Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A highly selective arylhydrazone based "ON–OFF" fluorescent chemosensor for Zn^{2+} ion in aqueous ethanol and their Molecular Docking, Cytotoxicity and DFT studies.

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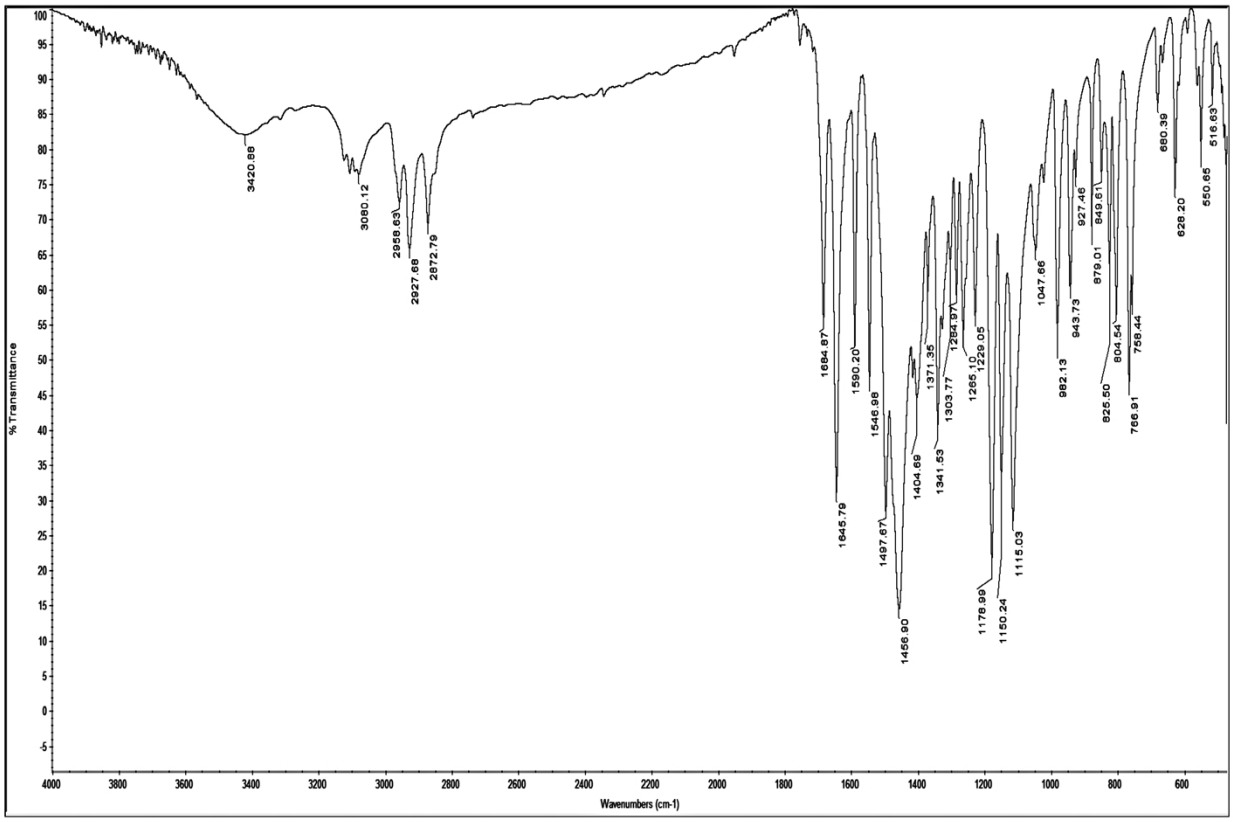


