Supporting information

Derivative of clove oil used as chemosensor for colorimetric and fluorometric detection of Al^{3+}: crystal structure description and live cell imaging

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Table S1 Crystal parameters and selected refinement details for chemosensor **H_3L**.

Chemosensor **H_3L**	
Empirical formula	$C_{37}H_{36}N_4O_4$
Formula weight	600.70
Temperature (K)	273(2)
Crystal system	Triclinic
Space group	*P-1*
a (Å)	9.3947(3)
b (Å)	12.3486(3)
c (Å)	14.4715(4)
α(°)	94.1270(10)
β(°)	103.7440(10)
γ(°)	94.6350(10)
Volume (Å^3)	1618.23(8)
Z	2
D_{calc} (g cm^{-3})	1.233
Absorption coefficient (mm^{-1})	0.081
F(000)	636
θ Range for data collection (°)	1.662-27.127
Reflections collected	52150
Independent reflection / R_{int}	5687/ 0.0419
Data / restraints / parameters	7140/0/406
Goodness-of-fit on F^2	1.042
Final *R* indices [I>2σ(I)]	R1 = 0.0726, wR2 = 0.2040
R indices (all data)	R1 = 0.0876 wR2 = 0.2181
Largest diff. peak / hole (e Å^{-3})	0.531/ -0.420

Table S2 Selected bond lengths (Å) and bond angles (°) for chemosensor **H_3L**.

Chemosensor **H_3L**			
N3-C10	1.494(3)	C8-C10-C11	110.55(17)
N3-N4	1.376(2)	C11-C10-C20	112.47(17)
N3-C26	1.372(3)	N3-C10-C8	110.83(17)
C8-C10	1.515(3)	N3-C10-C11	109.50(16)
C11-C10	1.516(3)	N3-C10-C20	99.40(16)
C20-C10	1.518(3)	C26-N3-C10	115.33(17)
C26-O2	1.214(3)	C26-N3-N4	129.50(18)
		C27-N4-N3	121.37(19)
		O2-C26-N3	126.4(2)

Table S3 Apparent binding constant (K), LOD, lifetime (τ_f) and quantum yield (Φ) values of **H_3L** and complex **1** from spectrofluorimetric measurement.

	K (M^{-1})	**LOD (M)**	**τ_f** (nS) (average)	**χ^2**	**Φ**
H_3L	-		0.26	0.990360	0.014
Complex **1**	2.01×10^5	2.82×10^{-6}	1.29	0.9031072	0.065

Table S4 First few strong and the lowest-lying absorption and emission band calculated wavelength (nm)/energies (eV), oscillator strength (*f*), major contribution, and the experimental wavelength (nm) for the investigated complex **1** in methanol media.

	Excited states	**Energy (eV)**	**Wavelength (nm)**	**Osc. Strength (*f*)**	**Major contributors**	**Experimental Wavelength (nm)**
Absorption						
	S_1	2.1516	576	0.3120	HOMO → LUMO (97.9%)	530
	S_3	2.9479	420	0.6588	HOMO → LUMO +2 (94%)	
	S_9	3.5893	345	0.2046	HOMO-4 → LUMO (72.8%)	350
Emission						
Opened spirolactam ring	S_1	2.4839	530	0.6441	HOMO → LUMO+2 (86.8%)	552
Closed spirolactam ring	S_1	2.5548	485	0.0004	HOMO-3 → LUMO (98.9%)	552

