

pK_a Modulation in Rhodamine Based Probes for Colorimetric Detection of Picric Acid

V. Nagarajan and Bamaprasad Bag

Department of Colloids and Materials Chemistry, CSIR-Institute of Minerals and Materials Technology, P. O.: R.R.L.; Bhubaneswar 751013, India.

Electronic Supplementary Information

Table of Contents

1. Materials and Methods	S2
2. Synthesis of 1 and 2 , Characterization data	S2
3. pH titration methods followed	S3
4. Figure S1. pH titration curves of 1	S3-S4
5. Table-ST1. The pK _a values of investigated acids in water	S4
6. Figure S2. pH titration curves of 2	S5
7. Figure S3. Kinetics experiment for 2 with PA	S6
8. Figure S4. Job's plot for 1 and 2 with PA	S6
9. Figure S5. Determination of association constant	S6
10. Figure S6. Limit of detection of PA with 1 and 2	S7
11. Figure S7. Competitive experiments for 1 and 2 with PA	S8
12. Figure S8. ¹ H NMR spectrum of 1 (CDCl ₃)	S8
13. Figure S9. ¹³ C NMR spectrum of 1 (CDCl ₃)	S9
14. Figure S10. ESI-MS spectrum of 1	S9
15. Figure S11. ¹ H NMR spectrum of 2 (CDCl ₃)	S10
16. Figure S12. ¹³ C NMR spectrum of 2 (CDCl ₃)	S10
17. Figure S13. ESI-MS spectrum of 2	S11
18. Figure S14. ESI-MS spectrum of 1 + PA	S11
19. Figure S15. ESI-MS spectrum of 2 + PA	S12
20. Figure S16. ¹³ C NMR spectrum of 1 + PA (acetone- <i>d</i> ₆).	S12
21. Figure S17. ¹³ C NMR spectrum of 2 + PA (acetone- <i>d</i> ₆).	S12
22. Figure S18 and S19. ¹ H NMR spectra of 2 and 2 + PA (acetone- <i>d</i> ₆)	S13

1. Materials and Methods

Rhodamine B hydrochloride, picric acid, nitro phenols and carboxylic acids were purchased from Sigma-Aldrich and used as received. Solvents and other chemicals, if not mentioned, were also used without further purification. The pH of the solutions were measured using Lab Man pH meter. The UV-Vis absorption experiments were carried out in Perkin-Elmer Lambda 650 spectrophotometer. The ^1H and ^{13}C -NMR spectra of **1** and **2** in CDCl_3 were recorded in a Bruker AC-200 NMR Spectrometer. The spectra of **1** and **2** with picric acid (PA) in acetone- d_6 were recorded in a Bruker 400 FT-NMR Spectrometer with Me_4Si as the internal standard. Electrospray mass spectral data were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer. The dissolved samples of the compounds in suitable solvents were introduced into the ESI source through a syringe pump at the rate of $5\mu\text{L}/\text{min}$, ESI capillary was set at 3.5 kV with 40V cone voltage and the spectra were recorded at 6 s scans.

2. Synthesis of 1

To the ethanol solution (20 mL) of rhodamine B hydrochloride (1.2g, 2.5 mmol) excess hydrazine hydrate (5 mL) was added drop wise and the resultant solution was refluxed for 2h. The reaction mixture was cooled down to room temperature and water was added to the reaction mixture to get a pale yellow pasty mass. The pasty mass obtained was dissolved in 20mL of methanol and excess of 37% formaldehyde in water stabilized with 10% methanol was added and stirred for 2h. The reaction mixture was evaporated to get solid which was washed with water. The solid obtained was recrystallized from methanol/water (1:1 ratio). Yield: 77%; ESI-MS($\text{C}_{29}\text{H}_{32}\text{N}_4\text{O}_2$) m/z^+ (%): 469.3 ($[\text{1}] + 1$) $^+$ (100), 470.3 ($[\text{1}] + 2$) $^+$ (38); ^1H NMR (200 MHz, CDCl_3) δ : 8.02 (dd, $J = 5.8, 2.6$ Hz, 1H), 7.64 – 7.33 (m, 2H), 7.26 – 6.98 (m, 2H), 6.80 – 6.14 (m, 7H), 3.37 (q, $J = 7.0$ Hz, 8H), 1.20 (t, $J = 7.0$ Hz, 12H); ^{13}C NMR (50 MHz, CDCl_3) δ : 165.64, 152.73, 152.63, 148.97, 137.82, 133.67, 128.19, 127.88, 127.76, 123.62, 108.13, 105.28, 98.08, 64.85, 44.35, 12.62.

