Electronic Supplementary Information (ESI)

A smart ratiometric red fluorescent chemodosimeter for fluoride based on anthraquinone nosylate

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EXPERIMENTAL

1.1 Apparatus:

The IR Spectra for the **AH** was recorded on JASCO-FTIR Spectrophotometer while ^{1}H and ^{13}C NMR spectra for the same were recorded on a JEOL AL 500 FT NMR Spectrometer. Mass spectrometric analysis was carried out on a MDS Sciex API 2000 LCMS/Brukar Compass data analysis spectrometer. Electronic spectra were recorded at room temperature (298 K) on a UV-1700 pharmaspec spectrophotometer with quartz cuvette (path length=1 cm). Emission spectra were recorded on JY HORIBA Fluorescence spectrophotometer.

1.2 Materials:

All reagents for synthesis were purchased from Sigma-Aldrich and were used without further purification.

1.3 General Methods:

All titration experiments were carried at room temperature. All anions were used as their tetrabutyl-ammonium (TBA) salts. The ^{1}H NMR spectra were recorded by using tetramethylsilane (TMS) as an internal reference standard. For the ^{1}H NMR titration spectra of **AH**, $\mathbf{5\times10^{-3}M}$ solution and tetrabutyl-ammonium fluoride (TBAF) were prepared in DMSO-d_6. For UV-visible/fluorescence titration experiments, the solutions of anions were prepared in DMSO. The stock solution of **10 mM** was prepared in DMSO which was used for fluorescence titration experiment in pure acetonitrile at 5μM concentration through dilution.

1.4 X-ray diffraction studies:

Single crystals of the **AH** were grown by slow evaporation of saturated solution in DMSO over a period of few weeks. The single crystal X-ray diffraction measurements were carried out on an Oxford Diffraction Xcalibur system with a Ruby CCD detector as well as on a Bruker SMART APEX CCD diffractometer using graphite-monochromated MoKa radiation (k = 0.71073 Å). All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo-Kα radiation (λ=0.71073 A°). The structures were solved by direct methods, using Fourier techniques and refined by full-matrix least-squares on F2 using the SHELXTL-97 program package. Crystal data and details of the structure determination for **AH** are summarized in **Table 1**.CCDC **1480047 (AH)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the **Cambridge Crystallographic Data Centre** via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi.

(DT1 lab) The corresponding Ortep diagram of the **AH** is shown in **Fig.1** while its supramolecular packing has been given in **Fig.2a, b.**

Electronic Supplementary Information (ESI)

