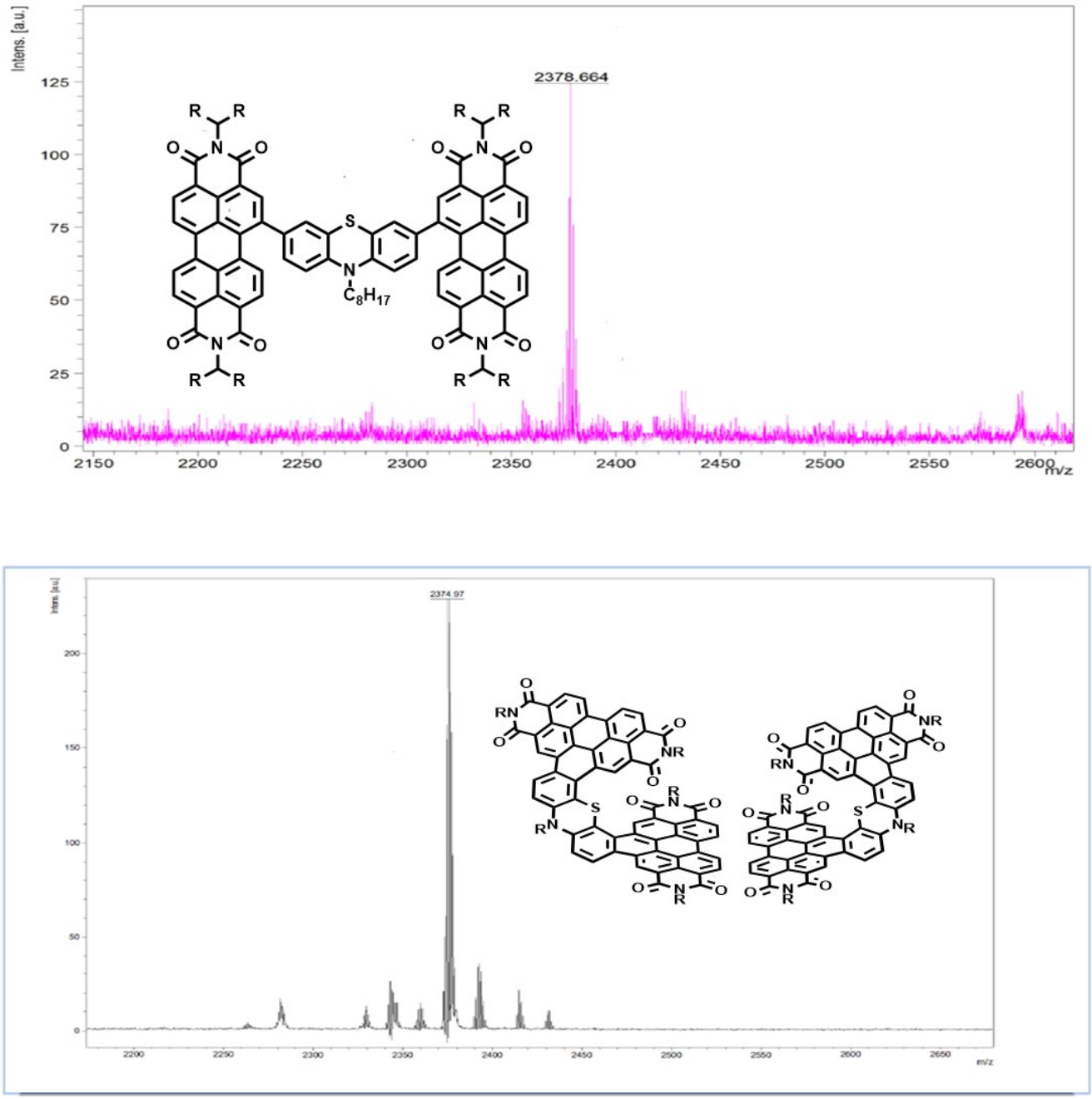


Fig. S23 MALDI-TOF of **PY-PT-Un and SPS-PY-PT.**

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