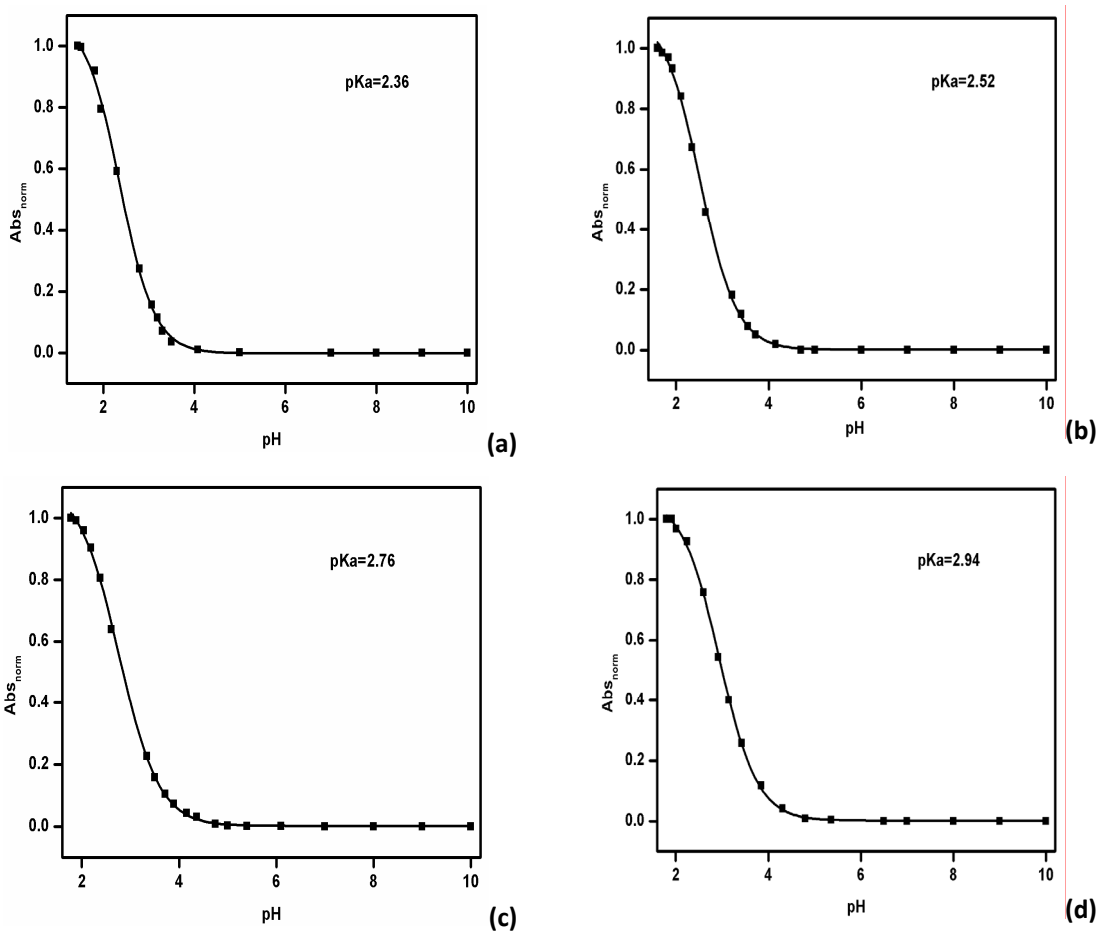
3. Synthesis of 2

To the ethanol solution (20mL) of rhodamine B hydrochloride (1.2g, 2.5mmol) excess ethylamine (4 mL) was added drop wise and the resultant solution was refluxed for 24h to get a colourless solution. The reaction mixture was cooled to room temperature and water was added to the reaction mixture to get a pasty mass which was dissolved in methanol. To the methanol solution water was added with constant stirring to get a pale pink coloured solid. The crude product was recrystallized from acetone. Yield: 62%; ESI-MS($\text{C}_{30}\text{H}_{35}\text{N}_3\text{O}_2$)

m/z^+ (%): 470.4 ($[2]+1$)⁺ (100), 471.3 ($[2]+2$)⁺ (47); ¹H NMR (200 MHz, CDCl₃) δ : 8.07 – 7.76 (m, 1H), 7.45 (dd, $J = 5.9, 2.8$ Hz, 2H), 7.21 – 6.93 (m, 1H), 6.64 – 6.13 (m, 6H), 3.38 (q, $J = 7.1$ Hz, 8H), 3.24 (q, $J = 7.2$ Hz, 2H), 1.20 (t, $J = 7.0$ Hz, 12H), 0.86 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ : 167.76, 153.75, 153.29, 148.73, 132.12, 131.49, 129.01, 127.88, 123.64, 122.66, 108.07, 105.98, 97.80, 64.76, 44.37, 35.08, 13.81, 12.59.

4. pH titration

The pH titration experiments were carried out for different percentage of water in water/acetone mixture, by maintaining the concentration at 10 μ M, for **1** and **2**. The pH of the solution is adjusted using 0.1N, 1N and 10N solution of HCl and KOH. Absorption was measured at 558 nm by varying the pH of the solution from 2-10, and for **1** the absorbance is measured instantaneously after pH adjustment, however, for **2** the measurements were done after 12h due to its slow reaction. The pKa was calculated by taking the pH value at which the absorbance is half from the maximum value (Ref 8, main text).



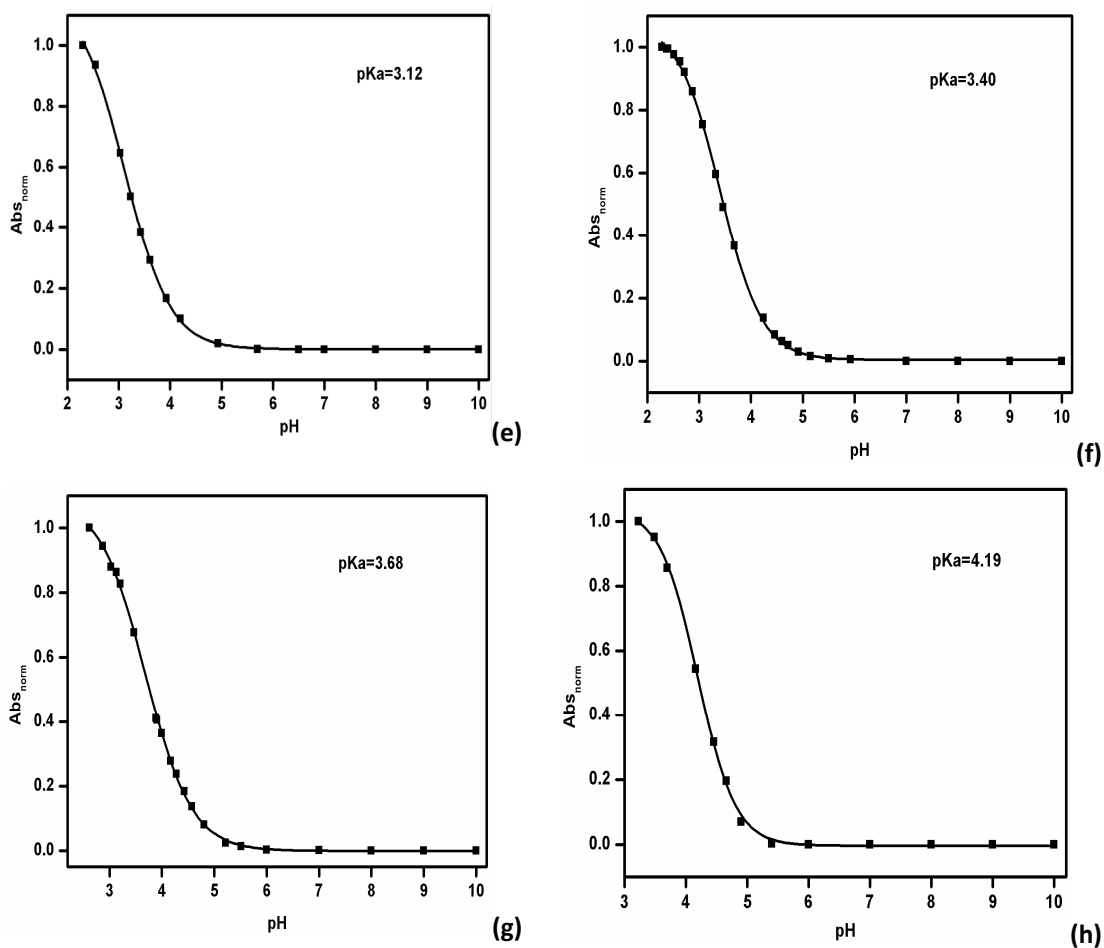


Figure S1. The pH titration plots for **1** with different percentage of water such as (a) 15, (b) 20, (c) 25, (d) 30, (e) 35, (f) 40, (g) 50 and (h) 60% of water in the water/acetone solvent medium.

Table-ST1. The pKa values of organic acids (used in this investigations) in water.