Table and Contents

Figure S1: FT-IR spectrum of **AHOH**

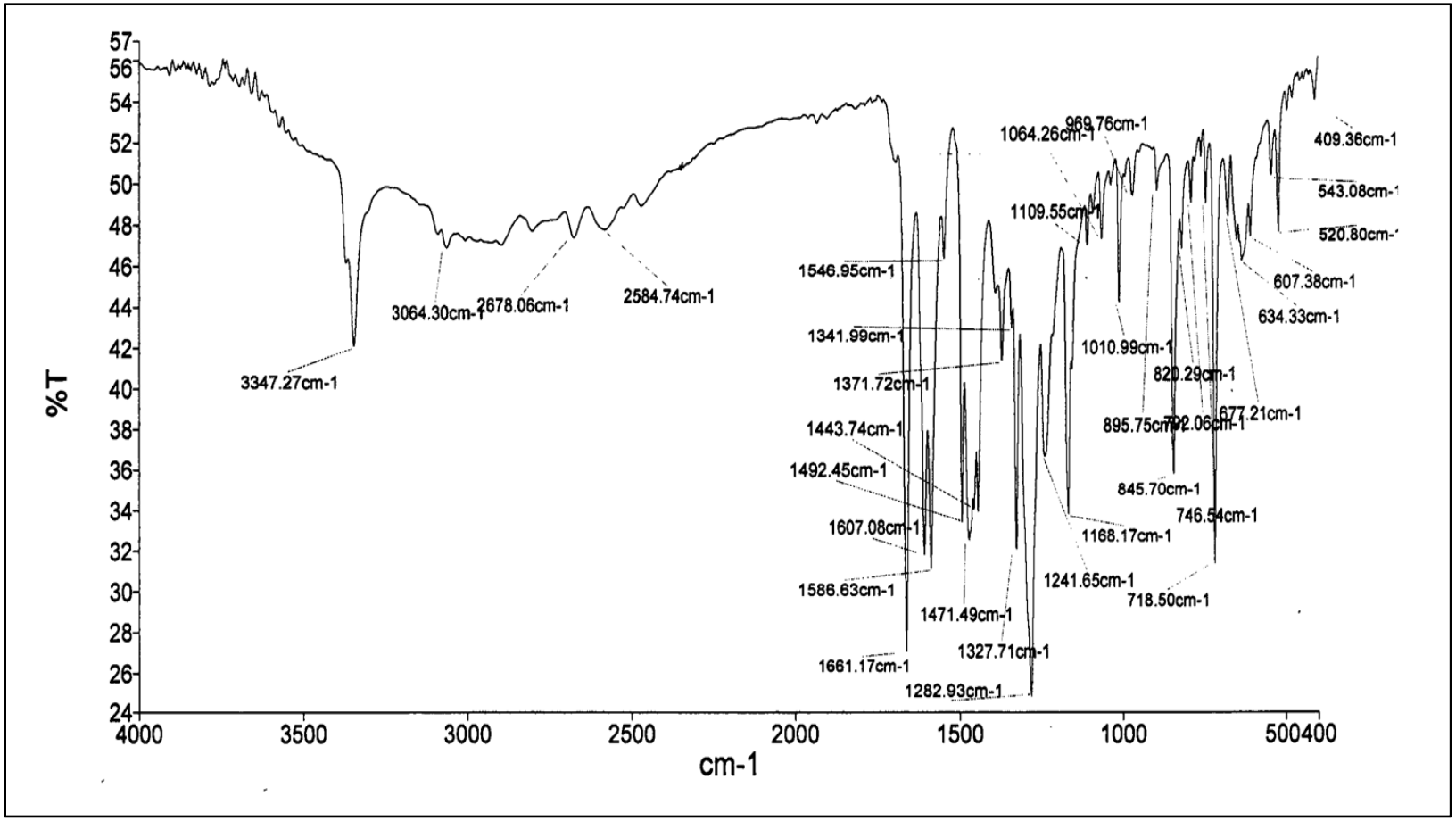


Figure S2: ^{1}H NMR spectrum of **AHOH**

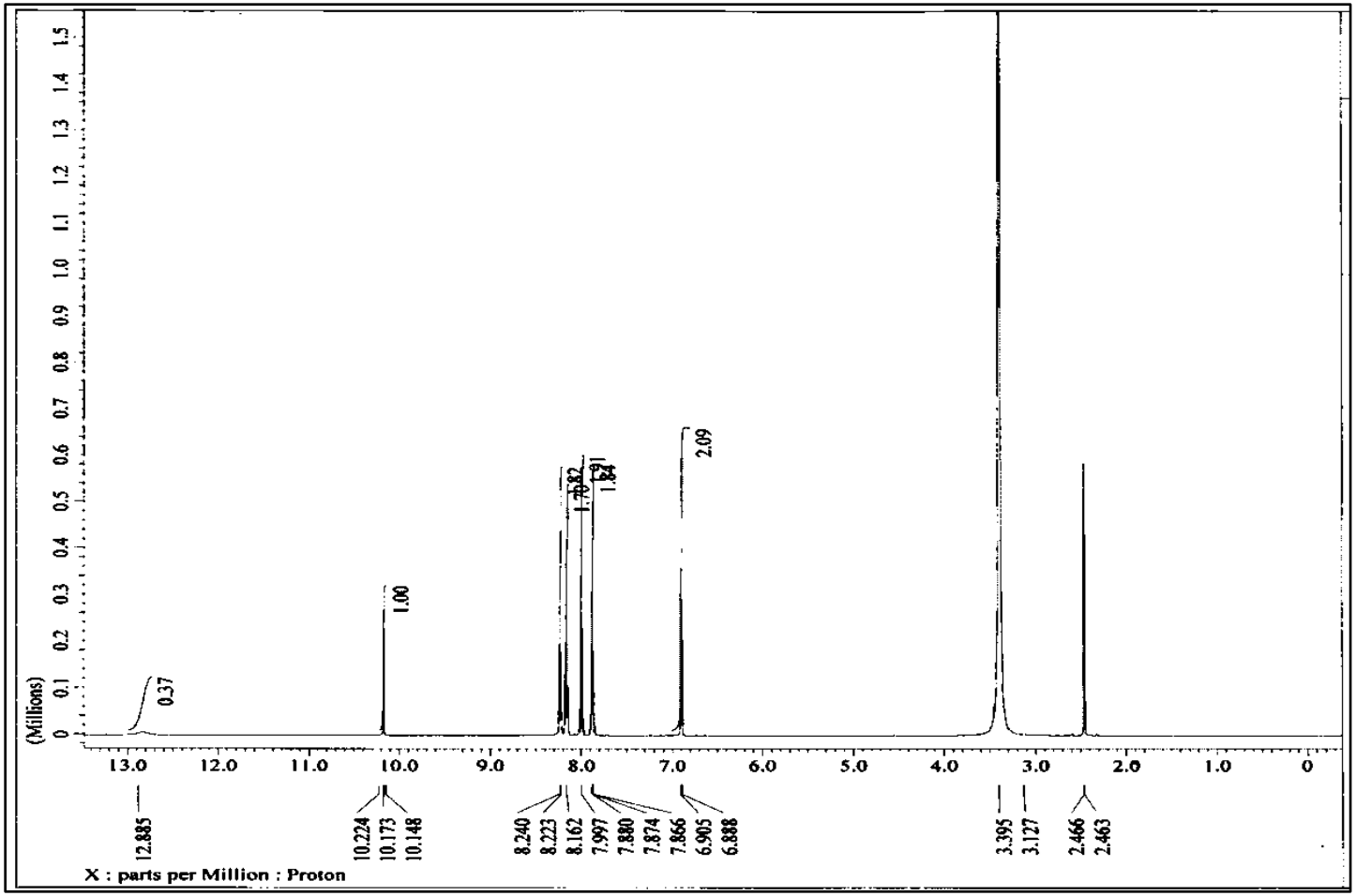


Figure S3: ^{13}C NMR spectrum of **AHOH**

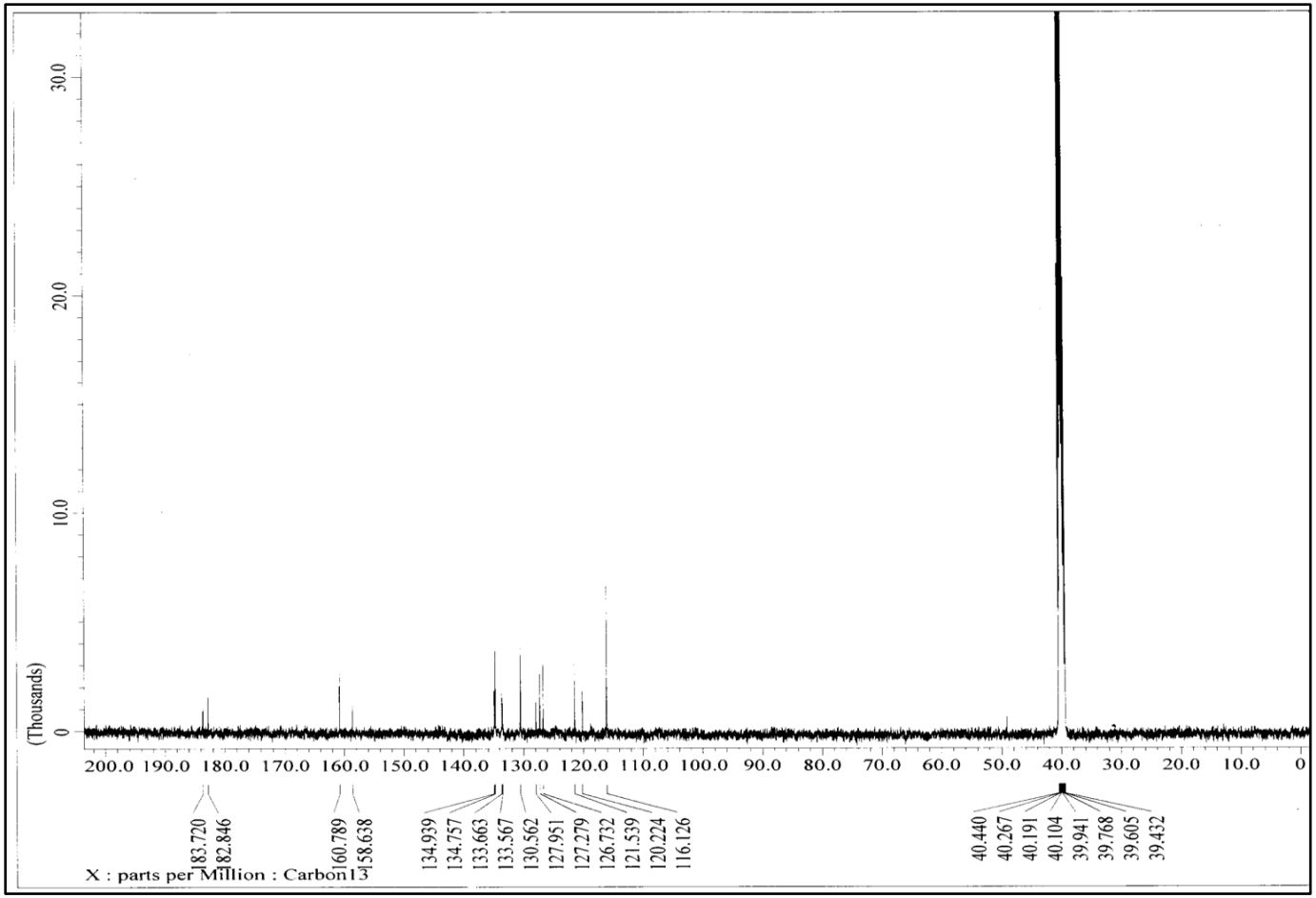