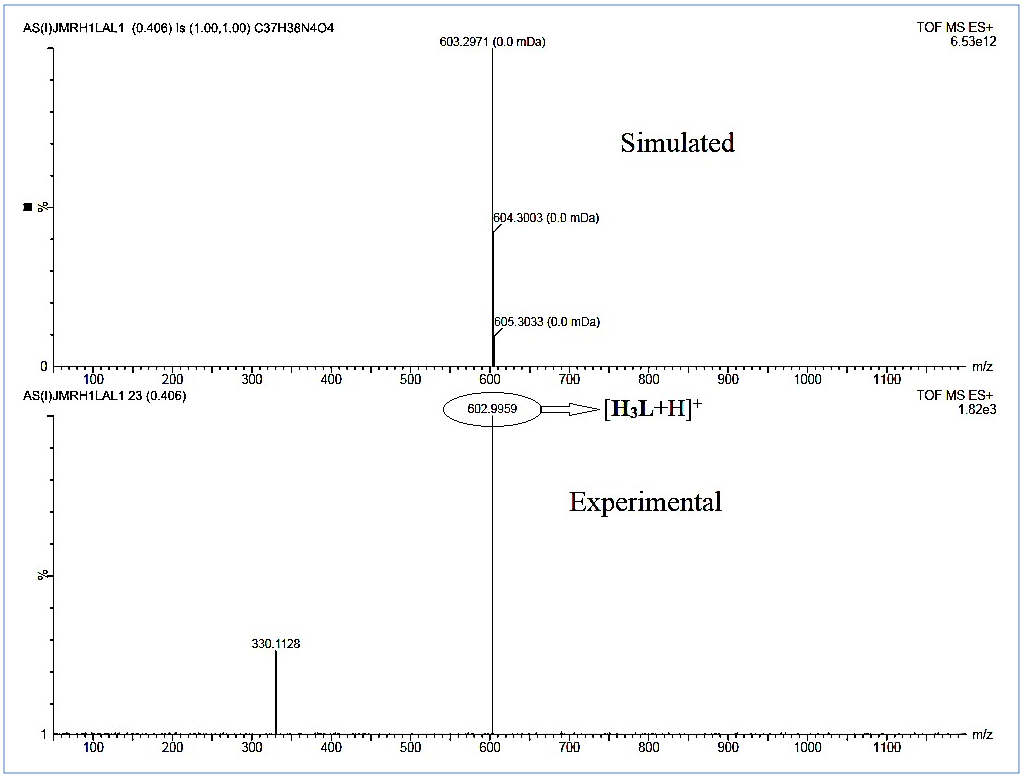


Fig. S1 ESI-MS$^+$ spectrum of [**H$_3$L**+H]$^+$.

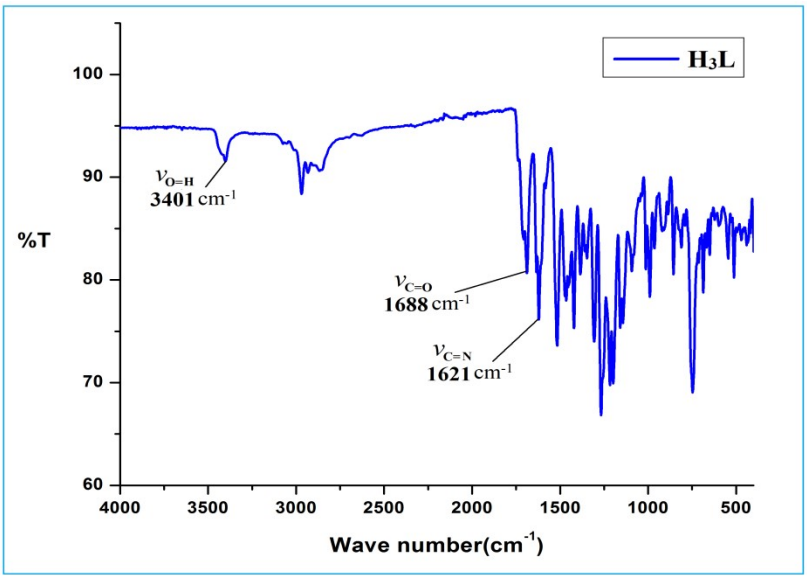


Fig. S2 FT-IR spectra of chemosensor **H$_3$L**.

