Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Pentacenequinone Derivatives: Aggregation-Induced Emission Enhancement, Mechanism and Fluorescent Aggregates for Superamplified Detection of Nitroaromatic Explosives

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Experimental

General information

All reagents were purchased from Aldrich and were used without further purification. The UV/vis and fluorescence spectra were recorded with Shimdzu UV-2450 spectrophotometer and Shimadzu RF-5301(PC) spectrofluorophotometer, respectively. The SEM images were recorded from Scanning Electron Microscope (SEM)-ZeissEV040. The time-resolved fluorescence spectra were recorded with a HORIBA time-resolved fluorescence spectrometer. Elemental analysis (C, H, N) was performed on a Flash EA 1112 CHNS-O analyzer (Thermo Electron Corp.). ^{1}H NMR were recorded on a JOEL-FT NMR–AL 300 MHz spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane $SiMe_4$ as internal standards. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet m = multiplet), coupling constants J (Hz), integration, and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography.

Calculations for quantum yield[1]:

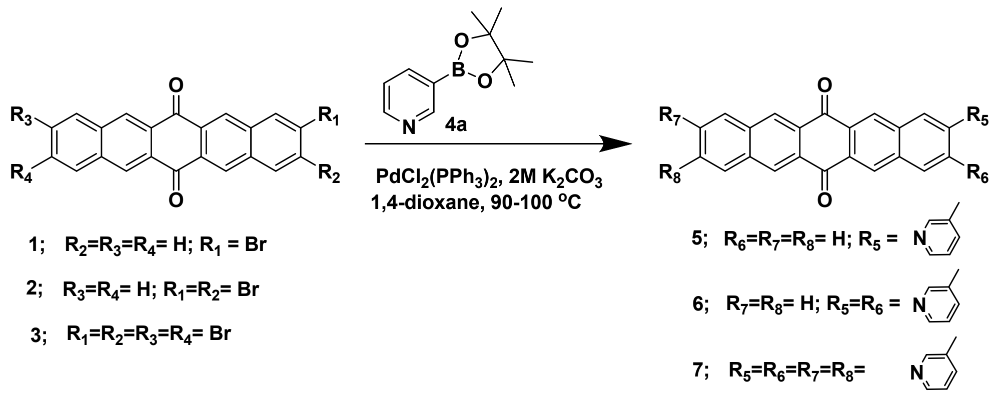
Fluorescence quantum yield was determined using optically matching solutions of diphenylanthracene (Φ_{fr} = 0.9 in cyclohexane) as standard at an excitation wavelength of 352 nm and quantum yield is calculated using the equation:

$$\Phi_{fs} = \Phi_{fr} \times \frac{1-10^{-ArLr}}{1-10^{-AsLs}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

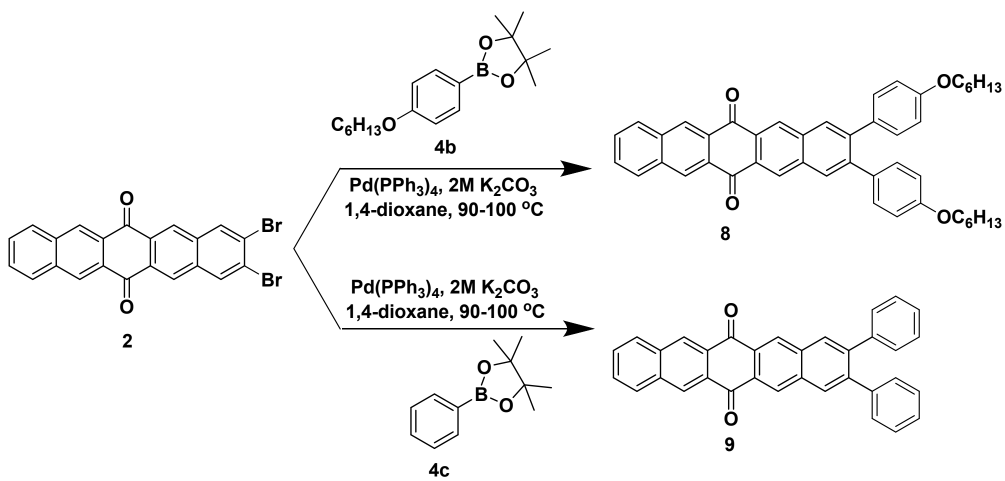
Φ_{fs} and Φ_{fr} are the radiative quantum yields of sample and the reference respectively, A_s and A_r are the absorbance of the sample and the reference respectively, D_s and D_r the respective areas of emission for sample and reference. Ls and L_r are the lengths of the absorption cells of sample and reference respectively. N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed respectively).

[1] Demas, J. N.; Grosby, G. A. *J. Phys. Chem*. **1971**, *75*, 991-1024.

Synthetic scheme of derivative5-9



Scheme 1. Pentacenequinone based derivatives **5-7**.



Scheme 2. Pentacenequinone based derivatives **8** and **9**.

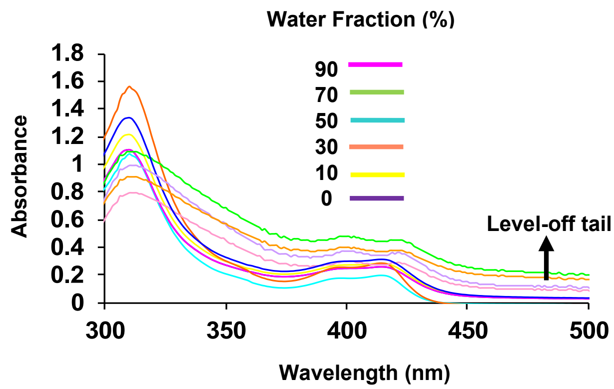


Fig. S1 Absorption spectra of derivative **5** (10 μM) showing the variation of absorption intensity in a H_2O/DMSO mixture with different water fractions.

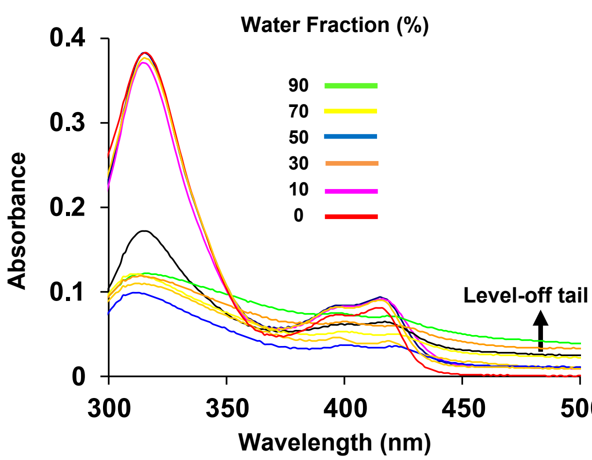


Fig. S2 Absorption spectra of derivative **6** (10 μM) showing the variation of absorption intensity in a H_2O/DMSO mixture with different water fractions.

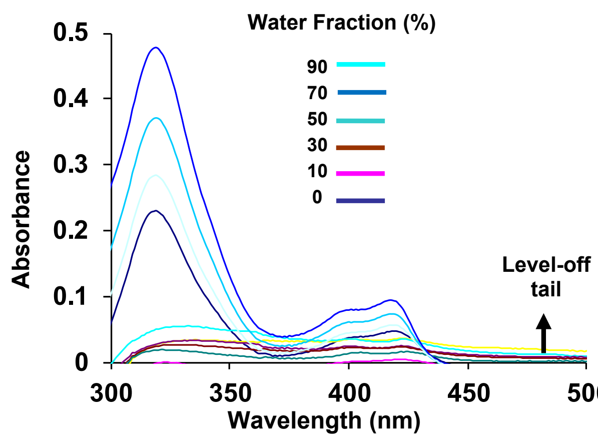


Fig. S3 Absorption spectra of derivative **7** (10 μM) showing the variation of absorption intensity in a H_2O/DMSO mixture with different water fractions.

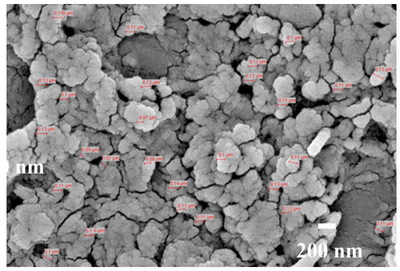


Fig. S4A SEM images of derivative **5** in H_2O/DMSO (1:1, v/v) solvent mixture. (Scale bar 200 nm)

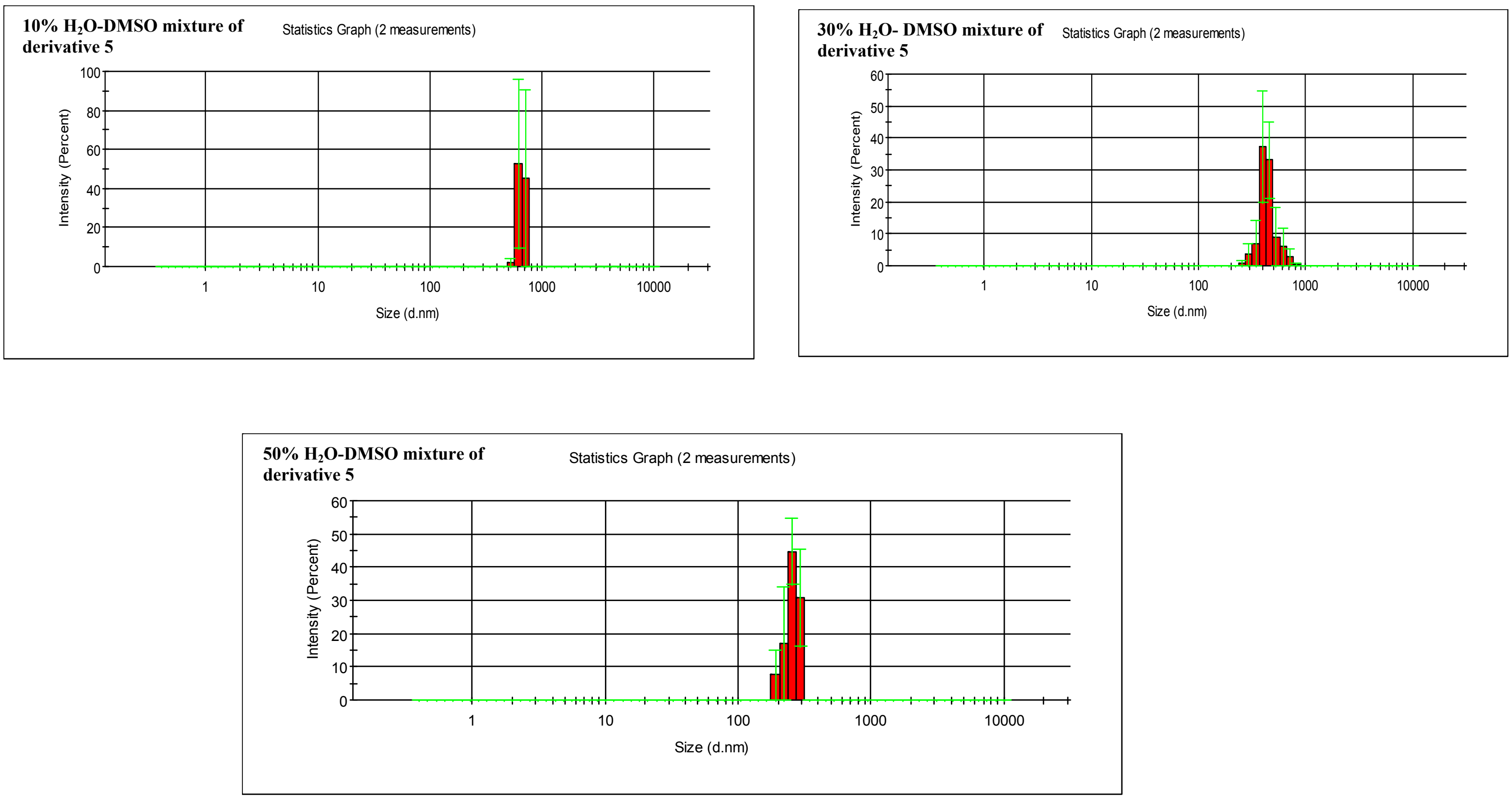


Fig. S4B: Dynamic light scattering (DLS) results showing the variation in particle size diameter with increasing water content in DMSO solution of **5**. (A) **10%** (B) **30%** and (C) **50%** water content in DMSO solution of **5**.