Figure S4: FT-IR spectrum of **AH**

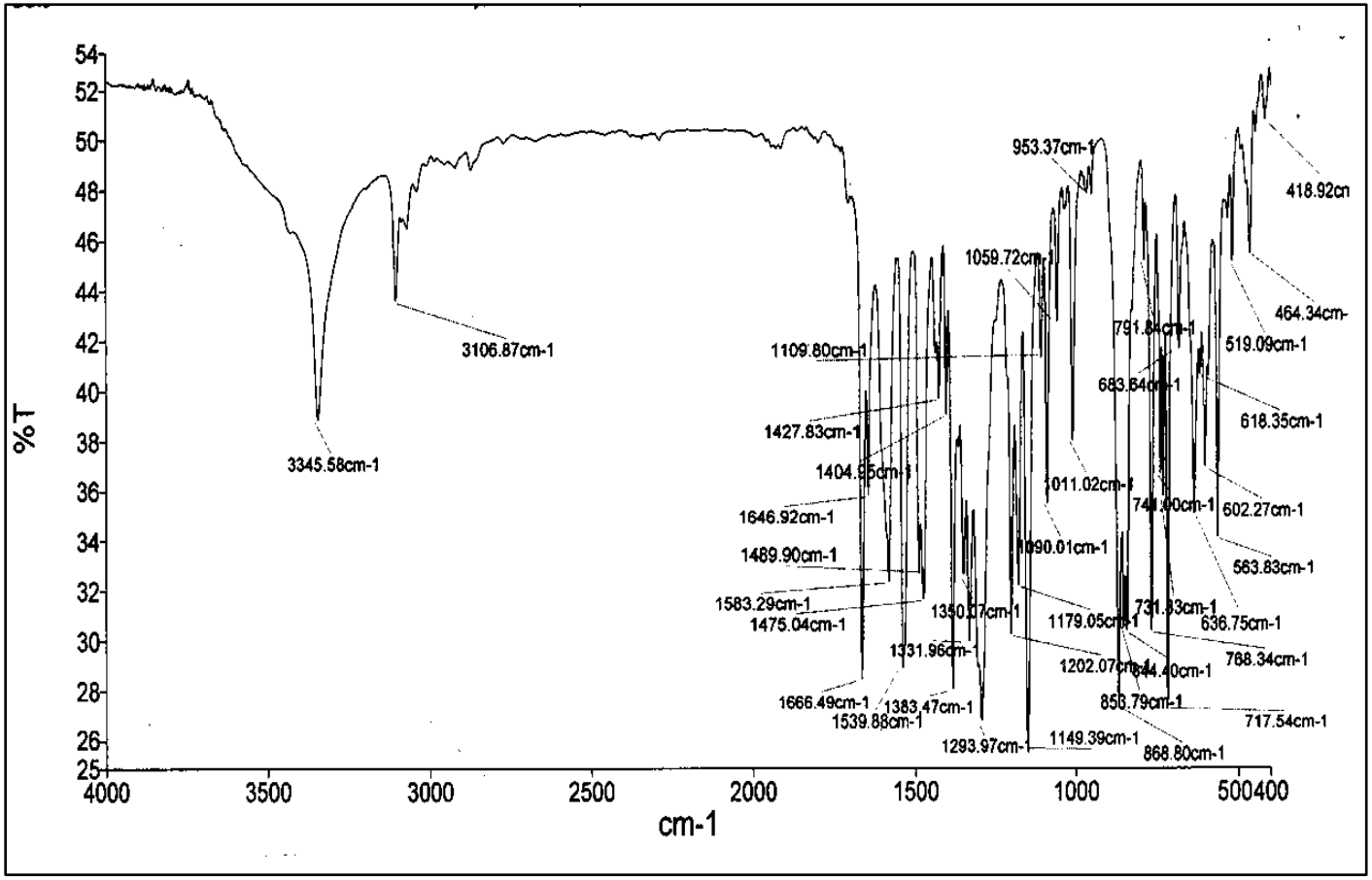


Figure S5: ^{1}H NMR spectrum of **AH**

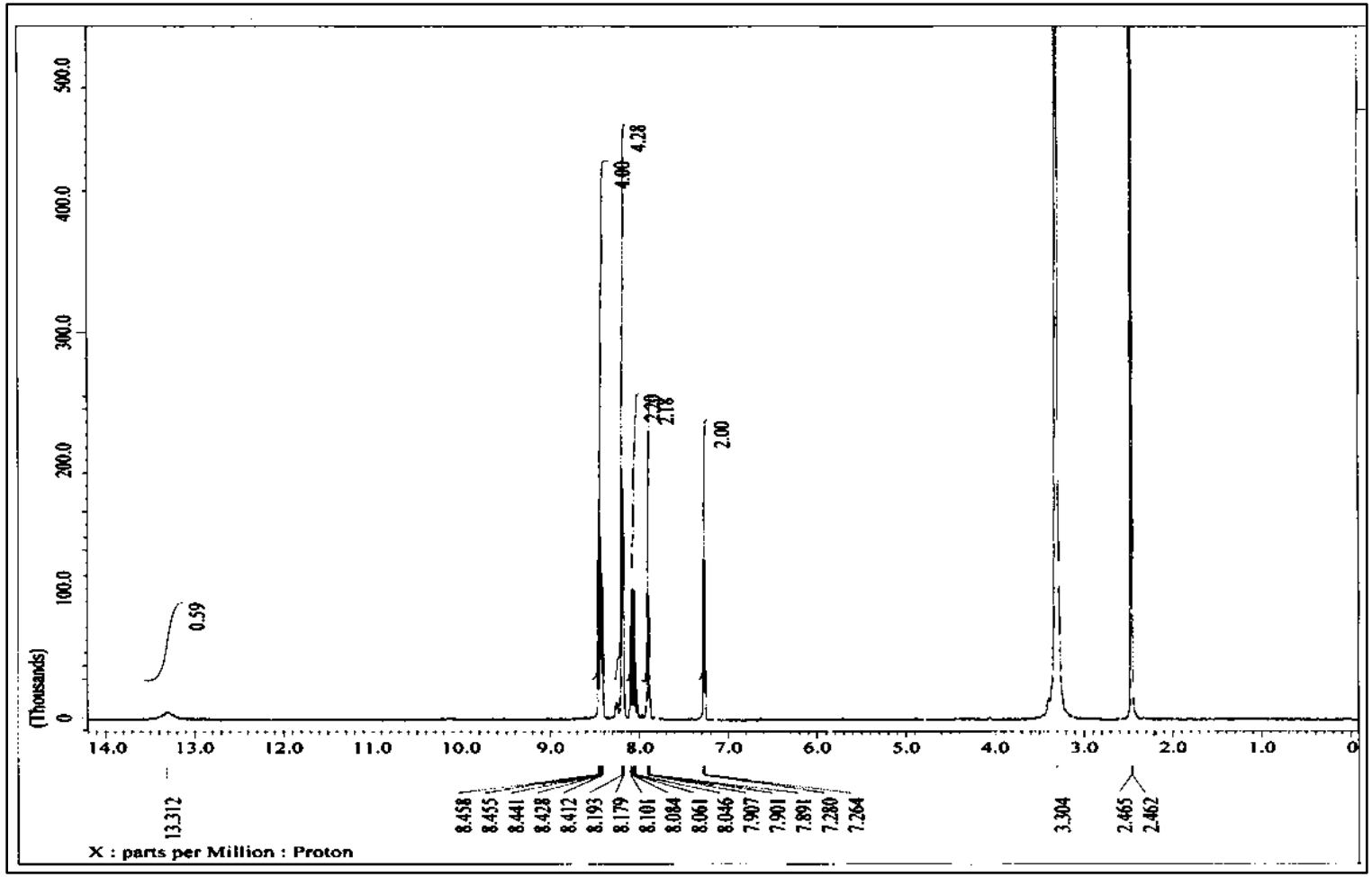


Figure S6: ^{13}C NMR spectrum of **AH**

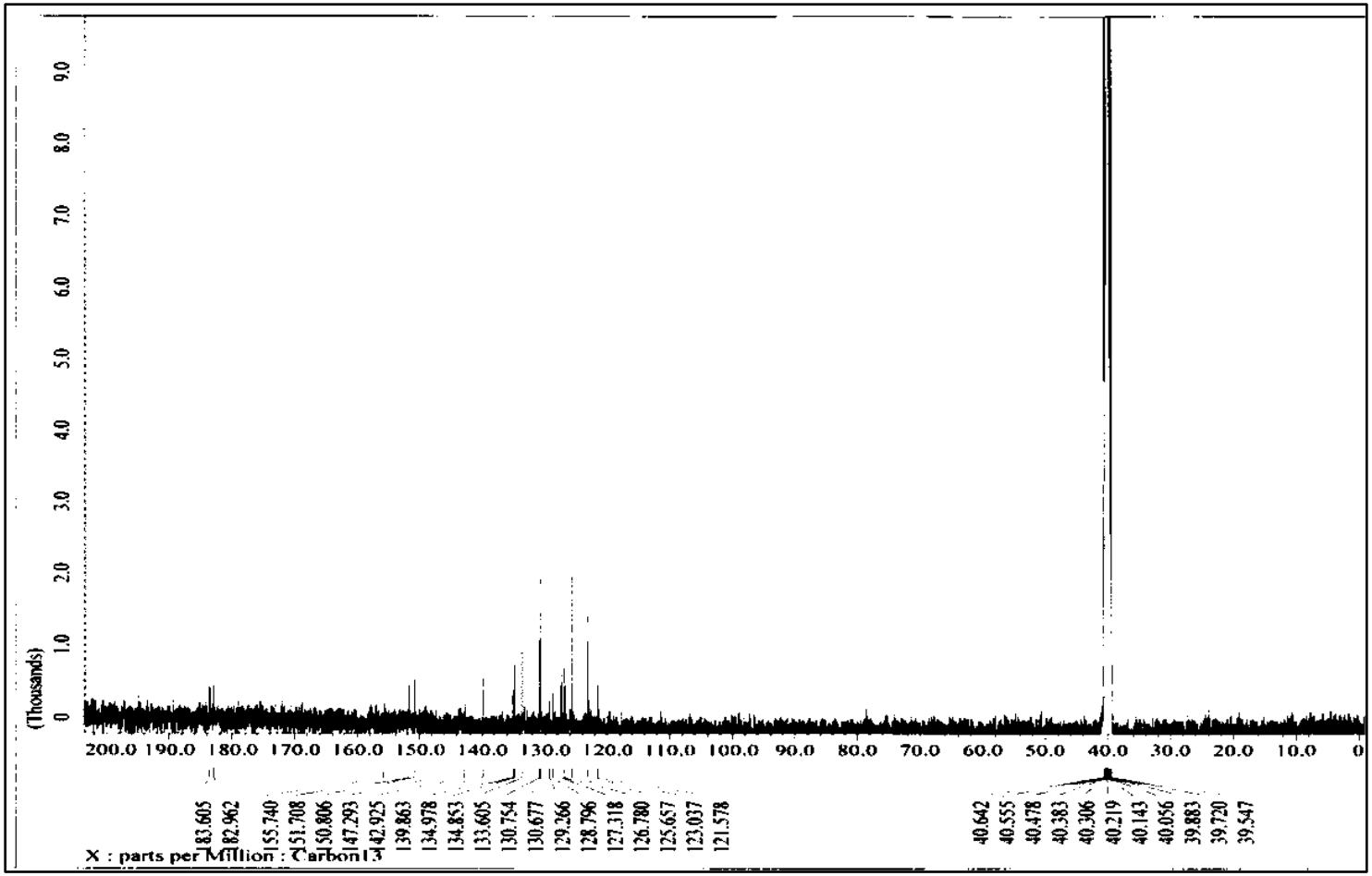


Figure S7: ESI-Mass spectrum of **AH**