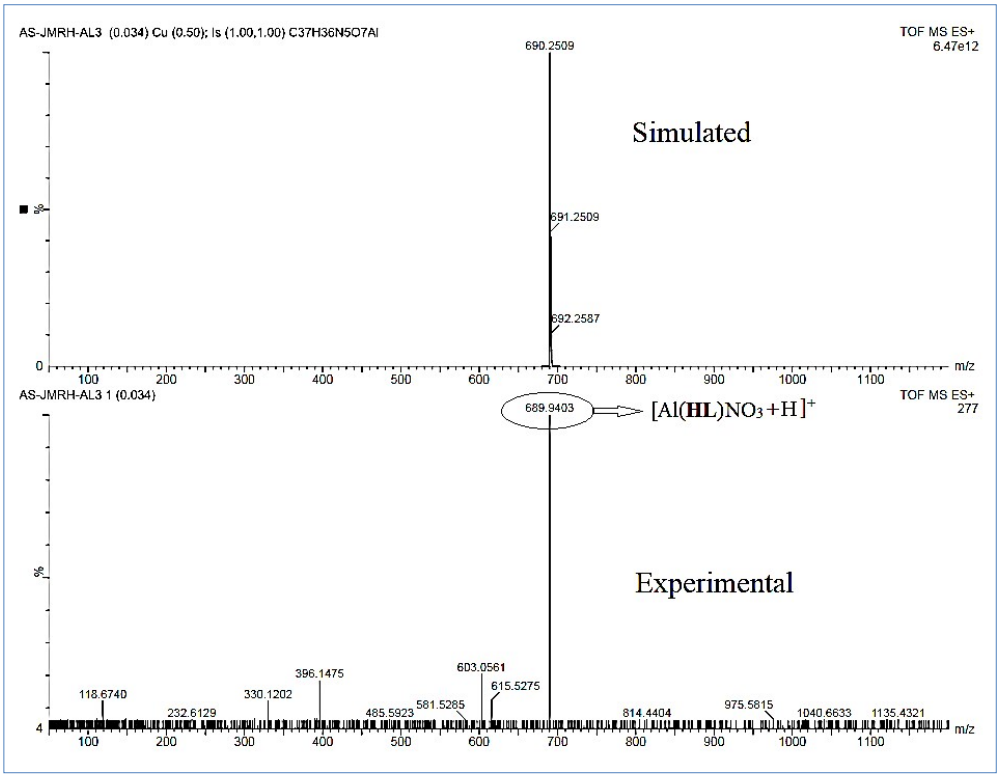


Fig. S3 ESI-MS$^+$ spectrum of complex **1**, {[Al(**HL**)NO_3+H]$^+$}.

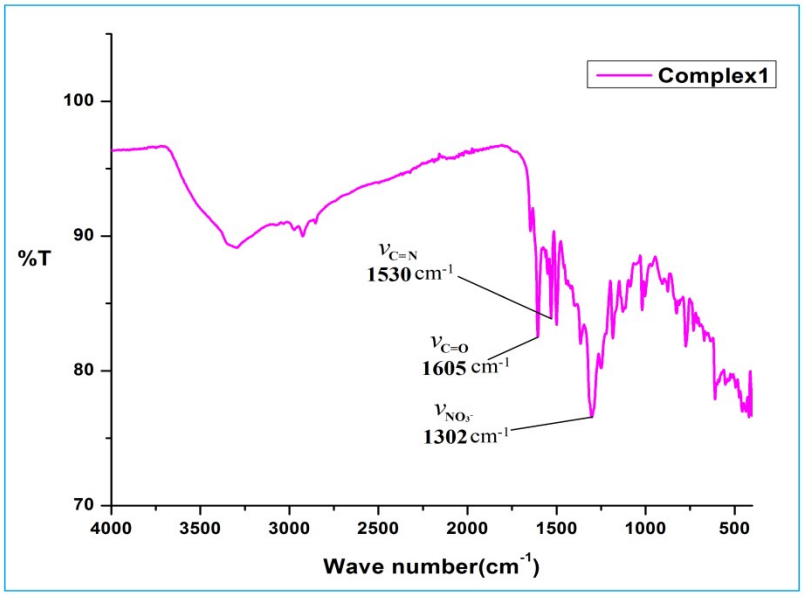


Fig. S4 FT-IR spectra of complex **1**.

