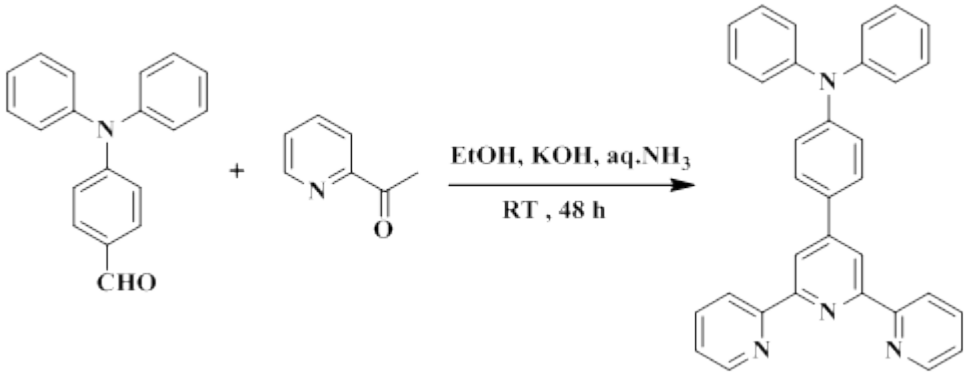
Electronic Supplementary Information (ESI)

Distinct fluorescence state, mechanofluorochromism of terpyridine conjugated fluorophores and the reusable sensing of nitroaromatics in aqueous medium

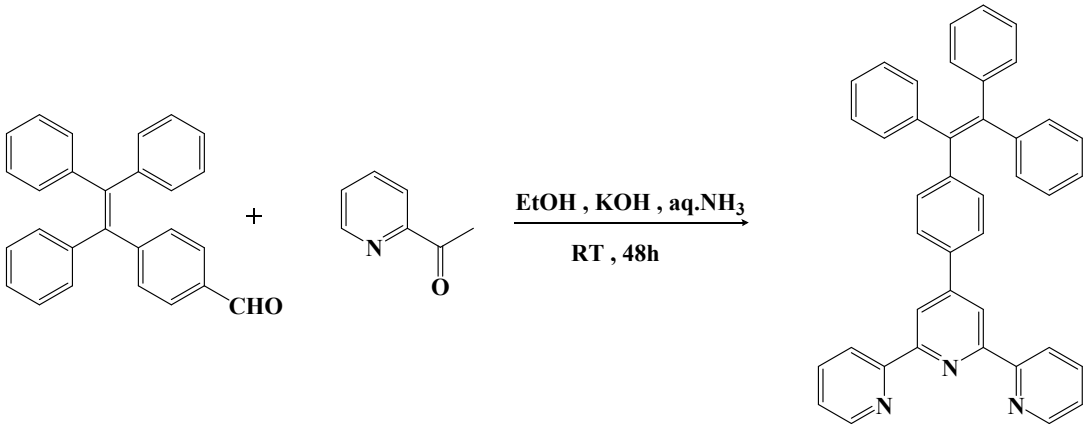
1. Experimental Section

Synthesis of 4-(2,6-di(pyridin-2-yl)pyridin-4-yl)-N,N-diphenylbenzenamine(TPA-TP)



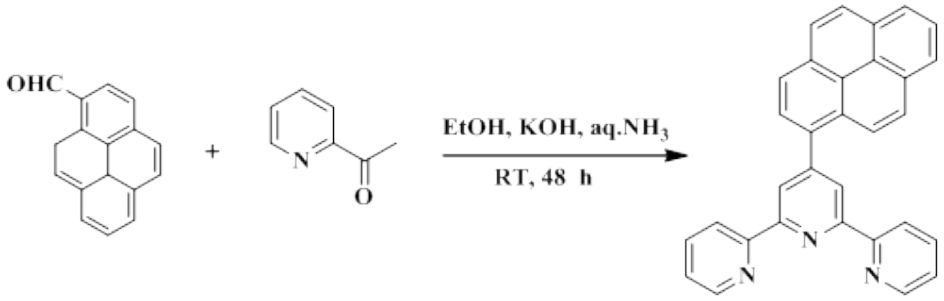
Scheme 1. Synthesis of TPA-TP.

Synthesis of 2,6-di(pyridin-3-yl)-4-(4-(1,2,2-triphenylvinyl)phenyl)pyridine (TPE-TP)



Scheme 2 Synthesis of TPE-TP.

Synthesis of 2-(4-(pyren-1-yl)-6-(pyridin-2-yl)pyridin-2-yl)pyridine (PY-TP)



Scheme 3 . Synthesis of PY-TP.

2. FT-IR analysis

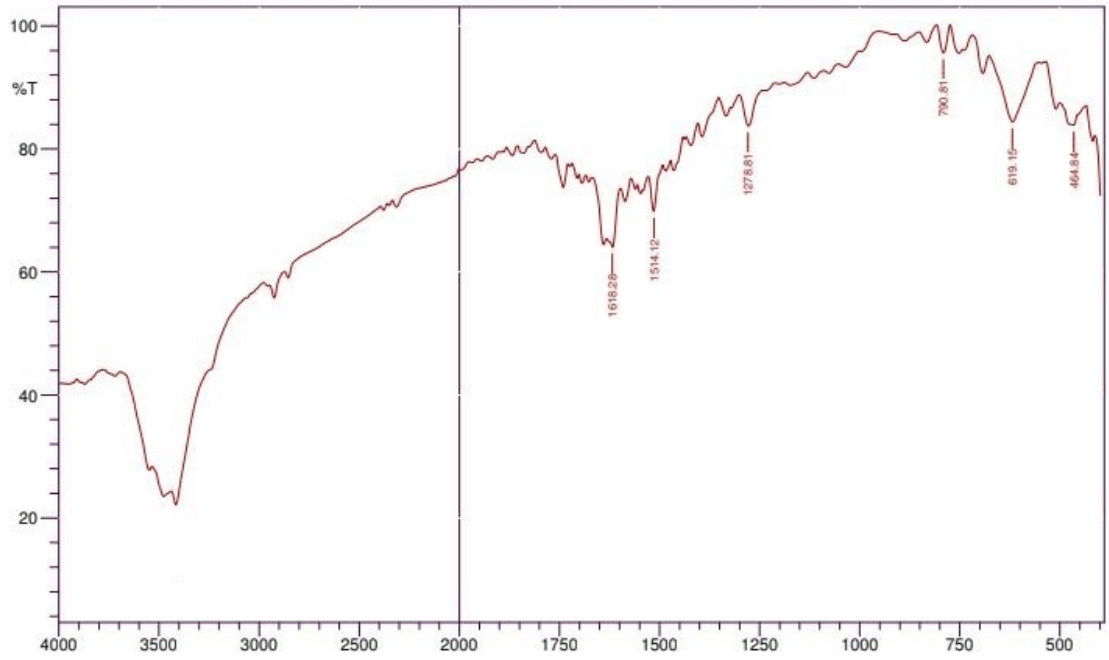


Fig. S1 FT-IR spectra of TPA-TP.

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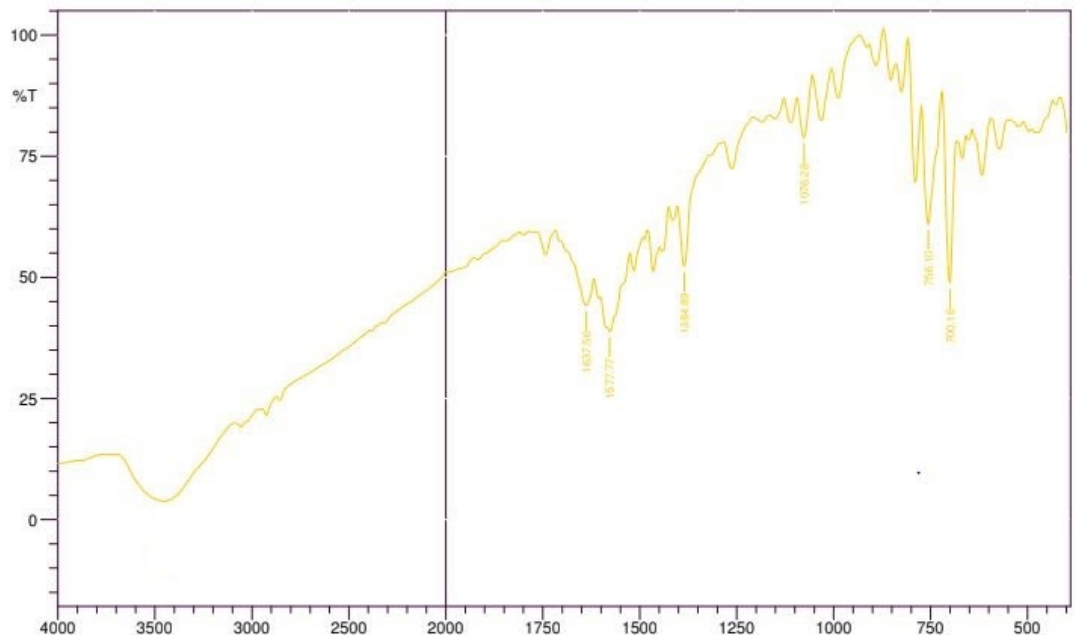


Fig. S2 FT-IR spectra ofTPE-TP.

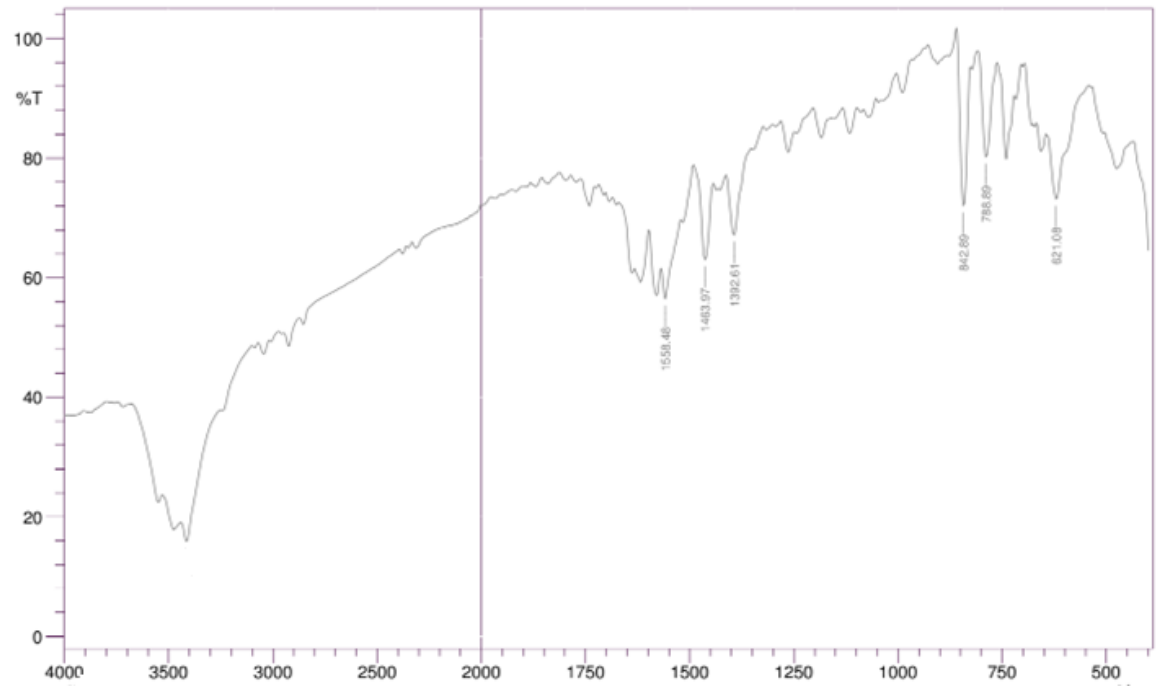


Fig. S3 FT-IR spectra ofPY-TP.