Fig. S1 IR spectra of compound **(1).**

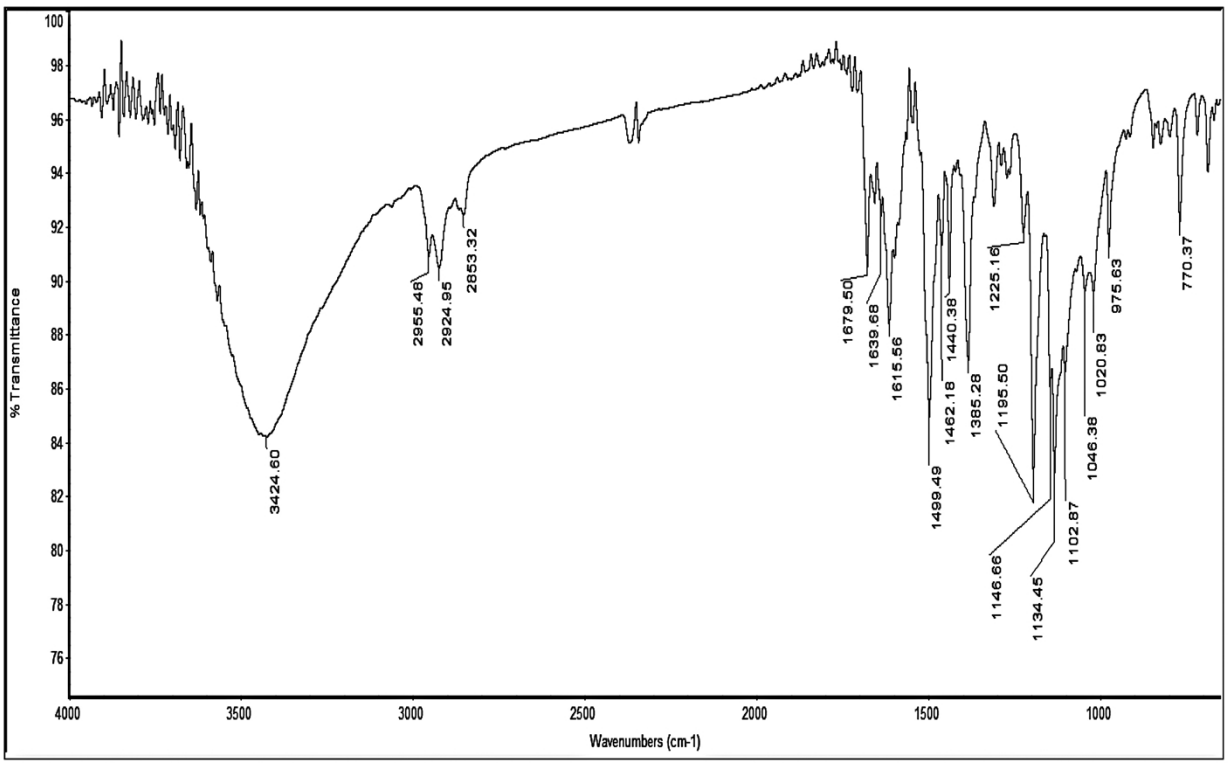


Fig. S2 IR spectra of compound **(2).**

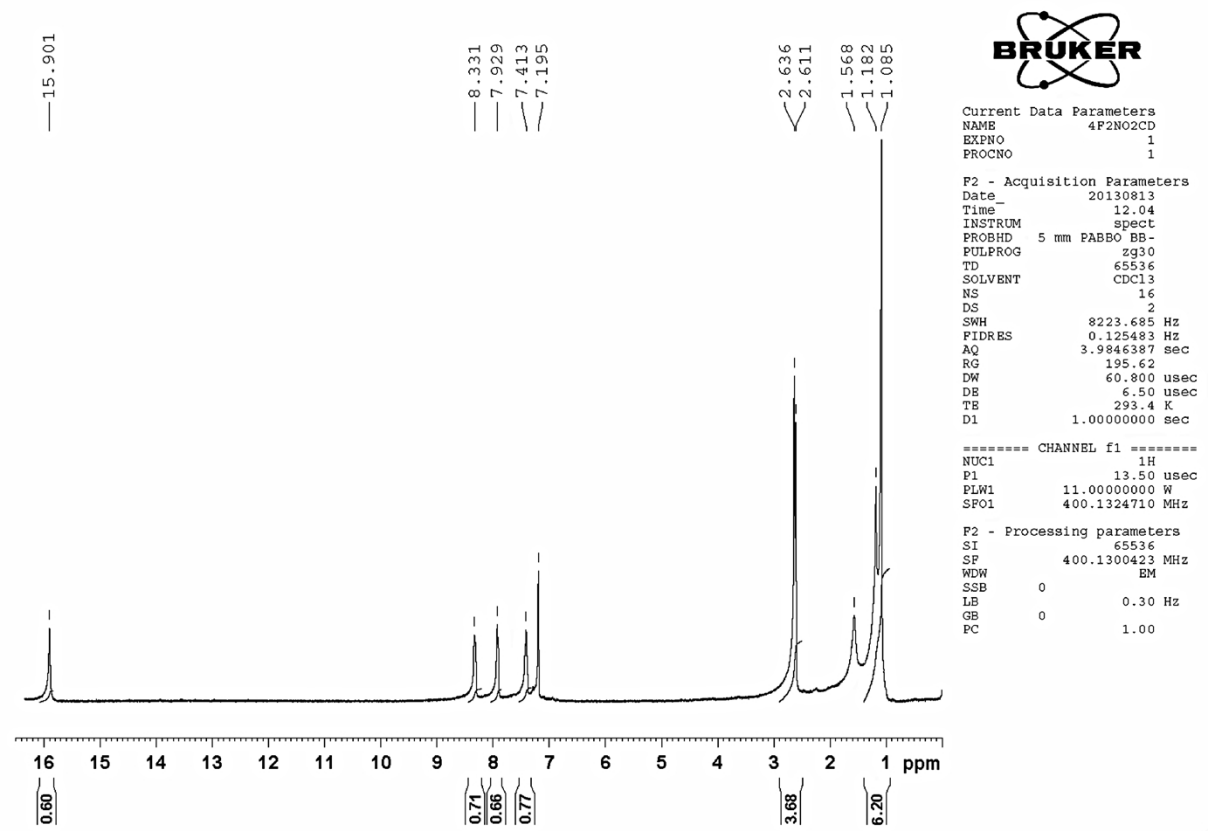


Fig. S3 ^{1}H NMR spectrum of compound **(1).**

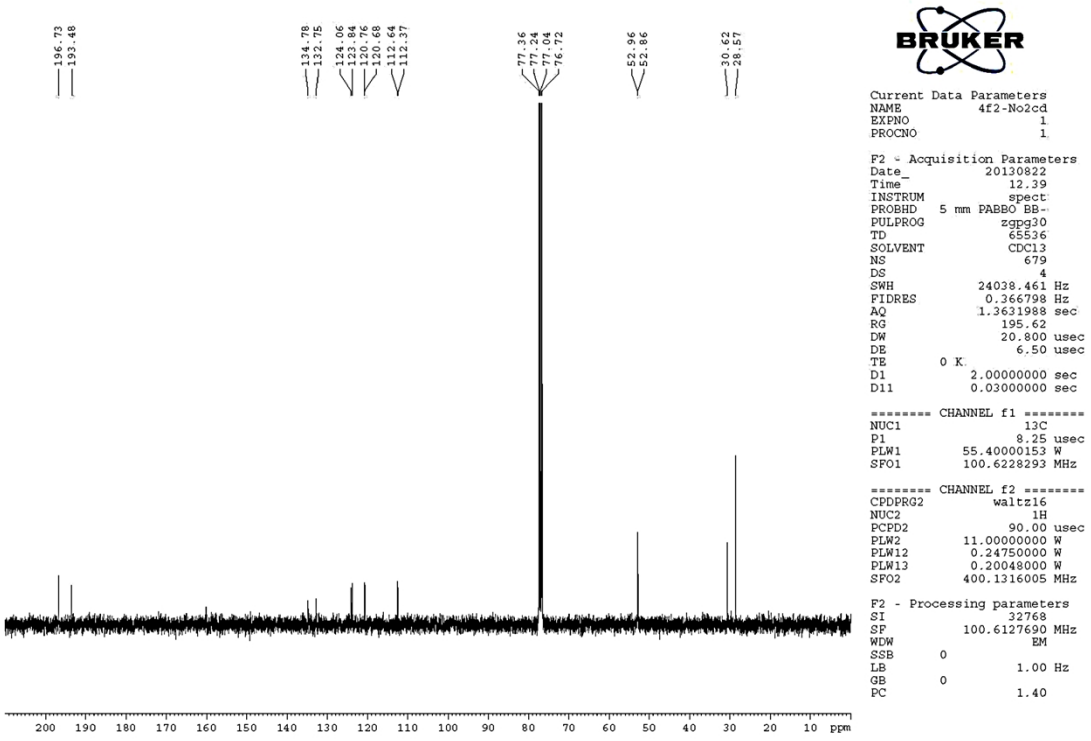


Fig. S4 ^{13}C NMR spectrum of compound **(1).**

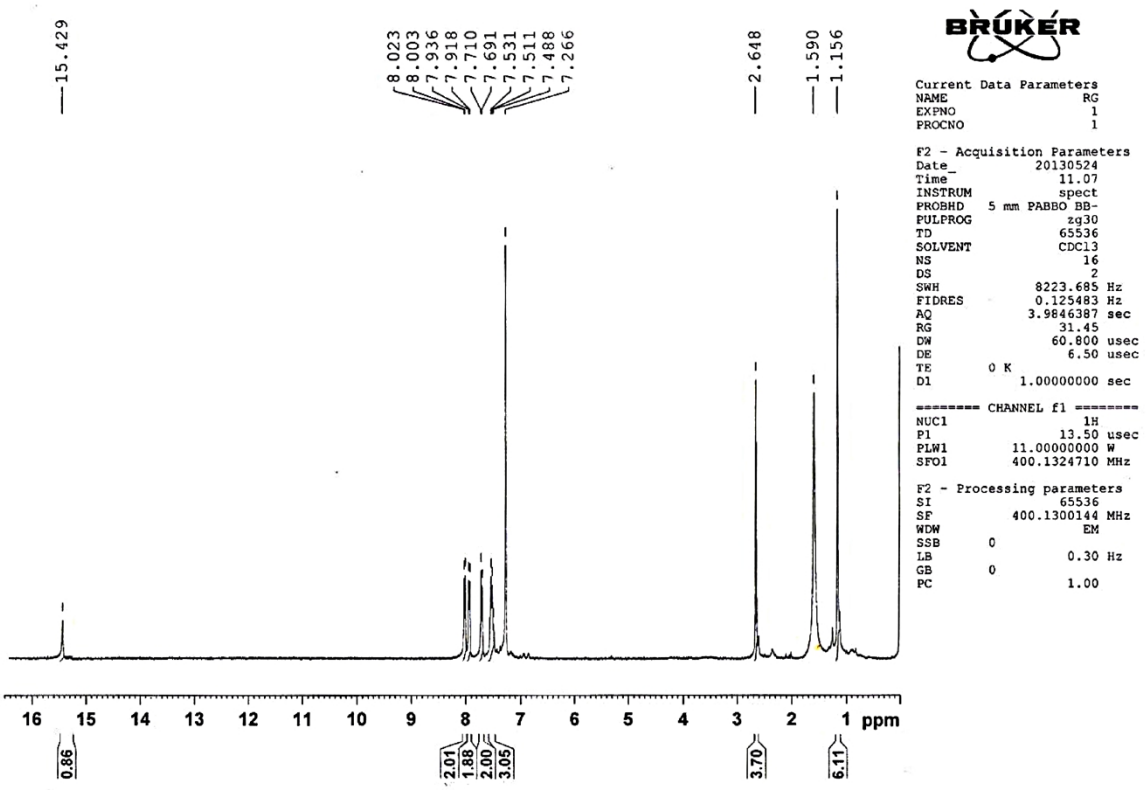


Fig. S5 ^{1}H NMR spectrum of compound **(2).**

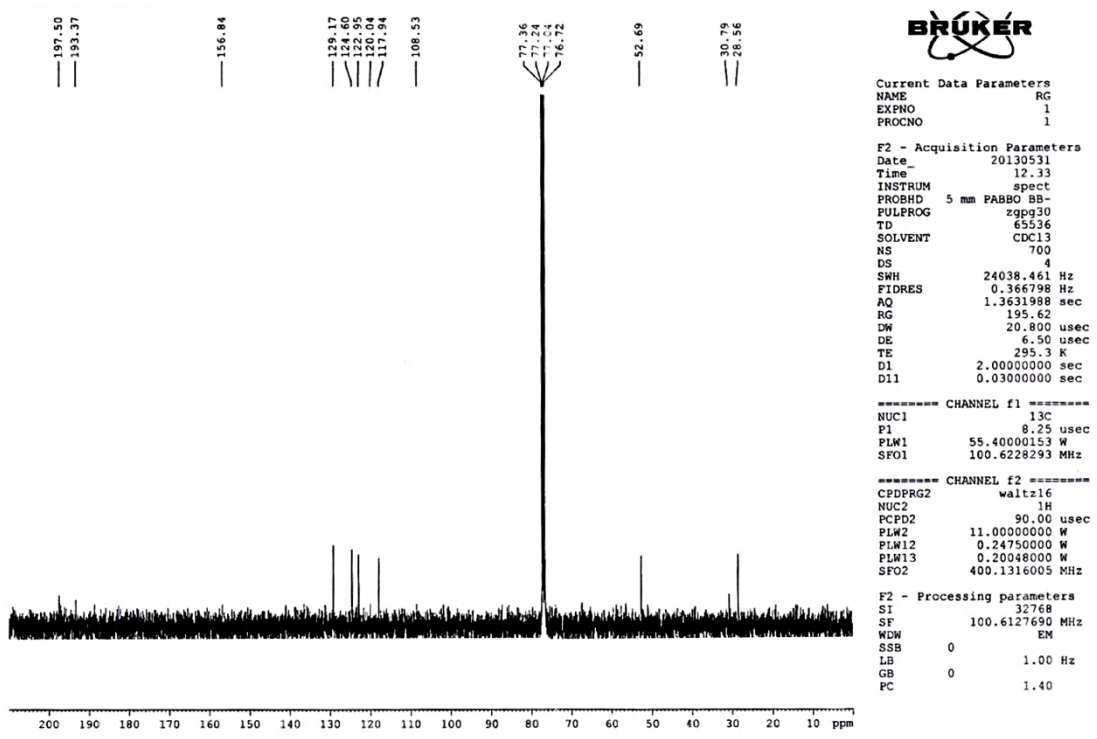


Fig. S6 ^{13}C NMR spectrum of compound **(2).**

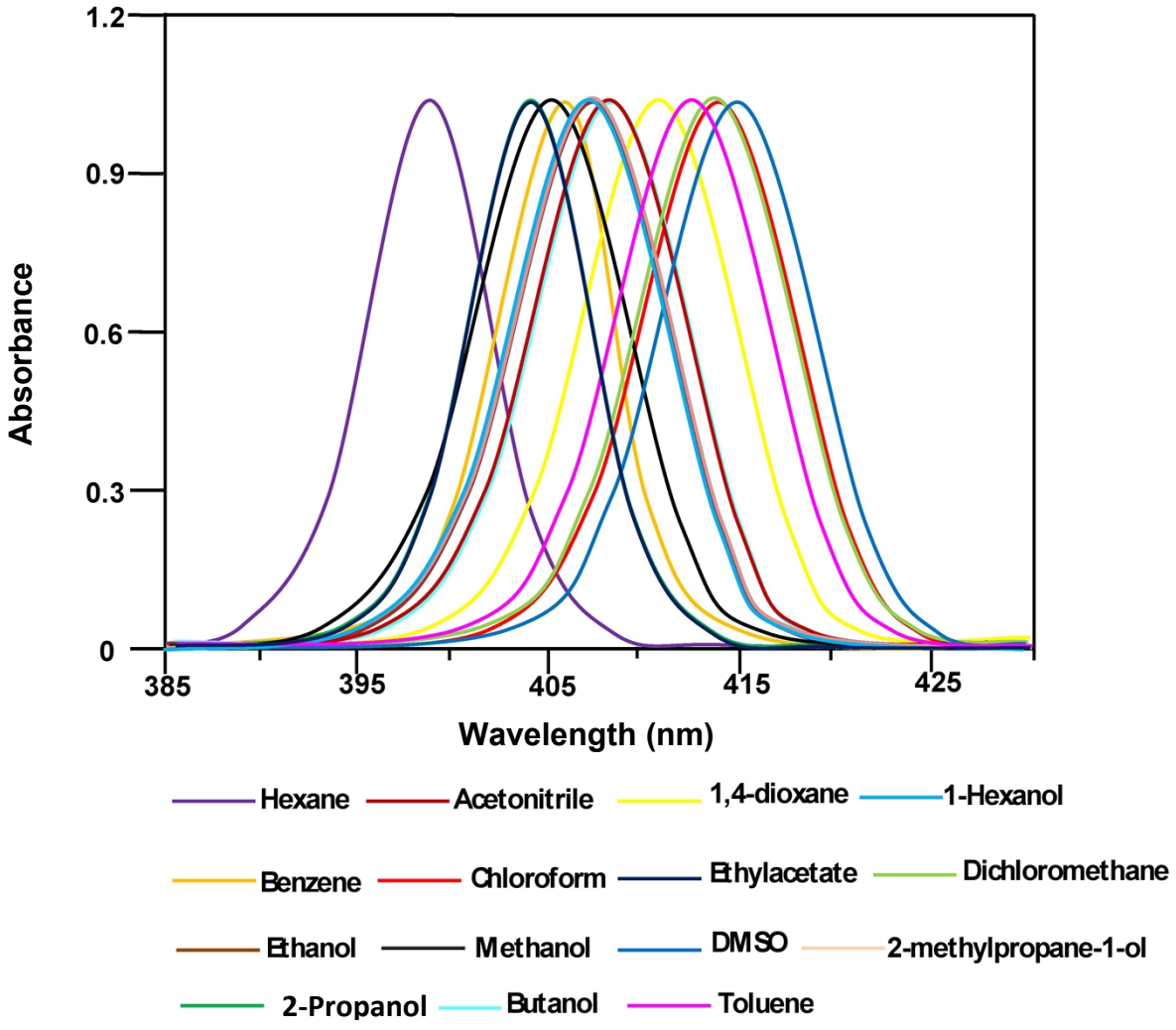


Fig. S7A Absorption spectrum of compound **(1).**

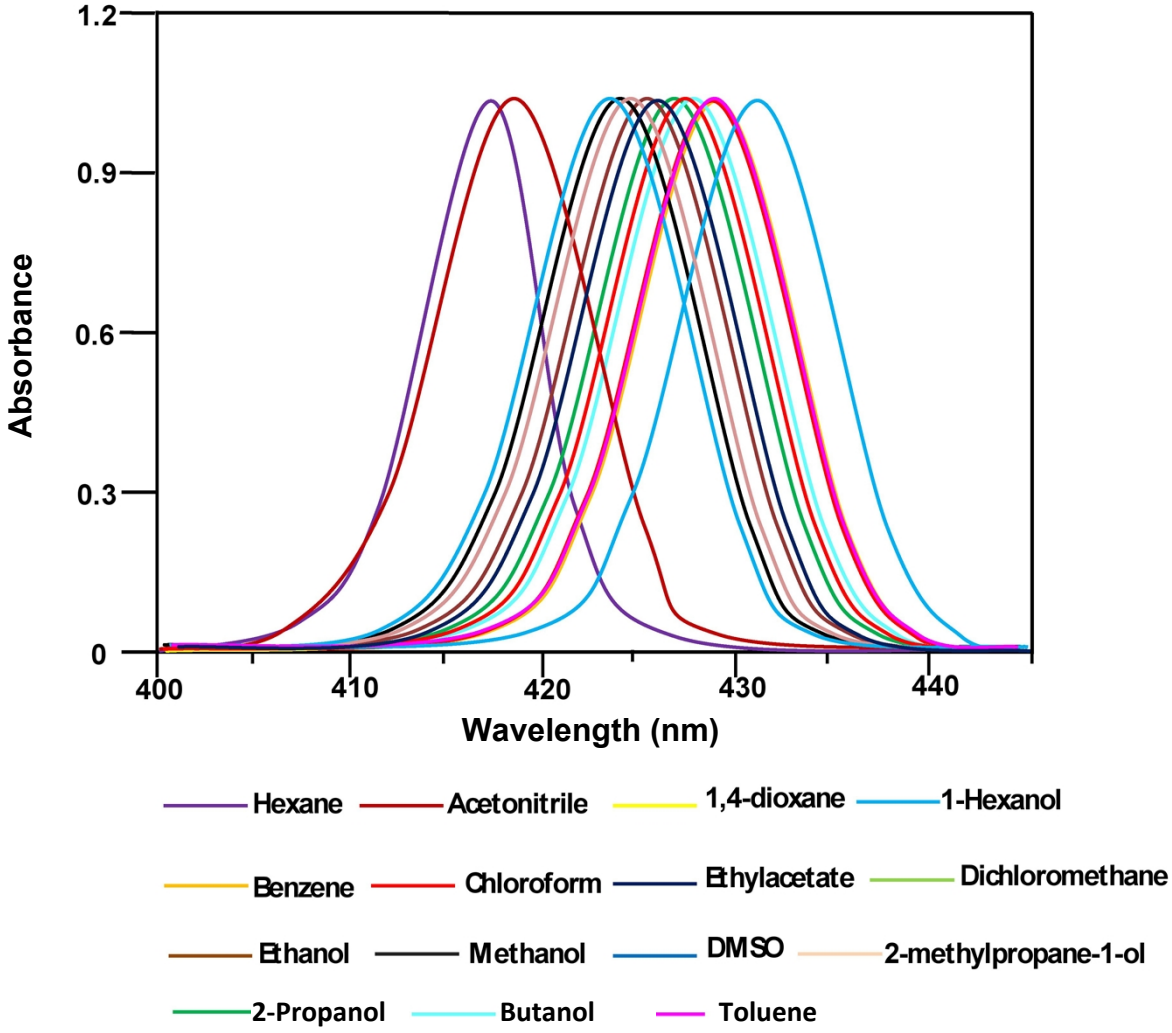


Fig. S7B Absorption spectrum of compound **(2).**

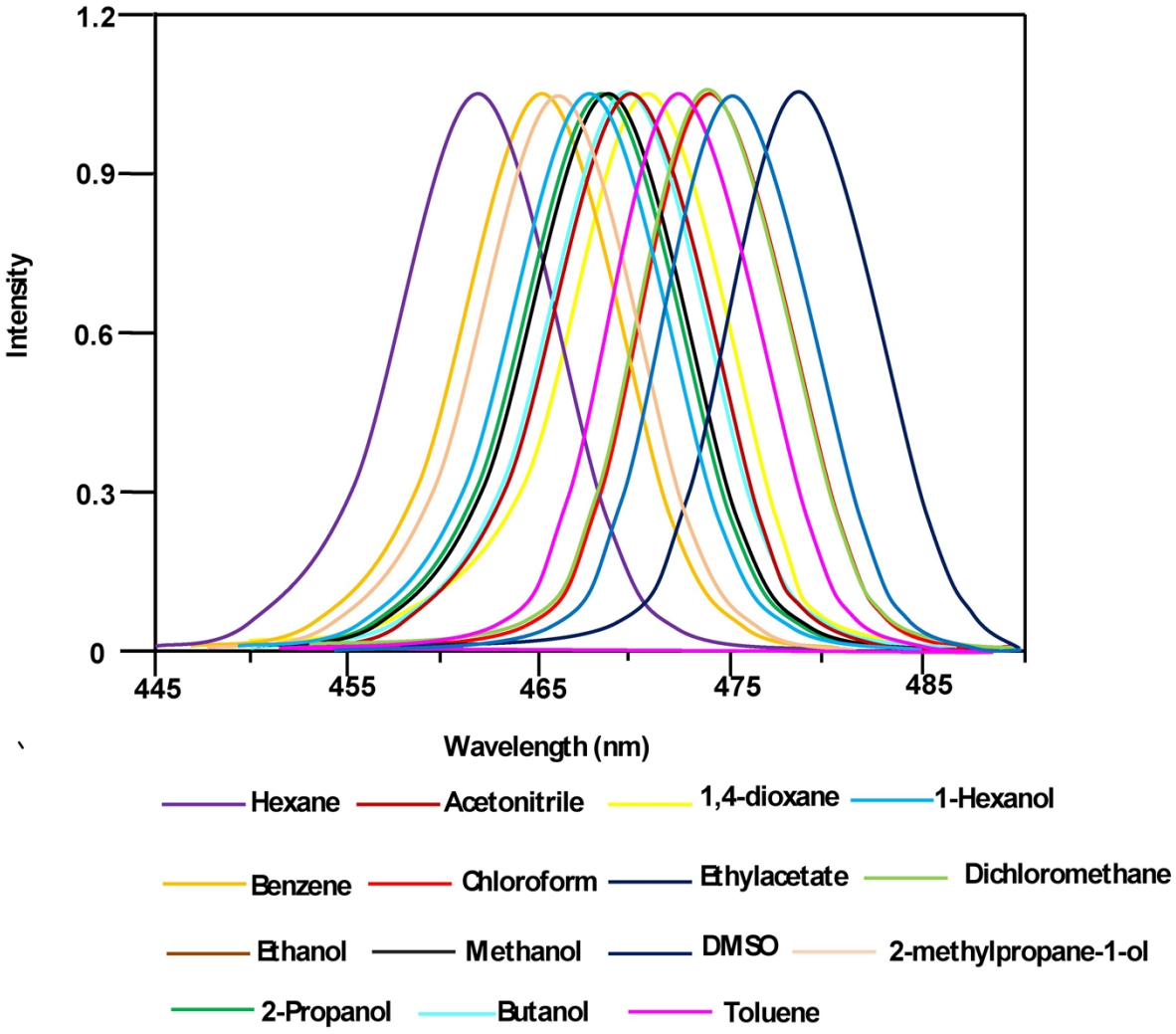


Fig. S8A Emission spectrum of compound **(1).**