Acids	pKa	Acids	pKa
Picric acid	0.38	Glutaric acid	4.34
2,4-Dinitrophenol	4.11	Adipic acid	4.42
2,6- Dinitrophenol	3.97	Benzoic acid	4.19
2,5- Dinitrophenol	5.15	4-Nitrobenzoic acid	3.41
4-Nitrophenol	7.15	3-Hydroxybenzoic acid	4.06
Phenol	9.95	4-Hydroxybenzoic acid	4.48
Oxalic acid	1.25	4-Aminobenzoic acid	4.65
Malonic acid	2.83	Trimesic acid	3.12
Succinic acid	4.24	Acetic acid	4.76

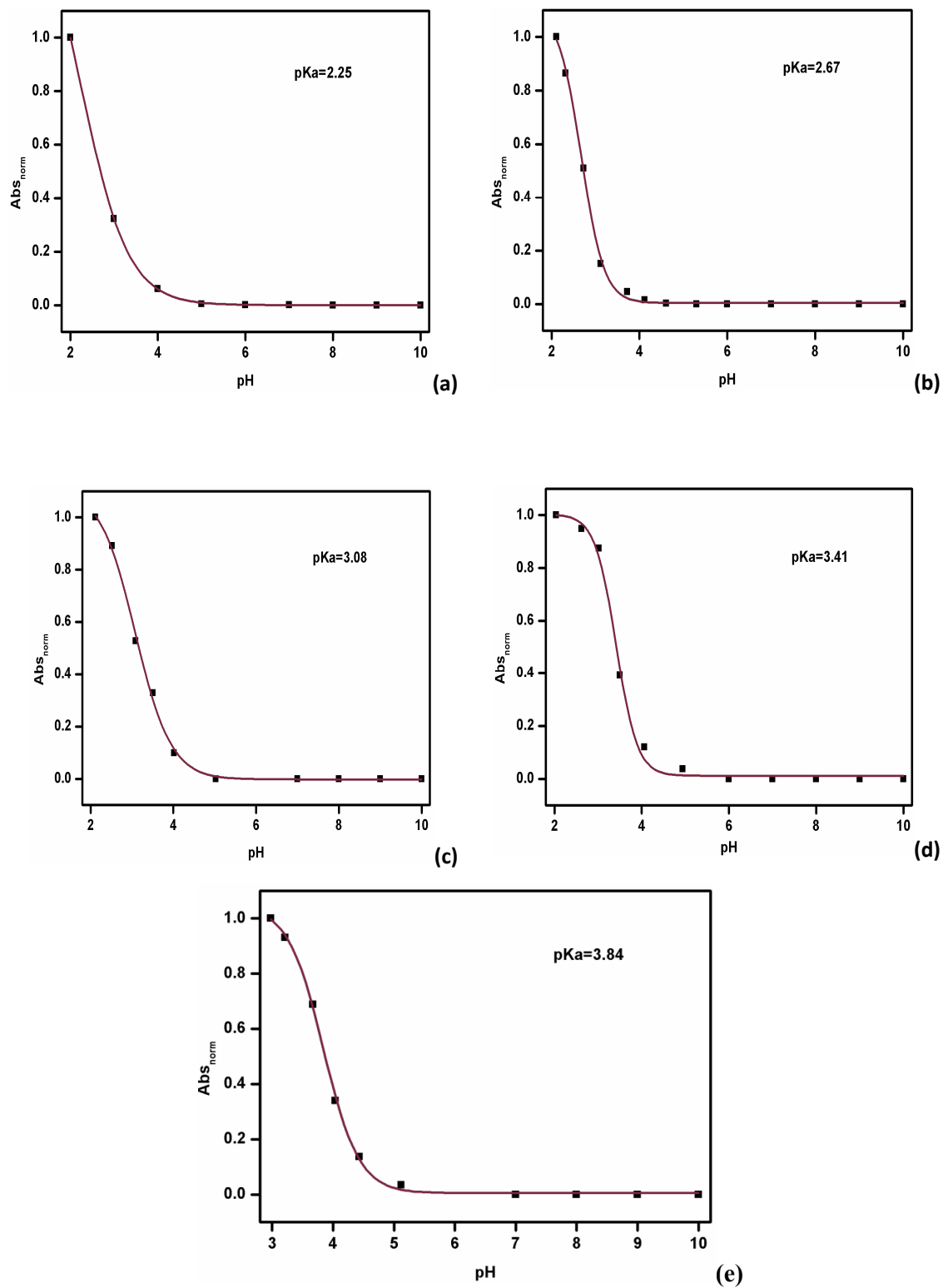


Figure S2. The pH titration plots for **2** with different percentage of water such as (a) 20, (b) 30, (c) 40, (d) 50 and (e) 60% of water in the water/acetone solvent medium.

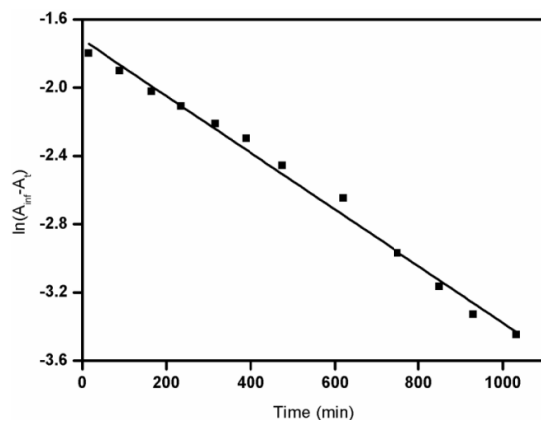


Figure S3. Kinetic experiment of **2** shows first order kinetics for the ring opening process mediated by PA.

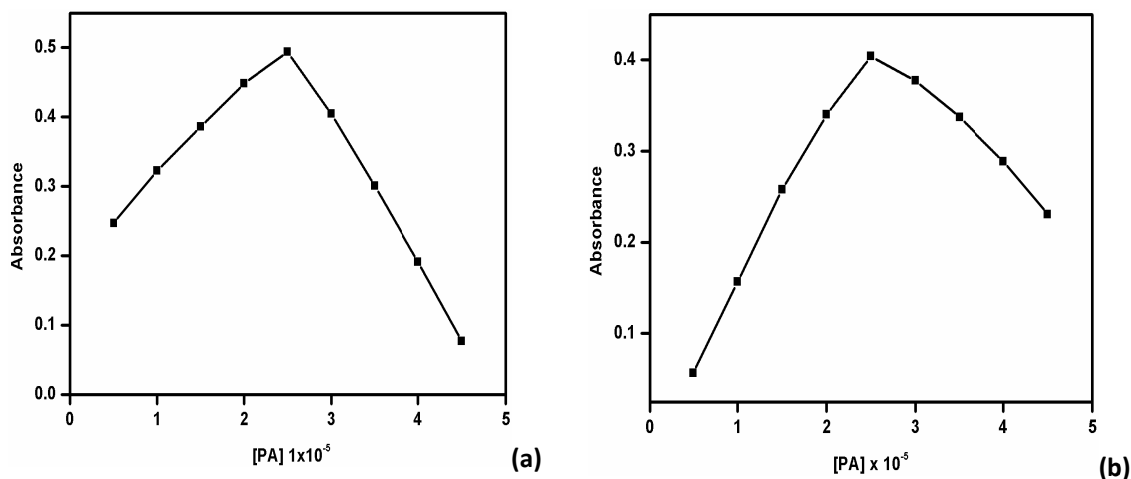


Figure S4. The Job's plots obtained for a) **1** and b) **2** with PA complexes. $\lambda_{\text{obs}} = 558\text{nm}$.