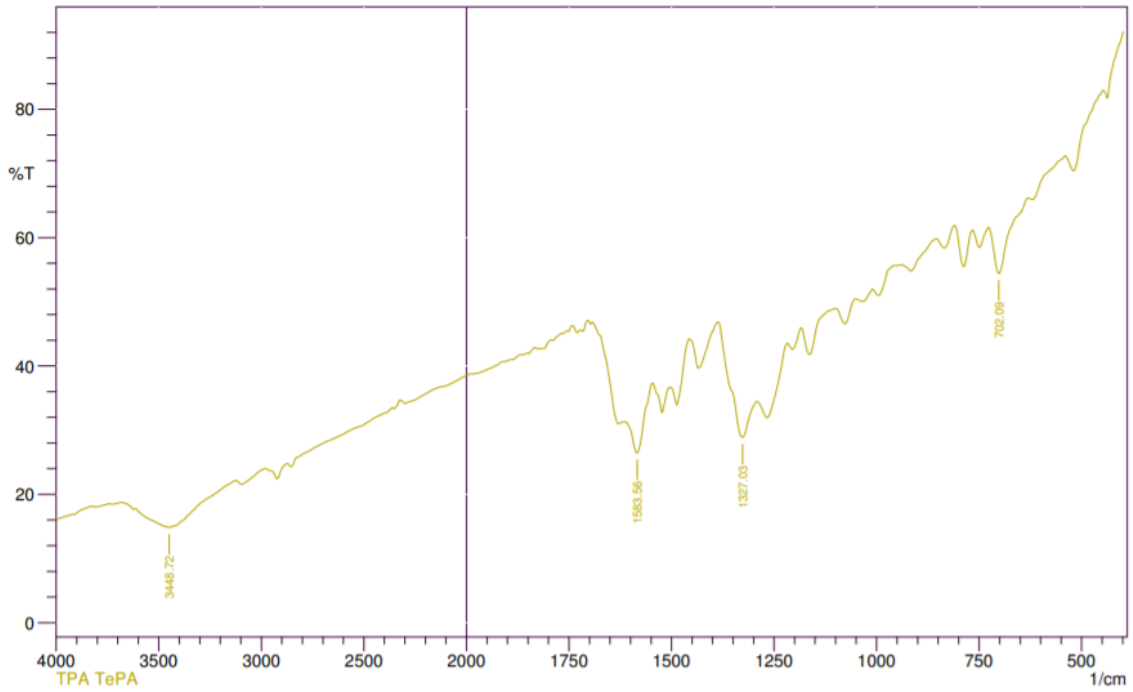


Fig. S4 FT-IR spectra ofTPA-TP.PA

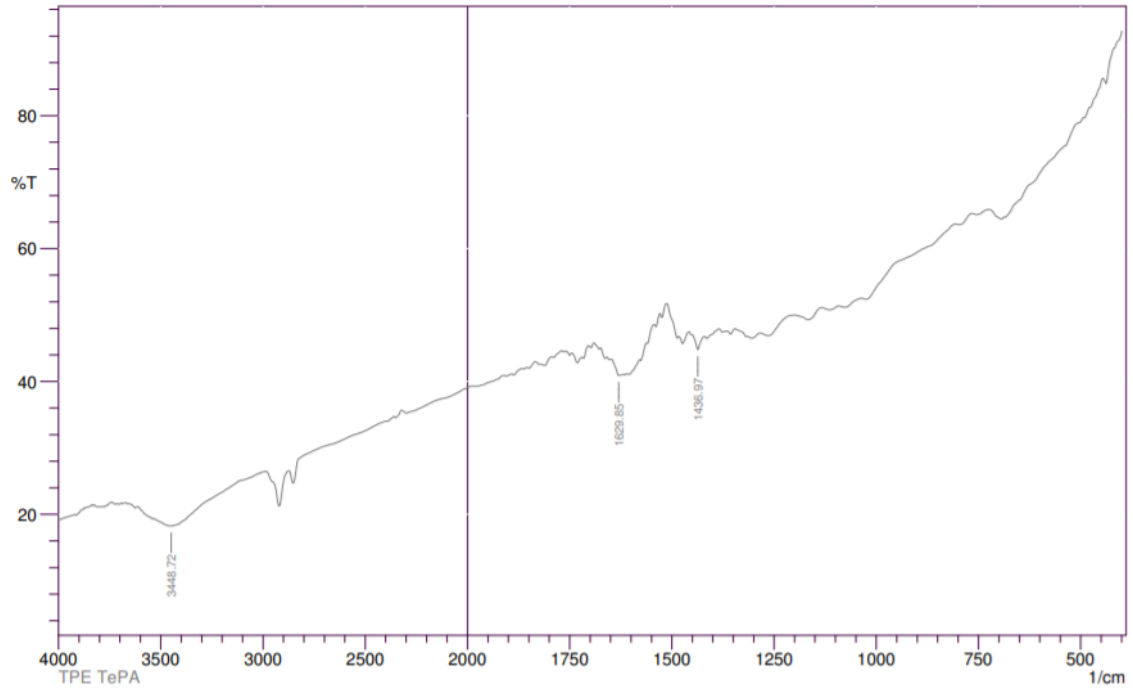


Fig. S5 FT-IR spectra ofTPE-TP.PA

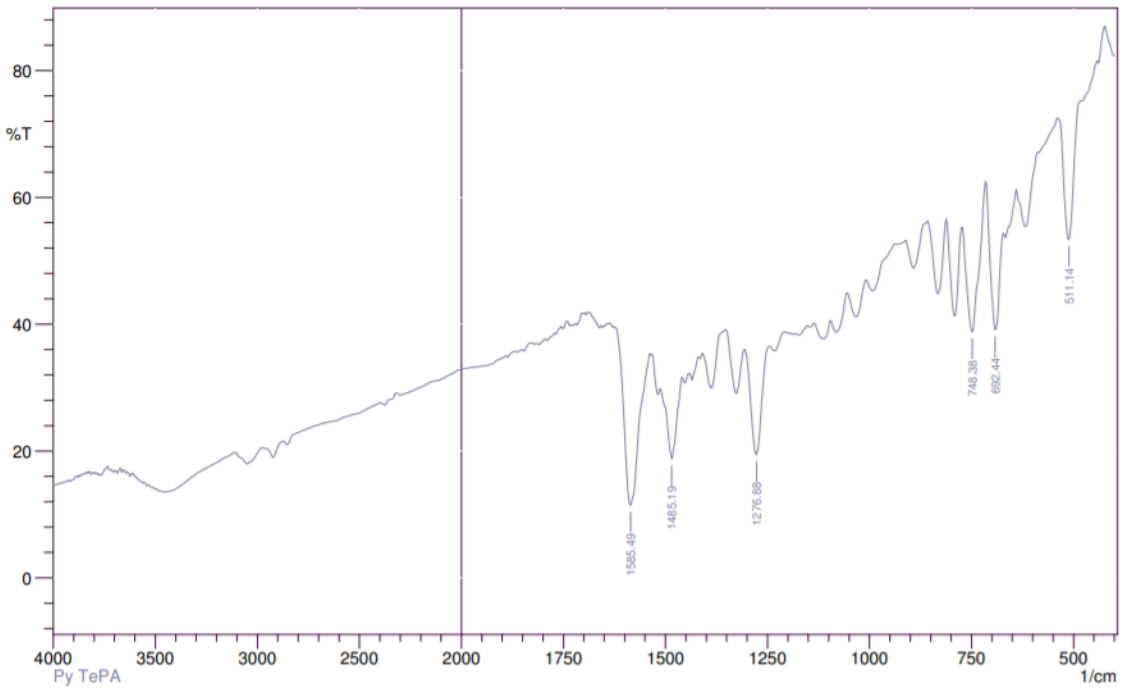


Fig. S6 FT-IR spectra ofPY-TP.PA

3. NMR studies