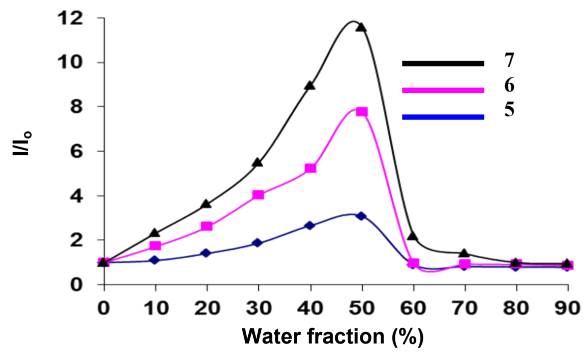


Fig. S5 Spectra of derivatives **5-7** showing the variation of fluorescence intensity in H_2O/DMSO mixture.

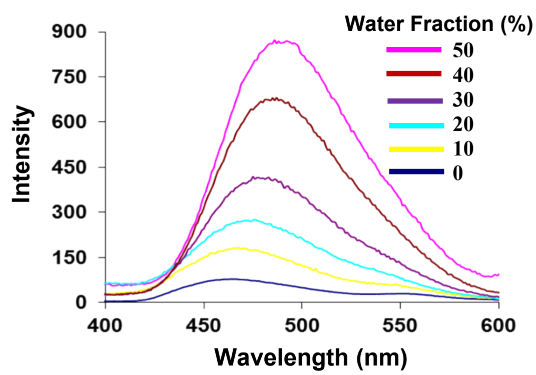


Fig. S6 Fluorescence spectra of derivative **7** (10 μM) showing the variation of fluorescence intensity in H_2O/DMSO mixtures. λex.=322 nm.

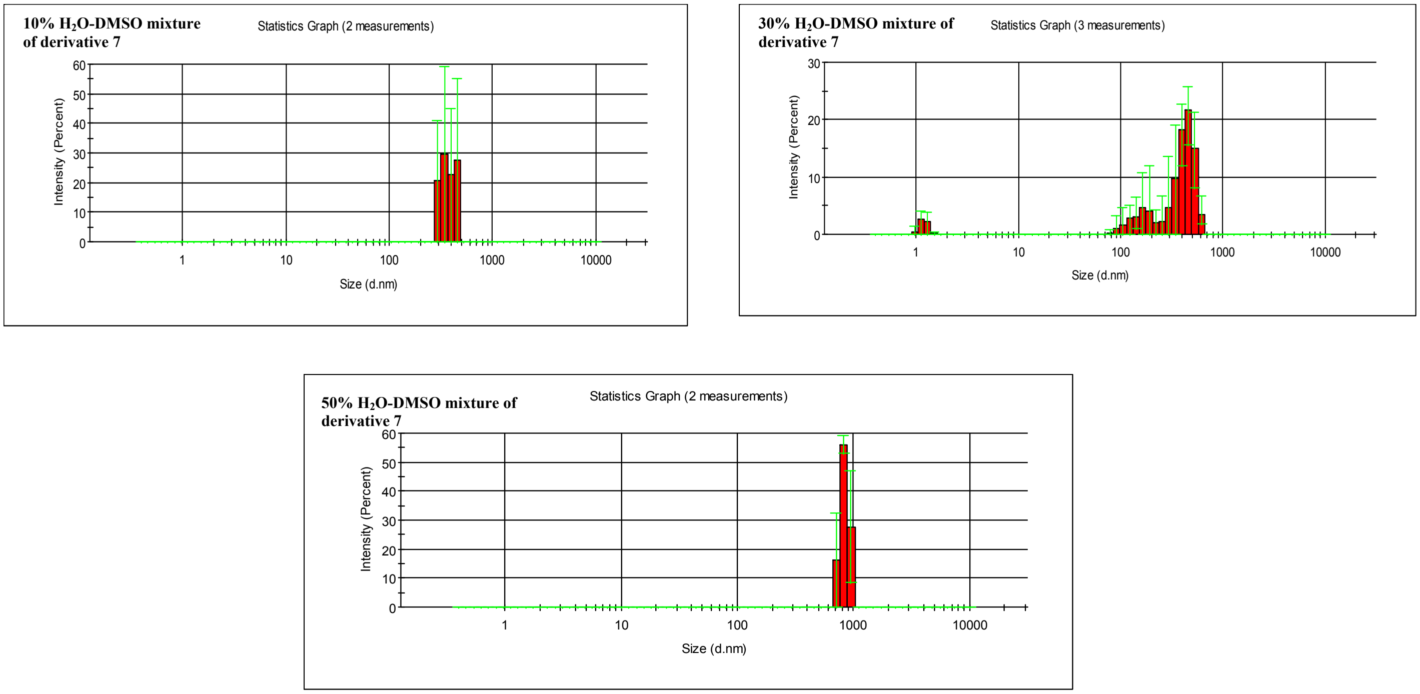


Fig. S7A: Dynamic light scattering (DLS) results showing the variation in particle size diameter with increasing water content in DMSO solution of **7**. (A) **10%** (B) **30%** and (C) **50%** water content in DMSO solution of **7**.

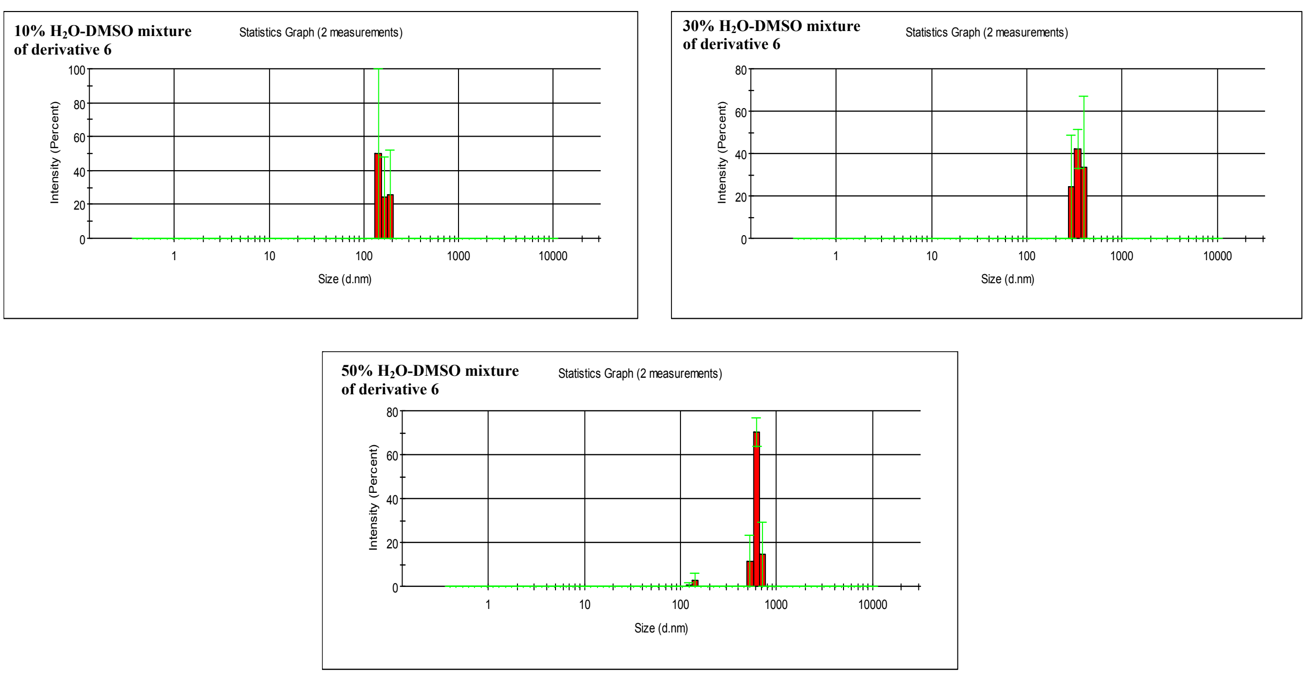


Fig. S7B: Dynamic light scattering (DLS) results showing the variation in particle size diameter with increasing water content in DMSO solution of **6**. (A) **10%** (B) **30%** and (C) **50%** water content in DMSO solution of **6**.

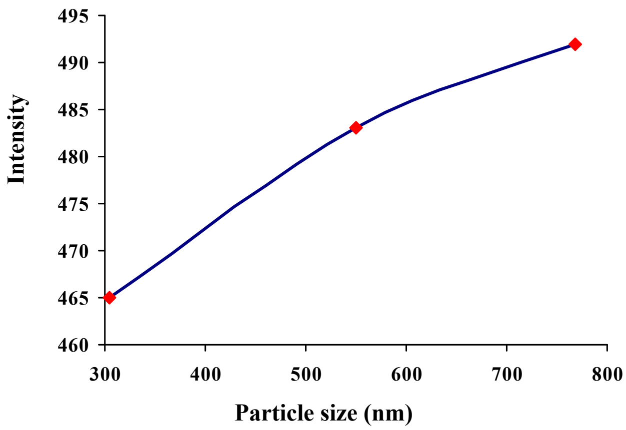


Fig. S8A Spectra of derivative **7** showing the variation of fluorescence intensity in *vs.* particle size.

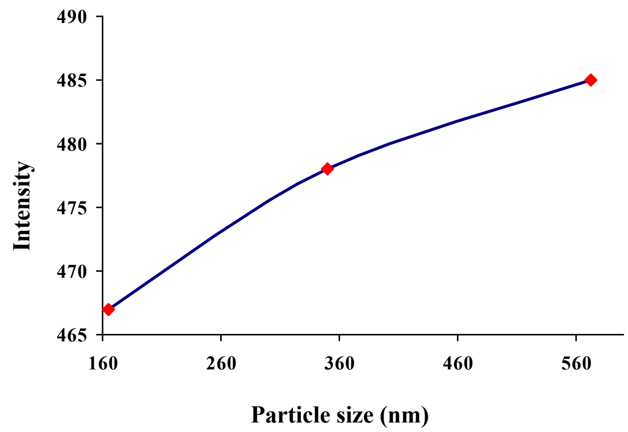


Fig. S8B Spectra of derivative **6** showing the variation of fluorescence intensity in *vs.* particle size.

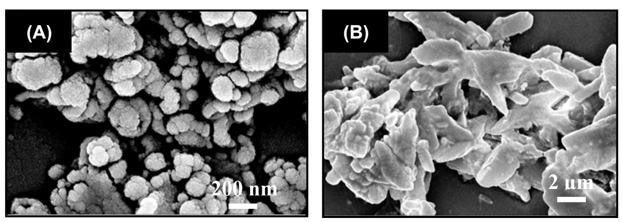


Fig. S9 SEM images of (A) **6** and (B) **7** showing the formation of aggregates. Scale bar (A) 200 nm and (B) 2 μm.

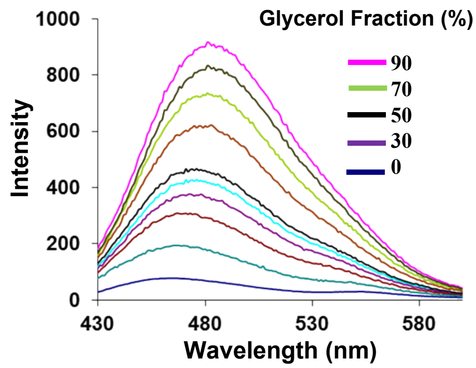


Fig. S10 Fluorescence spectra of derivative **7** (10 µM) showing the variation of fluorescence intensity in DMSO/Glycerol mixtures. λex.=322 nm.

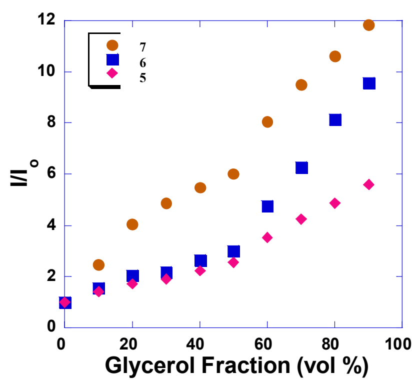


Fig. S11 Plot showing the variation in fluorescence intensity of derivatives **5-7** in DMSO/glycerol mixtures with different glycerol fractions.