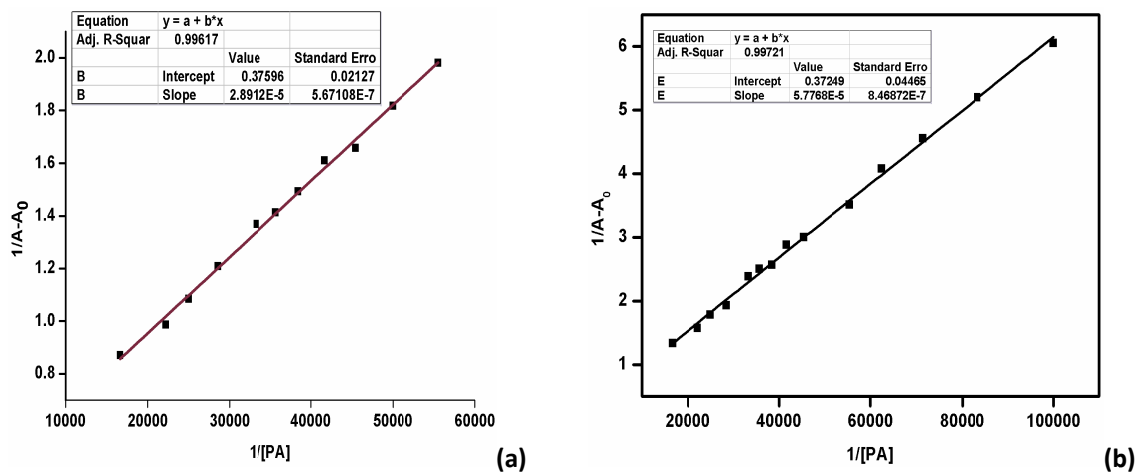


Figure S5. The linear regression plot obtained from the absorption titration for determination of association constant for (a) **1** and (b) **2** with PA.

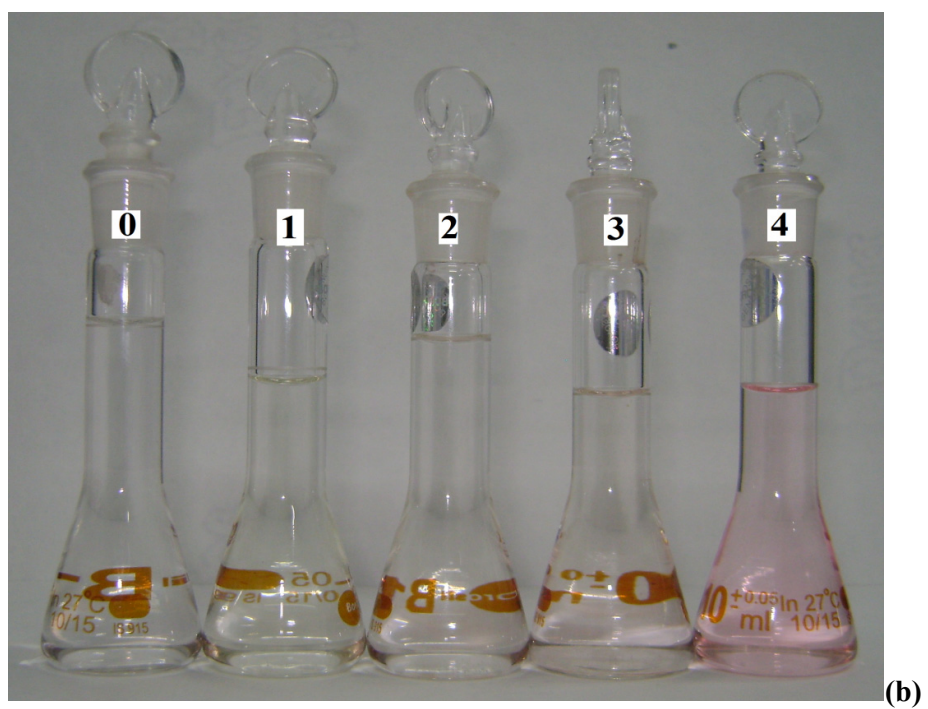
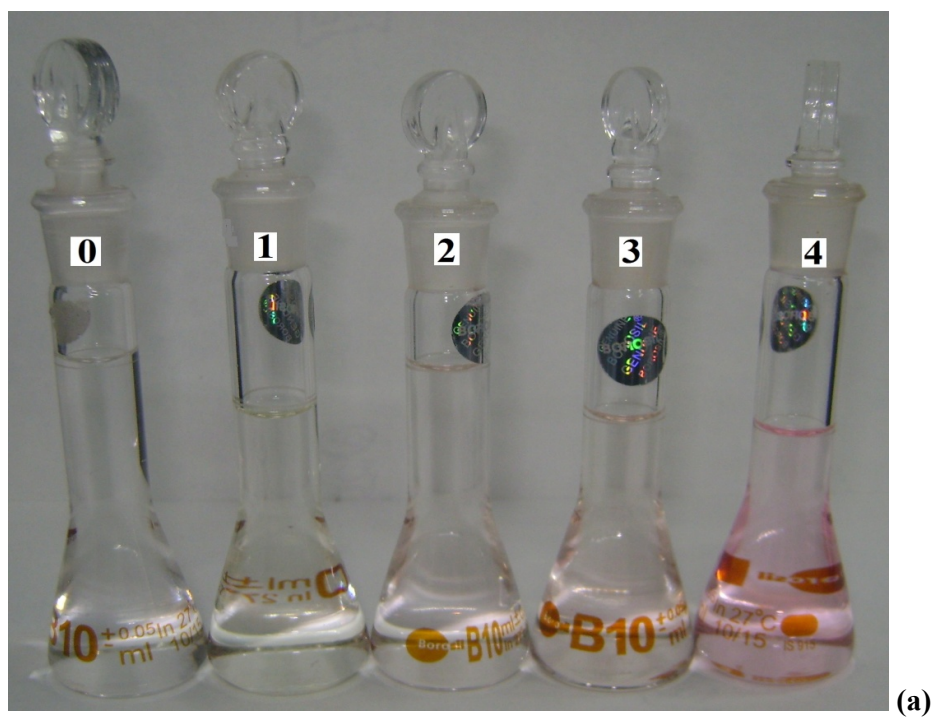


Figure S6. Naked eye detection limit of PA(0-4 μ M) with (a) 1 and (b) 2.

