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A Sensitive and Selective Sensor for Picric Acid Detection with a Fluorescence Switching Response

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Supporting information

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1. Materials and methods

All commercially obtained chemicals were used as received. As required the solvents were dried as per the standard protocols. Silica gel or neutral alumina used as stationery phase for column chromatography. Alluminium sheets coated with silica gel were used for thin layer chromatography (TLC) to monitor the reactions and column purifications. Infrared spectra were measured on a Perkin Elmer IR spectrometer at room temperature by preparing the KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. Mass spectrometry was carried out using MALDI-TOF mass spectrometer or High Resolution Mass Spectrometer. Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer was used to obtain UV-Vis spectra, while Fluoromax-4 fluorescence spectrophotometer and Perkin Elmer LS 50B spectrometer were used to obtain emission spectra in solution state and solid thin film state respectively. Steady State anisotropy experiment was performed on Horiba Scientific Fluoromax spectrofluorometer 4. Time resolved lifetime measurements were done on time correlated single photon counter from Horiba Jobin Yvon (excitation by 440 nm laser diode). Atomic Force microscopy (AFM) images were obtained for the spin-coated films using Agilent 5500-STM instrument. Field Emission Scanning Electron Microscope (FESEM) images were recorded on Zeiss Sigma microscope at an accelerating voltage of 2kV. The xerogel of the compounds were prepared from gel state, evaporating the solvent first in air for 2-3 days followed by vacuum. Then, the morphologies of the xerogel were examined by AFM and FESEM. We used B3LYP hybrid density functional and 6-31G(d) basis set for all the calculations. No imaginary frequencies were found in all these optimization calculations, suggesting that these structures are minmium points on the potential energy surface. More importantly we performed all these calculations considering the presence of solvent (DMSO) using Polarizable Continuum Model (PCM) as implemented in Gaussian 09. First in order to find the possible protonation site, we performed five calculations on the tetrazole molecule by bonding Hydrogen to Nitrogen atom one at a time. Out of all these five runs, one configuration (Hydrogen bonded to the nitogen atom of oxadiazole ring which is near to the trialkoxy benzene ring) found with minimum energy is proposed as the possible site for protonation. Using this protonated tetrazole and picrate anion, we performed a calculation for the total complex.

2. Experimental section

Caution! The nitroaromatic compounds used in this study, specially TNT and picric acid, are very powerful explosives. They must be handled with care and also in very small quantities.

Procedure for the synthesis of ethyl 3,4,5-trihexadecyloxy benzoate (5)[1]

A mixture of ethyl gallate (15.1 mmol, 1equiv.), anhydrous K_2CO_3 (99.9 mmol, 6.6 equiv.), *n*-bromohexadecane (49.83 mmol, 3.3 equiv.) were taken in dry DMF and heated at 80 ^oC for 24 h under nitrogen atmosphere. Then the reaction mixture was poured into water and extracted with ethyl acetate. The combined extract was washed with water and dried over anhydrous Na_2SO_4 and then concentrated. The crude product was purified by column chromatography on silica. Elution with hexanes followed by 2-5% ethyl acetate-hexane yielded the desired product.

R_f = 0.5 (5% EtOAc - hexanes); white solid; yield: 75%; IR (KBr pellet): ν_{max} in cm^{-1} 2922, 2850, 1716, 1583, 1468, 1426, 1331, 1218, 1110, 1041; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25 (s, 2H, H_{Ar}), 4.35 (q, 2H, J = 7.2 Hz, $COOCH_2$), 4.01 (t, 6H, 3 × OCH_2), 1.25-1.82 (m, 84H, 42 × CH_2), 0.87 (m, 12H, 4 × CH_3), ^{13}C NMR ($CDCl_3$, 100 MHz): 166.70, 153.04, 142.61, 125.28, 108.29, 73.72, 69.44, 61.17, 33.05, 32.16, 30.56, 29.94, 29.89, 29.87, 29.80, 29.63, 29.60, 29.57, 26.32, 26.29, 22.92, 14.63, 14.33. HRMS (ESI+) exact mass calculated for $C_{57}H_{107}O_5$ (M+1): 871.8119, Found: 871.8031.

Procedure for the synthesis of ethyl 3, 4, 5-tris (hexadecyloxy) benzhydrazide (4)[1]

A mixture of ethyl 3,4,5-tri-*n*-hexadecyloxybenzoate (10 mmol, 1equiv.), excess hydrazine hydrate (20 equiv.), in ethanol was refluxed for 48 h. Excess solvent was removed and water was added to it. Resulting precipitate was collected by filtration, washed with excess water, dried under vacuum, and recrystallization from ethanol gave white solid product.

R_f = 0.52 (20% EtOAc-hexanes); white solid, yield: 75%; IR (KBr pellet): ν_{max} in cm^{-1} 3448.94, 3248.41, 2921.55, 2850.68, 1635.32, 1579.85, 1466.26, 1427.84, 1238.90, 1122.06; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.22 (br s, 1H, CONH), 6.92 (s, 2H, H_{Ar}), 4.07 (s, 2H, NH_2), 3.99 (m, 6H, 3 × OCH_2), 1.26–1.80 (m, 84H, 42 × CH_2), 0.88 (m, 9H, 3 × CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 168.70, 153.54, 141.92, 127.68, 105.74, 69.60, 30.53, 29.97, 29.95, 29.88, 29.60, 26.30, 22.92, 14.33. HRMS (ESI+) exact mass calculated for $C_{55}H_{105}N_2O_4$ (M+1): 857.8074, Found: 857.8151.