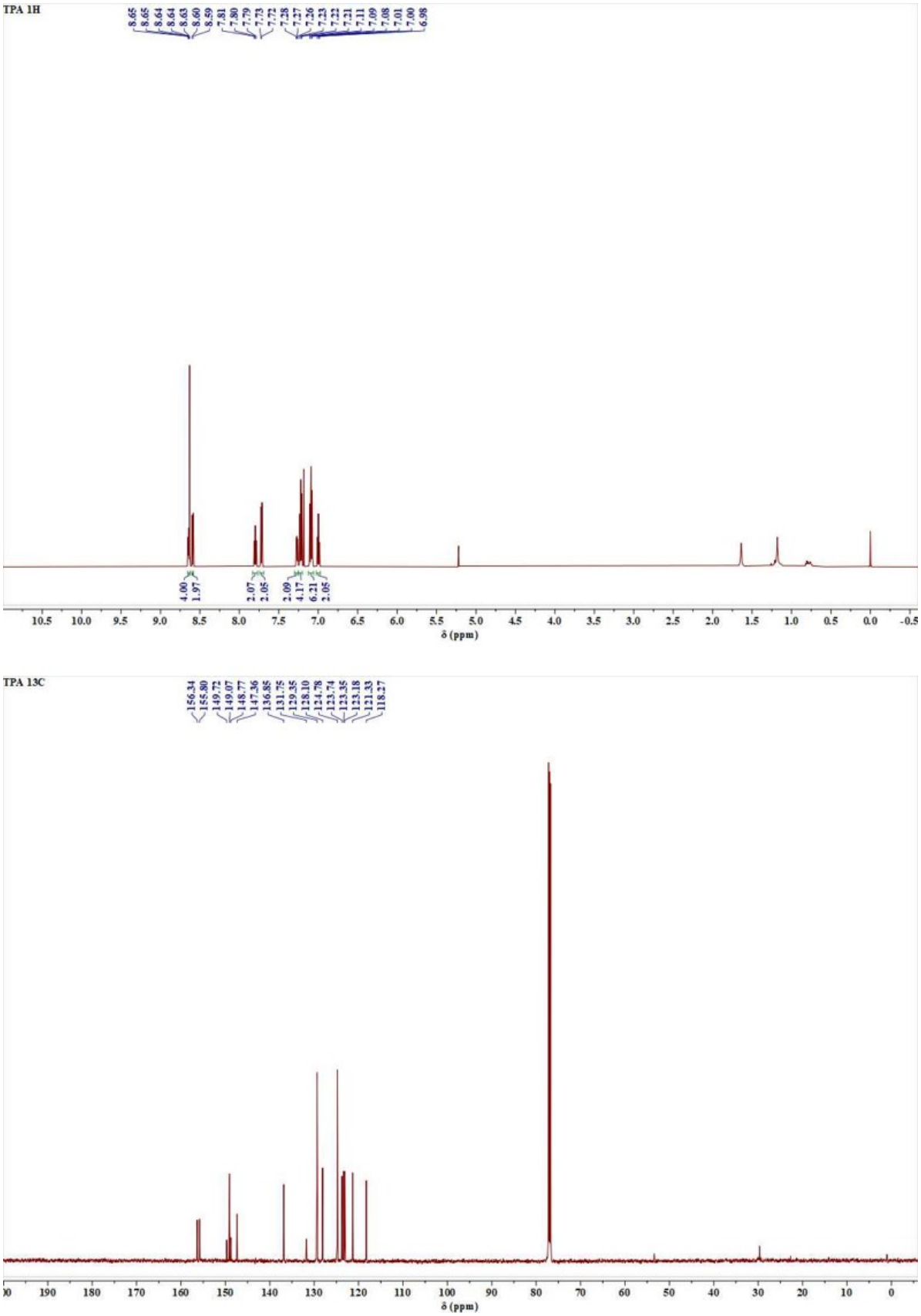
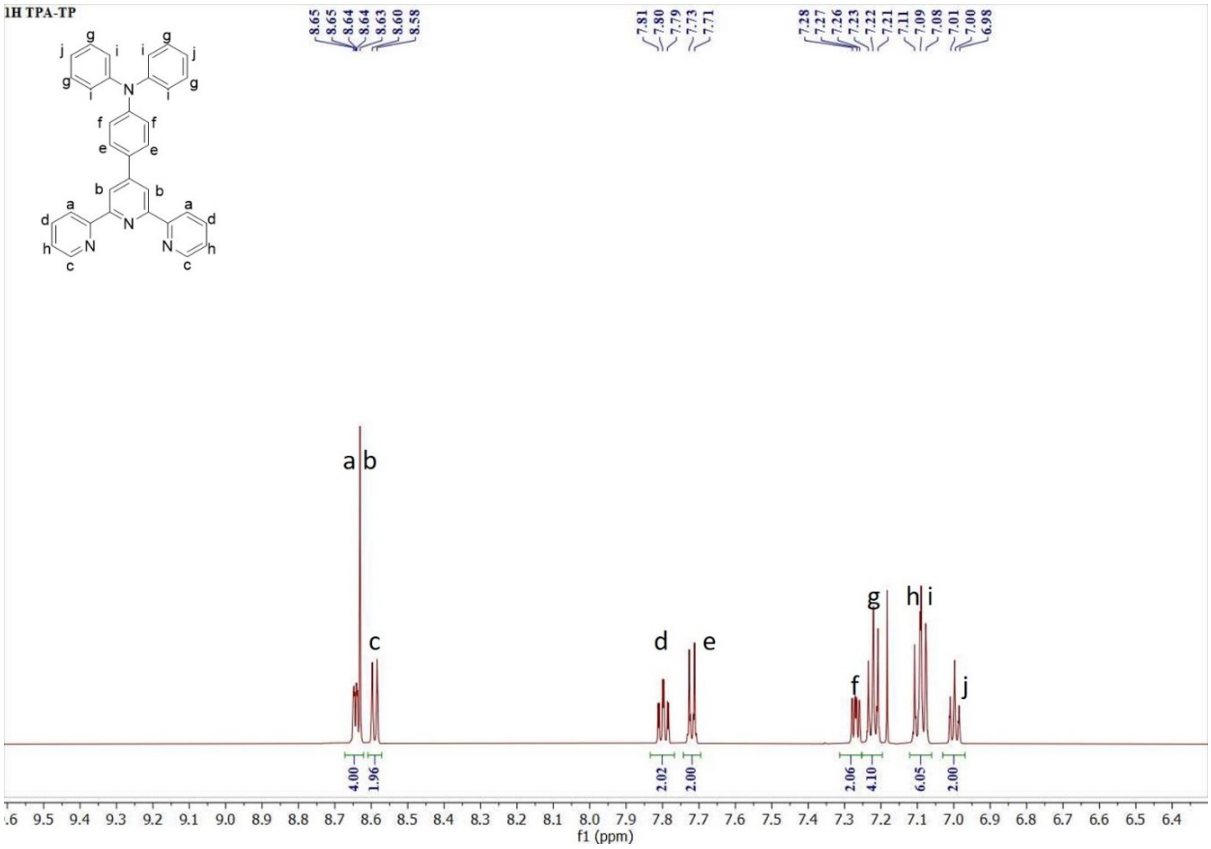


Fig. S7. ^{1}H &^{13}C NMR spectrum of TPA-TP.



The expanded ^{1}H NMR spectrum of TPA-TP along with peak assigning.

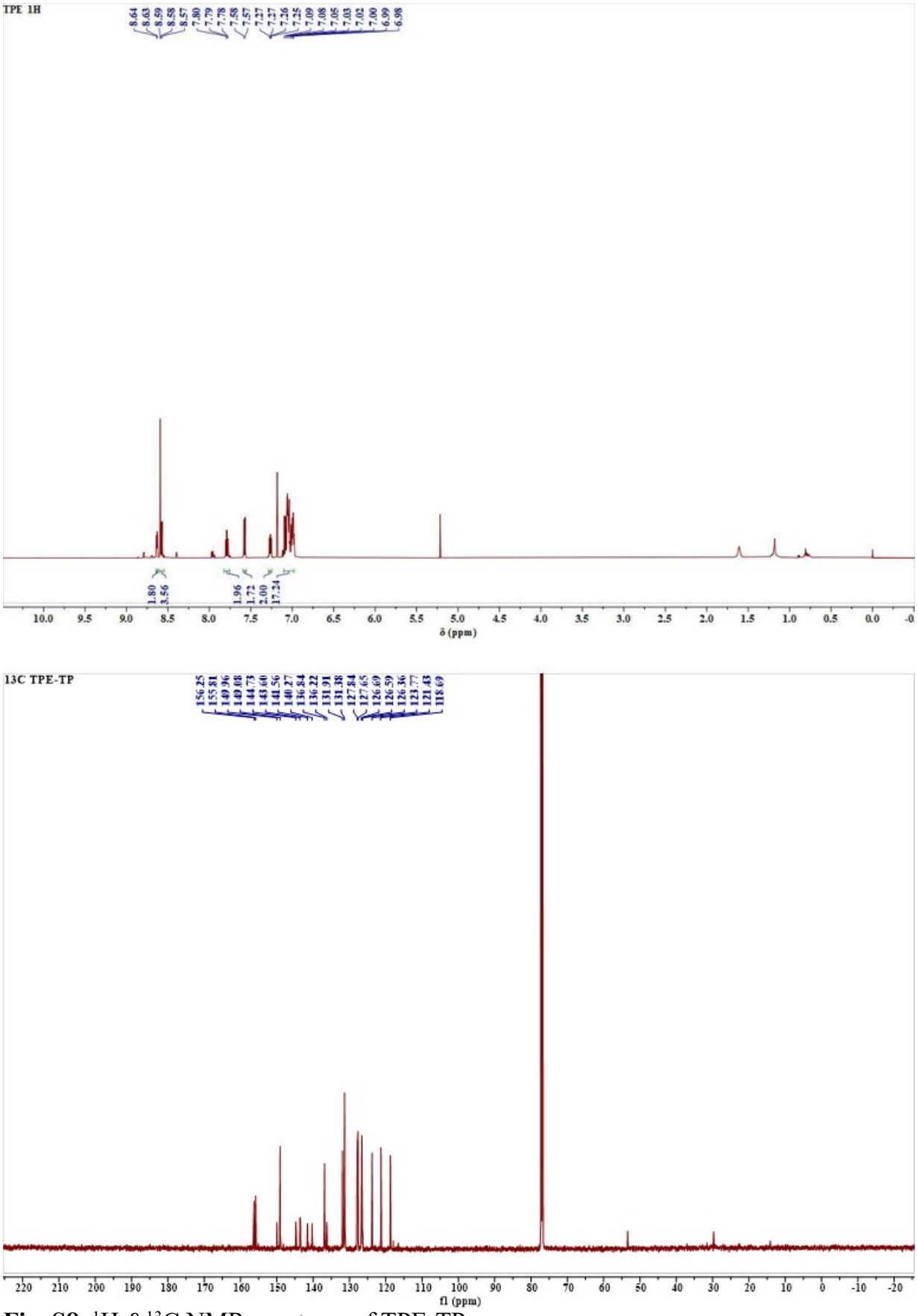
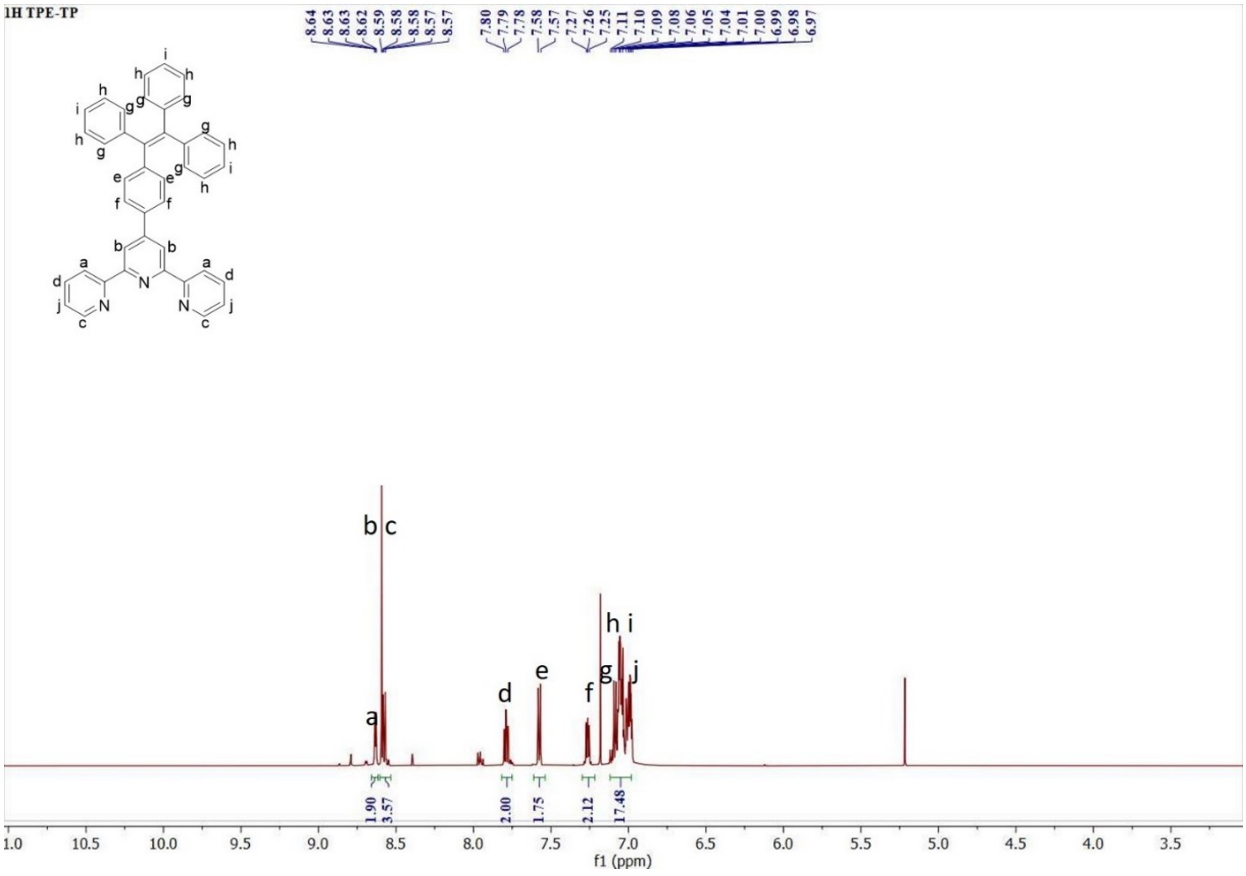