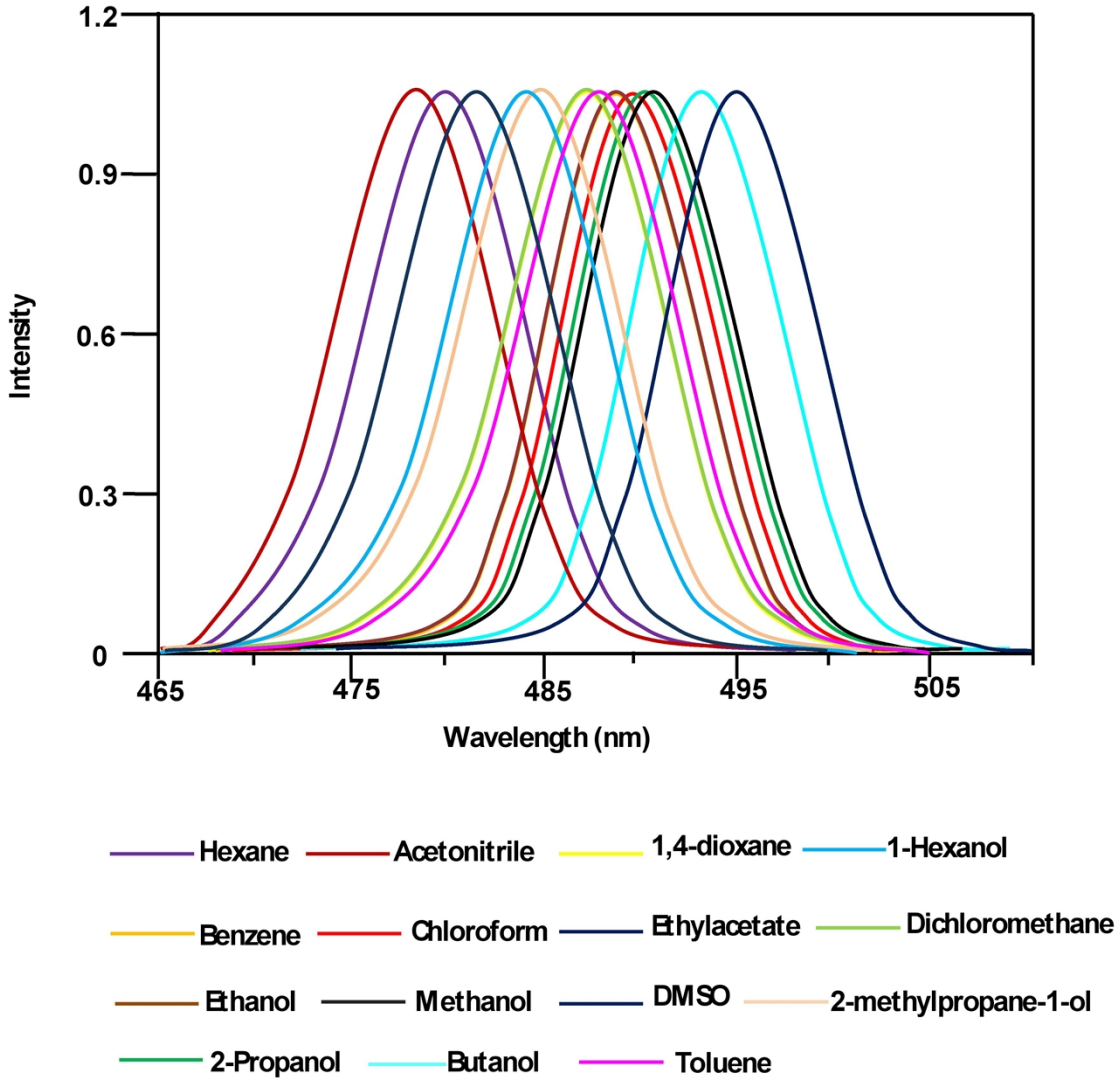


Fig. S8B Emission spectrum of compound **(2).**

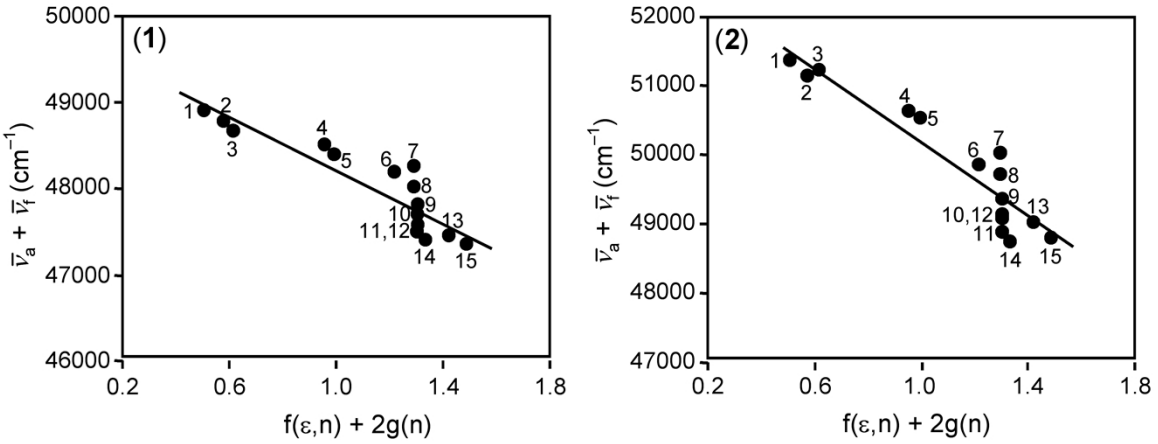


Fig. S9 Plot of Kawski correlation $\bar{\nu}_a + \bar{\nu}_f$ (cm^{-1}) *Vs* f(ε,n) + 2g(n) for compound (1) and (2). 1. Hexane, 2. 1,4-dioxane, 3. Benzene, 5. Chloroform, 6. Ethylacetate, 7. Ethanol, 8. Methanol, 9. 2-propanol, 11. 1-Butanol, 13. Dichloromethane, 14. Acetonitrile, 15. Dimethylsulfoxide.

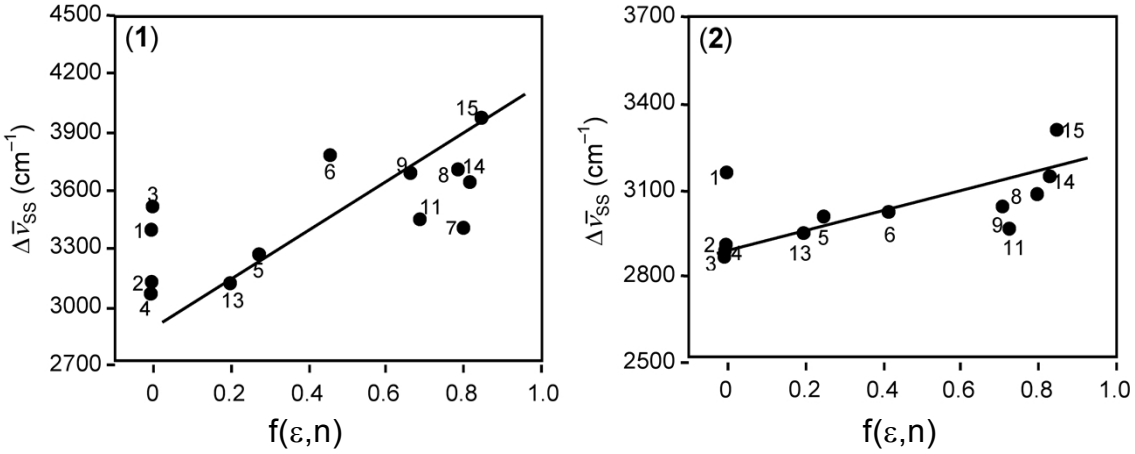


Fig. S10 Plot of Stokes shifts (cm^{-1}) *Vs* f(ε,n) for compound (2). 1. Hexane, 2.1,4-dioxane, 3. Benzene, 5. Chloroform, 6. Ethylacetate, 7. Ethanol, 8. Methanol, 9. 2-propanol, 11. 1-Butanol, 13. Dichloromethane, 14. Acetonitrile , 15 dimethylsulfoxide.