Procedure for the synthesis of 4-(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzonitrile (2)

4-Cyanobenzoic acid was refluxed with thionyl chloride (excess) in presence of DMF (few drops, as catalyst) for 4 h. Excess thionyl chloride was distilled out and the crude residue was taken in THF and slowly added into the THF solution of compound **4** (3.3 eqv.) and TEA (3 eqv.) under argon atmosphere and then refluxed for 6 h. The reaction mixture was extracted with chloroform, washed with 3 × 50 mL of water. The chloroform extract was dried over Na_2SO_4, evaporated and used as such without any purification. The residue was refluxed with $POCl_3$ for 12 h, and then the reaction mixture was cooled. This was carefully poured into ice-cold water and then extracted with chloroform. The chloroform extract was washed several times with water, dried over anhyd.Na_2SO_4, and concentrated. The compound was further purified by column chromatography over neutral alumina using 10-50% EtOAc:Hexane. Finally the compound was purified by recrystallization in DCM-ethanol mixture.

R_f = 0.5 (60% EtOAc - hexanes); white solid; m.p.: 94-96 ^oC; yield: 70%; IR (KBr pellet): ν_{max} in cm^{-1} 3448, 2919, 2851, 2230, 1594, 1546, 1492, 1469, 1439, 1122, ; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.26 (d, 2H, *J* = 6 Hz, H_{Ar}), 7.84 (d, 2H, *J* = 6 Hz, H_{Ar}) 7.31 (s, 2H, H_{Ar}), 4.08-4.04 (m, 6H, 3 × OCH_2), 1.87-1.25 (m, 84H, 42 × CH_2), 0.89-0.86 (m, 9H, 3 × CH_3), ^{13}C NMR ($CDCl_3$, 100 MHz): 165.74, 163.04,153.87, 141.99, 133.06, 128.03, 127.51, 118.15, 118.04, 115.23, 105.74, 73.88, 69.62, 32.14, 30.55, 29.97, 29.96, 29.94, 29.88, 29.86, 29.79, 29.62, 29.59, 29.52, 26.31, 26.28, 22.91, 14.34. MALDI-TOF exact mass calculated for $C_{63}H_{106}N_3O_4$ (M+H): 968.8183, Found: 968.689.

Procedure for the synthesis of 5-(4-(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)-2H-tetrazole (1)

A mixture of compound **2**, NaN_3 (1.5 eqv.) and NH_4Cl (1.3 eqv.) in DMF was heated at 120 ^oC for 36 h. DMF was removed in rotavapor and the solid compound was washed several times with water, then with ethanol and chloroform, dried in vacuum to obtain a white solid; yield: 56 %; m.p.: >300 ^oC IR (KBr pellet): ν_{max} in cm^{-1} 3443, 2918, 2850, 1649, 1588, 1556, 1496, 1466, 1379, 1126; ^1H NMR (DMSO-D_6, 600 MHz): δ 8.22 (d, 2H, *J* = 6 Hz, H_{Ar}), 8.13 (d, 2H, *J* = 6 Hz, H_{Ar}) 7.37 (s, 2H, H_{Ar}), 4.12 (t, 4H, J = 6Hz, 2 × OCH_2) 4.00 (t, 2H, 1 × OCH_2), 1.81-1.19 (m, 85H, 42 × CH_2, 1× NH), 0.87-0.84 (m, 9H, 3 × CH_3). MALDI-TOF exact mass calculated for $C_{63}H_{107}N_6O_4$ (M+1): 1011.8348, Found: 1012.440.