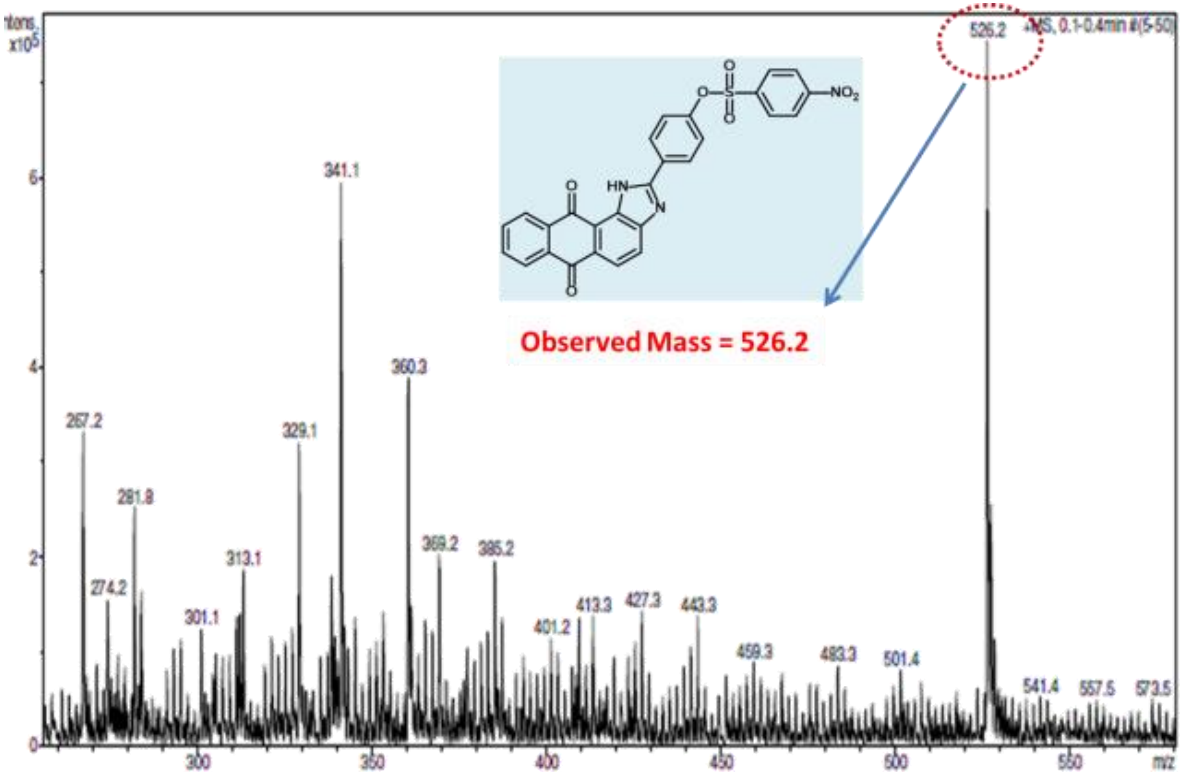


Figure S8: Visible colour changes of **AH** in acetonitrile (ACN) on addition of different anions (10 equiv.)

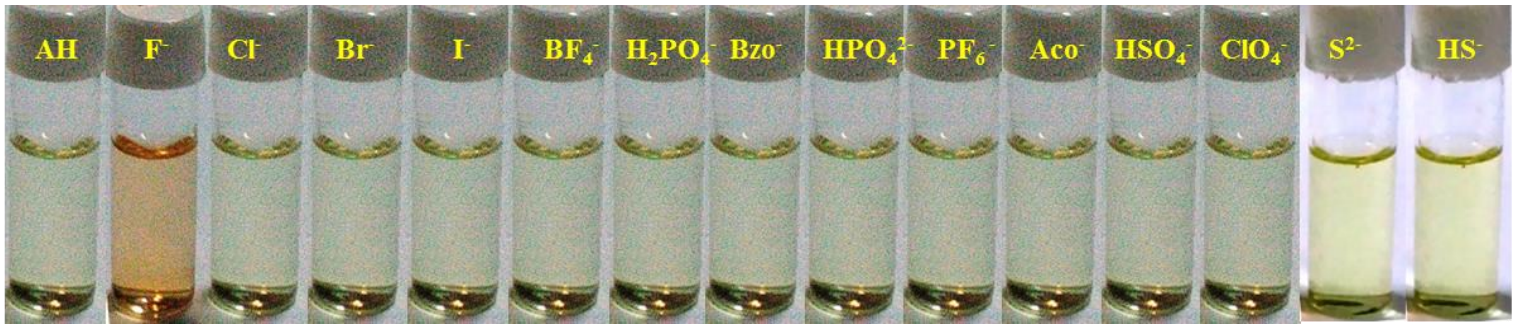
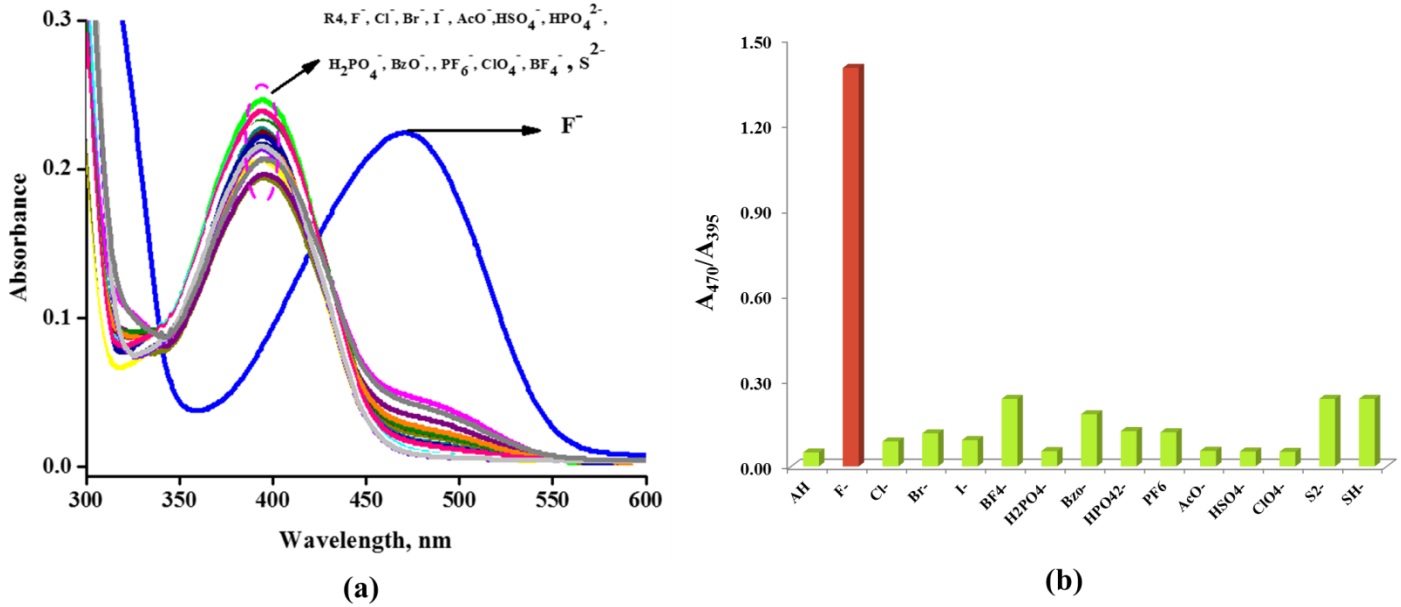


Figure S9: (a) UV-visible spectrum of **AH** (10 μM) with different anions in acetonitrile; (b) bar graph representation of ratio of absorbance at two different wavelengths with different anions



(a) (b)

Figure S10: Reaction time profile of **AH** with fluoride at ~ 395 nm and at ~ 470 nm through UV-Vis. study