Fig. S8. ^{1}H &^{13}C NMR spectrum of TPE-TP.



The expanded ^{1}H NMR spectrum of TPE-TP along with peak assigning.

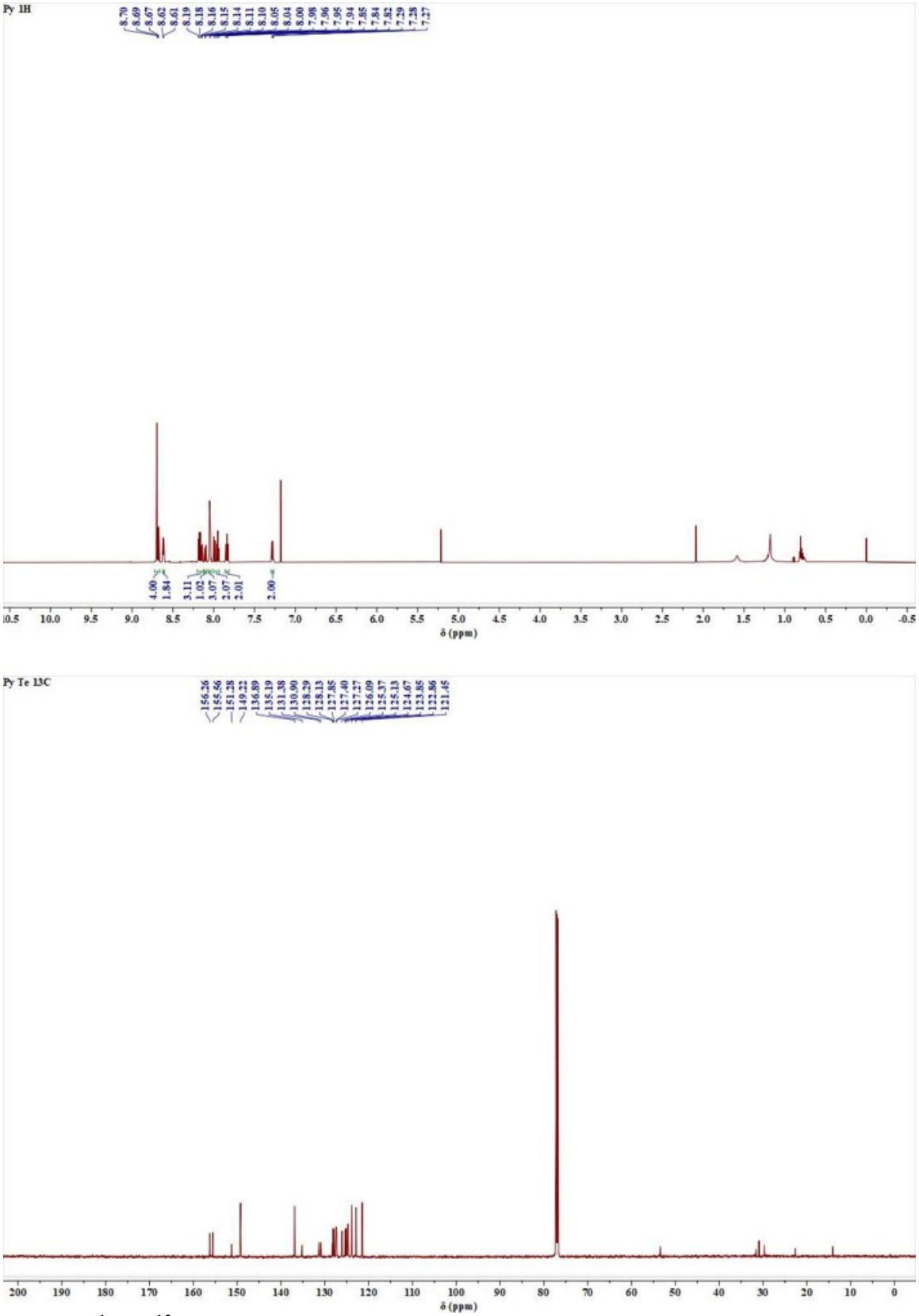
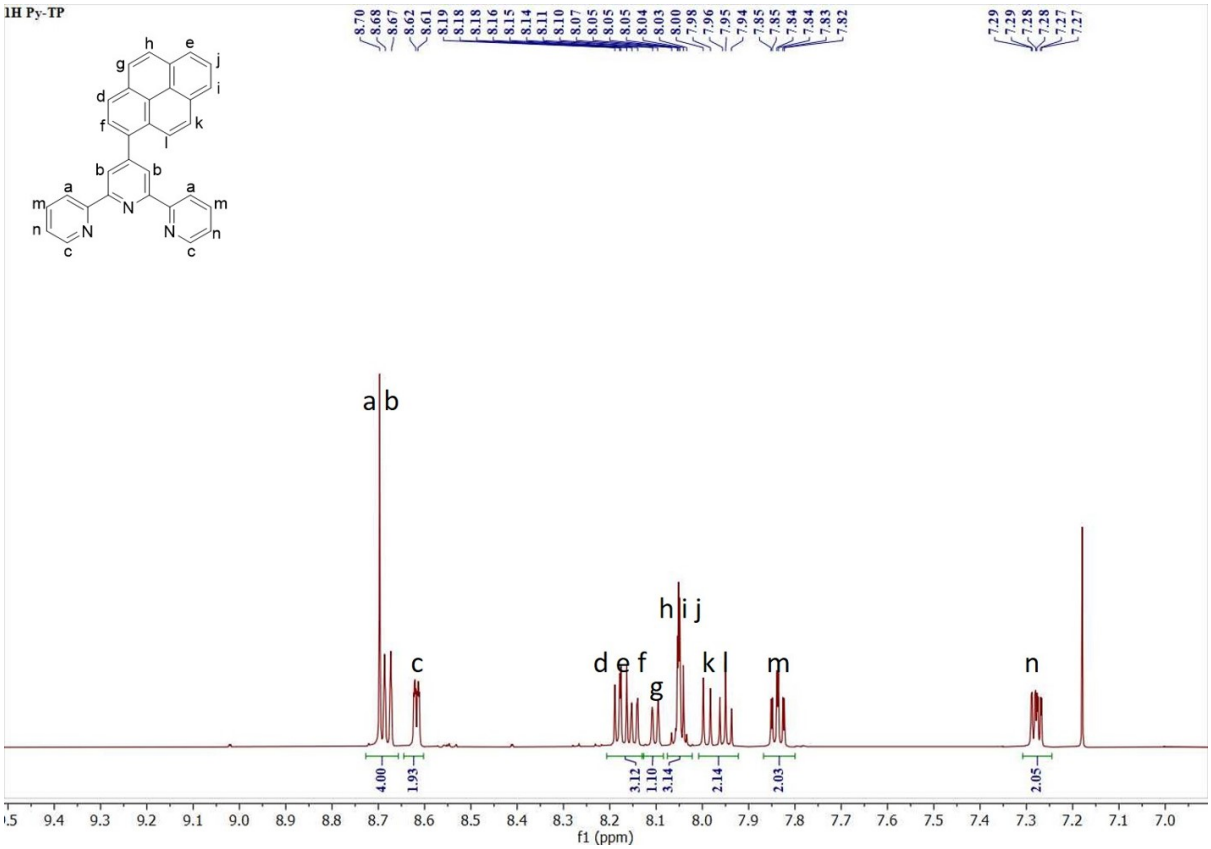


Fig. S9. ^{1}H &^{13}C NMR spectrum of Py-TP



The expanded ^{1}H NMR spectrum of Py-TP along with peak assigning.