3. NMR spectra

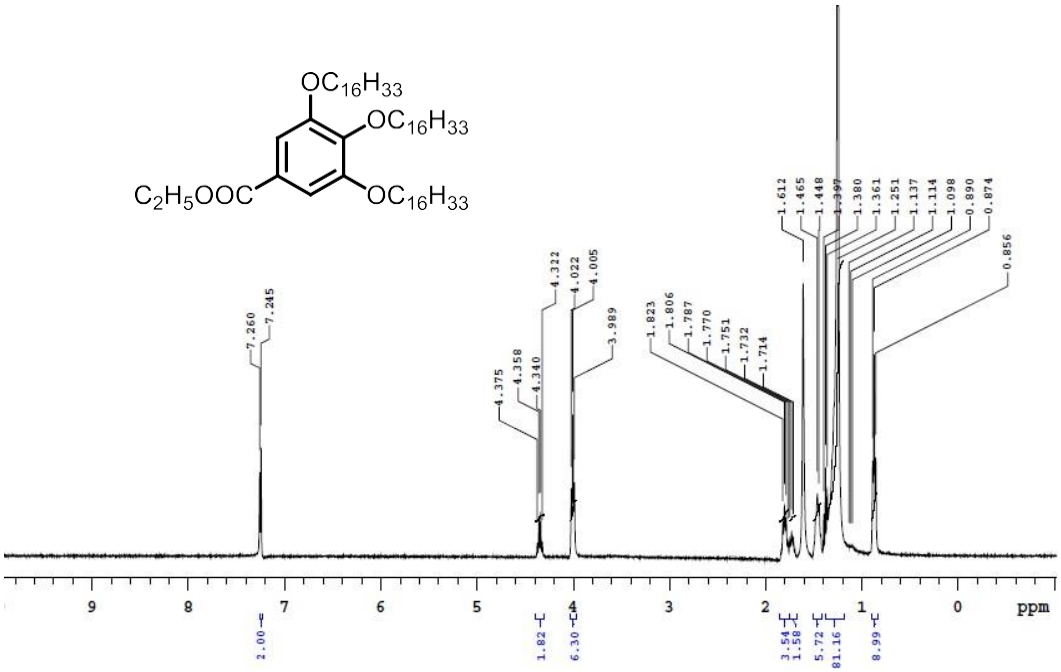


Figure S1. ^{1}H NMR (400 MHz) spectra of **5** in $CDCl_3$

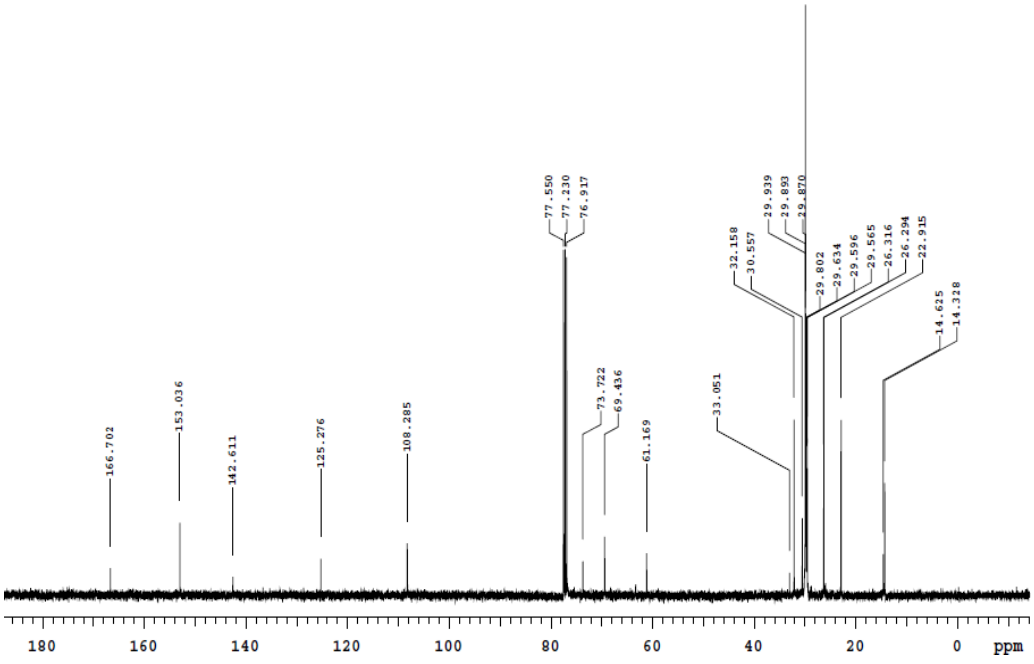


Figure S2. ^{13}C NMR (100 MHz) spectra of **5** in $CDCl_3$

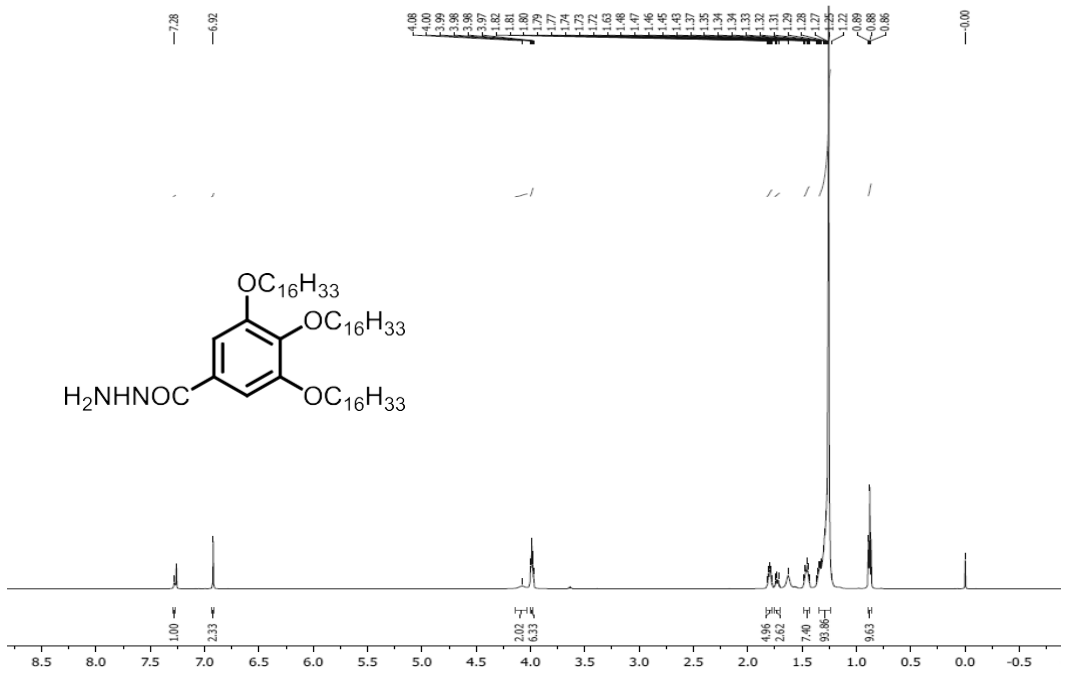