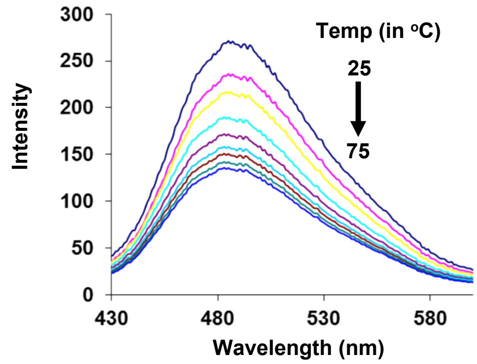


Fig. S12 Fluorescence spectra of derivative **5** (10 µM) showing the variation of fluorescence intensity with increase in temperature in H_2O/DMSO mixture (1:1, v/v). λex.=310 nm.

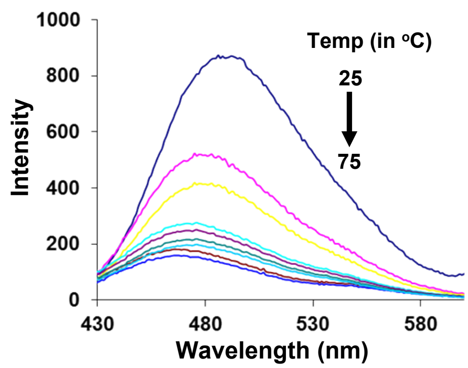


Fig. S13 Fluorescence spectra of derivative **7** (10 µM) showing the variation of fluorescence intensity with increase in temperature in H_2O/DMSO mixture (1:1, v/v). λex.=322 nm.

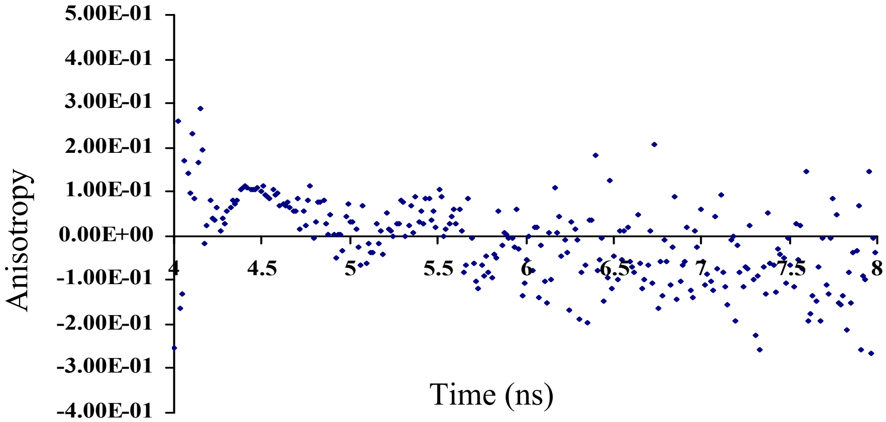


Fig. S14 Fluorescence anisotropy of derivative **7** in DMSO solution

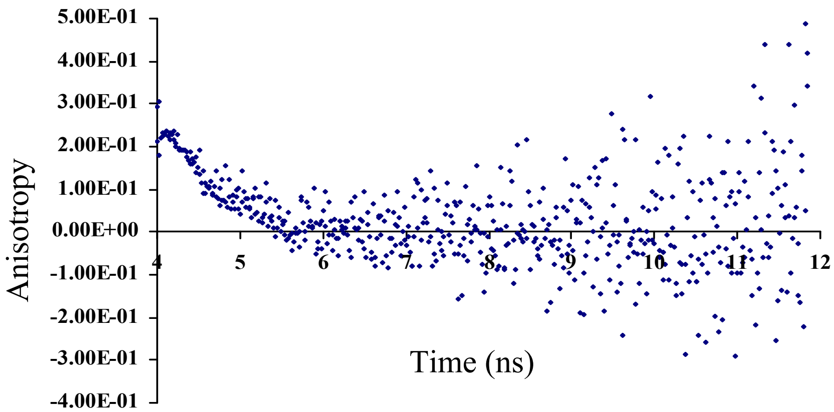


Fig. S15 Fluorescence anisotropy of derivative **7** in H_2O/ DMSO (1:1, V/V) mixture.

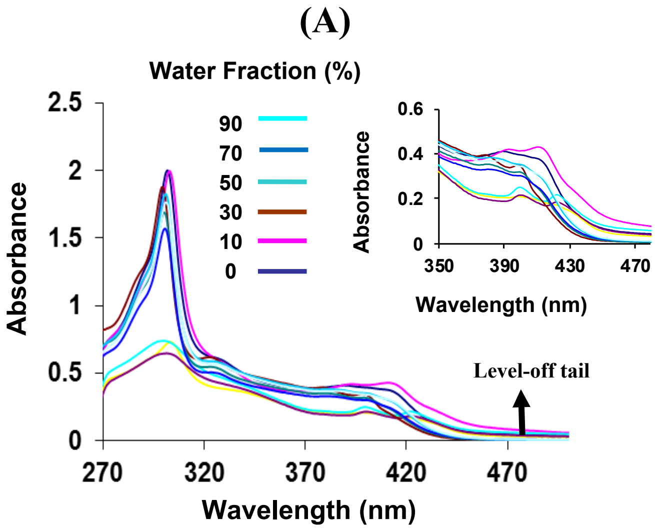


Fig. S16A Absorption spectra of derivative **8** (10 μM) showing the variation of absorption intensity in H_2O/THF mixture with different water fractions. (Inset photographs showing formation of new band at 420 nm)

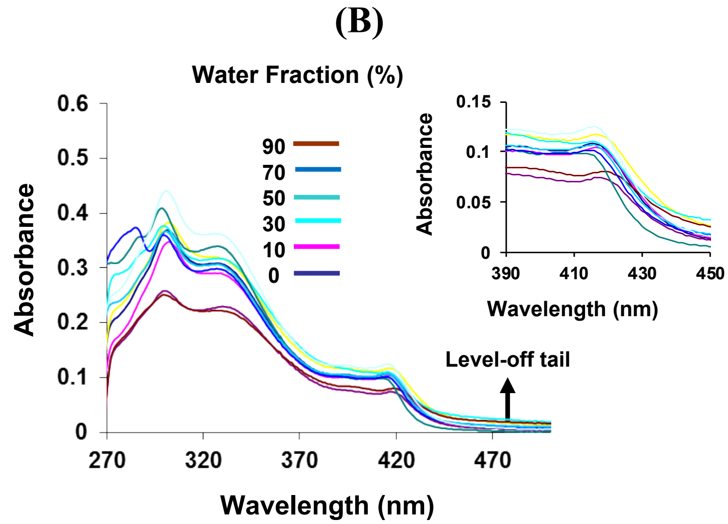


Fig. S16B Absorption spectra of derivative **9** (10 μM) showing the variation of absorption intensity in H_2O/THF mixture with different water fractions. (Inset photographs showing formation of new band at 420 nm)

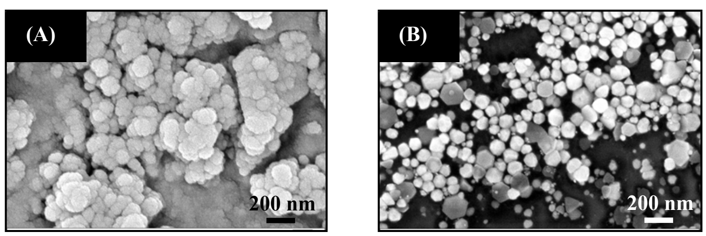


Fig. S17 SEM images of derivatives (A) **8** and (B) **9** showing formation of aggregates. Scale bar 200 nm

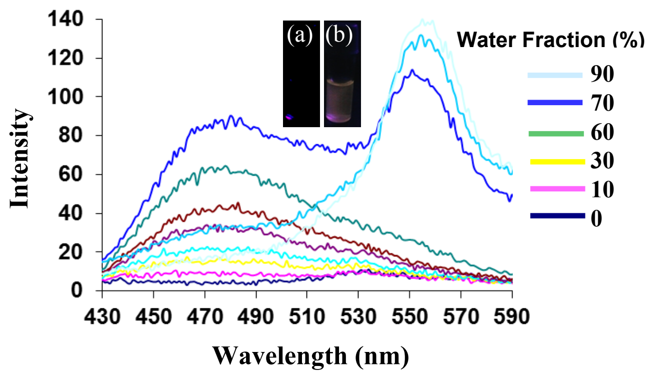


Fig. S18 Fluorescence spectra of **9** (10 μM) showing the variation of fluorescence intensity in H_2O/THF mixtures with different water fractions. Inset photographs (Under 365 nm UV-light) (a) in pure THF (b) with the addition of 90% water in THF.

Table S1. Fluorescence lifetimes (τ_F) of derivative **8-9** recorded at different H_2O/THF ratios (decay monitored at the corresponding λmax; excitation at 300 nm)

Derivative	H_2O/THF **ratio**	λ_{max} **(nm)**	τ_{F1} **(ns)**	τ_{F2}**(ns)**
Derivative 8	0/10	480	0.95	-
	7/3	480	0.283	1.96
	7/3	555	2.82	3.07
	9/1	555	3.53	6.54
Derivative 9	0/10	480	1.44	-
	7/3	480	0.00166	0.412
	7/3	555	0.429	2.31
	9/1	555	3.63	9.48

Table S2. Comparative photophysical properties of derivative **8-9:**

Derivative	Quantum yield (φ_F)[a] in solution	τ_F[b] in solution (ns)	A_1/A_2[c]	K_f[d] (s^{-1})	K_{nr}[e] ($10^9 s^{-1}$)	Quantum yield (φ_F)[f] in aggregates	A_1/A_2[g]	τ_{F1}[h] (ns)	τ_{F2}[h] (ns)	K_f[i] (s^{-1})	K_{nr}[j] ($10^9 s^{-1}$)
8	0.0039	0.957	100/0	4.07×10^6	1.04	0.24	71/29	3.53	6.54	6.7×10^7	0.21
9	0.0064	1.44	100/0	4.44×10^6	0.69	0.15	77/23	3.63	9.48	4.1×10^7	0.234

Table S2 [a] solution in THF. [b] monoexponential life time in THF. [c] A_1, A_2 : fractional amount of molecules in each environment in solution. [d] Radiative rate constant in solution ($K_f = \Phi_F/\tau_F$). [e] non-radiative rate constant in solution ($k_{nr} = (1-\Phi_F)/\tau_F$). [f] aggregates in H_2O/THF with 90 vol% of water. A_1, A_2: [g] fractional amount of molecules in each environment in aggregates. [h] τ_{F1} and τ_{F2}: biexponential life time of aggregates in 90 vol% of water in THF. [i] Radiative rate constant in aggregates ($K_f = \Phi_F/\tau_F$). [j] non-radiative rate constant in aggregates($K_{nr} = (1-\Phi_F)/\tau_F$).

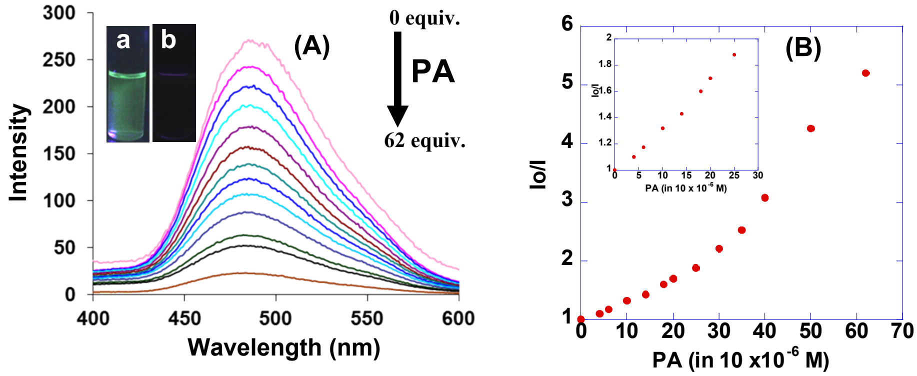


Fig. S19 (A) Change in fluorescence spectra of derivative **5** (10 μM) with the addition of PA in H_2O/DMSO (1:1) mixture, inset photograph shows the fluorescence intensity changes upon addition of PA from (a) 0 to (b) 62 equiv. (B) Stern-Volmer plot in response to PA, inset Fig. shows the Stern-Volmer plot obtained at lower concentration of PA.