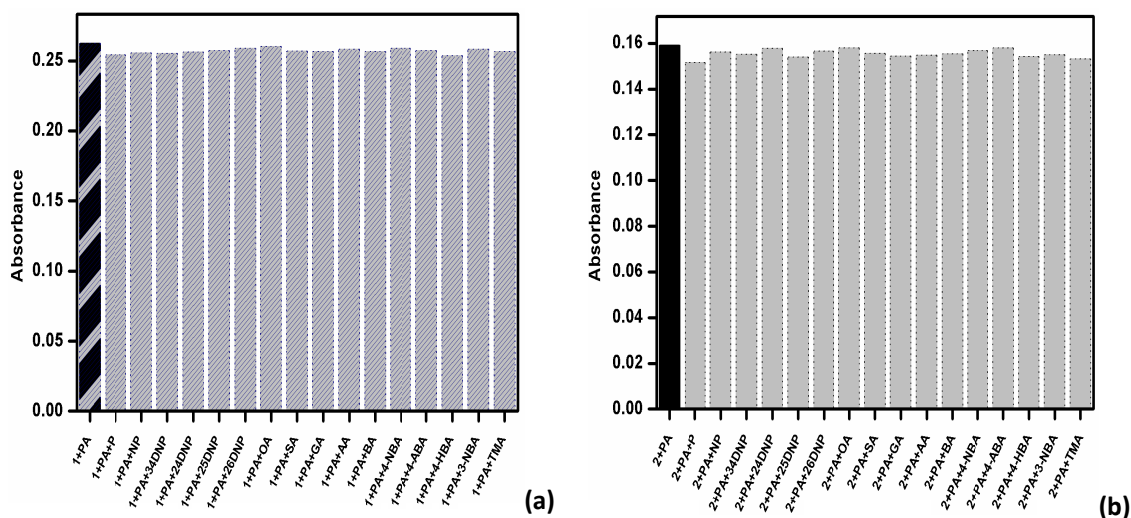


Figure S7. The competitive experiments are to understand the influence of the phenols and carboxylic acids in the absorbance intensity of (a) **1+PA** and (b) **2+PA**.

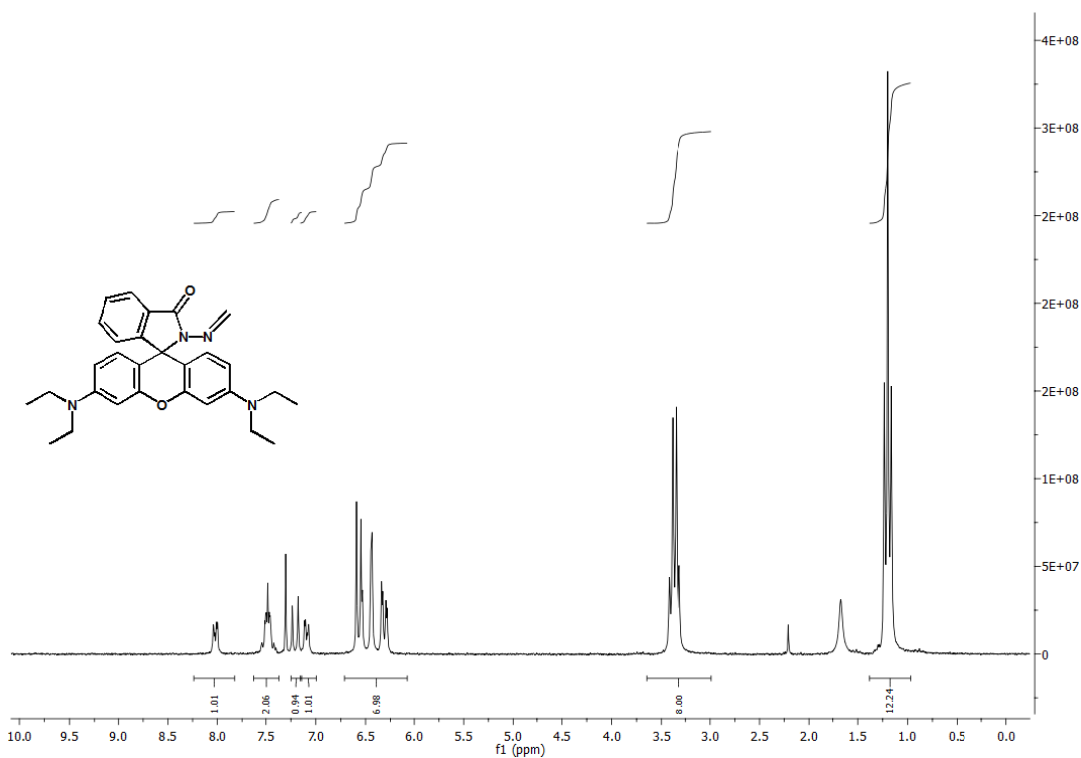


Figure S8. ^1H NMR spectrum of **1**(CDCl_3).

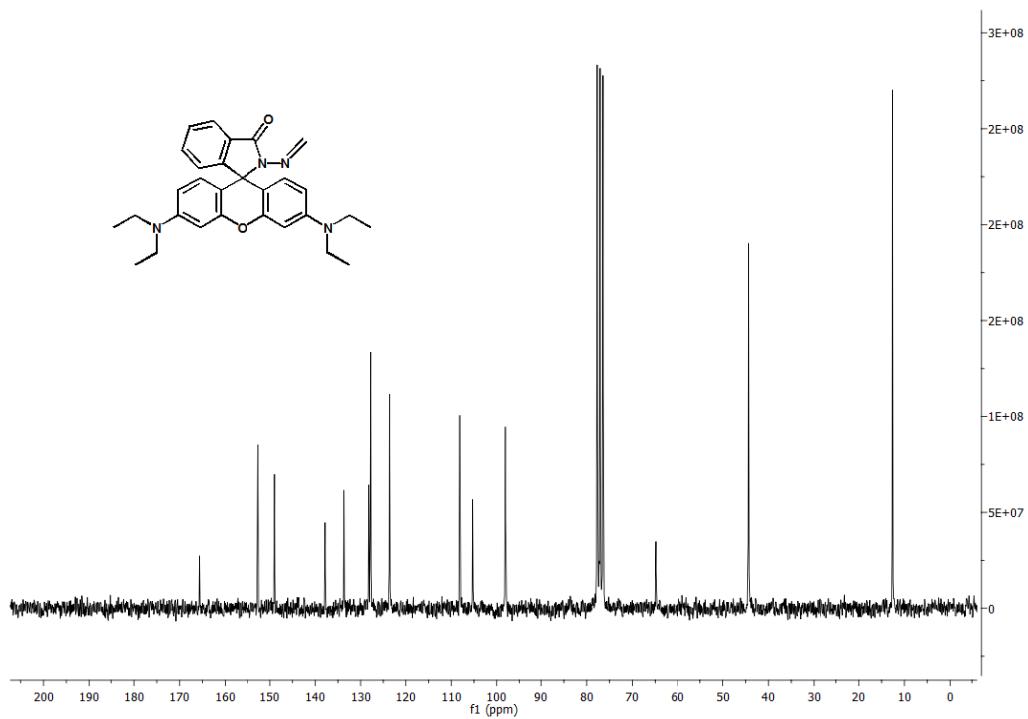


Figure S9. ^{13}C NMR spectrum of 1 (CDCl_3).