Figure S3. ^{1}H NMR (400 MHz) spectra of **4** in $CDCl_3$

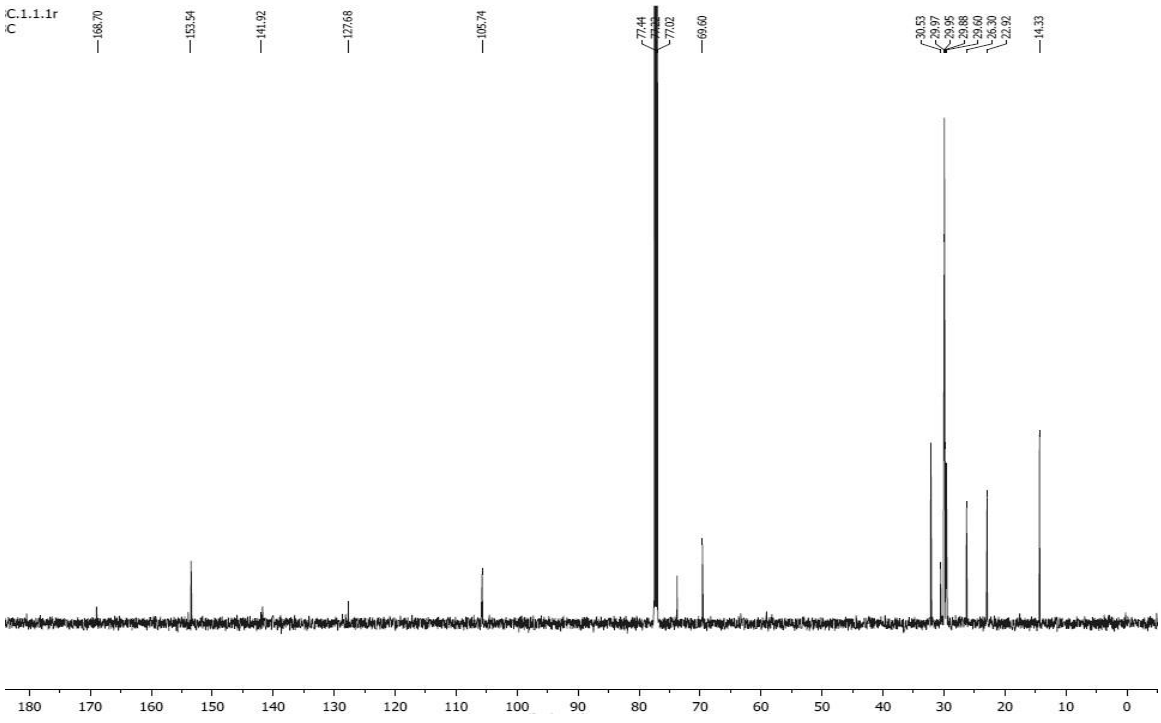


Figure S4. ^{13}C NMR (100 MHz) spectra of **4** in $CDCl_3$

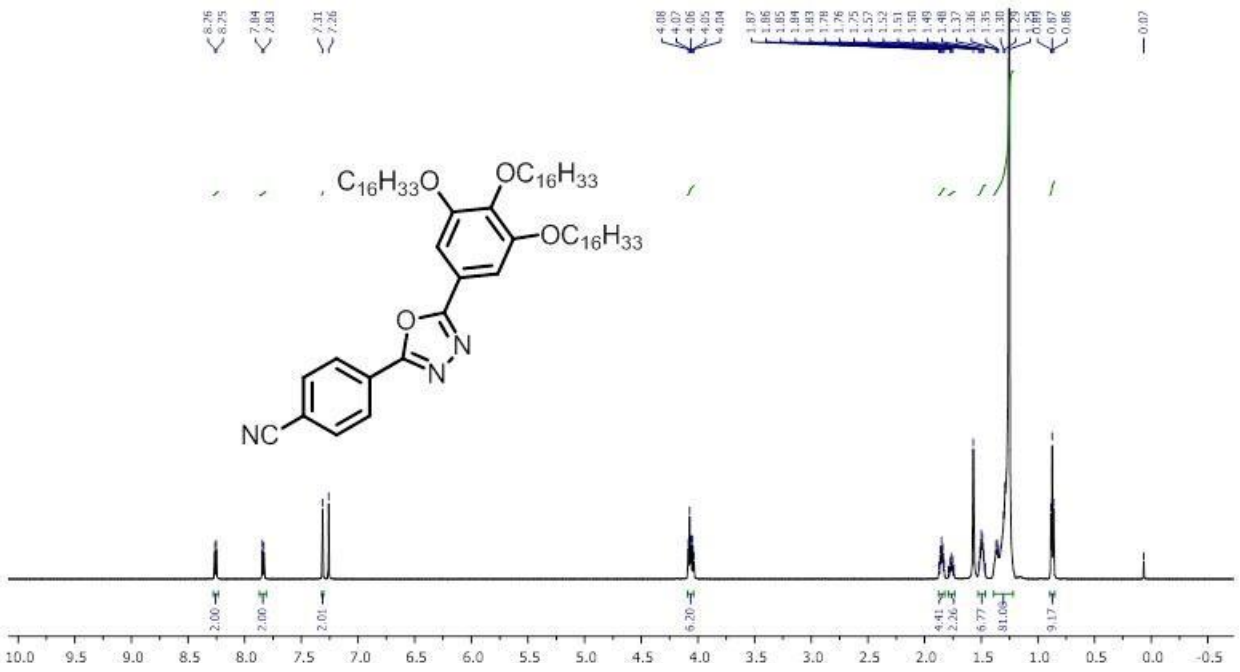


Figure S5. ^{1}H NMR (600 MHz) spectra of **2** in $CDCl_3$

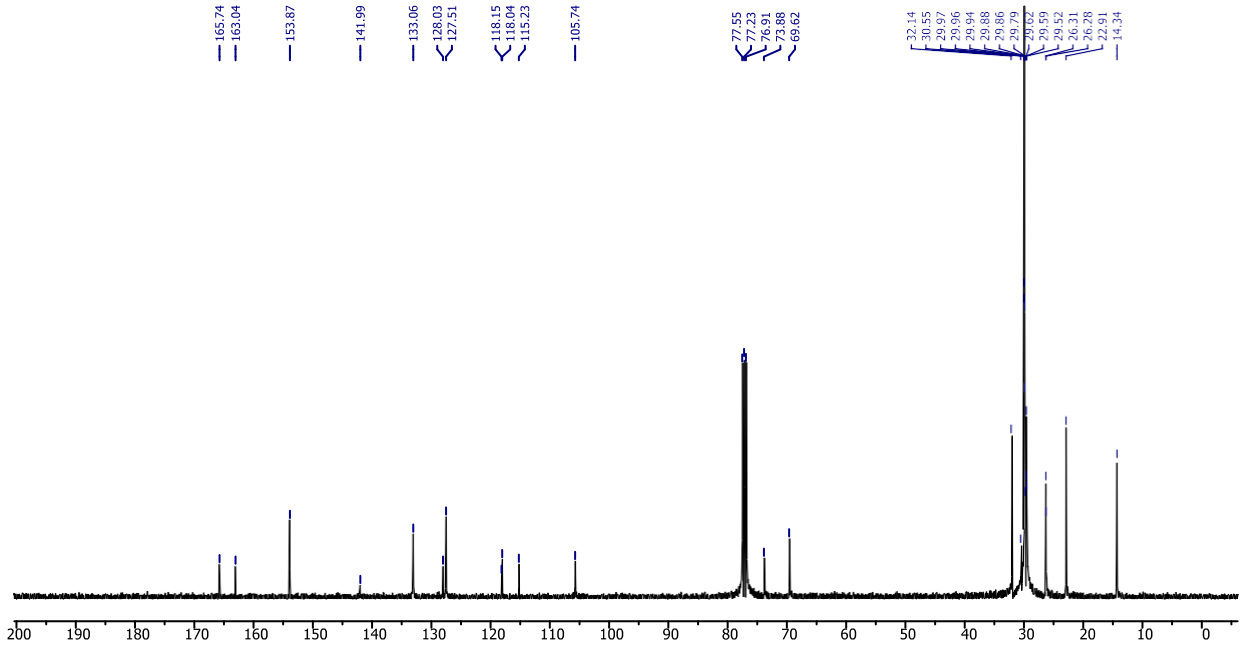