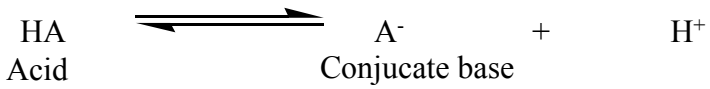
Spectroscopic determination of the pka for compounds (1) and (2)[1,2]

Buffer solutions ranging from pH 1-13 were prepared as per standard procedures and standardized by standard pH meter using a glass electrode. Absorbance of compound **(1)** and these buffer solutions were measured. The absorbance maximum at highest acidic pH 1 is considered as λ_1(acidic). Similarly the absorbance maximum at highest basic pH is pH13 is considered as λ_2(basic). Now the intensities at λ_1(acidic) and λ_2(basic) were determined for all other pH ranges. The values are tabulated in Table S3 and S4. The intensity correction at λ_1(acidic) and λ_2(basic) were done to avoid errors by the following method

Intensity of corrected absorption at λ_1 (acidic)= λ_1 intensity observed - λ_1 intensity minimum

Where, **λ_1** intensity minimum is the minimum intensity for λ_1(acidic). Similarly corrections are carried out at λ_2(basic) and the values are tabulated.

As we know



Hendersan-Hasselbach equation for the above reaction

$pH=pka + \log[A^-]/[HA]$

$\log[A^-]/[HA]=A\lambda_2 \,.\, A\lambda_1$ acidic/ $A\lambda_2$ basic. $A\lambda_1$

Where $A\lambda_2$= Corrected λ_2 absorption at a particular pH

$A\lambda_1$= Corrected λ_1 absorption at a particular pH

$A\lambda_1$ acidic= Acidic λ_1 absorption

$A\lambda_2$ basic= Basic λ_2 absorption

At equilibrium **pH=pKa**

A graph is ploted between pH Vs log[A-]/[HA]. From intersection straight line over y axis gives equilibrium pH which is the pKa value.