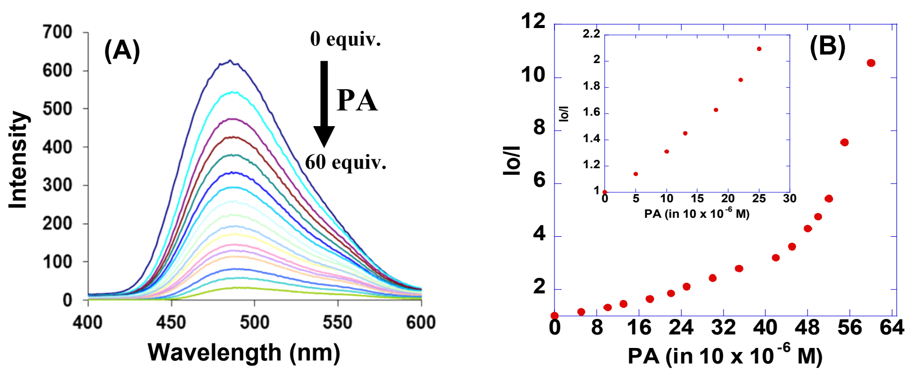


Fig. S20 (A) Change in fluorescence spectra of derivative **6** (10 μM) with the addition of PA in H_2O/DMSO (1:1) mixture, (B) Stern-Volmer plot in response to PA, inset Fig. shows the Stern-Volmer plot obtained at lower concentration of PA.

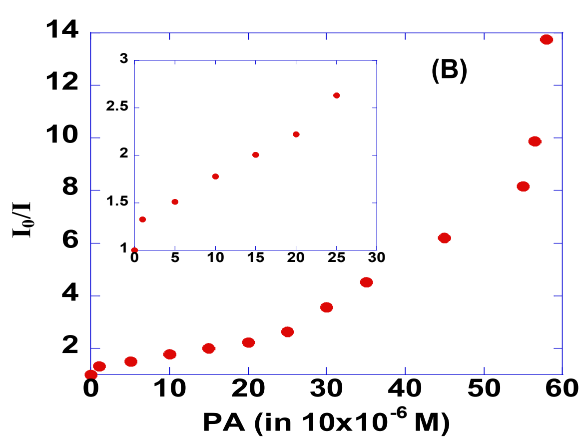


Fig. S21 Stern-Volmer plot in response to PA of derivative **7**; inset figure shows the Stern-Volmer plot obtained at lower concentration of PA.

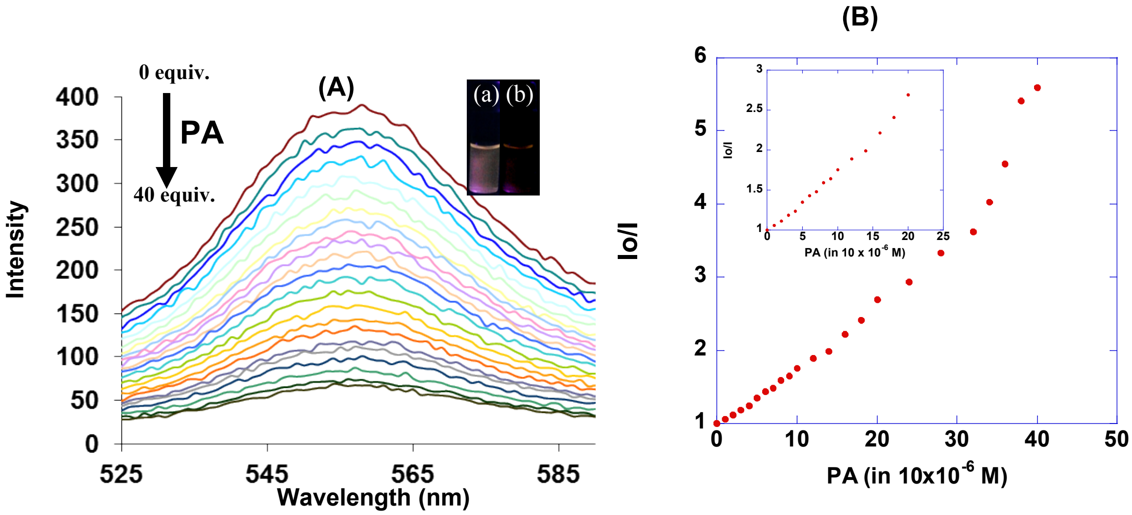


Fig. 22 (A) Change in fluorescence spectra of derivative **8** (10 μM) with the addition of PA in H_2O/THF (9:1) mixture, inset photograph shows the fluorescence intensity changes upon addition of PA from (a) 0 to (b) 40 equiv. (B) Stern-Volmer plot in response to PA, inset Fig. shows the Stern-Volmer plot obtained at lower concentration of PA.

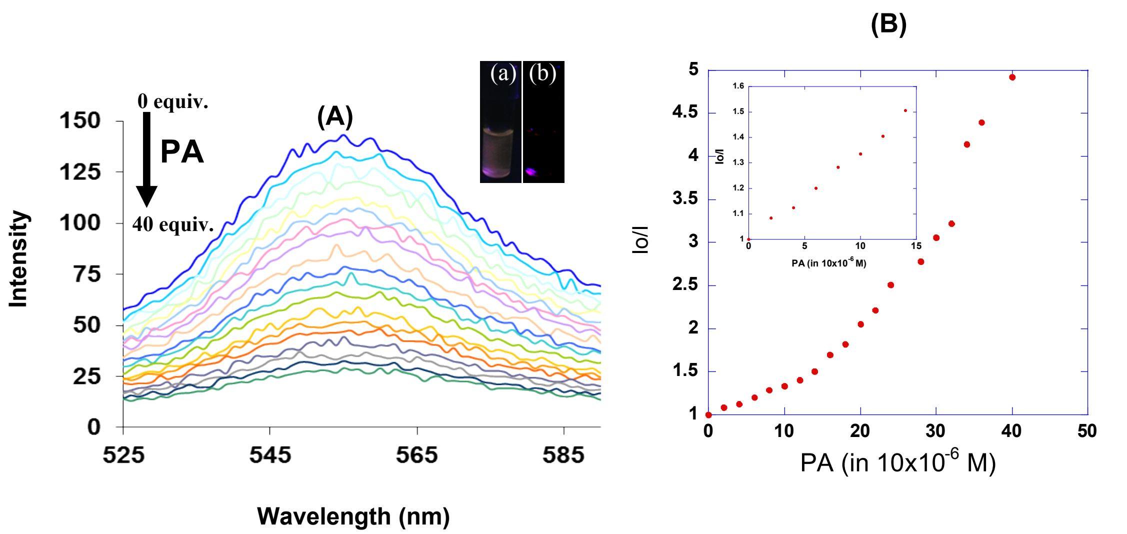


Fig. S23 (A) Change in fluorescence spectra of derivative **9** (10 μM) with the addition of PA in H_2O/THF (9:1) mixture, inset photograph shows the fluorescence intensity changes upon addition of PA from (a) 0 to (b) 40 equiv. (B) Stern-Volmer plot in response to PA, inset Fig. shows the Stern-Volmer plot obtained at lower concentration of PA.

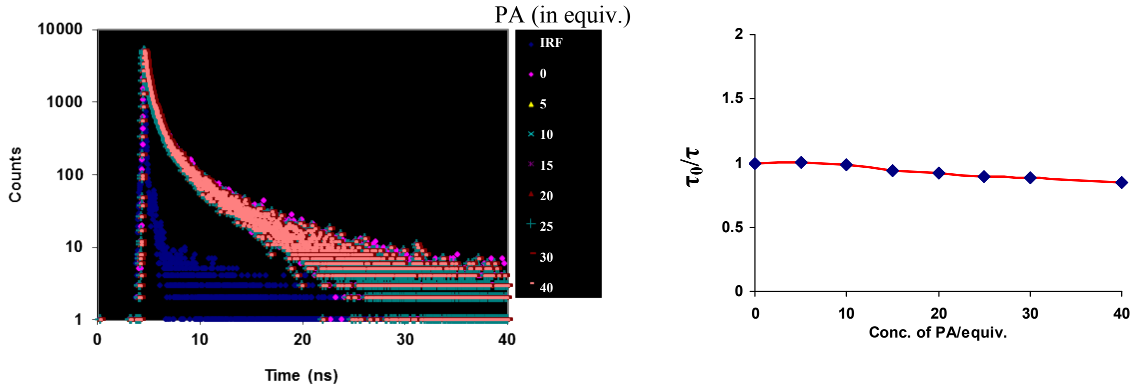


Fig. S24 Time resolved fluorescence emission spectra of aggregates of compound **5** with different concentrations of PA and showing the fluorescence lifetime of aggregates of **5** is invariant at different concentration of PA

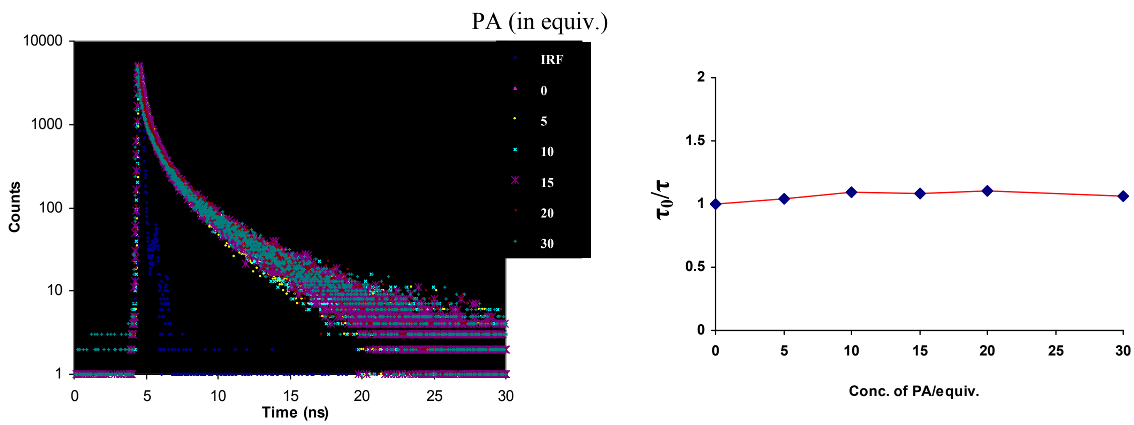


Fig.S25 Time resolved fluorescence emission spectra of aggregates of compound **6** with different concentrations of PA and showing the fluorescence lifetime of aggregates of **6** is invariant at different concentration of PA

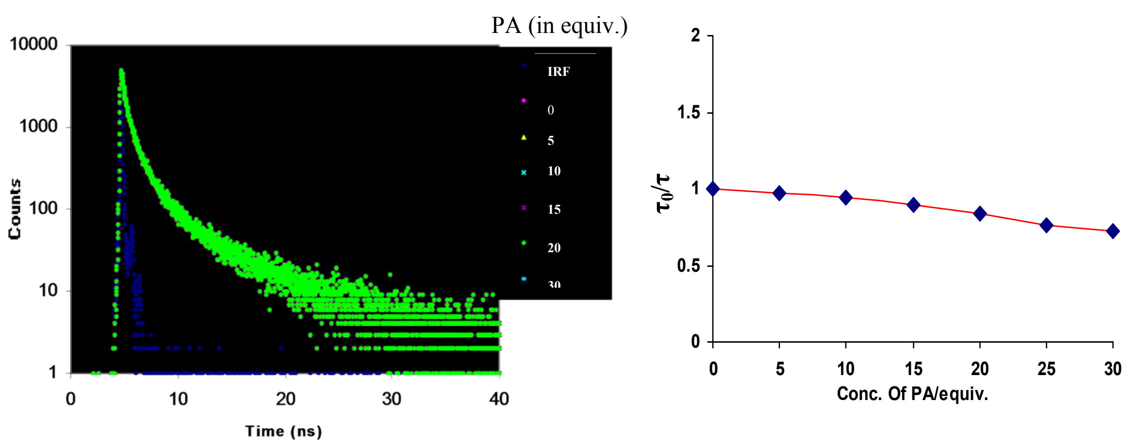


Fig. S26 Time resolved fluorescence emission spectra of aggregates of compound **7** with different concentrations of PA and showing the fluorescence lifetime of aggregates of **7** is invariant at different concentration of PA