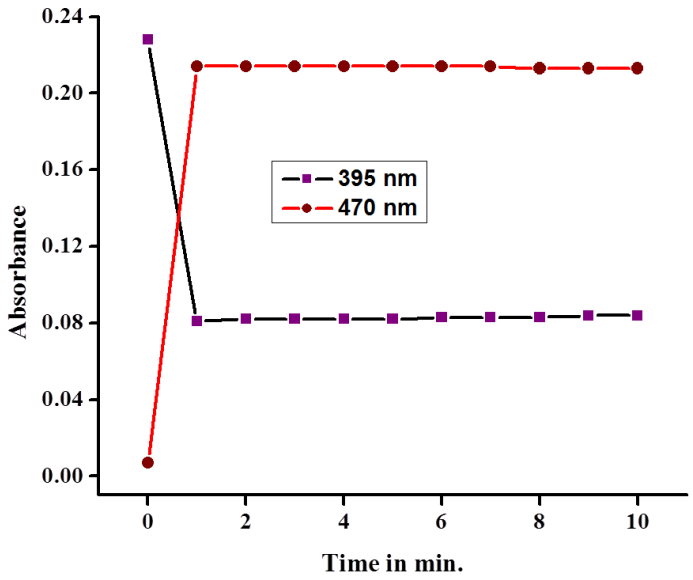


Figure S11: Visible colour changes of **AHOH** in acetonitrile (ACN) on addition of different anions

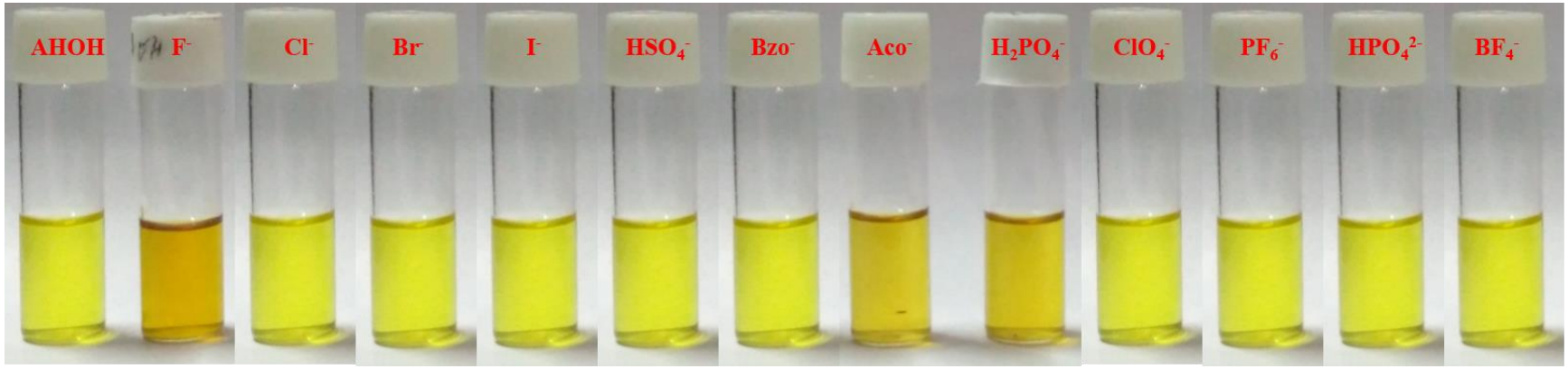


Figure S12: (a) Emission spectrum of **AH (**5 μM) with different anions (10 equiv.) in acetonitrile, λ_{ex} = 425 nm; **(b)** Corresponding bar graph with different anions;

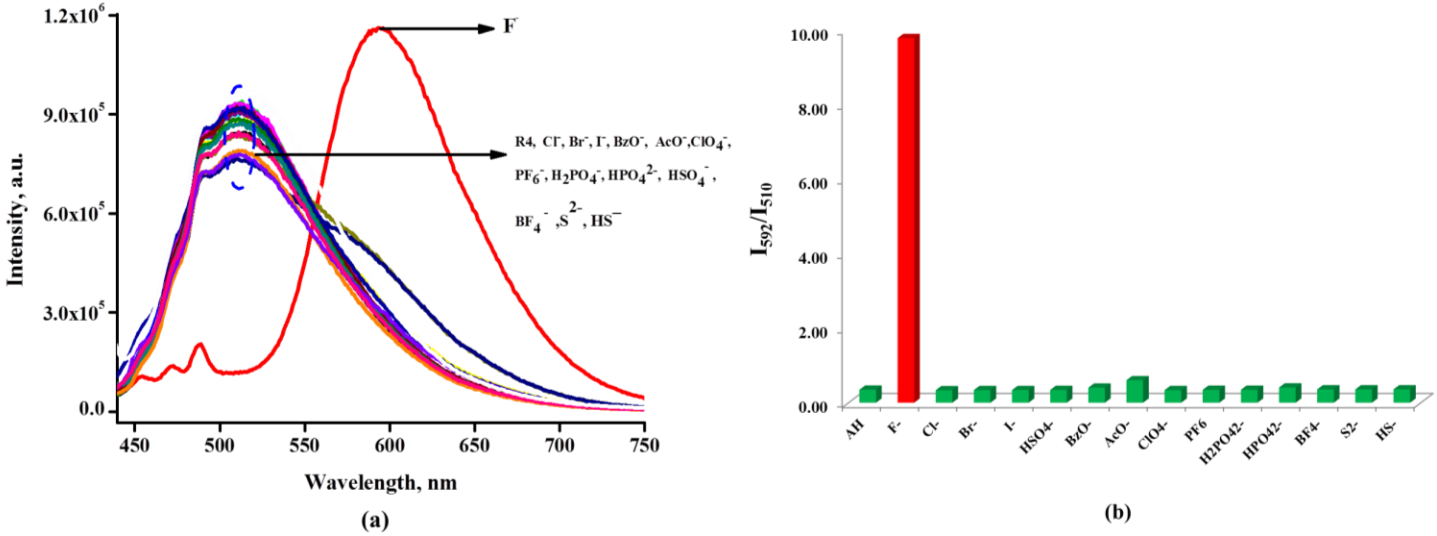


Figure S13: Optical response of **AH** in acetonitrile (ACN) with different anions (under UV light)