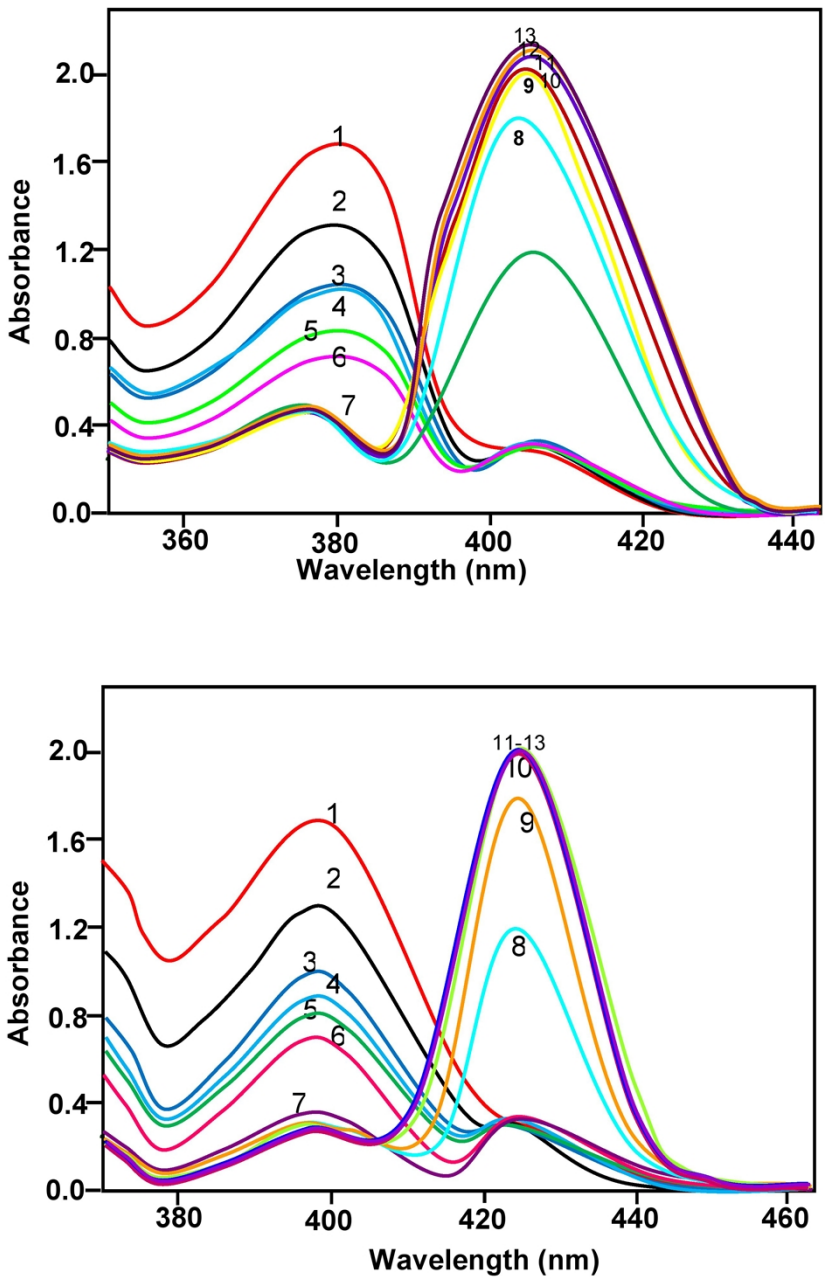


Fig. S11 A plot of absorbance as a function of pH for compounds (1) and (2)

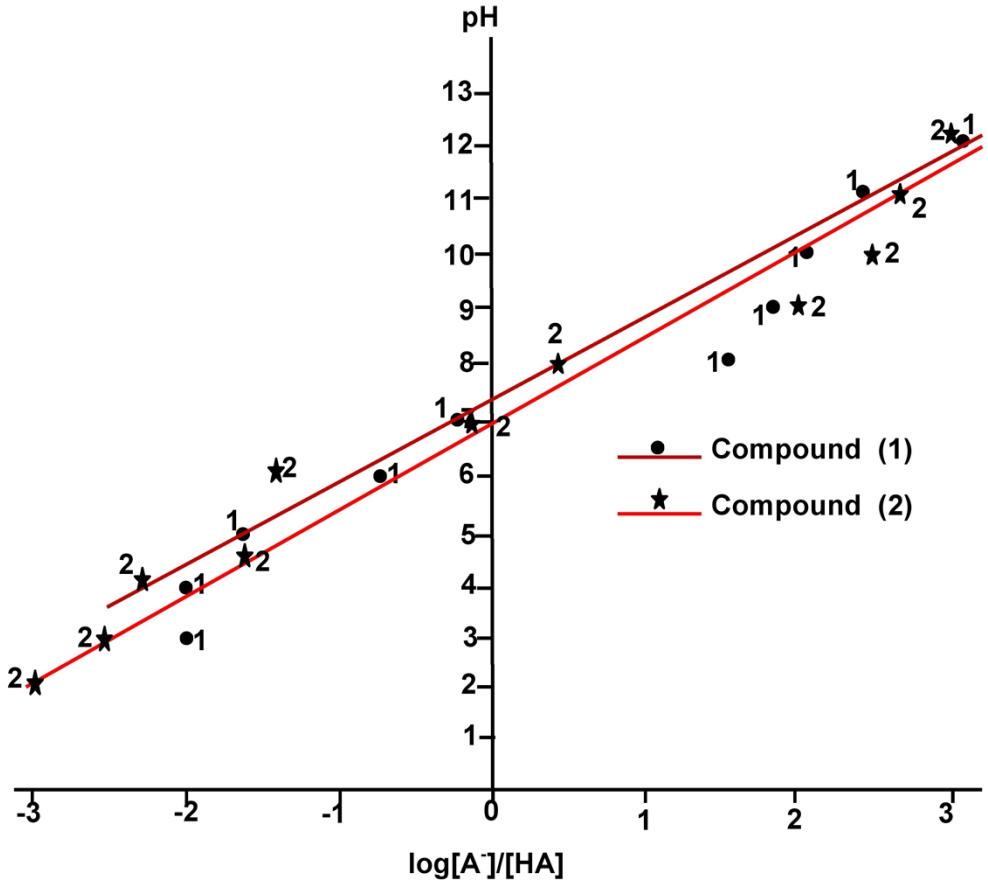


Fig. S12 Plot of pH as a function of log[A^-]/[HA]. The pKa of compounds **(1)** and **(2)** corresponds to the intersection of the straight line with the 'y' axis

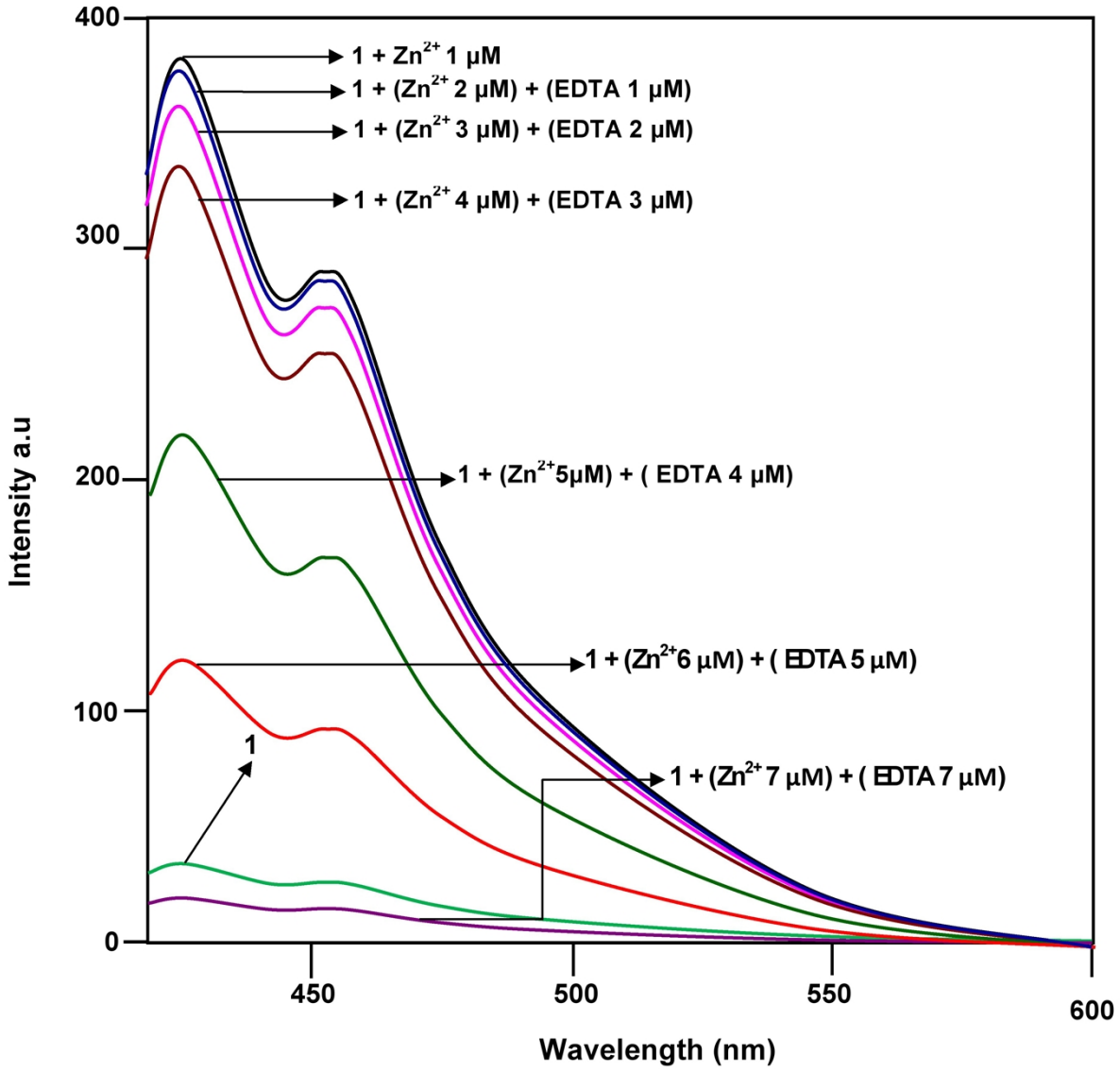


Fig. S13 Fluorescence spectra of compound (1) with various concentration of Zn^{2+} and EDTANa2 in ethanol solution.