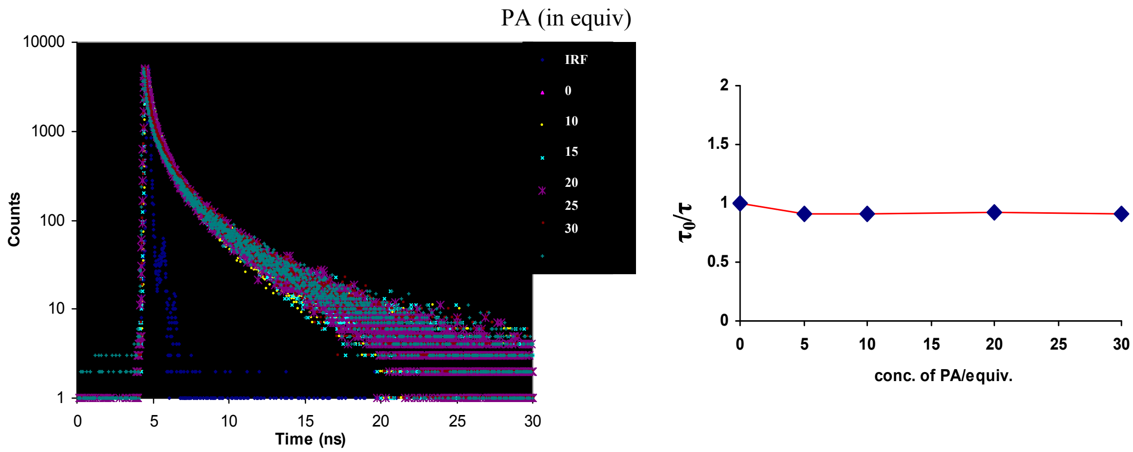


Fig. S27 Time resolved fluorescence emission spectra of aggregates of compound **8** with different concentrations of PA and showing the fluorescence lifetime of aggregates of **8** is invariant at different concentration of PA

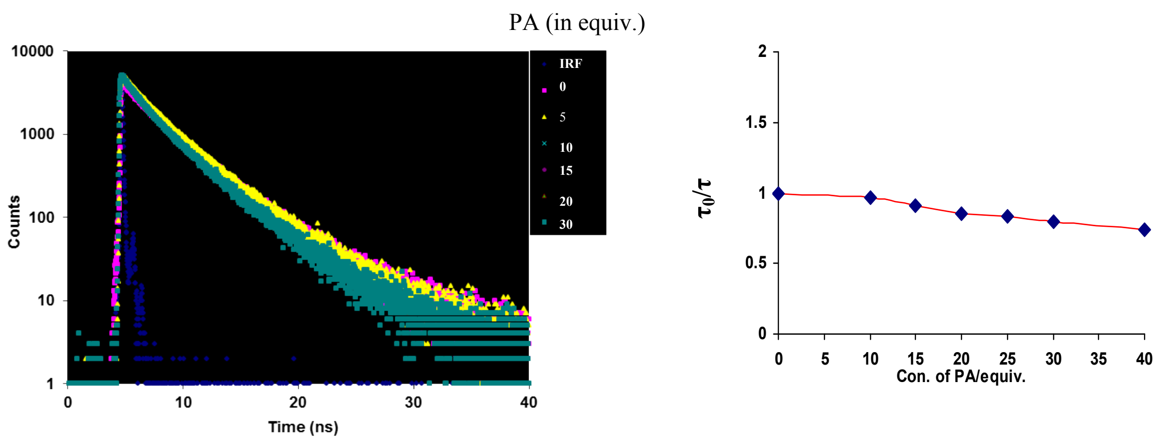


Fig. S28 Time resolved fluorescence emission spectra of aggregates of compound **9** with different concentrations of PA and showing the fluorescence lifetime of aggregates of **9** is invariant at different concentration of PA

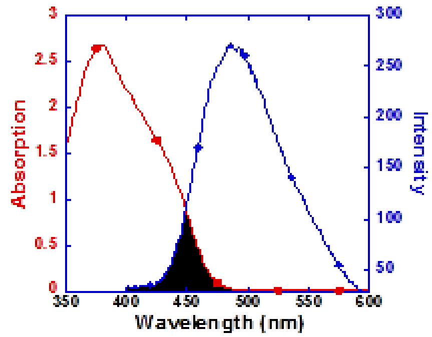


Fig. S29 Spectral overlaps of absorption spectrum of PA and fluorescence spectrum of aggregates of derivative **5**.

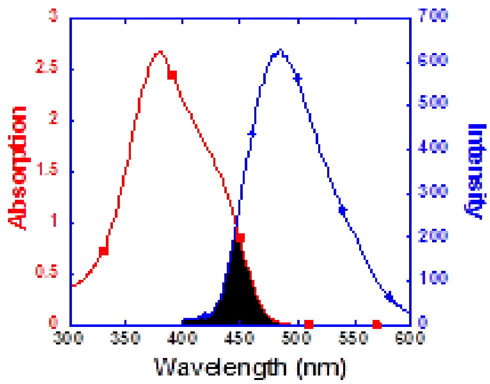


Fig. S30 Spectral overlaps of absorption spectrum of PA and fluorescence spectrum of aggregates of derivative **6**.

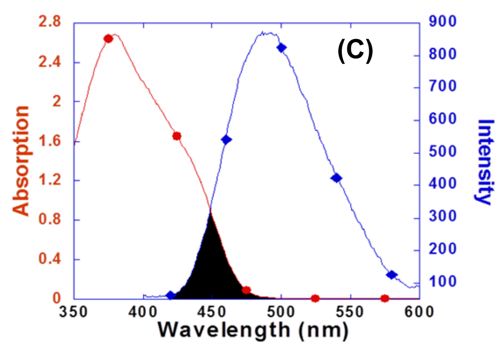


Fig. S31 Spectral overlap of absorption spectrum of PA and fluorescence spectrum of aggregates of compound **7**.

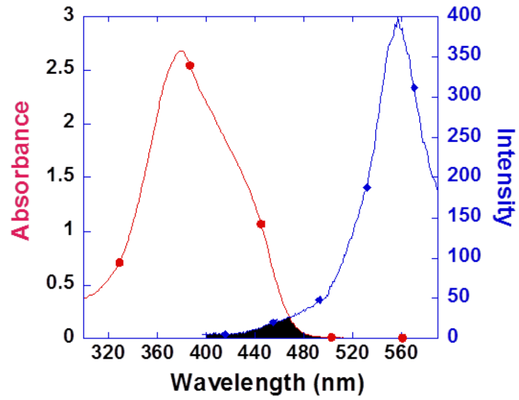


Fig. S32 Spectral overlaps of absorption spectrum of PA and fluorescence spectrum of aggregates of derivative **8**.

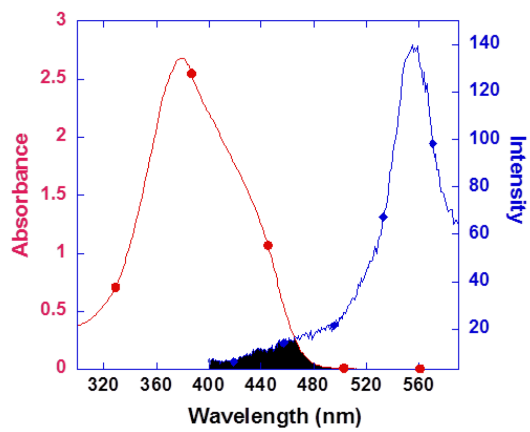


Fig. S33 Spectral overlaps of absorption spectrum of PA and fluorescence spectrum of aggregates of derivative **9**.

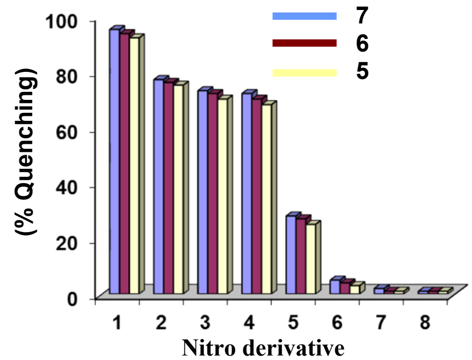


Fig. S34 Extent of fluorescence quenching of **5-7** (10 μM) observed in H_2O/DMSO (1:1) mixture after the addition of 62 equiv. of various nitroderivatives. 1=PA, 2=TNT, 3=DNT, 4=DNB, 5=DNBA, 6=BQ, 7=NM, 8=DMDNB

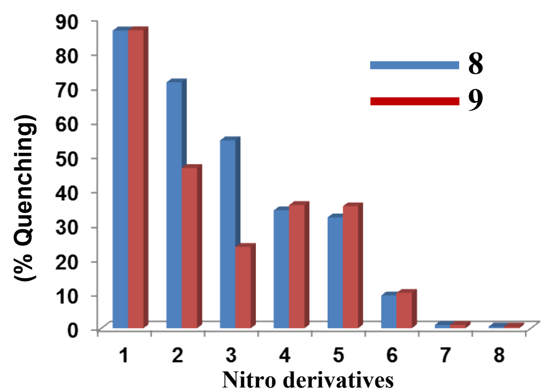


Fig. S35 Extent of fluorescence quenching of **8** and **9** (10 μM) observed in H_2O/THF (9:1) mixture after the addition of 40 equiv. of various nitroderivatives. 1=PA, 2=DNT, 3=DNB, 4=BQ, 5=DNBA, 6=TNT, 7=NM, 8=DMDNB

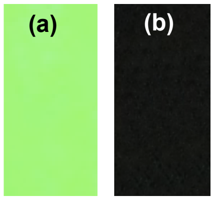


Fig. S36 Photographs (under 365 nm UV light) of derivative **5** on test strips (a) before and (b) after dipping into aqueous solutions of PA.

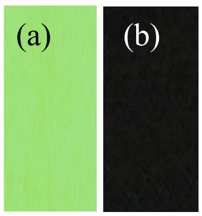


Fig. S37 Photographs of derivative **6** on test strips (a) before and (b) after dipping into aqueous solutions of PA.

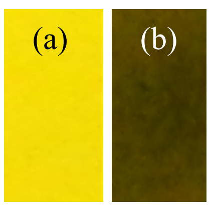


Fig. S38 Photographs of derivative **8** on test strips (a) before and (b) after dipping into aqueous solutions of PA.

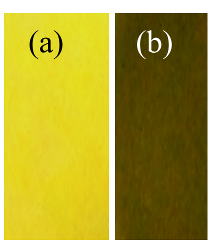


Fig. S39 Photographs of derivative **9** on test strips (a) before and (b) after dipping into aqueous solutions of PA.

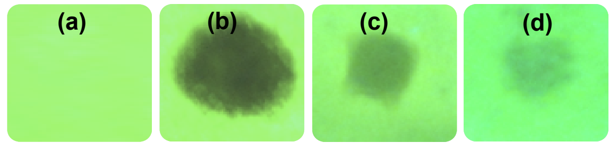


Fig. S40 Photographs (under 365 nm UV light) of fluorescence quenching of aggregates of derivative **5** on test strips for the visual detection of small amount of PA (a) test strip; PA of different concentration (b) 10^{-4} M (c) 10^{-6} M (d) 10^{-8} M.

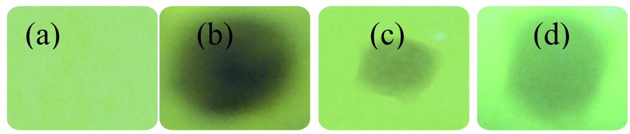


Fig. S41 Photographs (under 365 nm UV light) of fluorescence quenching of nanoaggregates of derivative **6** on test strips for the visual detection of small amount of PA (A) test strip; PA of different concentration (b) 10^{-4} M (c) 10^{-6} M (d) 10^{-8} M.

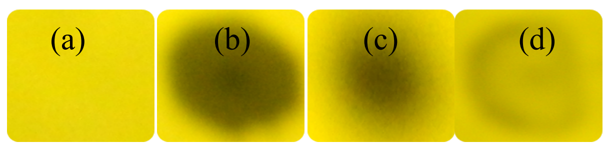


Fig. S42 Photographs (under 365 nm UV light) of fluorescence quenching of nanoaggregates of derivative **8** on test strips for the visual detection of small amount of PA (A) test strip; PA of different concentration (b) 10^{-4} M (c) 10^{-6} M (d) 10^{-8} M.

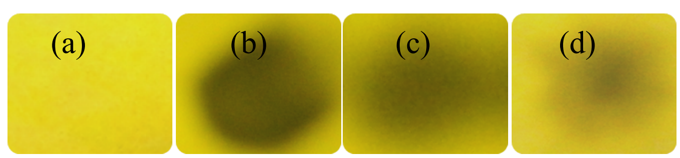


Fig. S43 Photographs (under 365 nm UV light) of fluorescence quenching of nanoaggregates of derivative **9** on test strips for the visual detection of small amount of PA (A) test strip; PA of different concentration (b) 10^{-4} M (c) 10^{-6} M (d) 10^{-8} M.