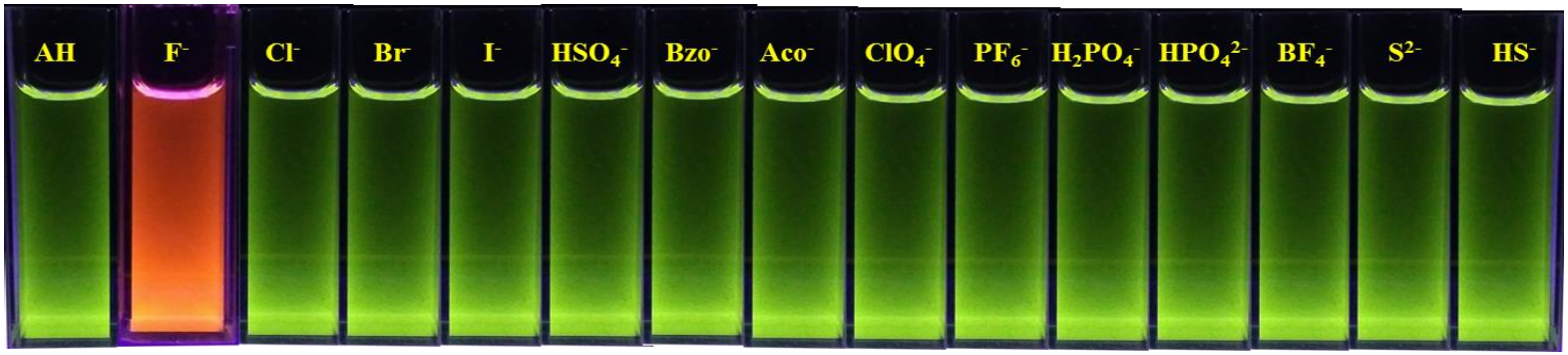


Figure S14: Competition experiment of **AH** with different anions

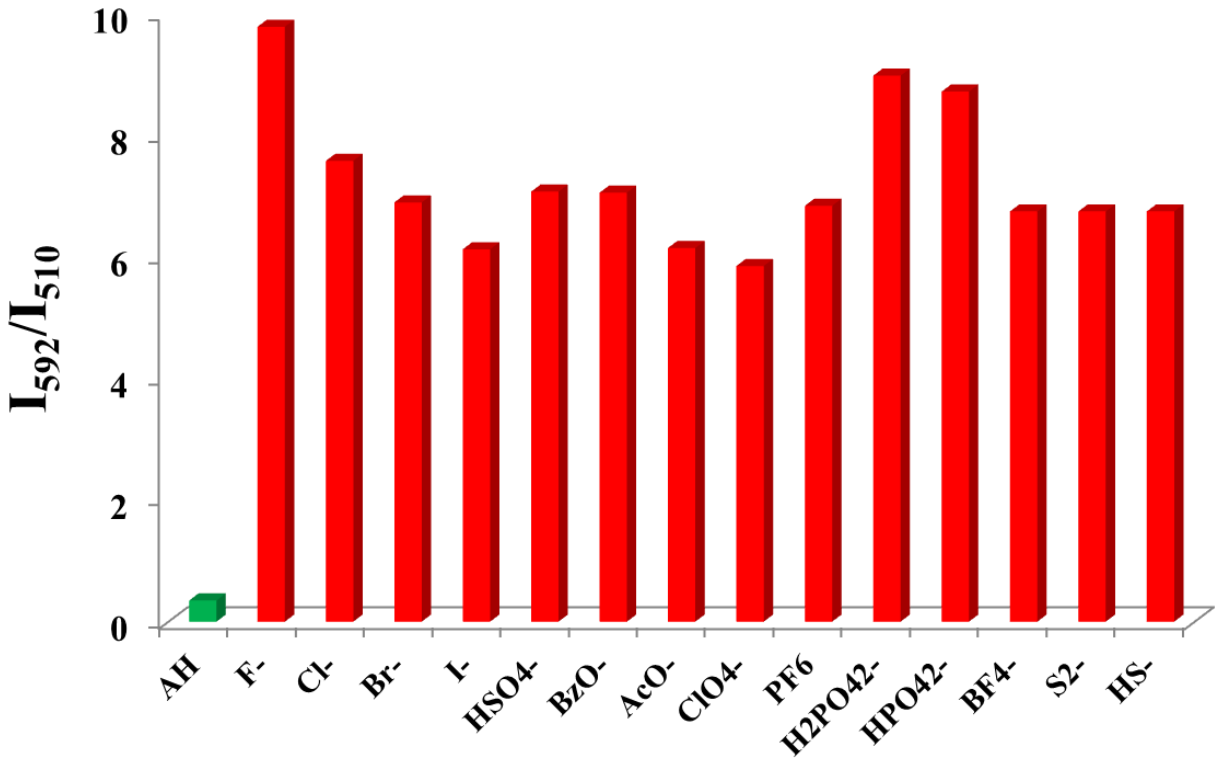


Figure S15: Relative time response study of **AH** with F^- and S^{2-} ion through UV-visible