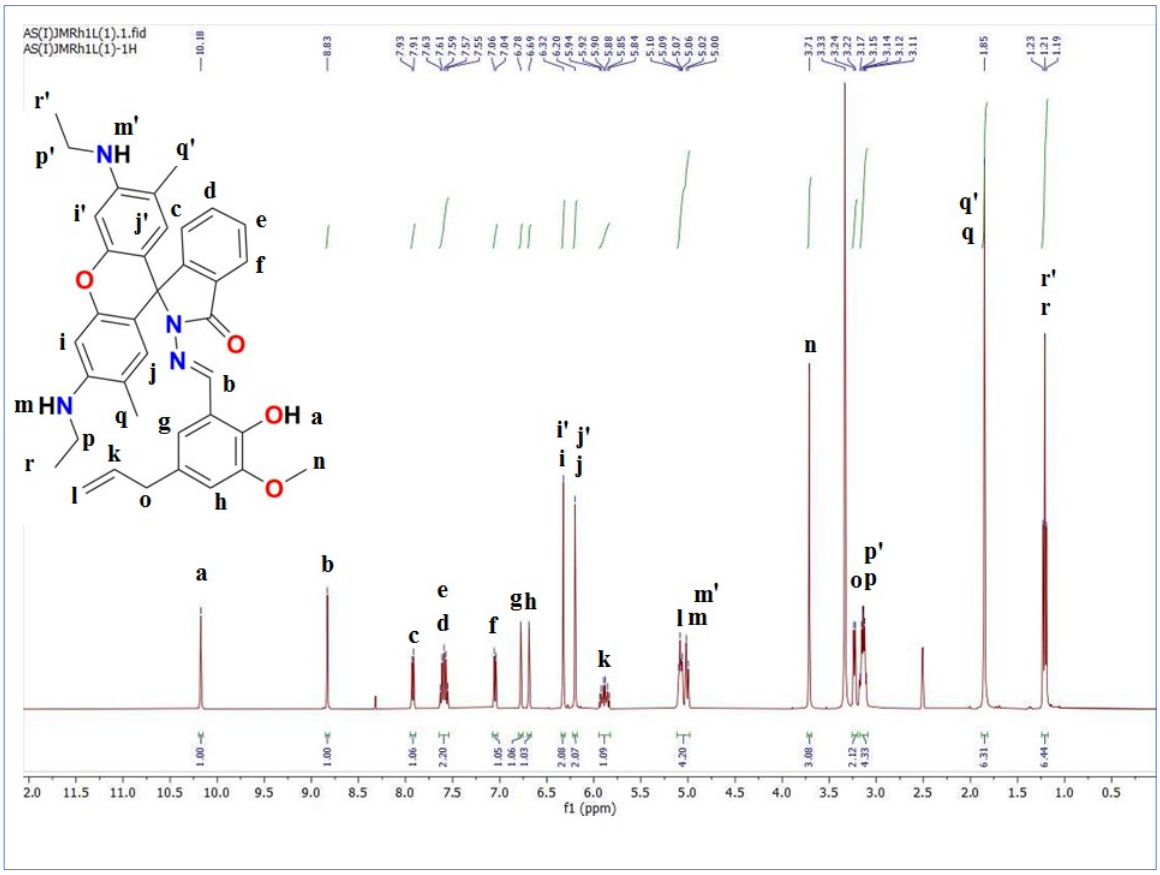


Fig. S5 ^{1}H NMR spectra of $\mathbf{H_3L}$ in DMSO-d_6 solvent.