^{1}H NMR spectrum of derivative **5** in $CDCl_3$

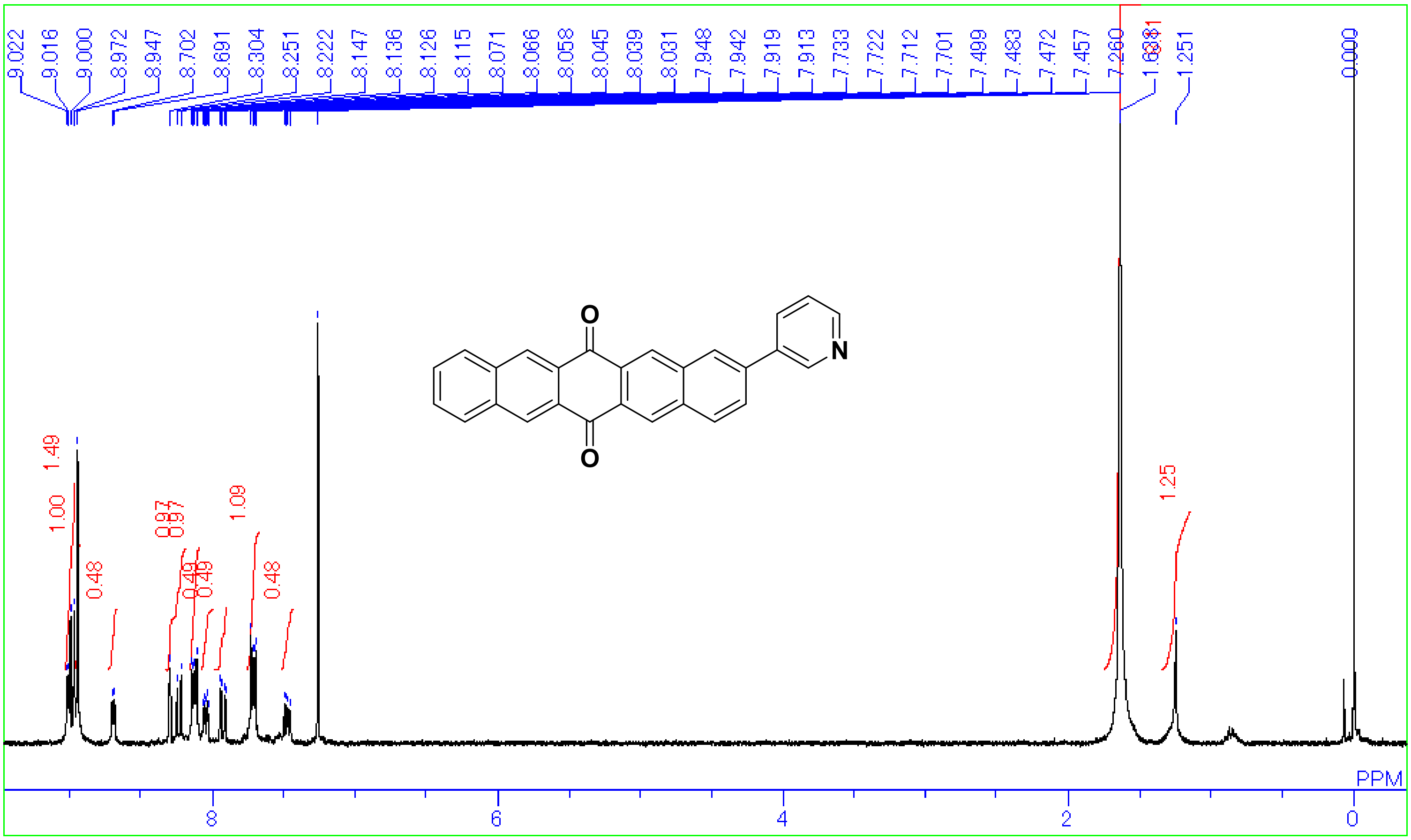


Fig. S44 ^{1}**H** NMR spectrum of derivative **5** in $CDCl_3$

Mass spectrum of derivative **5**

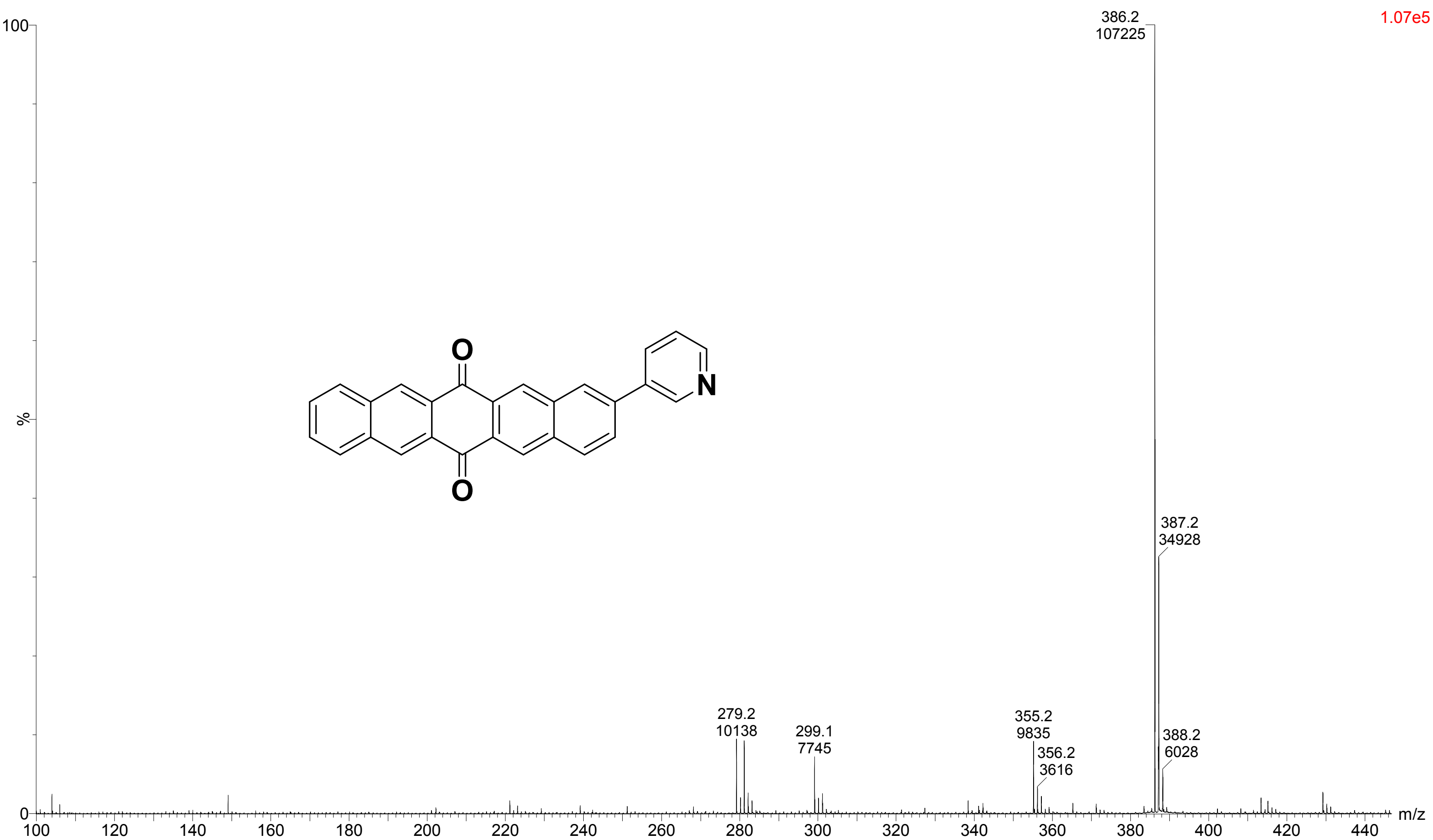


Fig. S45 Mass spectrum of derivative **5**

^{1}H NMR spectrum of derivative **7** in $CDCl_3$

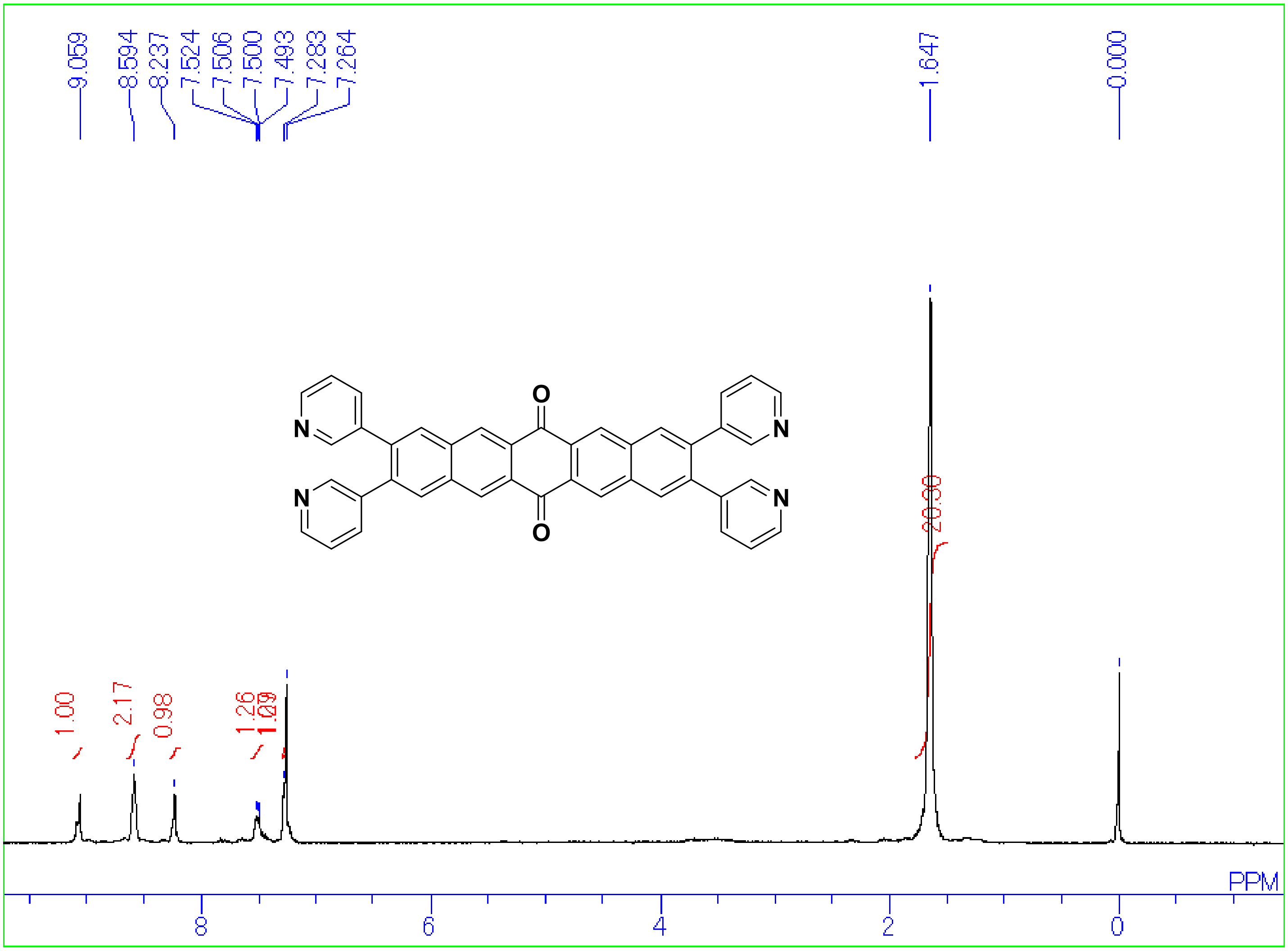


Fig. S46 ^{1}H NMR spectrum of derivative **7** in $CDCl_3$