Figure S6. ^{13}C NMR (150 MHz) spectra of **2** in $CDCl_3$

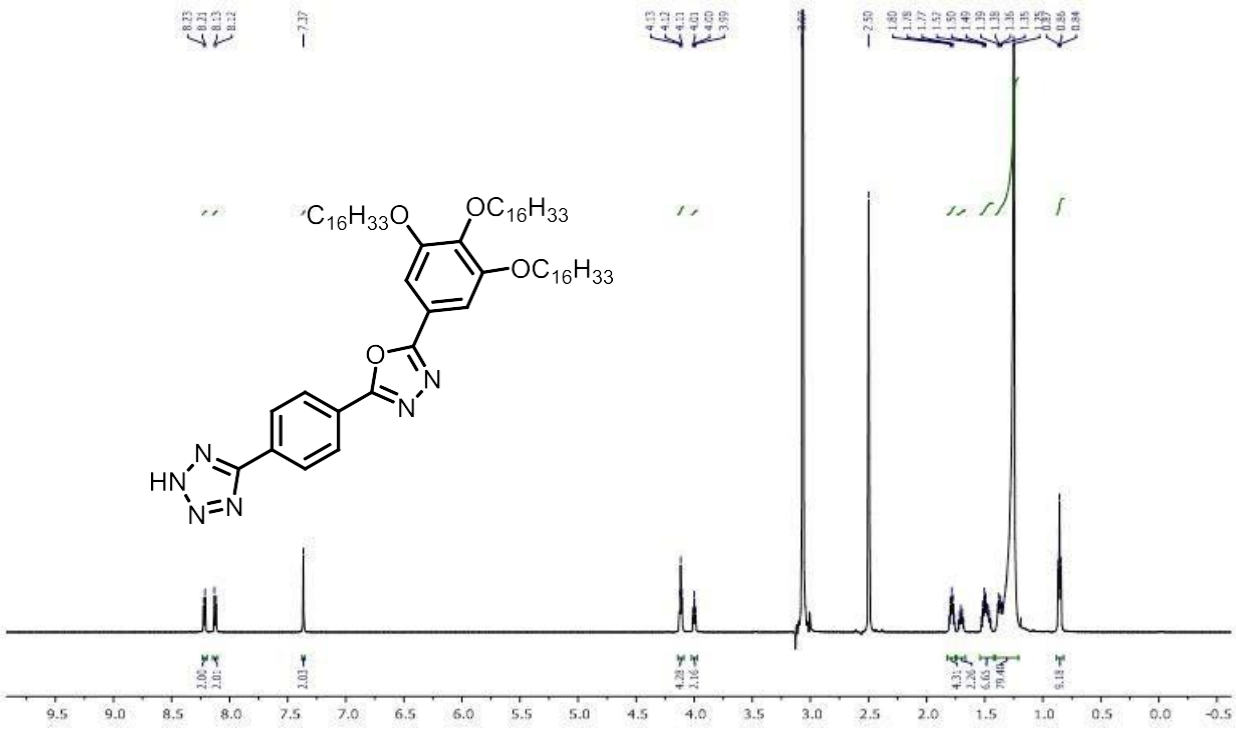


Figure S7. ^{1}H NMR (600 MHz) spectra of **1** in DMSO-d_6

4. Photophysical properties

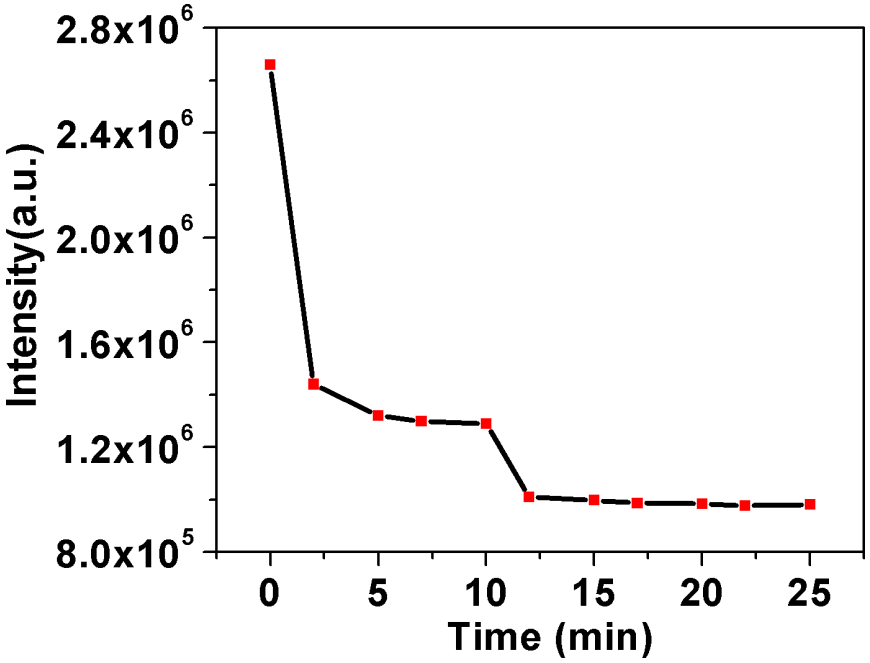


Figure S8. Change in the emission intensity *vs* time on gelation.