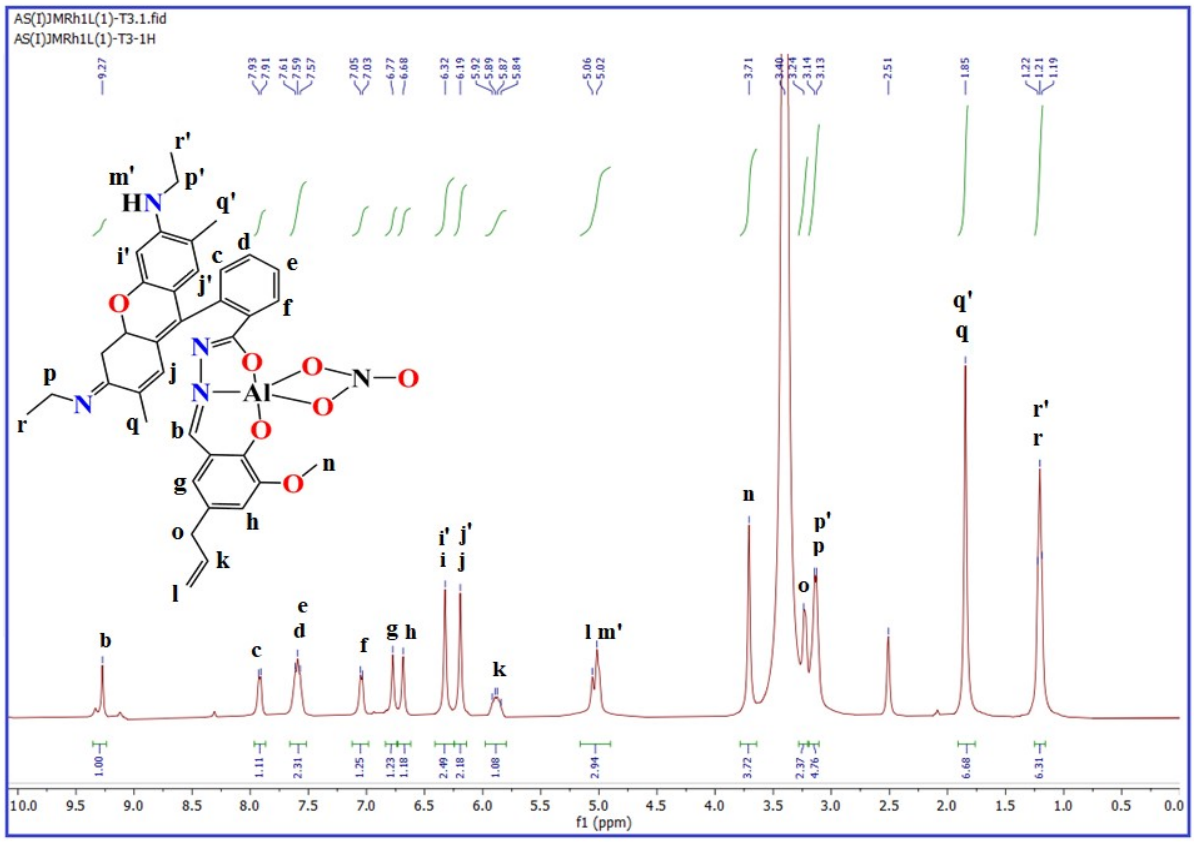


Fig. S6 ^{1}H NMR spectra of complex **1** in DMSO-d_6 solvent.