Mass spectrum of derivative **7**

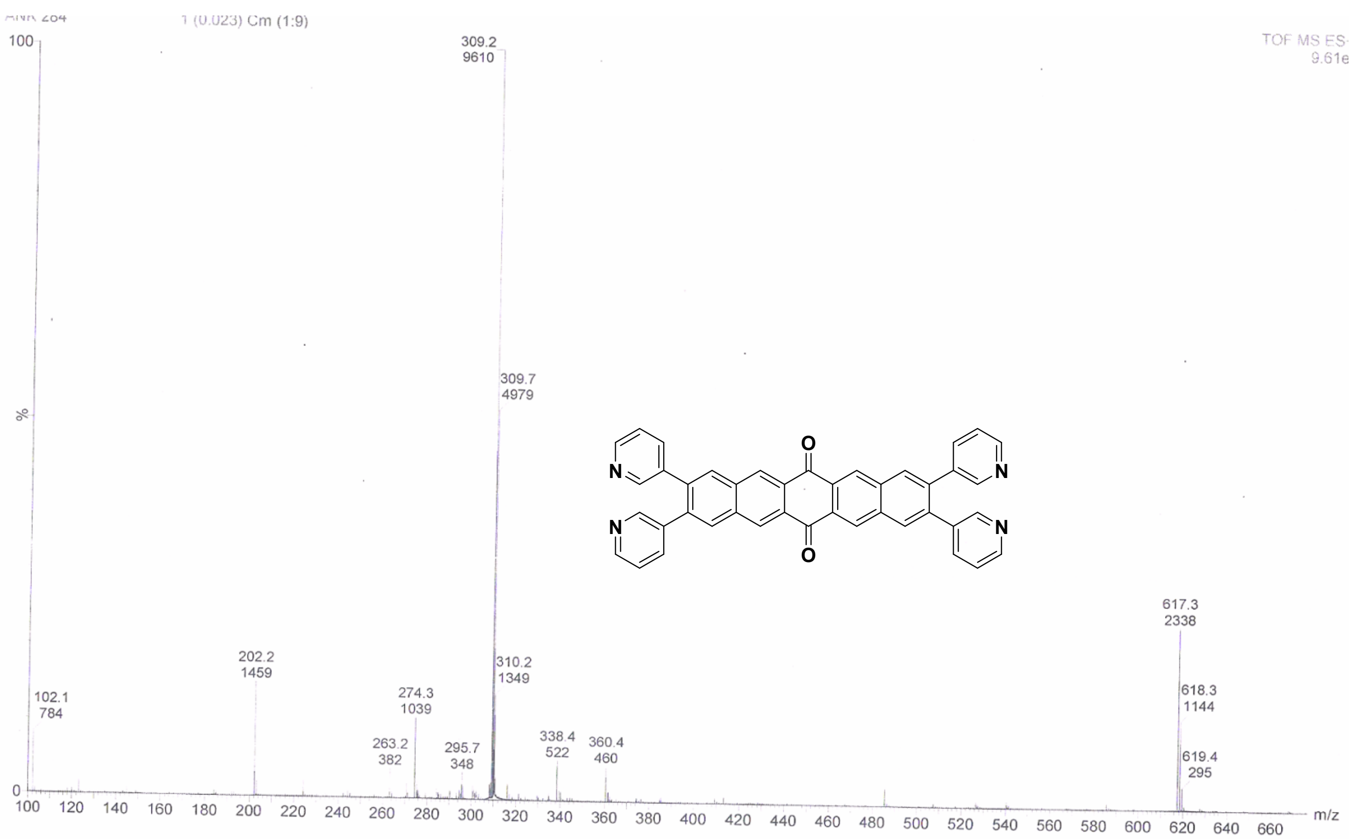


Fig. S47 Mass spectrum of derivative **7**

^1H NMR spectrum of derivative **8** in $CDCl_3$

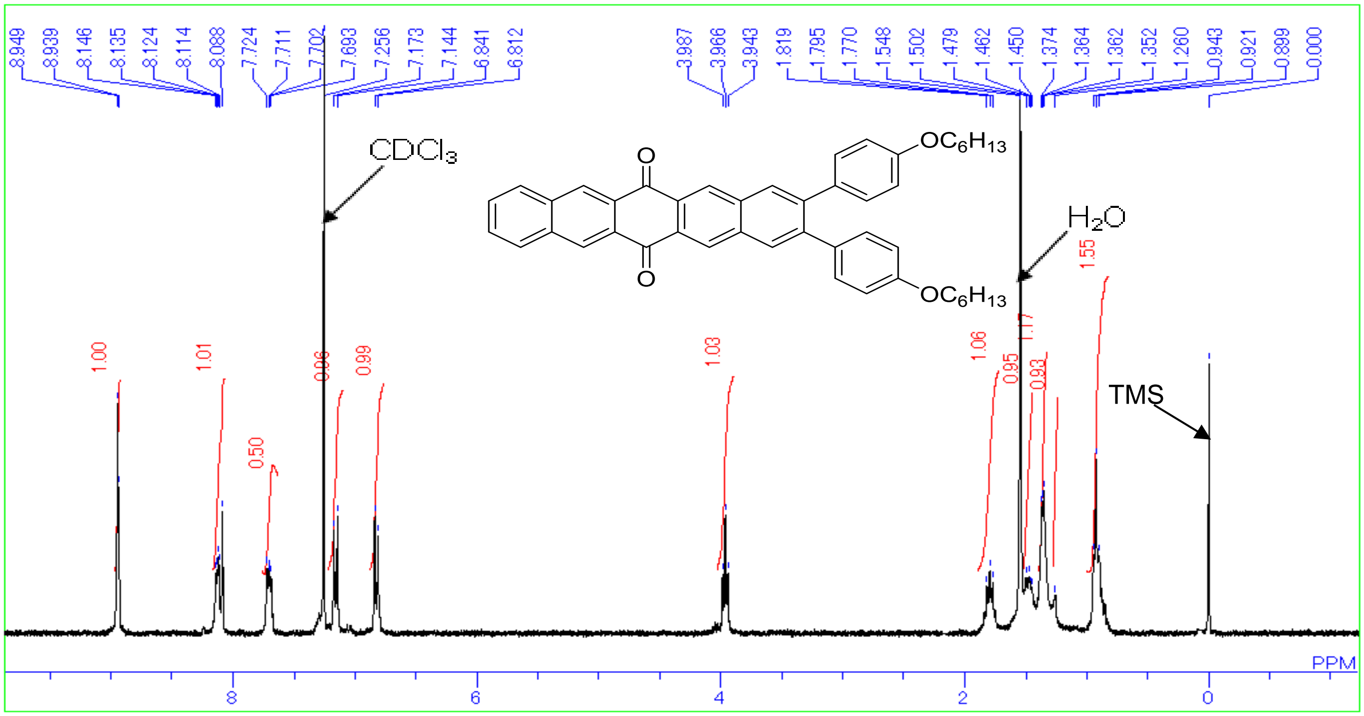


Fig. S48 ^1H NMR spectrum of derivative **8** in $CDCl_3$

^{13}C NMR spectrum of derivative **8** in $CDCl_3$

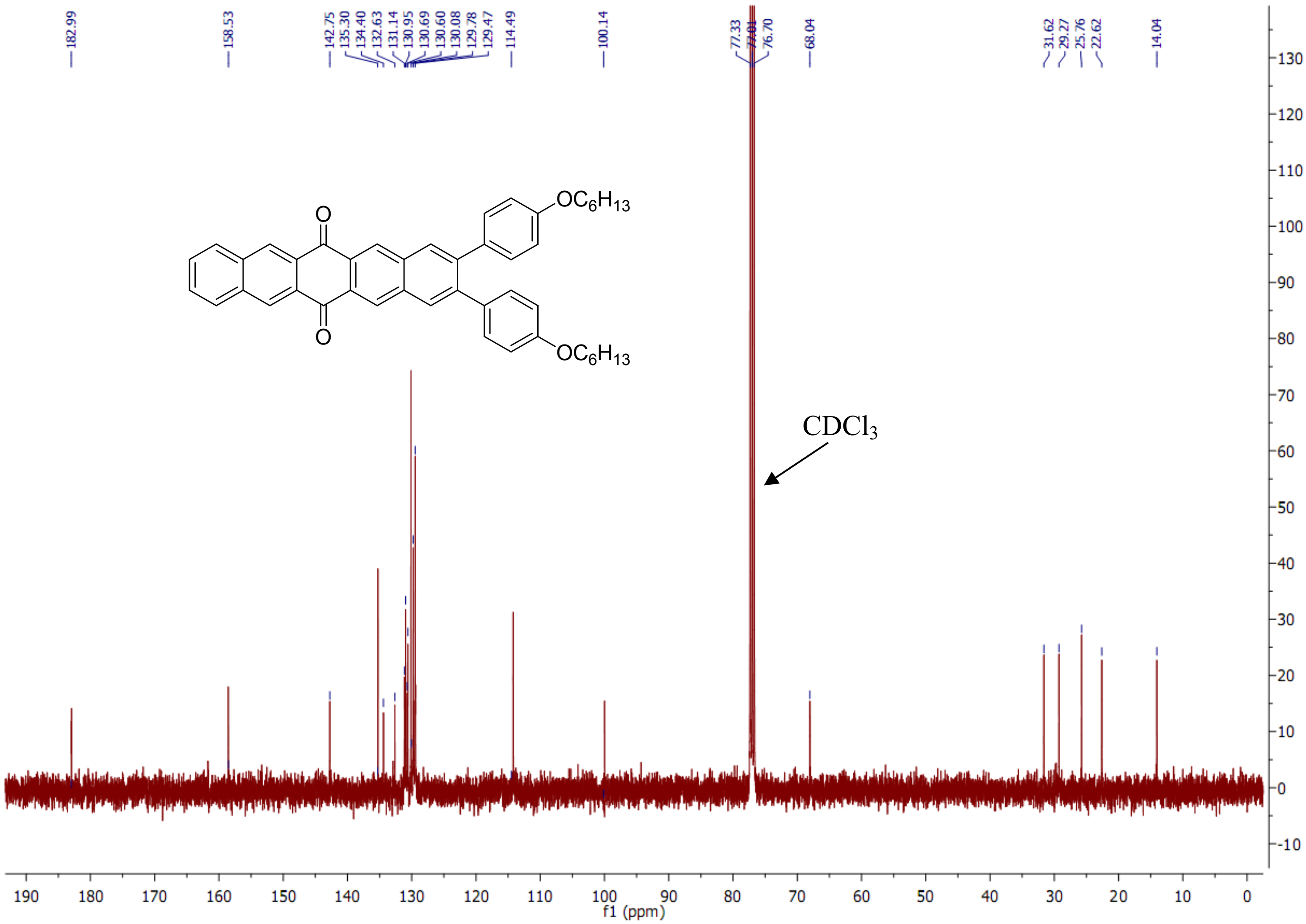


Fig. S49 ^{13}C NMR spectrum of derivative **8** in $CDCl_3$.