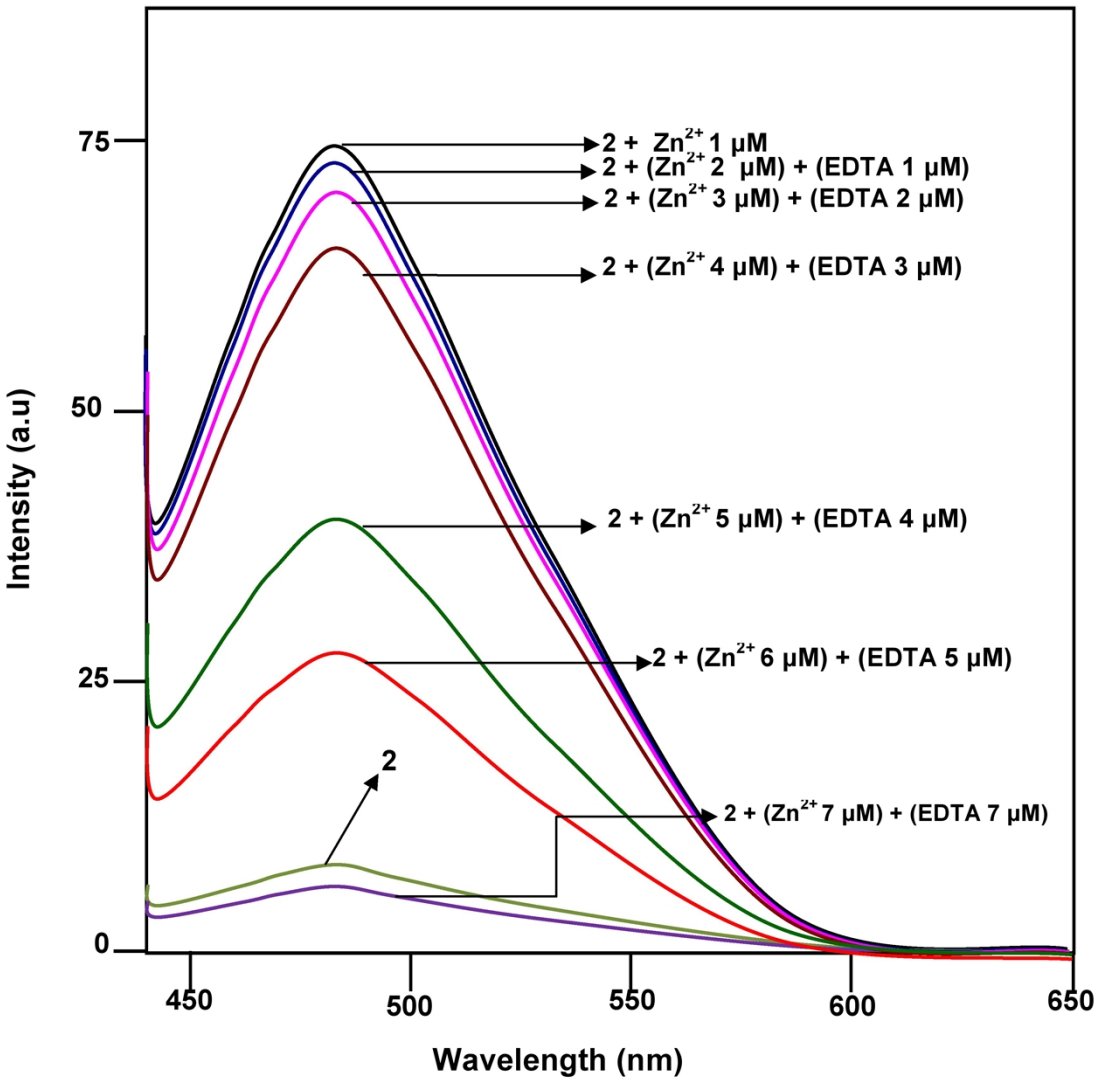


Fig. S14 Fluorescence spectra of compound (2) with various concentration of Zn^{2+} and EDTANa2 in ethanol solution.

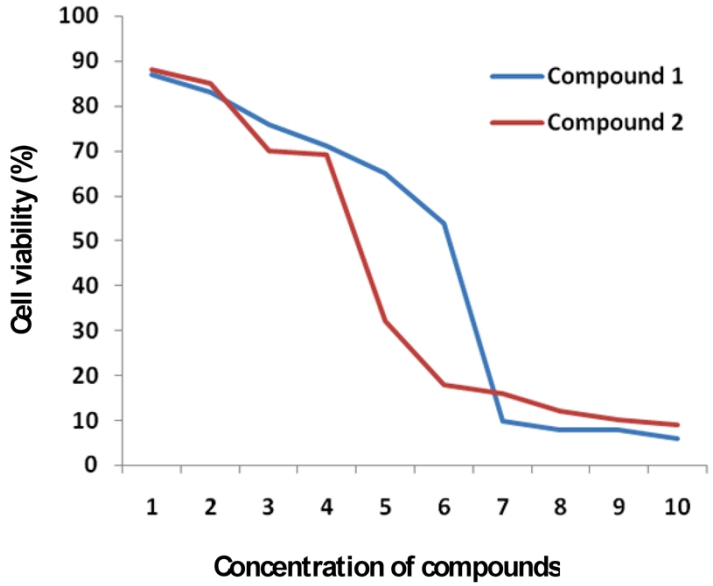


Fig. S15 Cytotoxic activity of compounds (1) and (2) against KB cell line.

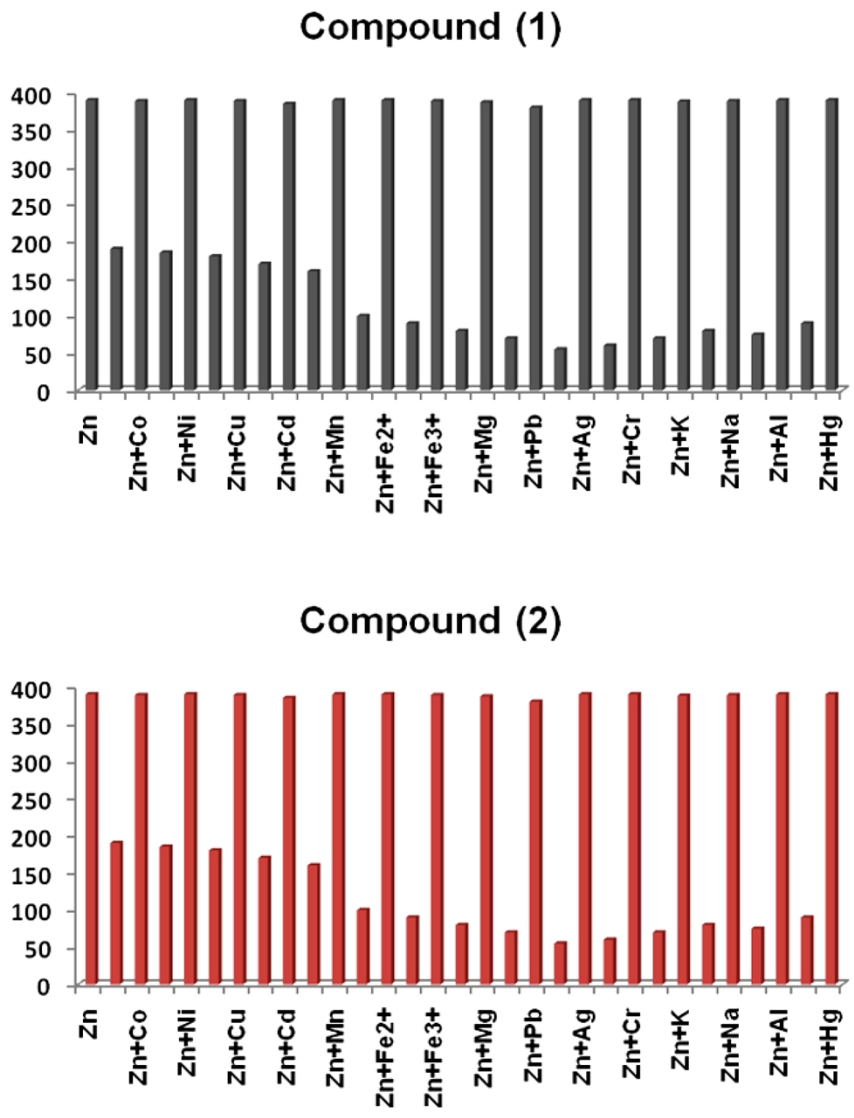


Fig. S16 Metal-ion selectivity of 1 (top) in 1: 1 v/v 0.01 M CH_3CH_2OH-H_2O, pH 7.0. The SHORT bars represent the fluorescence emission of a solution of compound (1) and (2) (10 mM) and 5 equiv. of other metal ions. The lengthy bars represents the fluorescence emission after the

addition of 1 equiv. of Zn(II) to the solution containing 1 and 2 (10 mM) and different metal ions (50 mM).