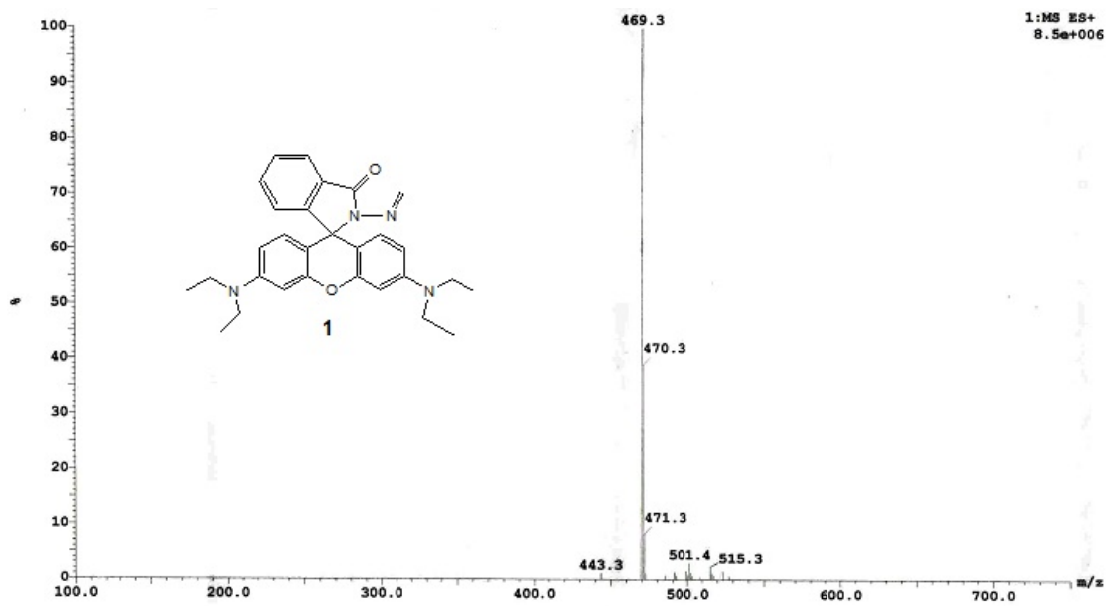


Figure S10. ESI-MS spectrum of 1

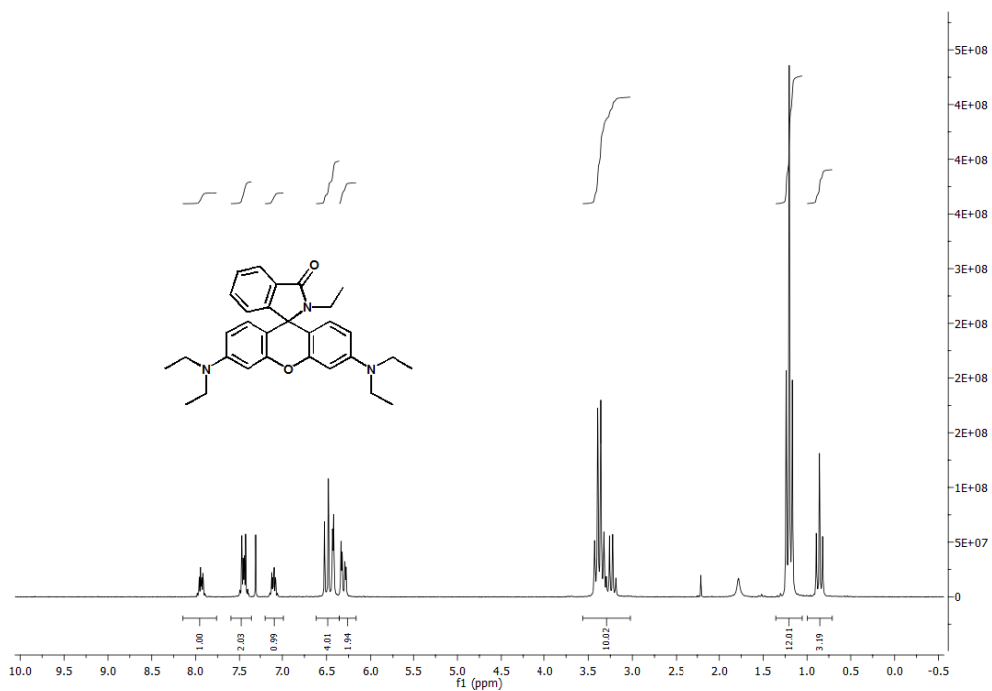


Figure S11. ^1H NMR spectrum of **2**(CDCl_3).

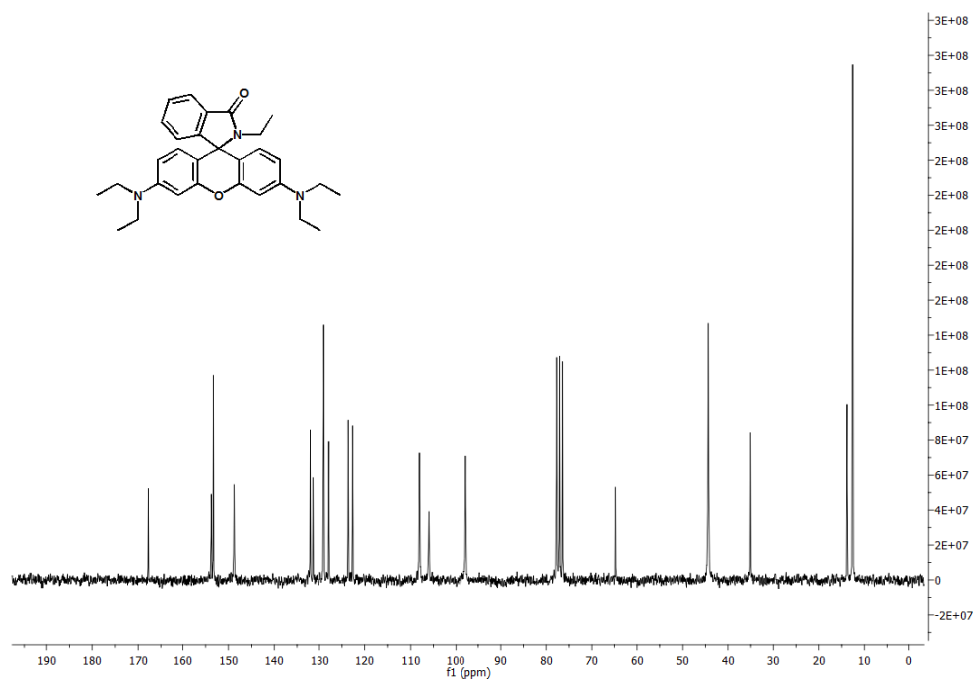


Figure S12. ^{13}C NMR spectrum of **2** (CDCl_3).