4. Mass analysis

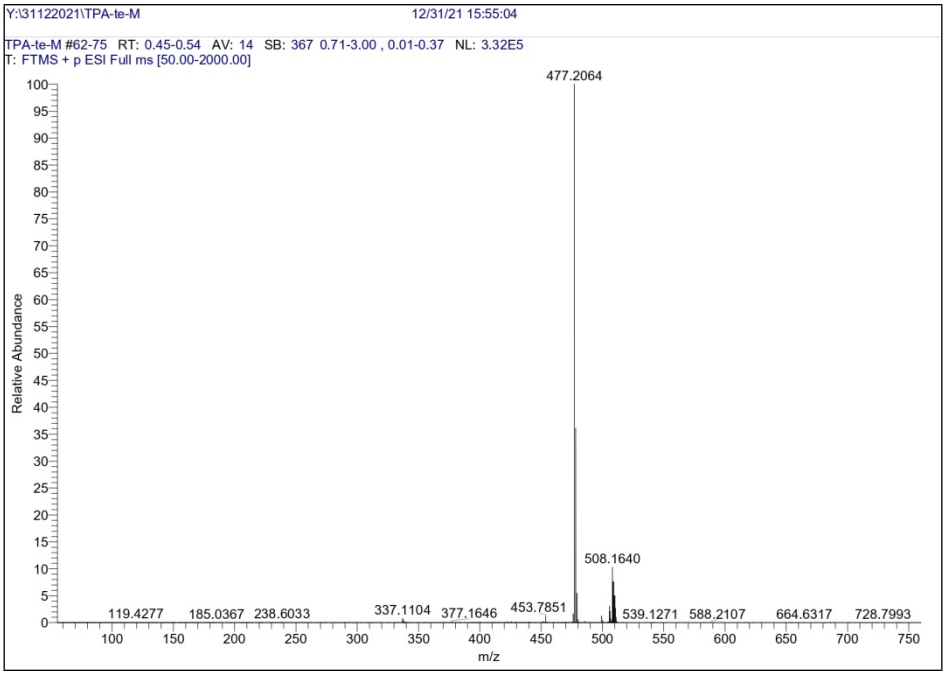


Fig. S10 Mass spectrum of TPA-TP

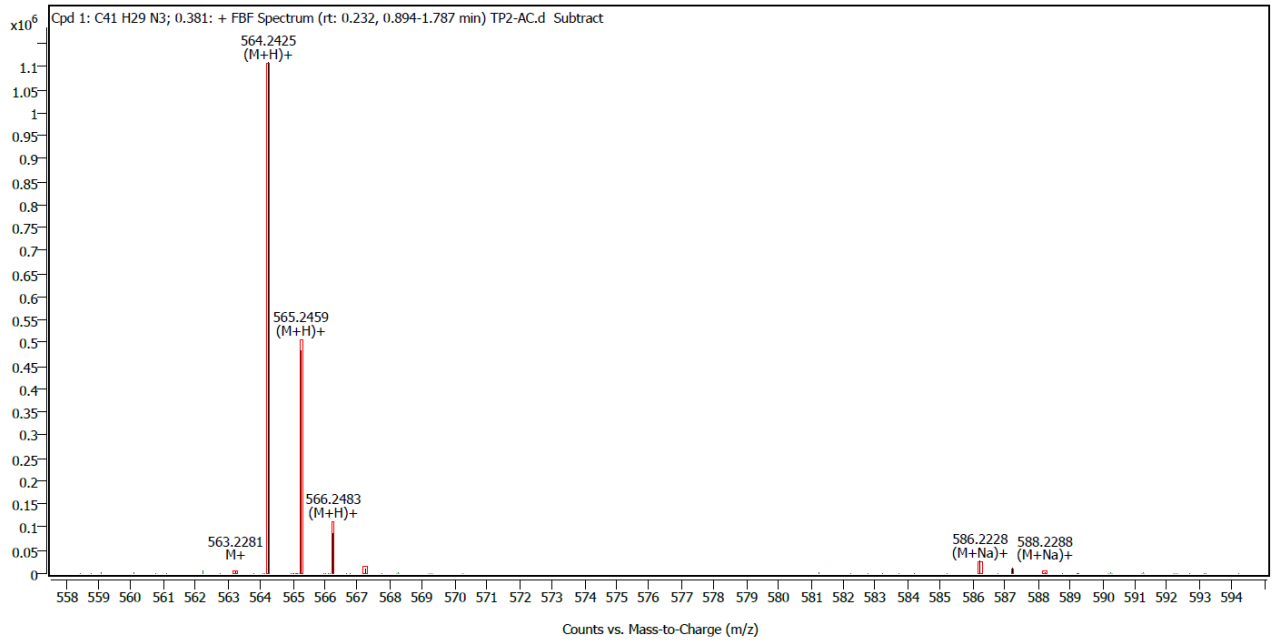


Fig. S11 Mass spectrum of TPE-TP

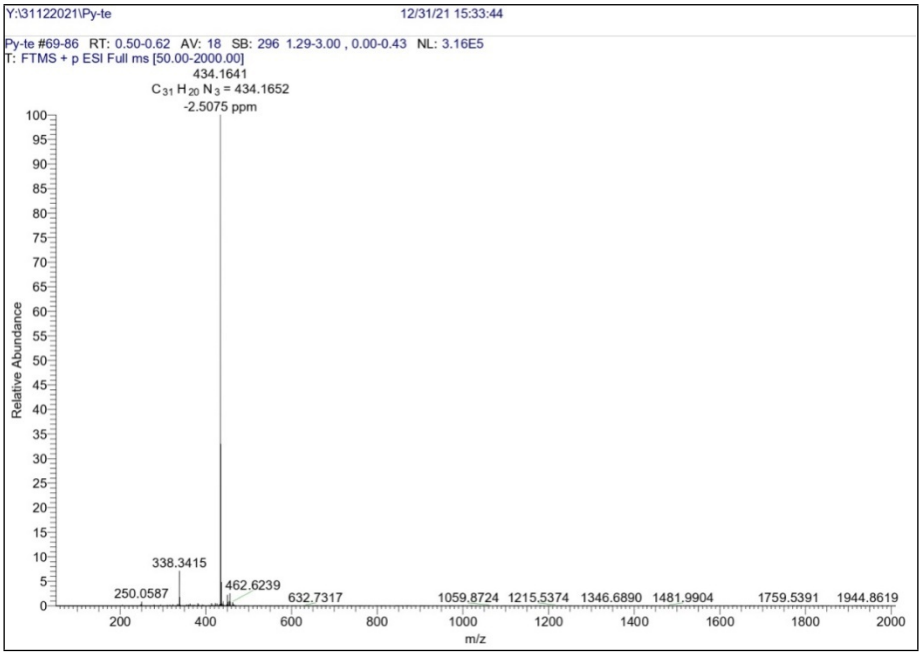


Fig. S12 Mass spectrum of PY-TP

5. Photophysical studies

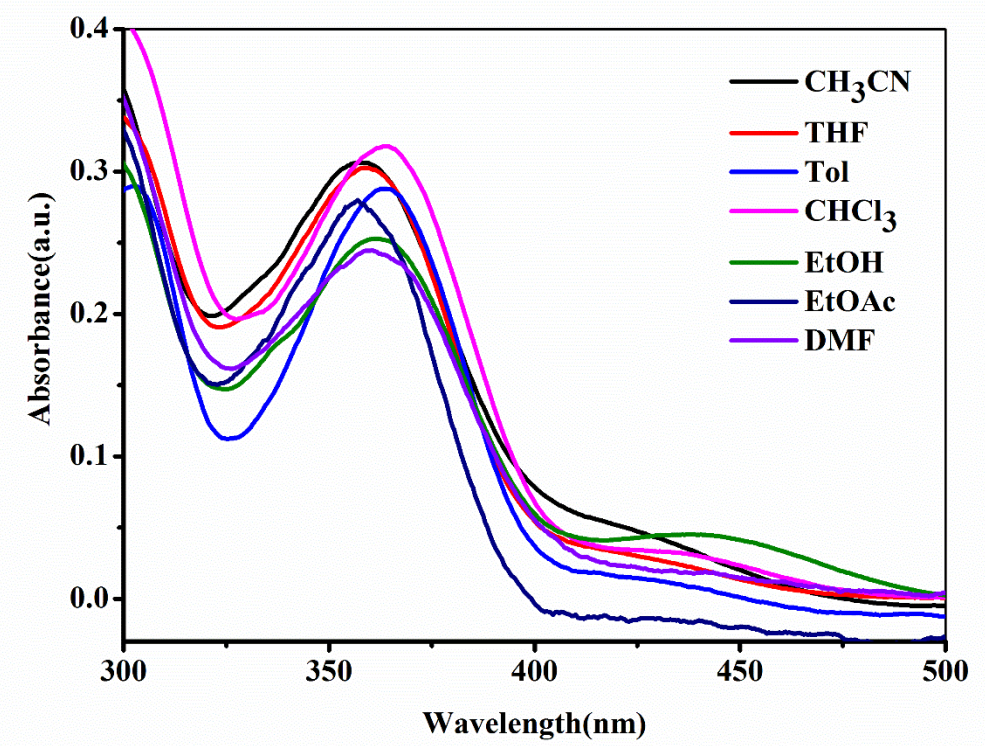


Fig. S13 Absorption spectrum of TPA-TP in different solvent

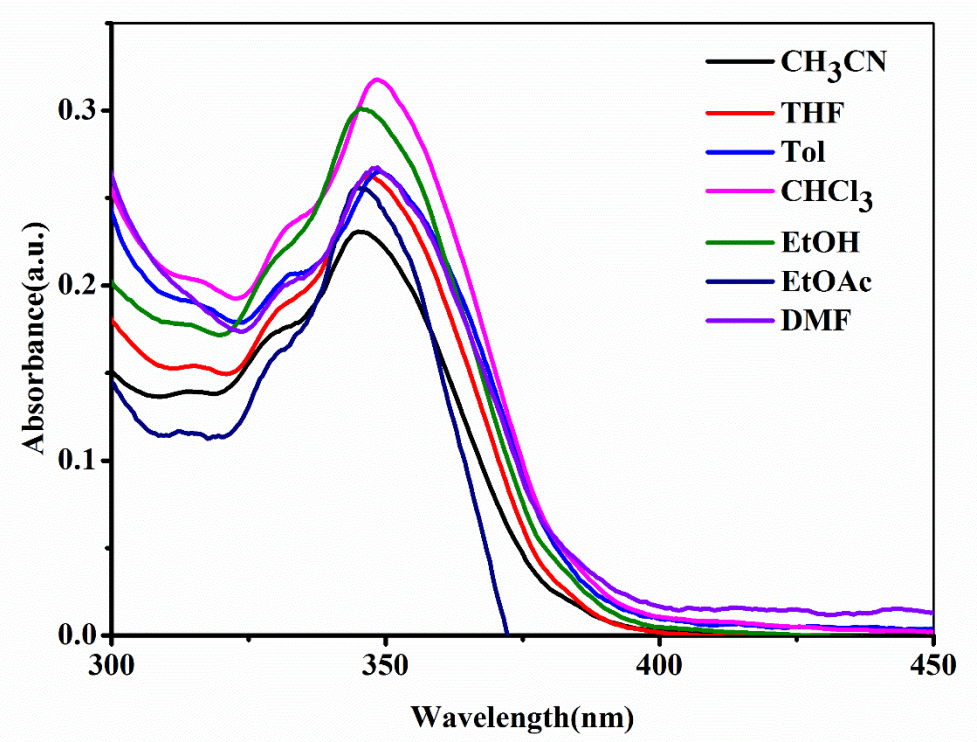


Fig. S14 Absorption spectrum of Py-TP in different solvent

Table S1. The absorbance data for **TPA-TP** in the different solvents

Solvent	Dielectric constant	λ_{max1} (nm)
Toluene	2.39	363
$CHCl_3$	4.81	364
EtOAc	6.02	356
THF	7.58	358
EtOH	24.3	361
CH_3CN	36.5	356
DMF	36.7	359

Table S2. The absorbance data for **Py-TP** in the different solvents

Solvent	Dielectric constant	λ_{max} (nm)
Tolune	2.39	348
$CHCl_3$	4.81	348
EtOAc	6.02	344
THF	7.58	347
EtOH	24.3	345
CH_3CN	36.5	345
DMF	36.7	348

Table S3. The emission data for **TPA-TP** in the different solvents. Quantum yield is compared to quinine sulphate standard.