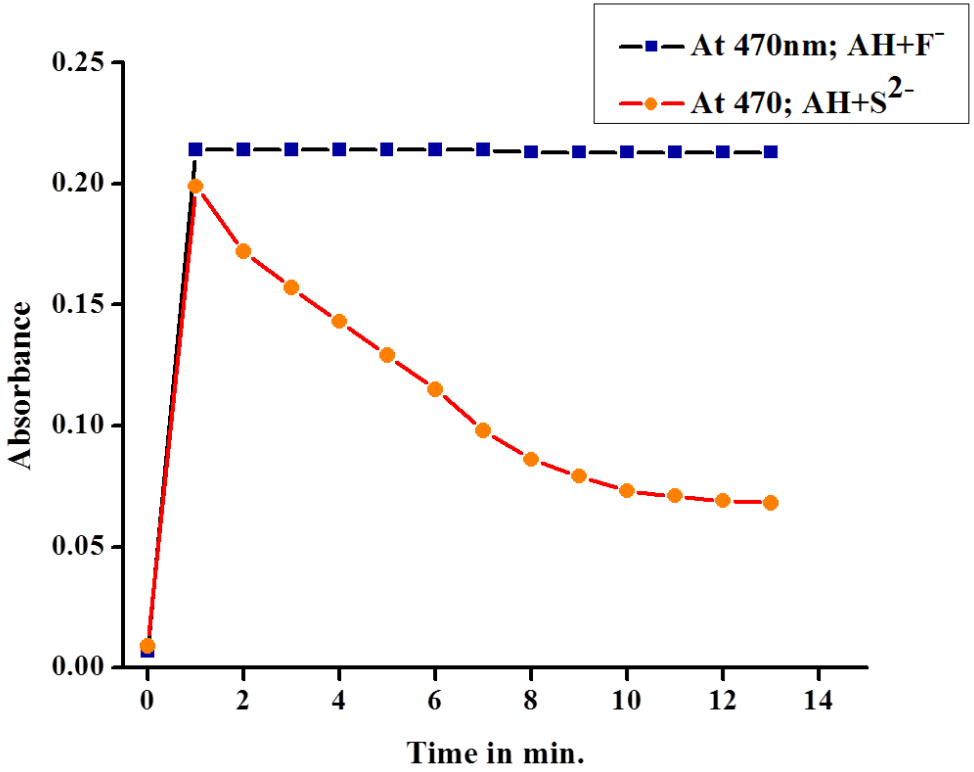


Figure S16: ESI-Mass spectrum of **A1**

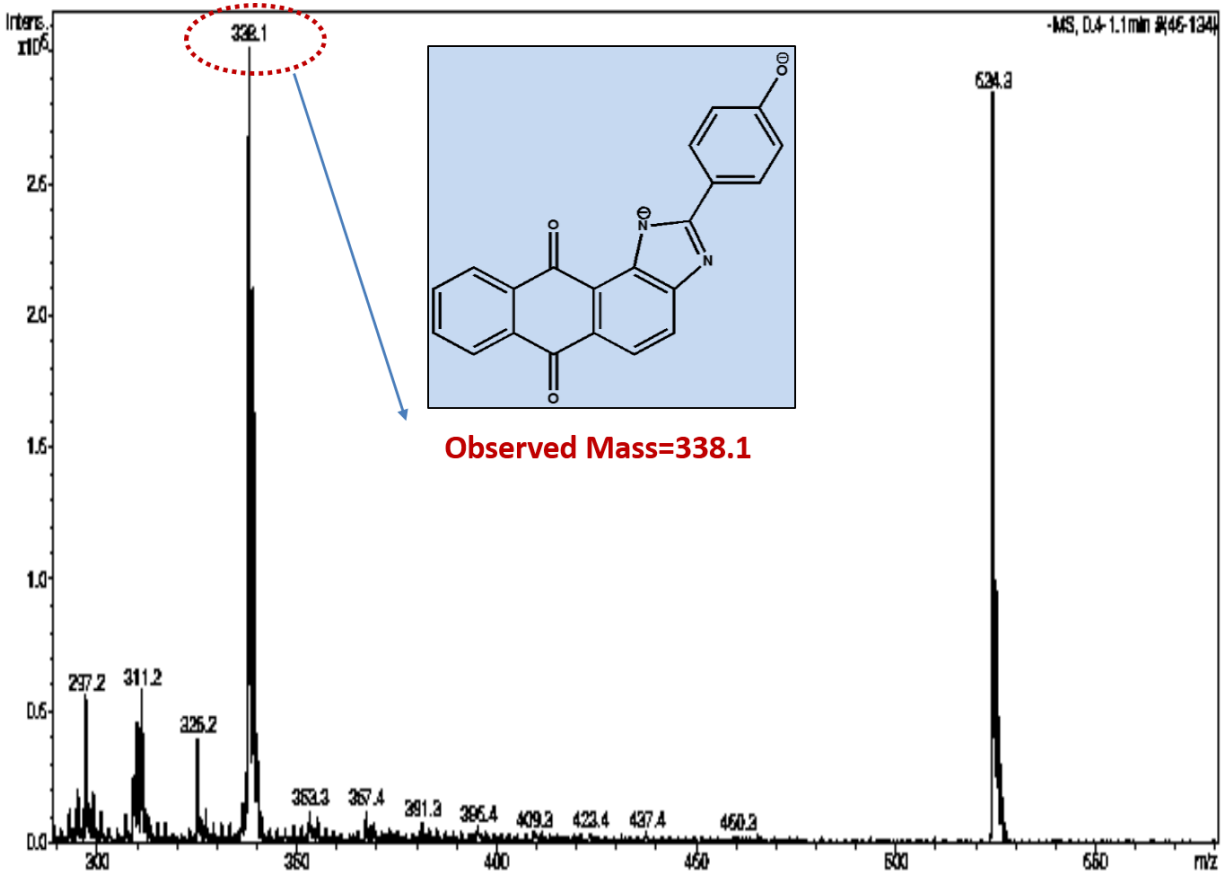


Table S1: Structural refinement details of **AH**

CCDC No.	**1480047**
Empirical formula	$C_{54}H_{30}N_6O_{14}S_2$
Formula weight	1050.96
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 43.418(11) Å alpha = 90 deg. b = 7.5014(18) Å beta = 105.777(8) deg. c = 14.333(4) Å, gamma = 90 deg.
Volume	4492.4(19) A^3
Absorption coefficient	0.203 mm^{-1}
Z, Calculated density	4, 1.554 mg/m^3
Theta range for data collection	3.9 to 56.574 deg.
Limiting indices	$-57 \leq h \leq 43$, $-9 \leq k \leq 9$, $-19 \leq l \leq 18$
Reflections collected / unique	13475 / 5177 [Rint = 0.0709]
Completeness to theta = 28.240	98.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5177/0/343
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R_1 = 0.0575, wR_2 = 0.1378
R indices (all data)	R_1 = 0.0999, wR_2 = 0.1685

Table S2: Selected important bond lengths and angles for **AH**

Atoms	Bond Length (Å)	Atoms	Angle (deg.)
S(1)-O(5)	1.603(2)	O(5)-S(1)-O(3)	109.4(1)
S(1)-O(3)	1.419(2)	O(5)-S(1)-O(4)	103.0(1)
S(1)-O(4)	1.421(2)	O(5)-S(1)-C(4)	101.6(1)
S(1)-C(4)	1.760(2)	O(3)-S(1)-O(4)	120.6(1)
O(6)-C(20)	1.230(3)	O(3)-S(1)-C(4)	109.5(1)
O(5)-C(7)	1.423(3)	O(4)-S(1)-C(4)	110.8(1)
O(7)-C(21)	1.223(3)	S(1)-O(5)-C(7)	119.5(1)
O(2)-N(1)	1.226(3)	C(13)-N(2)-C(14)	104.7(2)
N(2)-C(13)	1.326(3)	H(3)-N(3)-C(15)	126.5(2)
N(2)-C(14)	1.371(3)	H(3)-N(3)-C(13)	126.7(2)
N(3)-H(3)	0.880(2)	C(15)-N(3)-C(13)	106.8(2)
N(3)-C(15)	1.376(4)	O(2)-N(1)-O(1)	124.4(3)
N(3)-C(13)	1.380(3)	O(2)-N(1)-C(1)	118.0(2)
O(1)-N(1)	1.229(3)	O(1)-N(1)-C(1)	117.6(2)
N(1)-C(1)	1.475(4)	N(2)-C(13)-N(3)	112.9(2)

Table S3: Some selected transitions of **AH** and **A1** obtained from theoretical calculations

	Theoretical				**Experimental (Acetonitrile)**	
S. No.	**Transitions: AH (some selected transitions)**		**Transitions: A1 (some selected transitions)**		**AH**	**AH+ TBAF= A1**
1.	135 (H)→136 (L)	435 nm f=0.3716	86 (H-1)→88 (L) 87 (H) →88 (L)	702 nm f=0.0085	**395 nm**	**470 nm**
2.	134 (H-1) →136 (L) 134 (H-1) →137 (L+1)	**394 nm** f=0.1273	82 (H-5) →88 (L) 86 (H-1) →88 (L) 86 (H-1) →89 (L+1)	**482 nm** f=0.6423		
3.	130 (H-5) →139 (L+3) 132 (H-3) →136 (L) 132 (H-3) →137 (L+1)	334 nm f=0.0676	82 (H-5) →88 (L) 86 (H-1) →88 (L) 87 (H) →89 (L+1)	457 nm f=0.6710		
4.	128 (H-7) →136 (L) 130 (H-5) →136 (L)	316 nm f=0.0699	82 (H-5) →88 (L) 86 (H-1) →89 (L+1) 87 (H) →89 (L+1)	388 nm f=0.0451		
5.	130 (H-5) →136 (L) 131(H-4) →136 (L) 131 (H-4) →137 (L+1)	312 nm f=0.0200	76 (H-11) →88 (L) 86 (H-1) →89 (L) 87 (H) →89 (L+1)	342 nm f=0.1798		