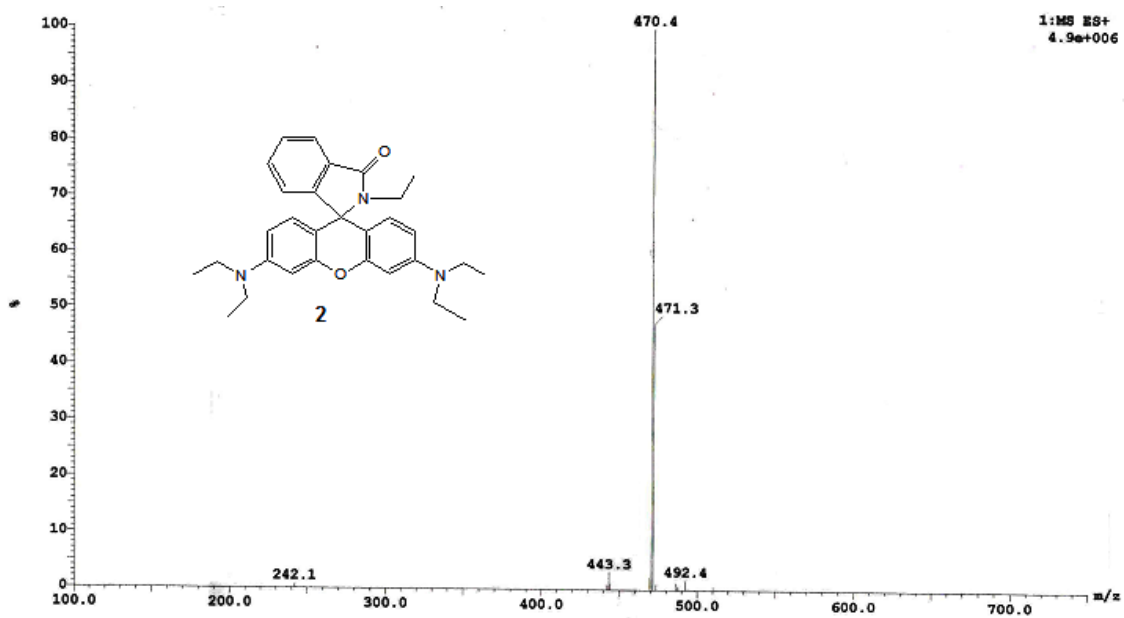


Figure S13. ESI-MS spectrum of 2.

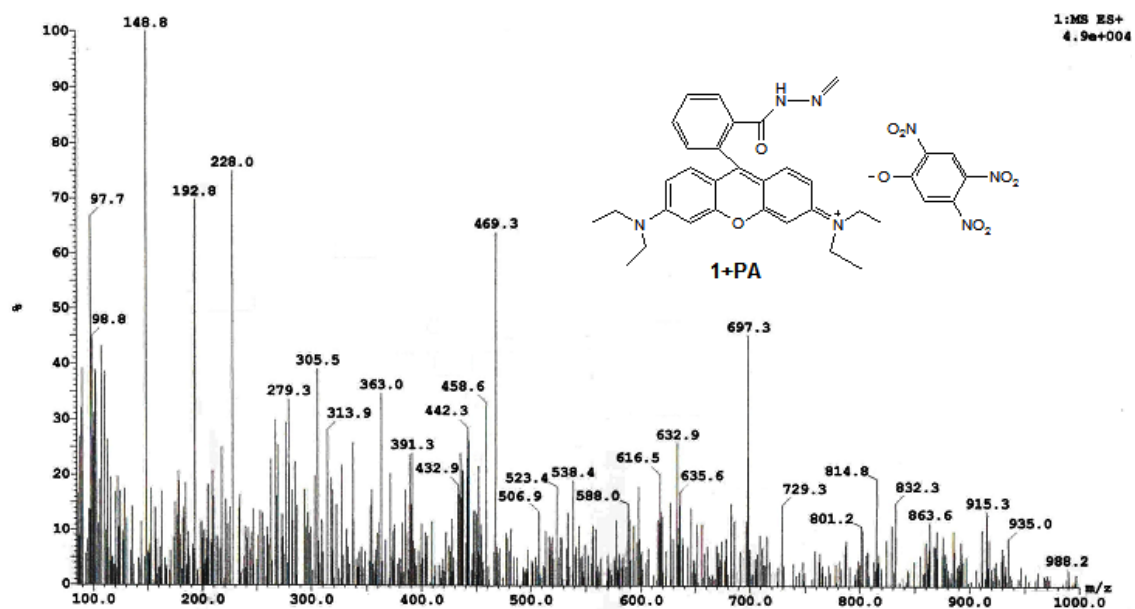


Figure S14. ESI-MS spectrum of 1+PA.

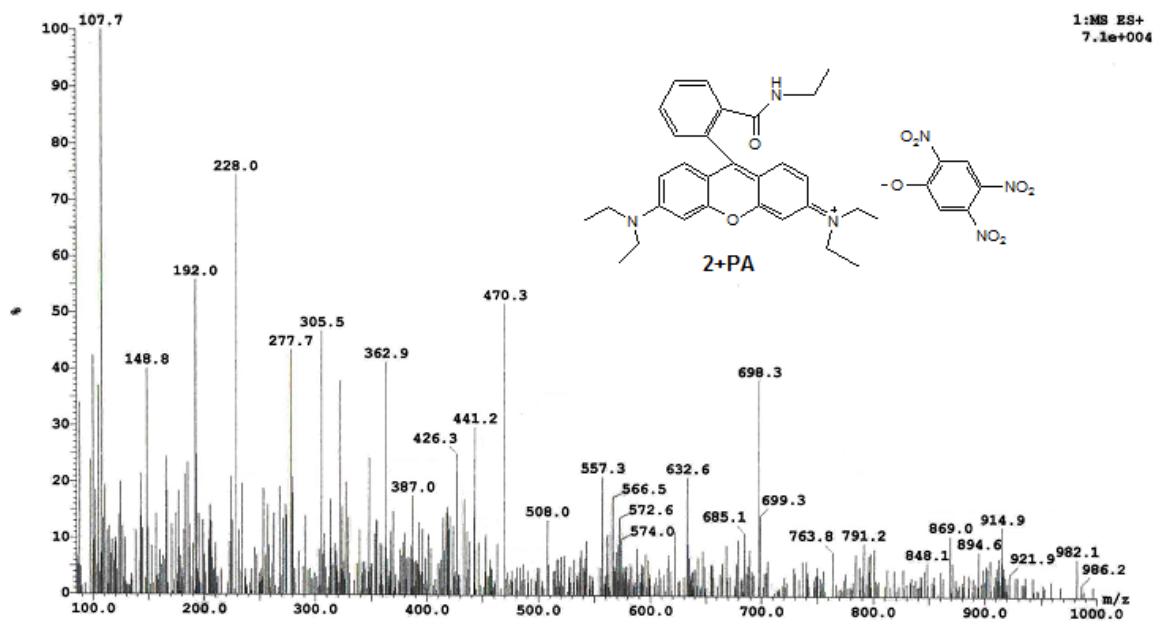


Figure S15. ESI-MS spectrum of 2+PA.