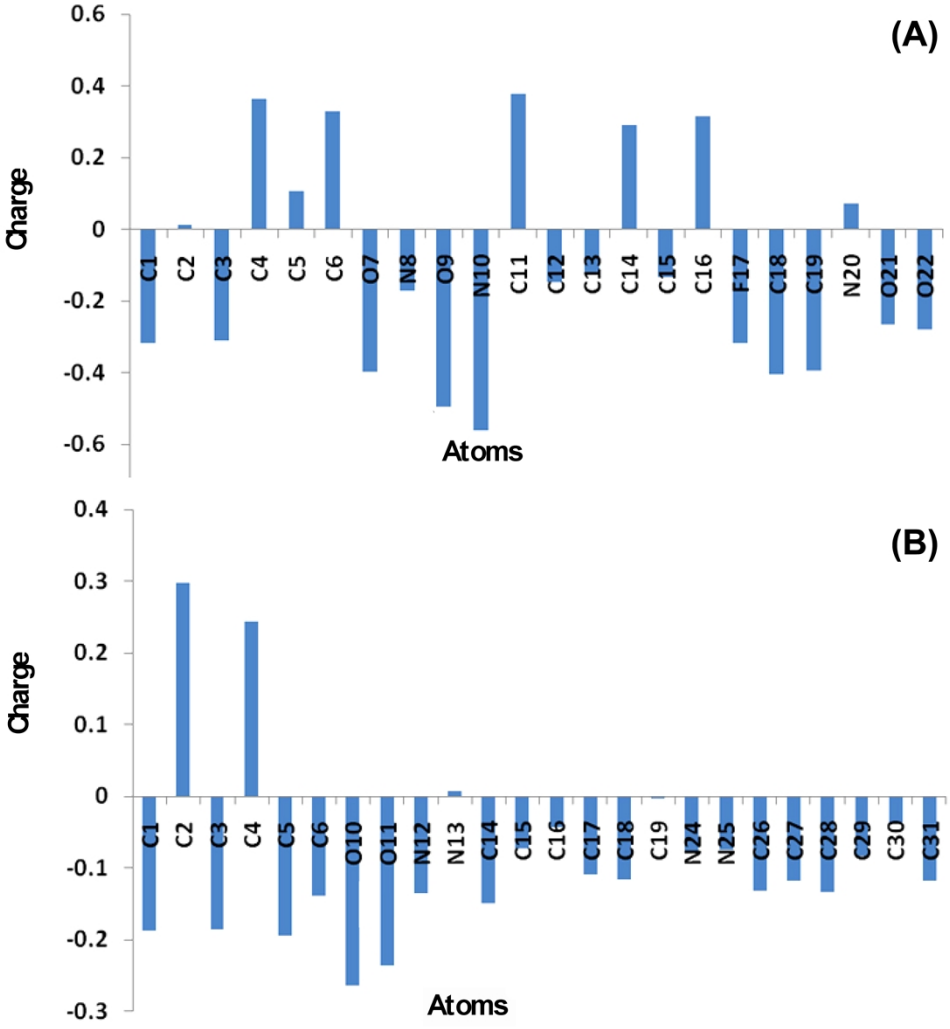


Fig. S17 Bar diagram of Mulliken atomic charges (A) compound **(1)** and (B) compound **(2)**.

Table S1 . Absorbtion and emission values of compound 1 and compound 2

Solvent	**Polarity index**	**1**		**2**	
		Λ_{abs} nm	**Λ_{flu} nm**	**Λ_{abs} nm**	**Λ_{flu} nm**
Hexane	0	399	462	417	480
1,4-dioxane	0.2	409	472	427	487
1-hexanol	0.5	407	467	424	484
1-butanol	0.6	408	469	428	488
Toluene	2.4	413	473	428	488
Benzene	2.7	401	465	429	489
Dichloromethane	3.1	414	474	427	487
2-propanol	3.9	404	468	426	486
2-methylpropane1-ol	3.9	407	466	425	485
Chloroform	4.1	414	474	429	490
Ethylacetate	4.4	404	475	422	482
Methanol	5.1	405	468	424	491
Ethanol	5.2	406	467	426	489
Acetonitrile	5.8	408	470	418	478
DMSO	7.2	415	478	431	495

Table S2. The IC50 values of compounds 1 and 2 against KB cell lines.

Anticancer effect of compounds(1) and (2) on KB cell line		
	Viability %	
Concentration (µM)	**Compound (1)**	**Compound (2)**
1.5	87	88
2	83	85
3.8	76	70
7.6	71	69
15.3	65	32
30.6	54	18
61.25	10	16
125	8	12
250	8	10
500	6	9

Table S3. Intensities and corrected intensities for λ acidic and λ basic for compound **(1)**

Compound (1)						
pH	**Observed Intensity of $\lambda_{1\ acidic}$**	**Corrected intensity of acid**	**Observed Intensity of $\lambda_{2\ basic}$**	**Corrected intensity of base**	**$[A^-]/[HA]$**	**$\log[A^-]/[HA]$**
1	1.698		0.291	0	0	0
2	1.344	1.267	0.292	0.001	0.000746	-3.12721
3	1.038	0.913	0.296	0.005	0.005611	-2.25096
4	1.014	0.607	0.296	0.005	0.005842	-2.23343
5	0.833	0.583	0.301	0.01	0.016945	-1.77096
6	0.765	0.402	0.355	0.064	0.130526	-0.8843
7	0.5	0.334	1.201	0.068	0.671311	-0.17308
8	0.458	0.069	1.868	1.577	39.78612	1.599732
9	0.445	0.027	2.03	1.739	84.61263	1.927435
10	0.44	0.014	2.07	1.779	134.6471	2.129197
11	0.435	0.009	2.121	1.83	311.6411	2.493655
12	0.432	0.004	2.142	1.851	1260.869	3.10067
13	0.431	0.001	2.151	1.86	0	
		λ1=380		**λ2**=406		

Table S4. Intensities and corrected intensities for λ acidic and λ basic for compound **(2)**

Compound (2)						
pH	**Observed Intensity of $\lambda_{1\ acidic}$**	**Corrected intensity of acid**	**Observed Intensity of $\lambda_{2\ basic}$**	**Corrected intensity of base**	**$[A^-]/[HA]$**	**$\log[A^-]/[HA]$**
1	1.692	1.349	0.326	0	0	
2	1.354	1.011	0.327	0.001	0.000674	-3.17149
3	1.01	0.667	0.328	0.002	0.002043	-2.68983
4	0.99	0.647	0.331	0.005	0.005264	-2.27867
5	0.794	0.451	0.34	0.014	0.021145	-1.67478
6	0.75	0.407	0.349	0.023	0.038494	-1.4146
7	0.382	0.039	0.37	0.044	0.768514	-0.11435
8	0.369	0.026	1.208	0.882	23.10782	1.363759
9	0.352	0.009	1.864	1.538	116.4066	2.065977
10	0.346	0.003	2.008	1.682	381.9165	2.581968
11	0.345	0.002	2.02	1.694	576.9618	2.761147
12	0.344	0.001	2.027	1.701	1158.692	3.063968
13	0.343	0	2.066	1.74		
		λ_1=399		λ_2=425		

References

1 R. D. Barun, Introduction to chemical Analysis; Mc Graw-Hill, New York, 1982, 197- 199

2 G. H. Jeffery, H. Bassett, J. Mendam, R.C. Denny, " Vogel's Text books of quantitative chemical Analysis Ed. 5, 1989, 46-49