Solvent	Dielectric constant	λ_{max} (nm)	Quantum yield
Toluene	2.39	426	0.30
$CHCl_3$	4.81	451	0.22
EtOAc	6.02	452	0.30
THF	7.58	451	0.16
EtOH	24.3	491	0.05
CH_3CN	36.5	489	0.08
DMF	36.7	484	0.18

Table S4. The data of emission for the compound **Py-TP** in the different solvents. Quantum yield is compared to quinine sulphate standard.

Solvent	Dielectric constant	λ_{max1} (nm)	Quantum yield
Toluene	2.39	402	0.30
$CHCl_3$	4.81	413	0.36
EtOAc	6.02	409	0.34
THF	7.58	409	0.19
EtOH	24.3	430	0.20
CH_3CN	36.5	420	0.28
DMF	36.7	421	0.24

6. Single crystal X-ray crystallography studies

Table S5. Crystal data and structure refinement for **TPA-TP** (CCDC: 2173855)

Identification code	SPA698	
Empirical formula	$C_{33}H_{24}N_4$	
Formula weight	476.56	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.1150(18) Å	α= 90°.
	b = 9.1470(18) Å	β= 90°.
	c = 29.340(6) Å	γ = 90°.
Volume	2446.2(8) $Å^3$	
Z	4	
Density (calculated)	1.294 Mg/m^3	
Absorption coefficient	0.061 mm^{-1}	
F(000)	1000	
Crystal size	0.041 x 0.021 x 0.008 mm^3	
Theta range for data collection	2.067 to 24.998°.	
Index ranges	-12<=h<=12, -12<=k<=12, -39<=l<=39	
Reflections collected	22108	
Independent reflections	6030 [R(int) = 0.1143]	
Completeness to theta = 22.210°	98.0 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.905	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6030 / 0 / 336	
Goodness-of-fit on F^2	0.827	
Final R indices [I>2sigma(I)]	R1 = 0.0507, wR2 = 0.0912	
R indices (all data)	R1 = 0.1215, wR2 = 0.1085	
Absolute structure parameter	0(5)	
Extinction coefficient	0.0165(14)	
Largest diff. peak and hole	0.189 and -0.174 $e.Å^{-3}$	

Table S6. Crystal data and structure refinement for **TPE-TP** (CCDC: 2173857)

Identification code	SPA681	
Empirical formula	C41 H29 N3	
Formula weight	563.67	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.174(2) Å	α= 100.57(3)°.
	b = 12.366(3) Å	β= 108.39(3)°.
	c = 12.944(3) Å	γ = 92.60(3)°.
Volume	1509.8(6) $Å^3$	
Z	2	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.057 mm^{-1}	
F(000)	592	
Crystal size	0.155 x 0.128 x 0.105 mm^3	
Theta range for data collection	1.494 to 24.999°.	
Index ranges	-13<=h<=13, -16<=k<=16, -17<=l<=17	
Reflections collected	14387	
Independent reflections	7229 [R(int) = 0.0127]	
Completeness to theta = 22.210°	95.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.946	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7229 / 0 / 397	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1485	
R indices (all data)	R1 = 0.0541, wR2 = 0.1526	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.308 and -0.312 $e.Å^{-3}$	

Table S7. Crystal data and structure refinement for **TPA-TP-PA** (CCDC: 2180021)

Identification code	SPA726	
Empirical formula	C39H27 N7O7	
Formula weight	704.66	
Temperature	220(2) K	
Wavelength	0.700 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 25.421(5) Å	a= 90°.
	b = 7.0150(14) Å	b= 96.02(3)°.
	c = 19.406(4) Å	g = 90°.
Volume	3441.5(12) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	1504	
Crystal size	0.094 x 0.018 x 0.015 mm^3	
Theta range for data collection	1.587 to 24.999°.	
Index ranges	-30<=h<=30, -8<=k<=8, -23<=l<=23	
Reflections collected	22724	
Independent reflections	6204 [R(int) = 0.0556]	
Completeness to theta = 24.835°	97.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.848	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6204 / 343 / 742	
Goodness-of-fit on F^2	1.360	
Final R indices [I>2sigma(I)]	R1 = 0.1155, wR2 = 0.3327	
R indices (all data)	R1 = 0.1532, wR2 = 0.3620	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.549 and -0.656 $e.Å^{-3}$	

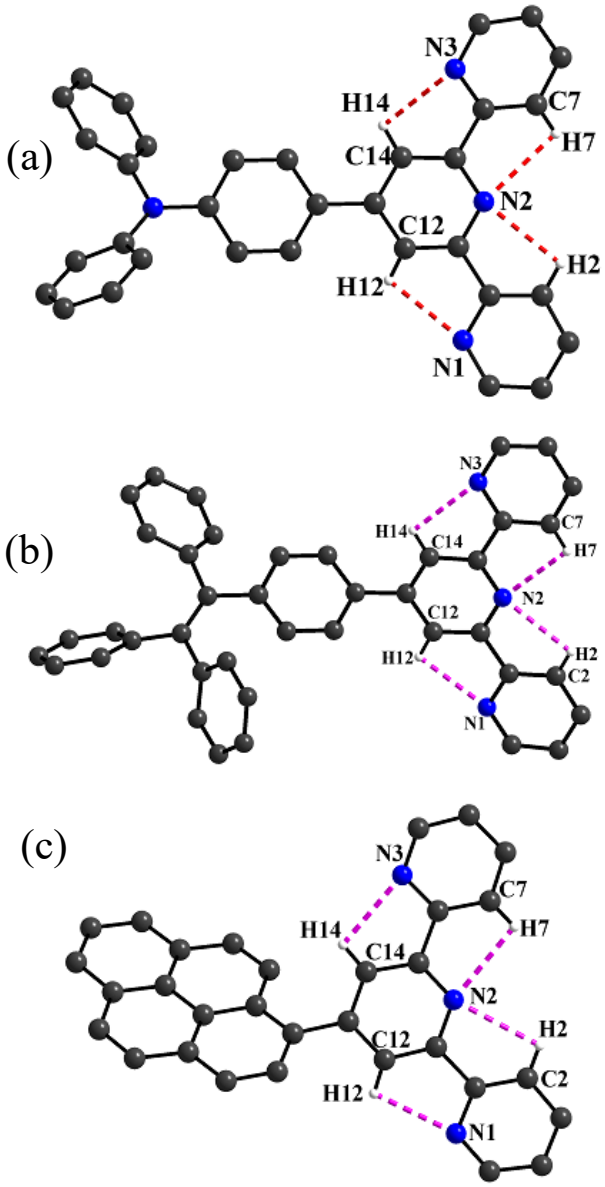


Fig. S15C-H•••N intramolecular hydrogen bonding interactions in (a) TPA-TP (b) TPE-TP and (c) Py-TP

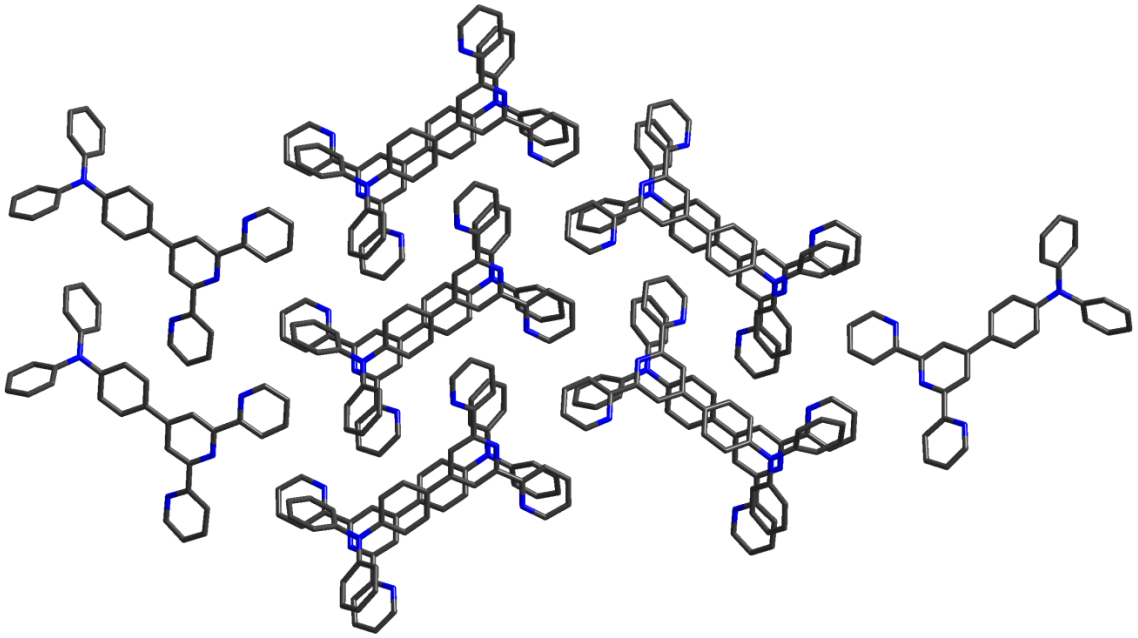


Fig. S16 Molecular packing of **TPA-TP** in crystal lattice.