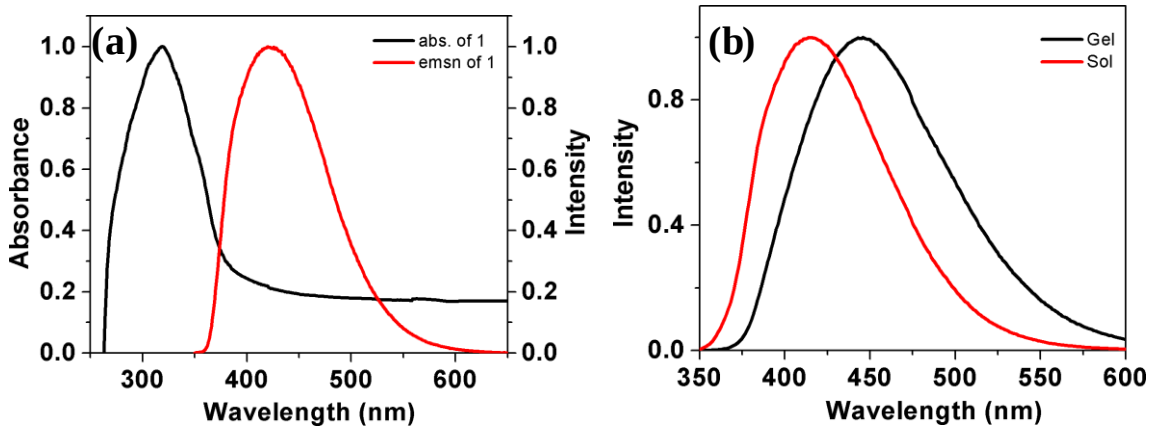


Figure S9. Absorption and emission of the compound **1** in micromolar solution of DMSO (a); emission spectra of compound **1** in solution and gel state (concentration: 7.2 mM in DMSO, λ_{exc} = 318 nm)

5. Gelation studies

Table S1. Gelation behavior of compound **1** in different solvents

Sl. No	Solvent	Compound **1**		
		Properties	CGC (wt%)	T_{gel} (^{o}C)
1	DMSO	G(O)	0.58	45
2	Hexane	I	.....	.....
3	Chloroform	I	.....	.....
4	Dichloromethane	I	.....	.....
5	Ethylacetate	I	.....	.....
6	Methanol	I	.....	.....
7	Ethanol	I	.....	.....
8	Benzene	I	.....	.....
9	Toluene	I	.....	.....
10	THF	I	....	.....
G: Gel; O: Opaque; I: Insoluble				

6. Sensing studies

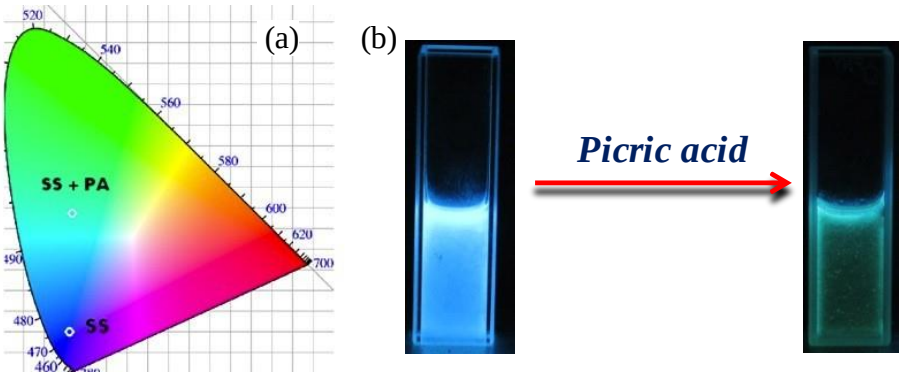


Figure S10. CIE co-ordinate of compound **1** before and after addition of Picric acid (a). Emission change of compound **1** from blue to green after addition of picric acid (b)

Table S2. CIE co-ordinates of compound **1** with different nitroaromatics and the color corresponding to each addition.

Sl.no	Compound	X-coordinate	y-coordinate	Color
1	1	0.156477	0.103152	
2	1 + 2,4-DNBA	0.156832	0.111007	
3	1 + 2,4-DNT	0.15669	0.10952	
4	1 + 2,6-DNT	0.15669	0.10952	
5	1 + 4-NBA	0.156477	0.103152	
7	1 + 4-NT	0.15669	0.10952	
8	1 + BA	0.156477	0.103152	
9	1 + m-DNB	0.156541	0.108646	
10	1 + NB	0.156541	0.108646	
11	1 + NM	0.156832	0.111007	
12	1 + PA	0.164059	0.39057	