Mass spectrum of derivative **8**

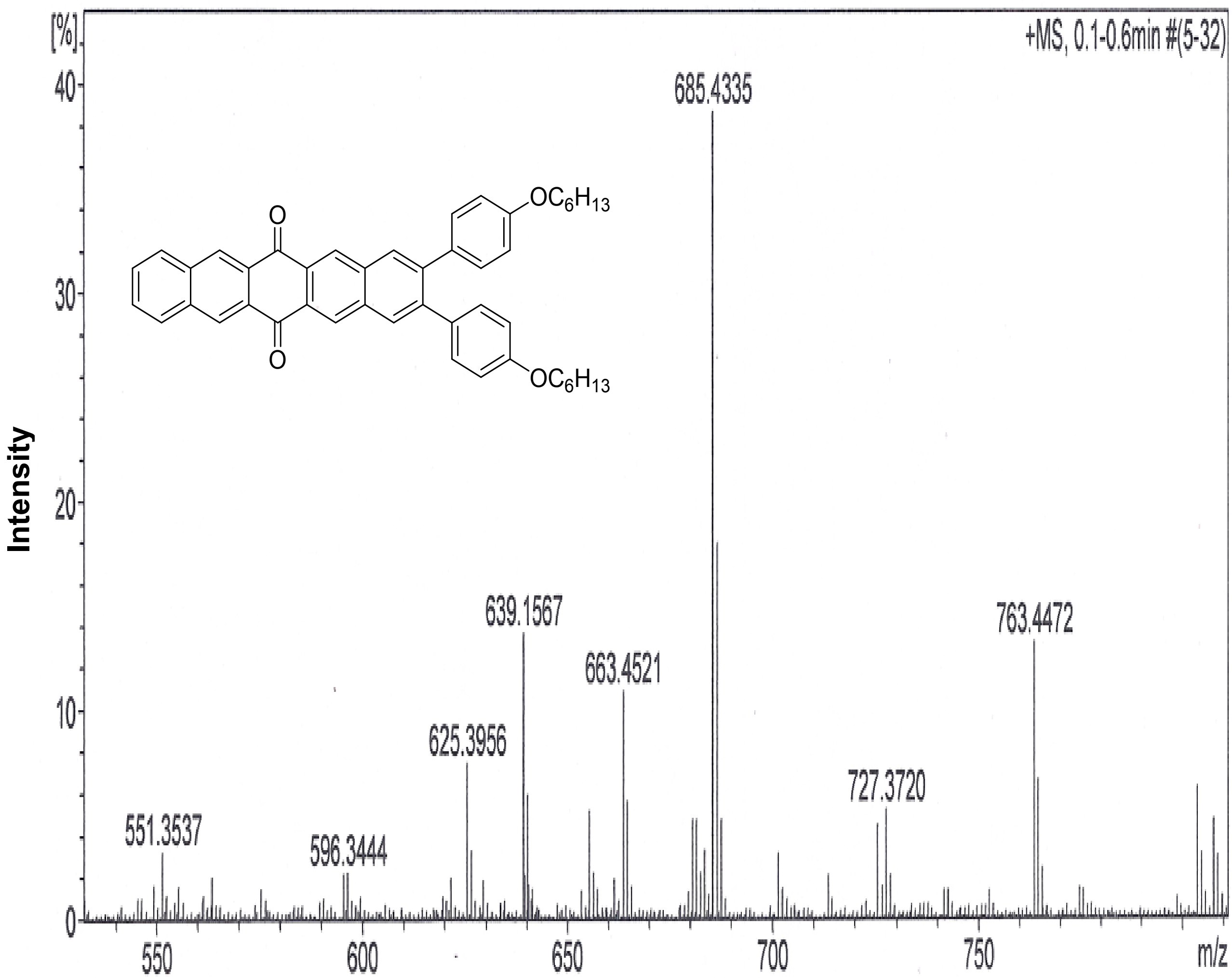


Fig. S50 Mass spectrum of derivative **8**

^{1}H NMR spectrum of derivative **9** in $CDCl_3$

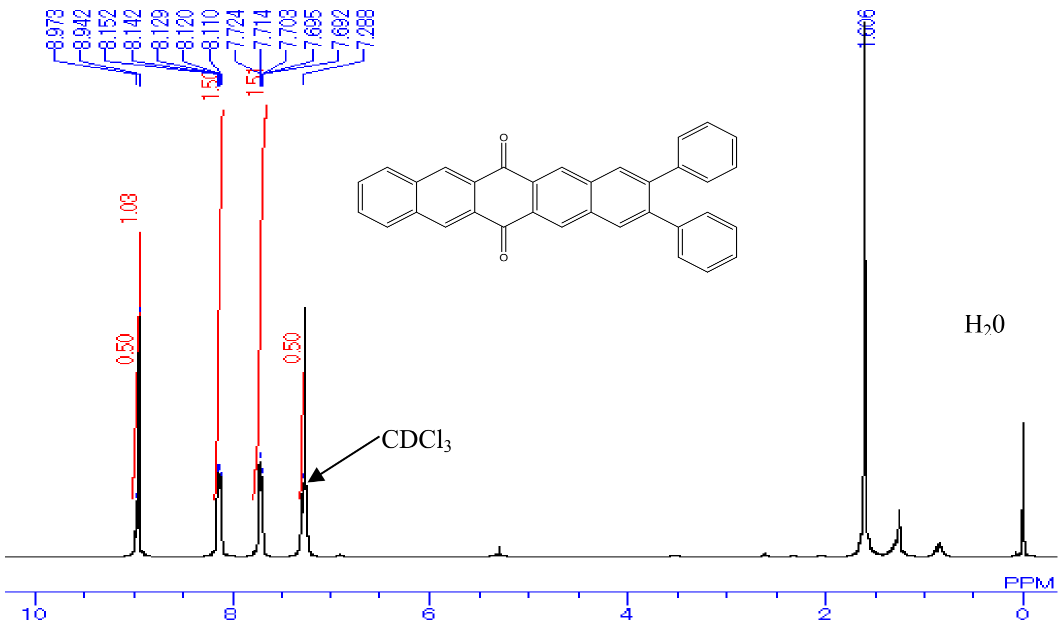


Fig. S51 ^{1}H NMR spectrum of derivative **9** in $CDCl_3$

^{13}C NMR spectrum of derivative **9**

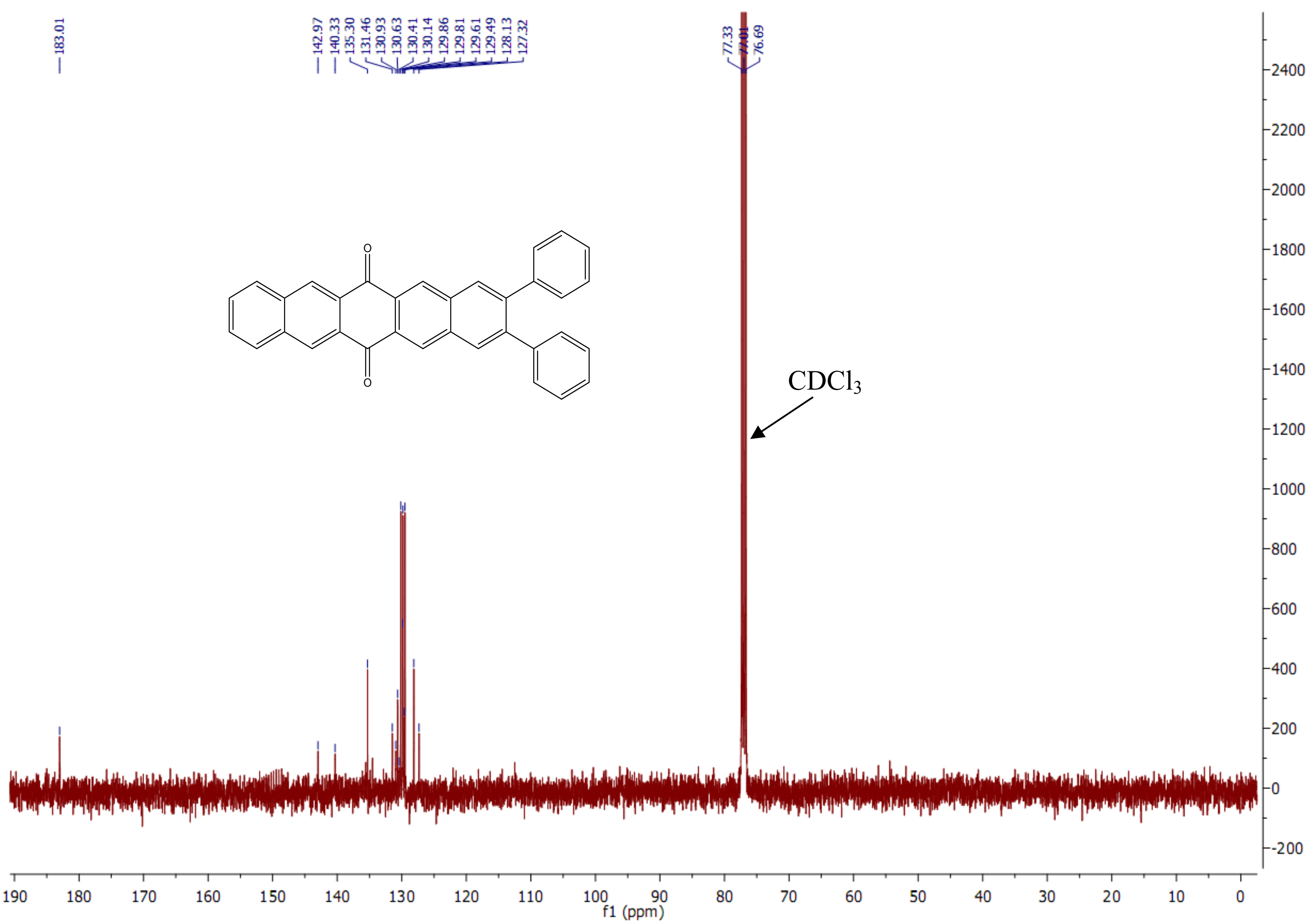


Fig. S52 ^{13}C NMR spectrum of derivative **9** in $CDCl_3$

Mass spectrum of derivative **9**

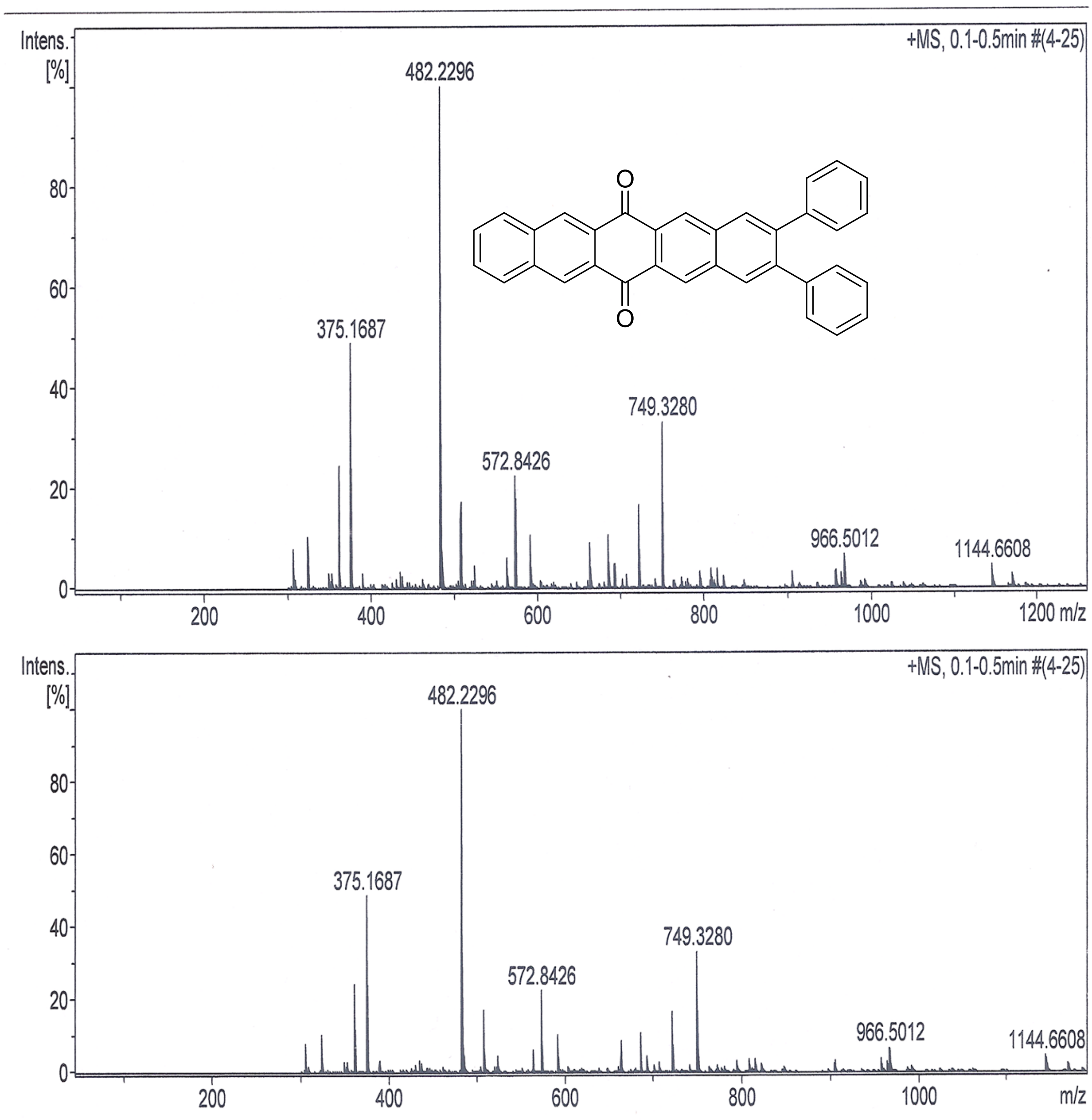


Fig. S53 Mass spectrum of derivative **9**