7. DSC studies

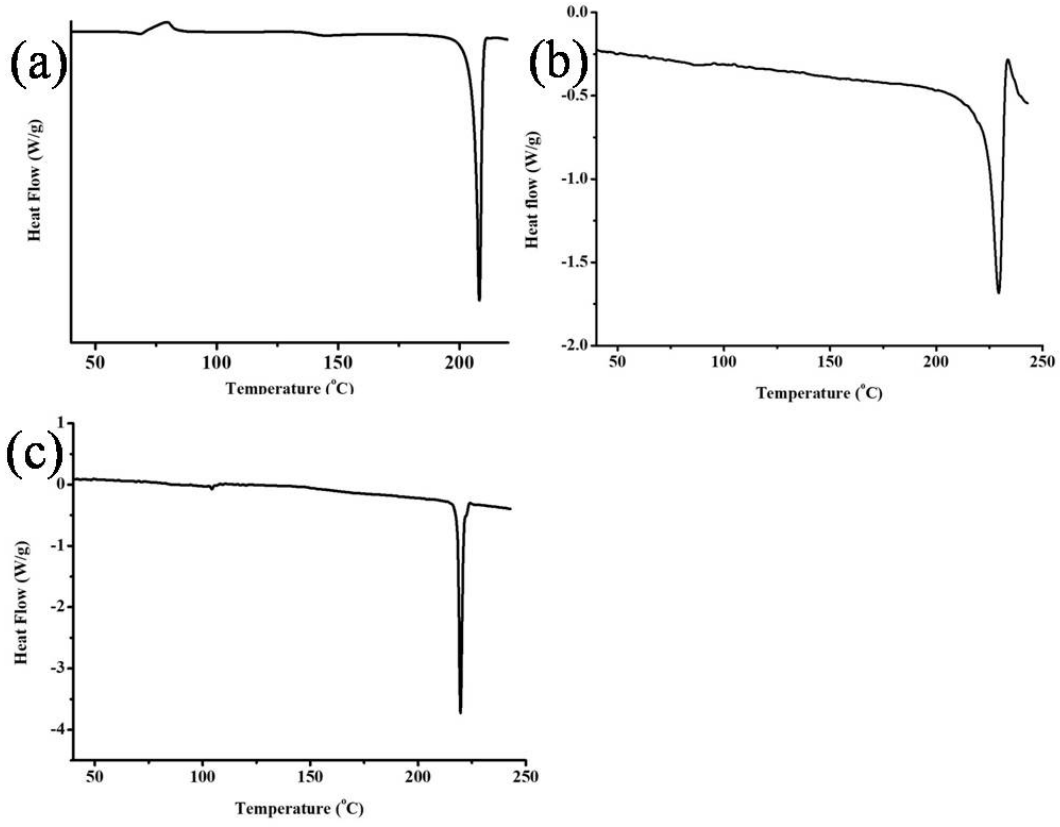


Fig. S17. DSC of (a) **TPA-TP,** (b) **TPE-TP** and (c) **Py-TP**.

7. Fluorescence sensing studies of nitroaromatics

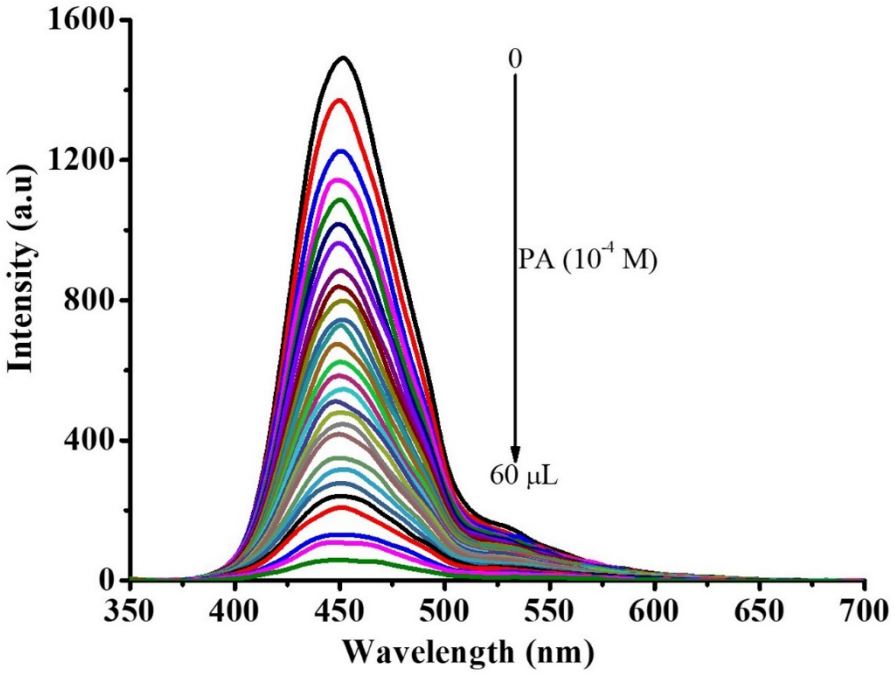


Fig. S18 Concentration dependent fluorescence quenching of **TPA-TP** by PA.λ_{exc} = 350 nm.

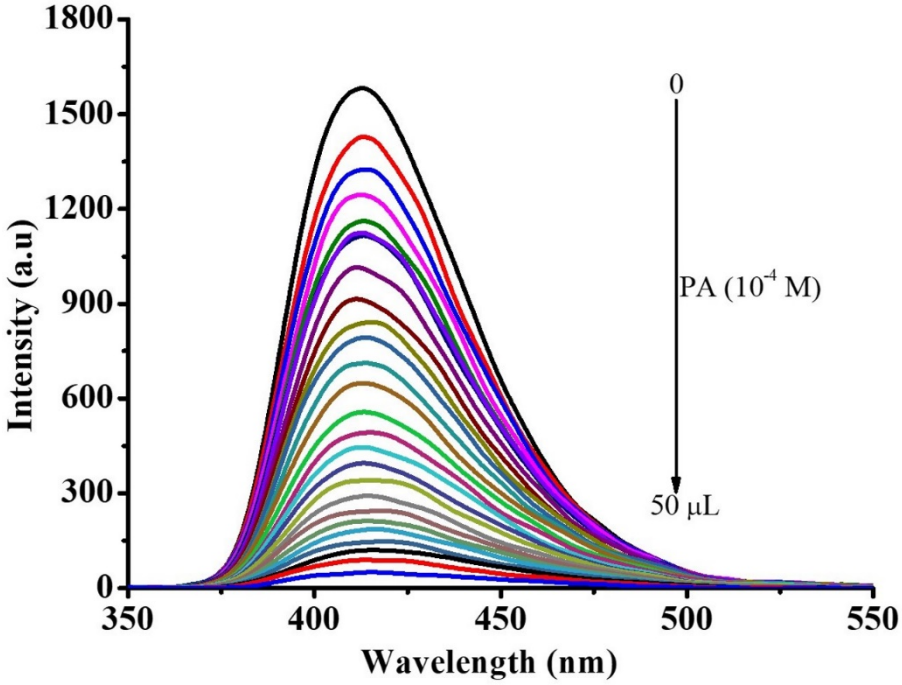


Fig. S19 Concentration dependent fluorescence quenching of **Py-TP** by PA.λ_{exc} = 350 nm.

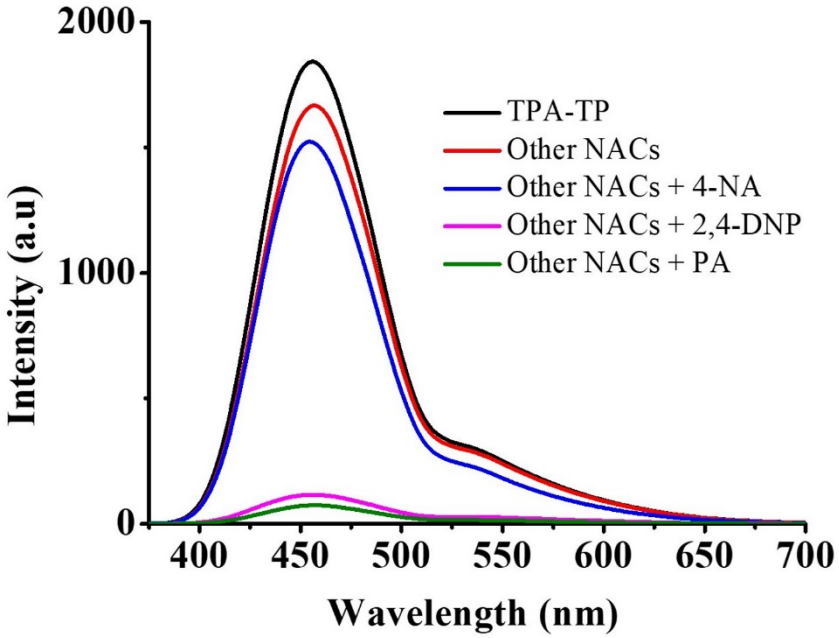


Fig. S20 Interference studies of **TPA-TP** probe PA fluorescence sensing in presence of other NACs.λ_{exc} = 350 nm.

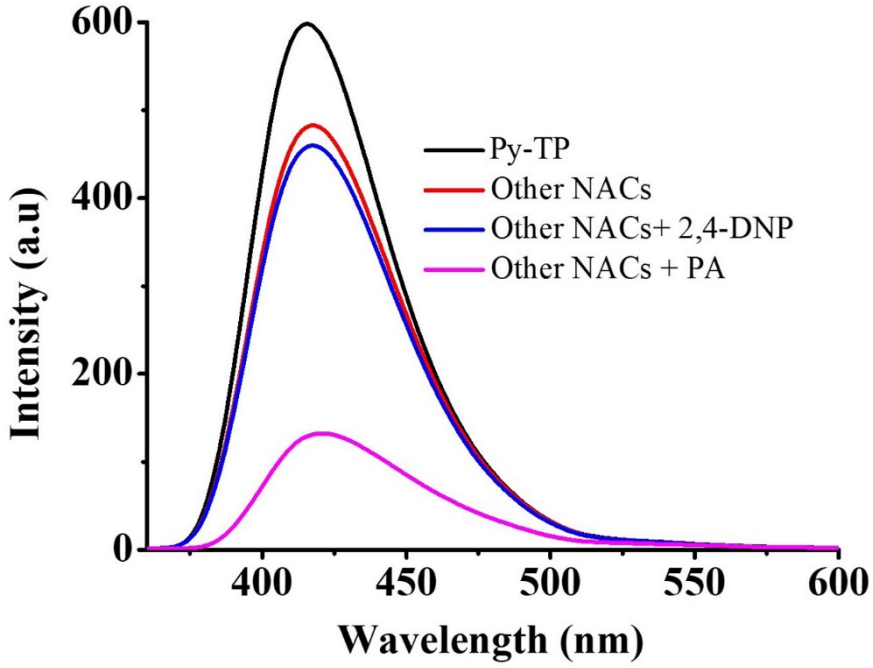


Fig. S21 Interference studies of **Py-TP** probe PA fluorescence sensing in presence of other NACs.λ_{exc} = 350 nm.