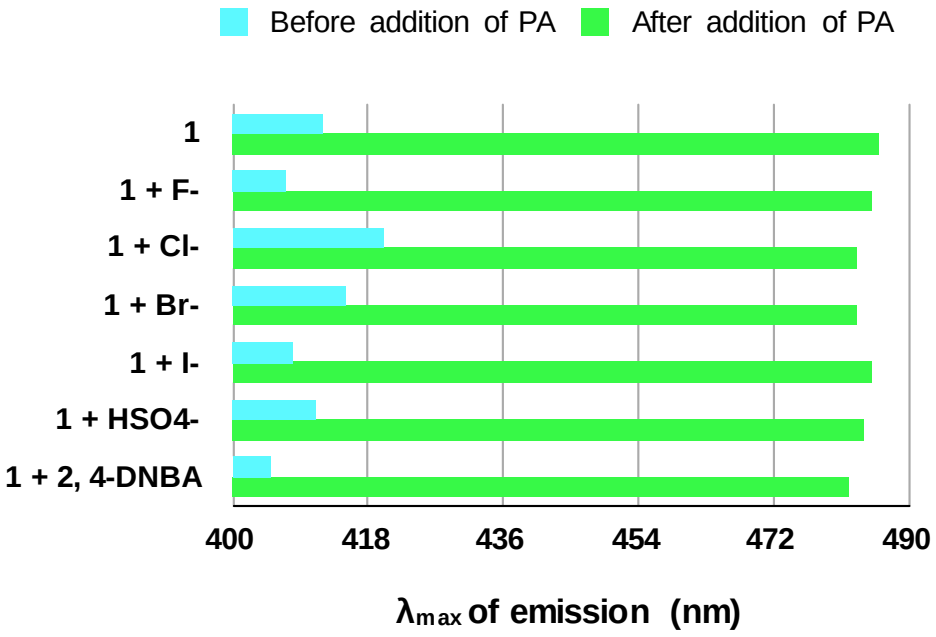


Figure S11. Fluorescence response to the PA in presence of different anions by DMSO solution of **1**.

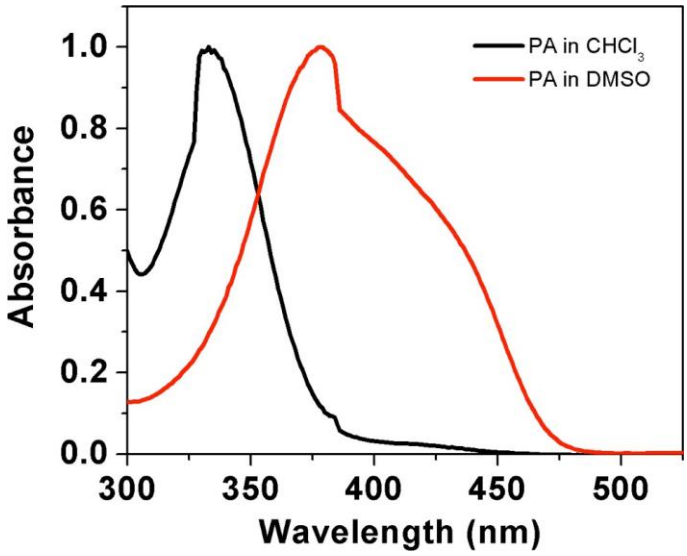


Figure S12. The normalized absorption spectra of picric acid in chloroform and DMSO.

7. Thermogravimetric Analysis

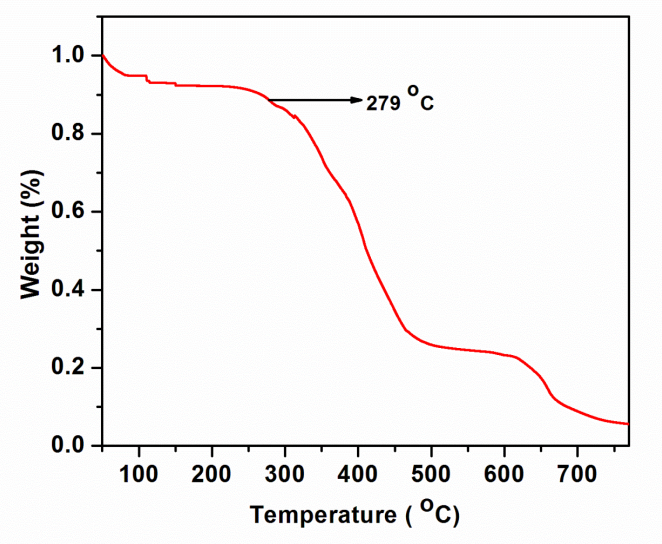
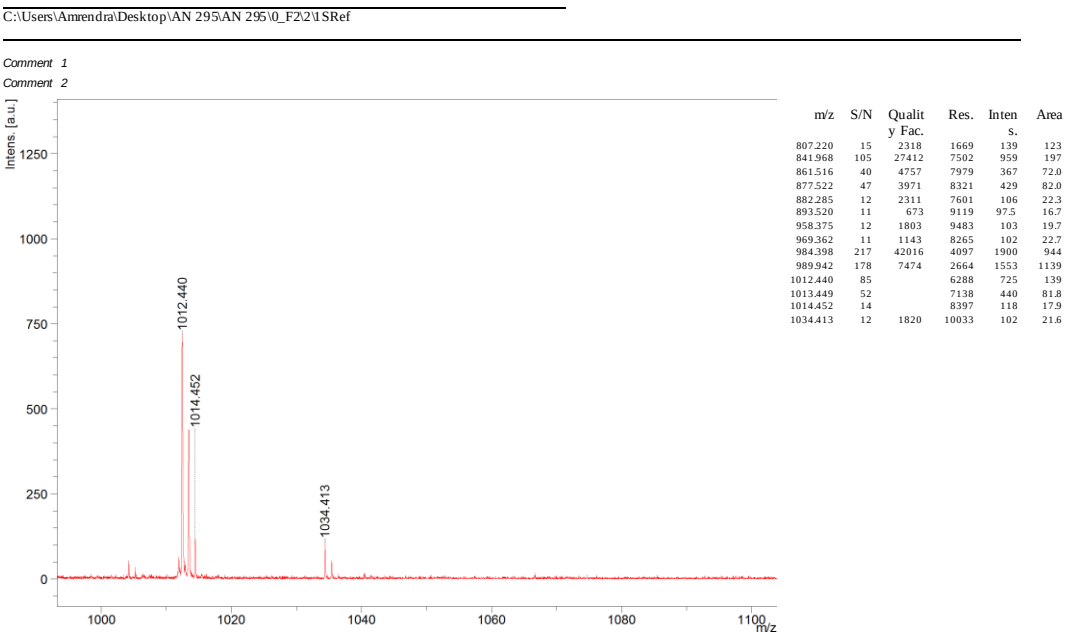


Figure S13. TGA graph showing the stability of compound **1** upto 279 °C.