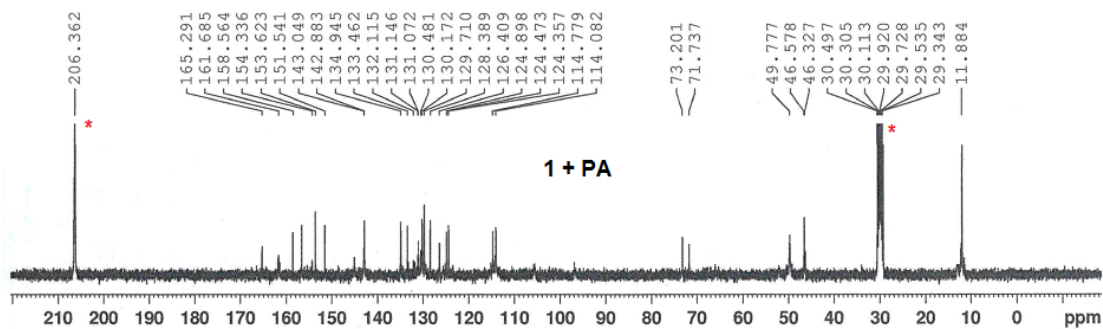


Figure S16. ^{13}C NMR spectrum of 1+ PA (acetone- d_6). Peaks marked with asterisk (*) are solvent residual peak.

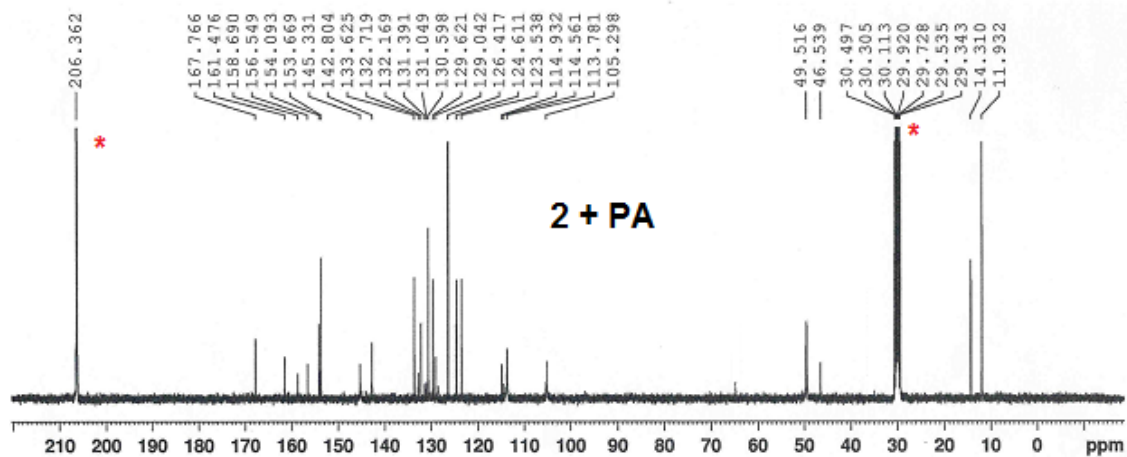


Figure S17. ^{13}C NMR spectrum of 2+ PA (acetone- d_6). Peaks marked with asterisk (*) are solvent residual peak.

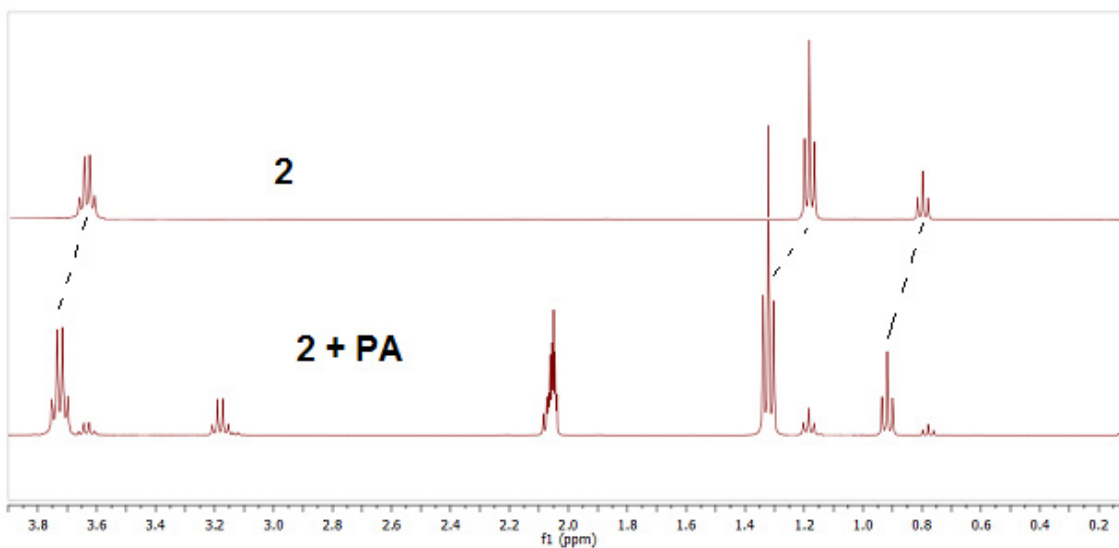


Figure S18. ^1H NMR spectra of **2** and **2+ PA** (acetone- d_6) in 0.1-3.8 ppm range.

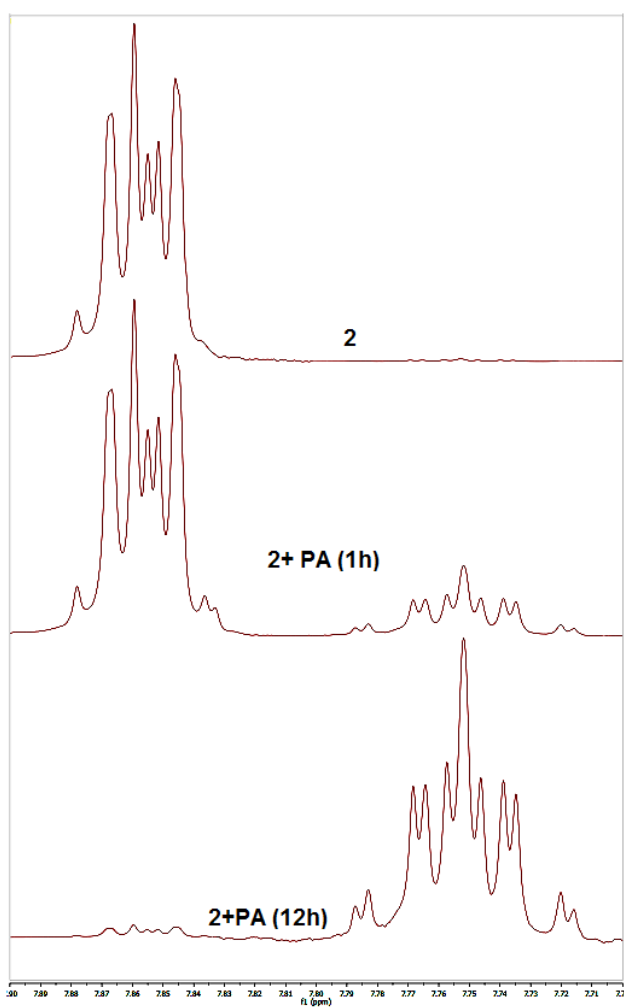


Figure S19. ^1H NMR spectra of **2** and **2+ PA** (acetone- d_6) in 7.7-7.9 ppm range.