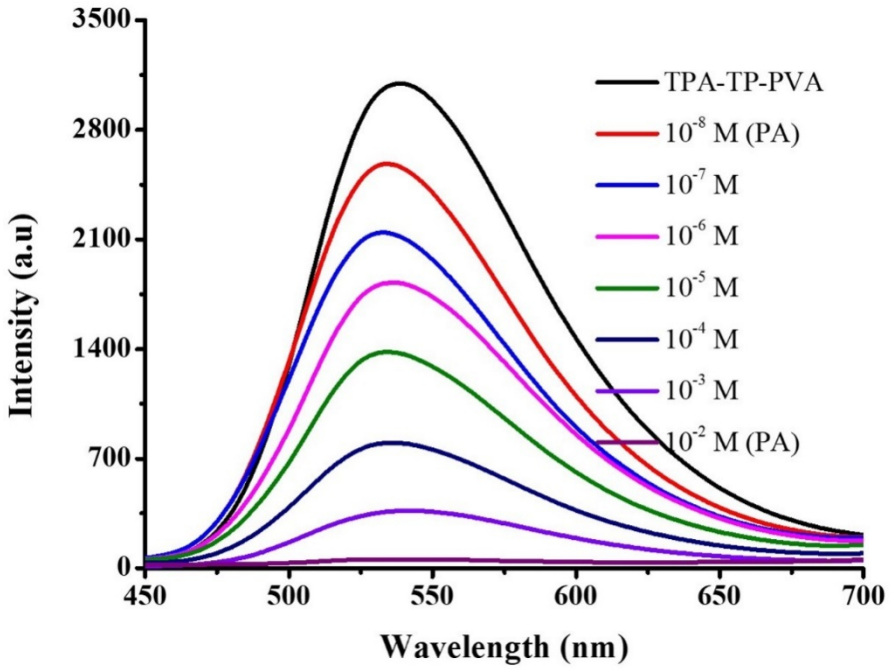


Fig. S22 Fluorescence quenching of **TPA-TP**-PVA upon into different concentration of PA.λ_{exc} = 350 nm.

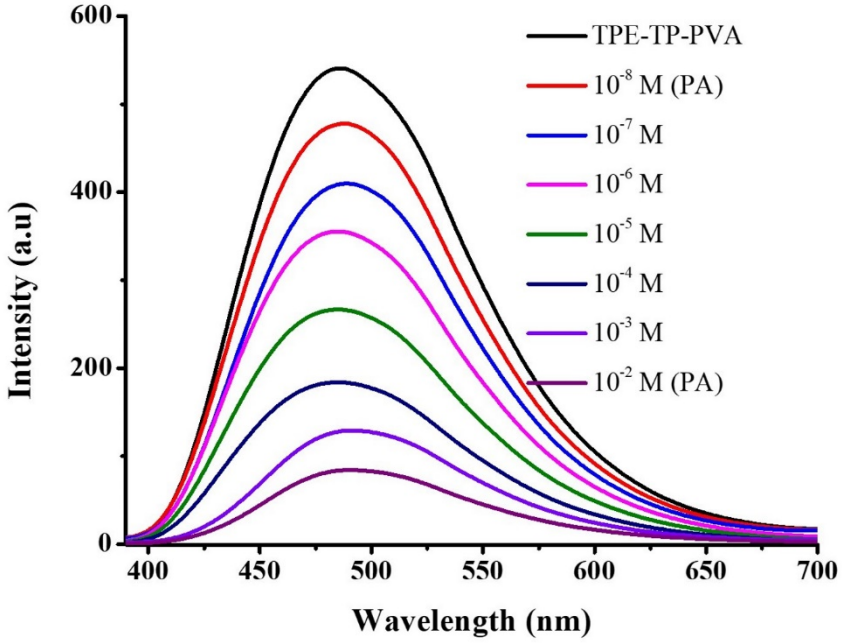


Fig. S23 Fluorescence quenching of **TPE-TP**-PVA upon into different concentration of PA.λ_{exc} = 350 nm.

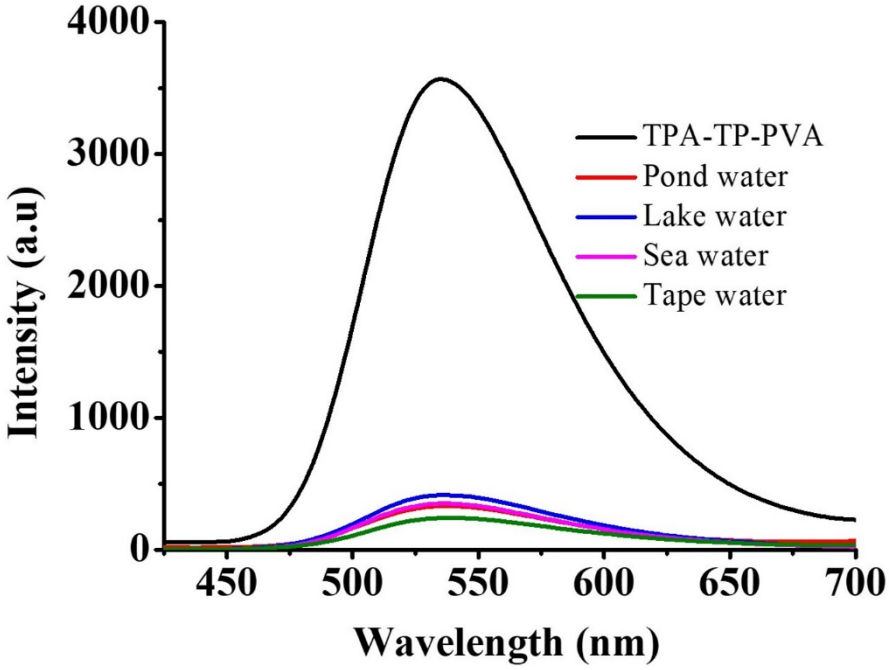


Fig. S24 Fluorescence sensing of PA dissolved in real water samples using **TPA-TP-**PVA thin films.λ_{exc} = 350 nm.

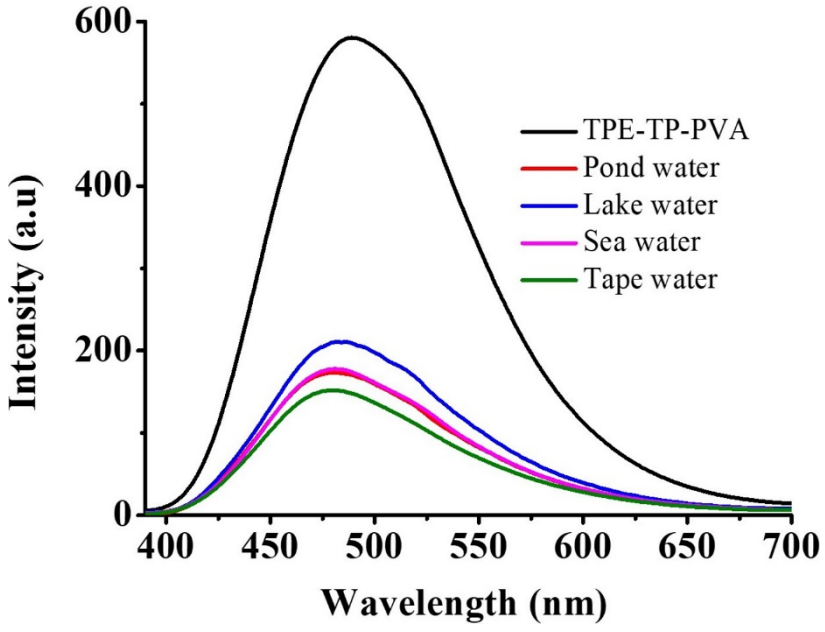


Fig. S25 Fluorescence sensing of PA dissolved in real water samples using **TPE-TP-**PVA thin films.λ_{exc} = 350 nm.

Table S8.TPA-TP-PVA thin film sensing of PA in real water samples with known concentration.

Sample	Spiked (M)	Detected (M)	Recovery (%)
Sea water	10^{-3}	$0.94x10^{-3}$	94%
	10^{-6}	$0.97x10^{-6}$	97%
River water	10^{-3}	$0.98x10^{-3}$	98%
	10^{-6}	$0.96x10^{-6}$	96%
Pond water	10^{-4}	$0.99x10^{-4}$	99%
	10^{-7}	$0.97x10^{-7}$	97%
Lake water	10^{-4}	$0.96x10^{-4}$	96%
	10^{-7}	$0.98x10^{-7}$	98%

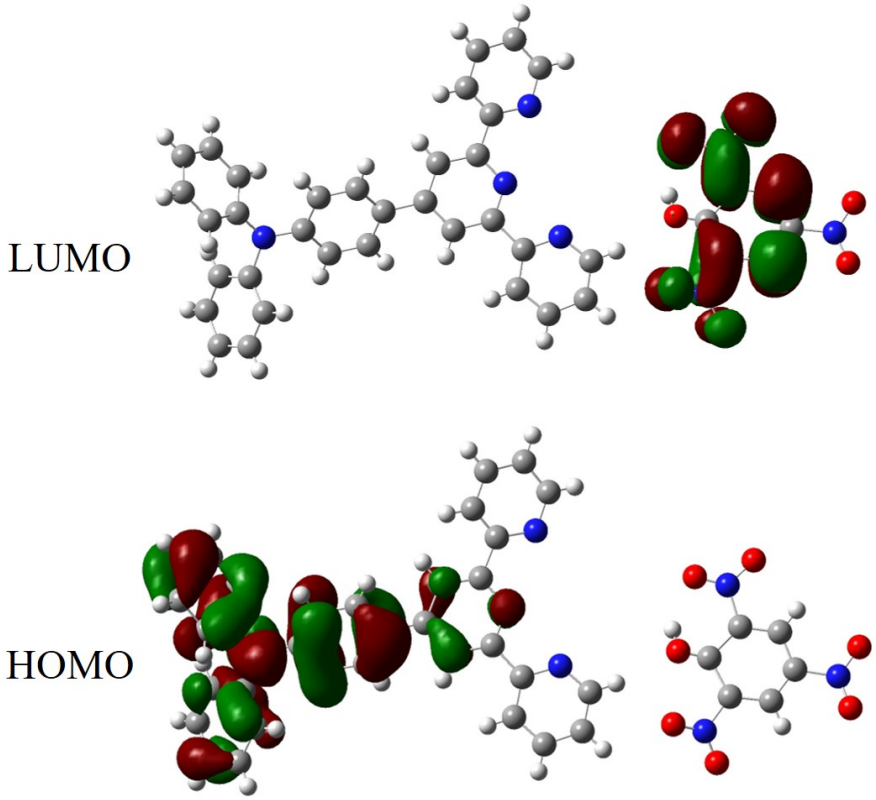


Fig. S26 HOMO-LUMO of **TPA-TP**-PA.