8. MALDI-TOF studies



m/z	S/N	Quality Fac.	Res.	Intens.	Area
807.220	15	2318	1669	139	123
841.968	105	27412	7502	959	197
861.516	40	4757	7979	367	72.0
877.522	47	3971	8321	429	82.0
882.285	12	2311	7601	106	22.3
893.520	11	673	9119	97.5	16.7
958.375	12	1803	9483	103	19.7
969.362	11	1143	8265	102	22.7
984.398	217	42016	4097	1900	944
989.942	178	7474	2664	1553	1139
1012.440	85		6288	725	139
1013.449	52		7138	440	81.8
1014.452	14		8397	118	17.9
1034.413	12	1820	10033	102	21.6

Figure S14. MALDI-TOF spectrogram of compound **1**

9. DFT studies

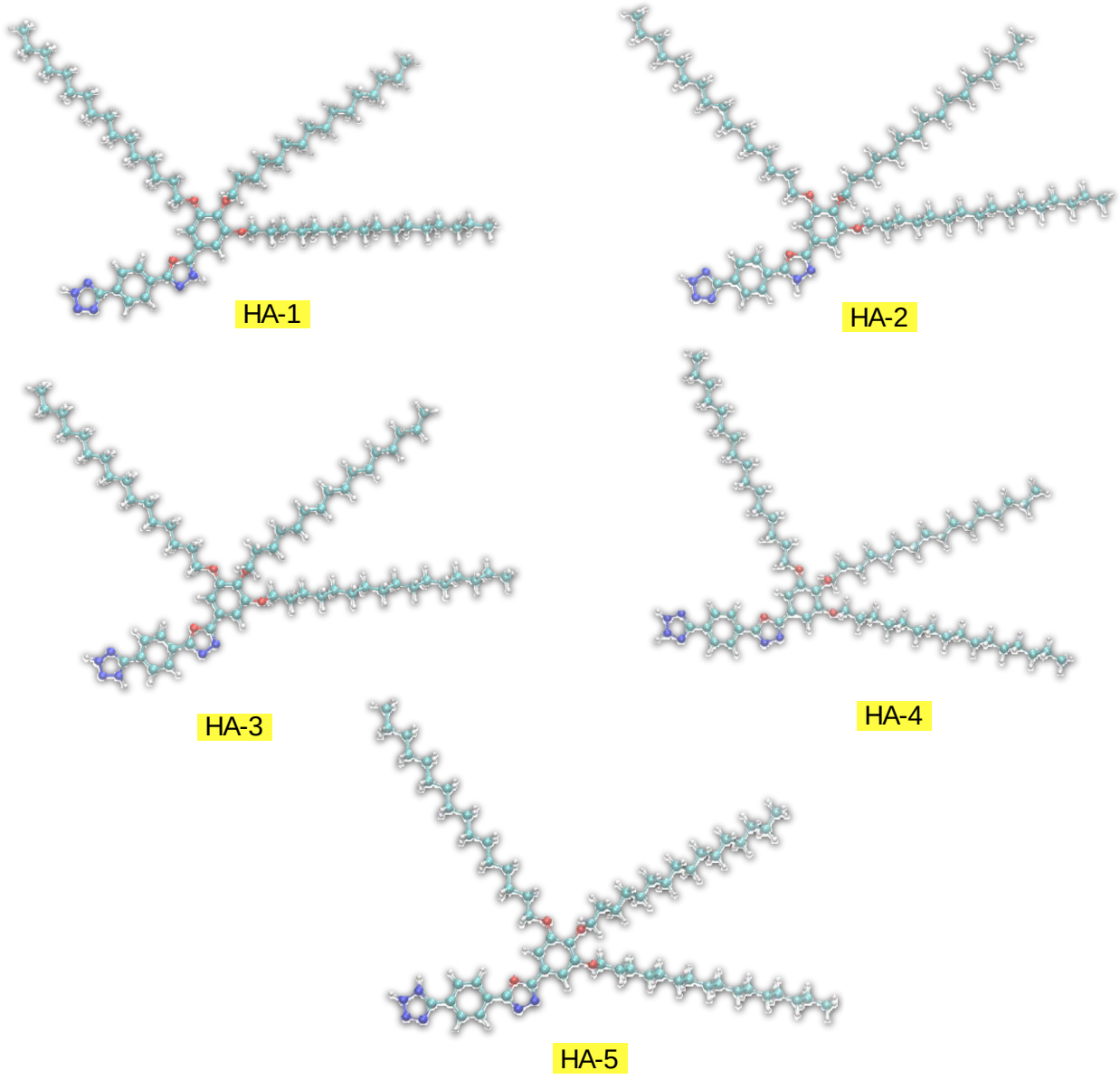


Figure S15. Energy minimized structures of possible protonated forms of compound **1**.

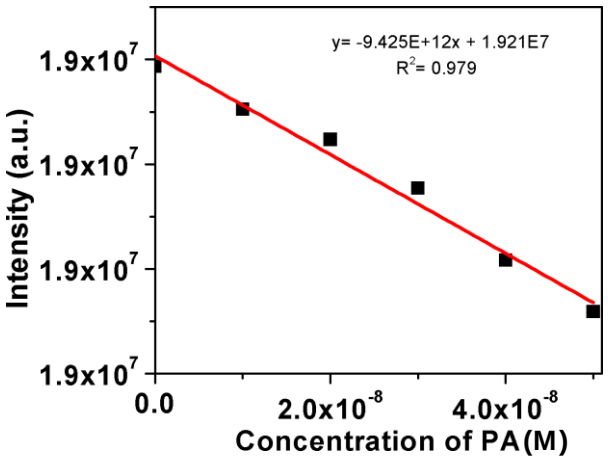


Figure S16. Fluorescence intensity of compound **1** (100 μM) in DMSO as a function of PA concentration (1 μM in DMSO) (Excitation wavelength = 318 nm).

10. References

1. B. Pradhan, S. K. Pathak, R. K. Gupta, M. Gupta, S. K. Pal and A. S. Achalkumar, *J. Mater. Chem. C*, 2016, 4, 6117-6130.