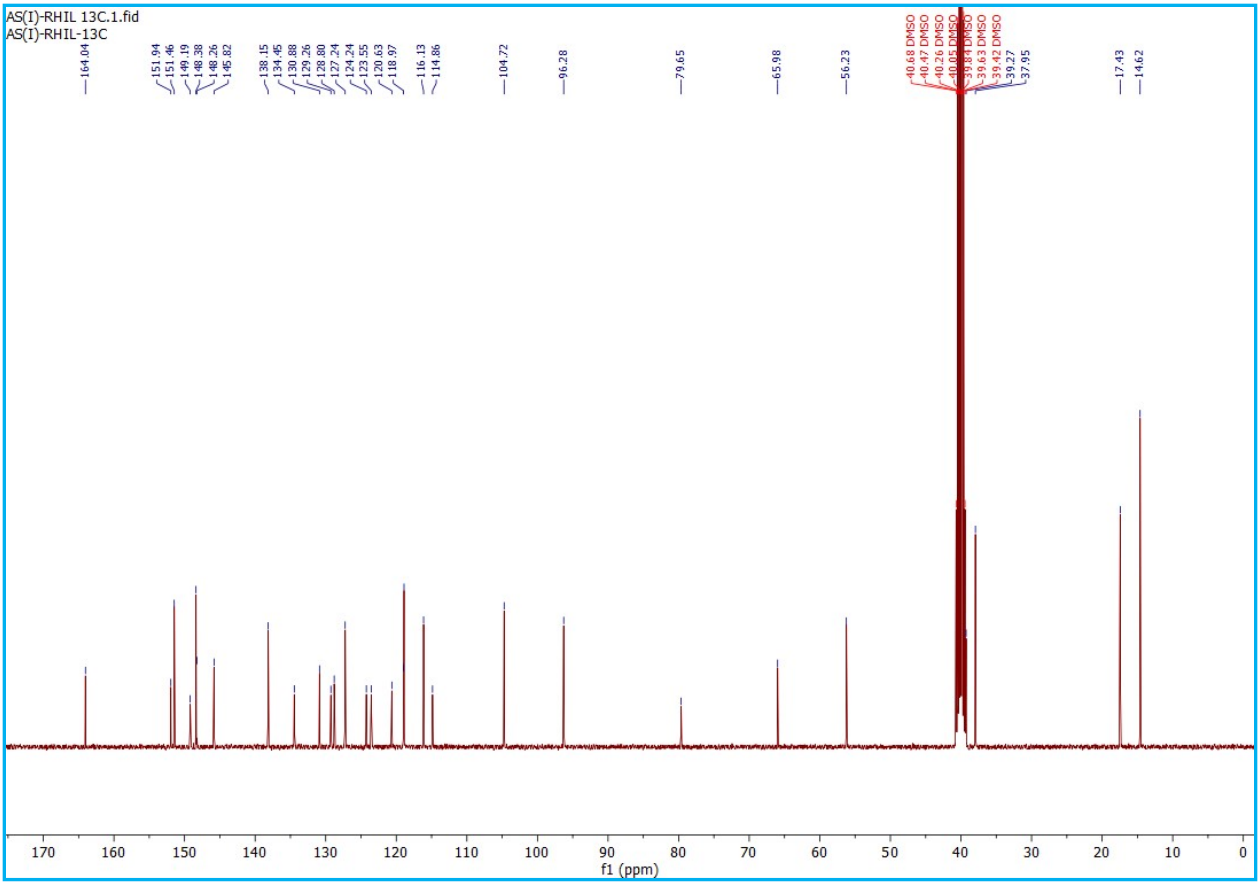


Fig. S7 ^{13}C NMR spectra of chemosensor **H_3L** in DMSO-d_6 solvent.

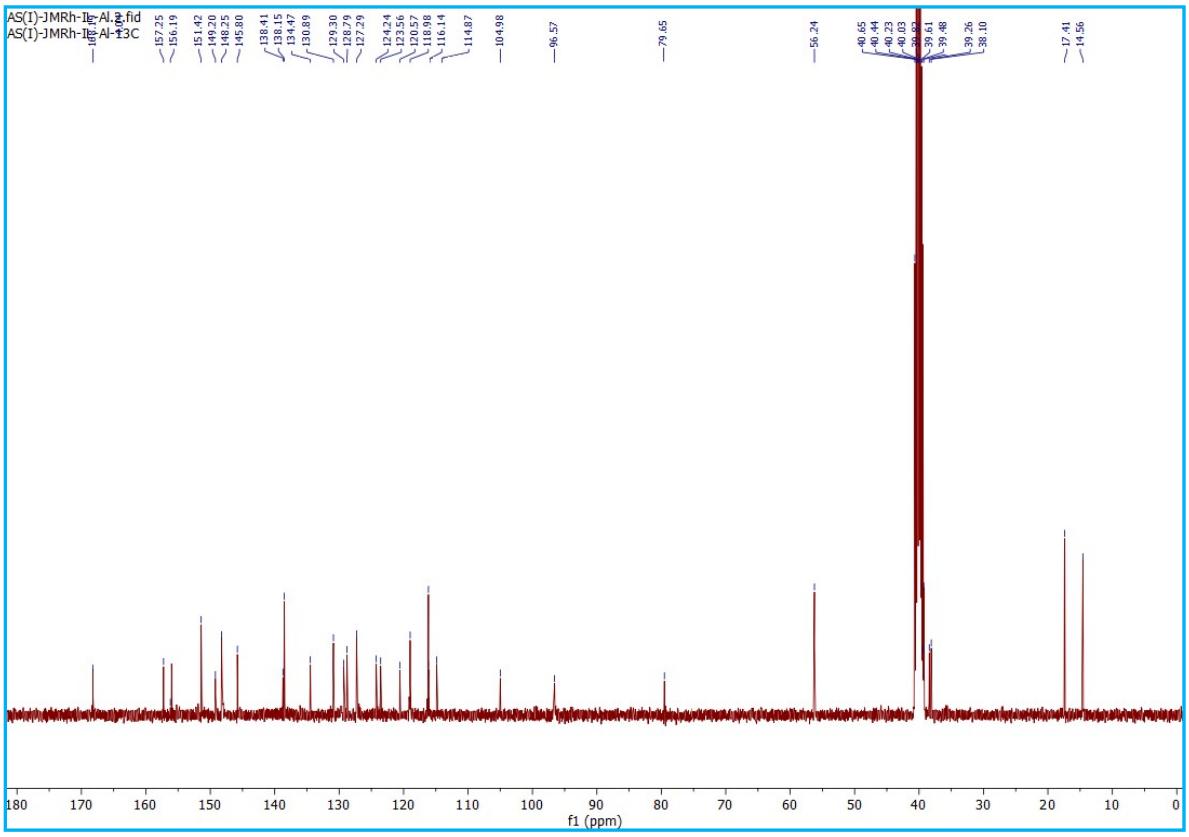


Fig. S8 ^{13}C NMR spectra of complex **1** in DMSO-d_6 solvent.

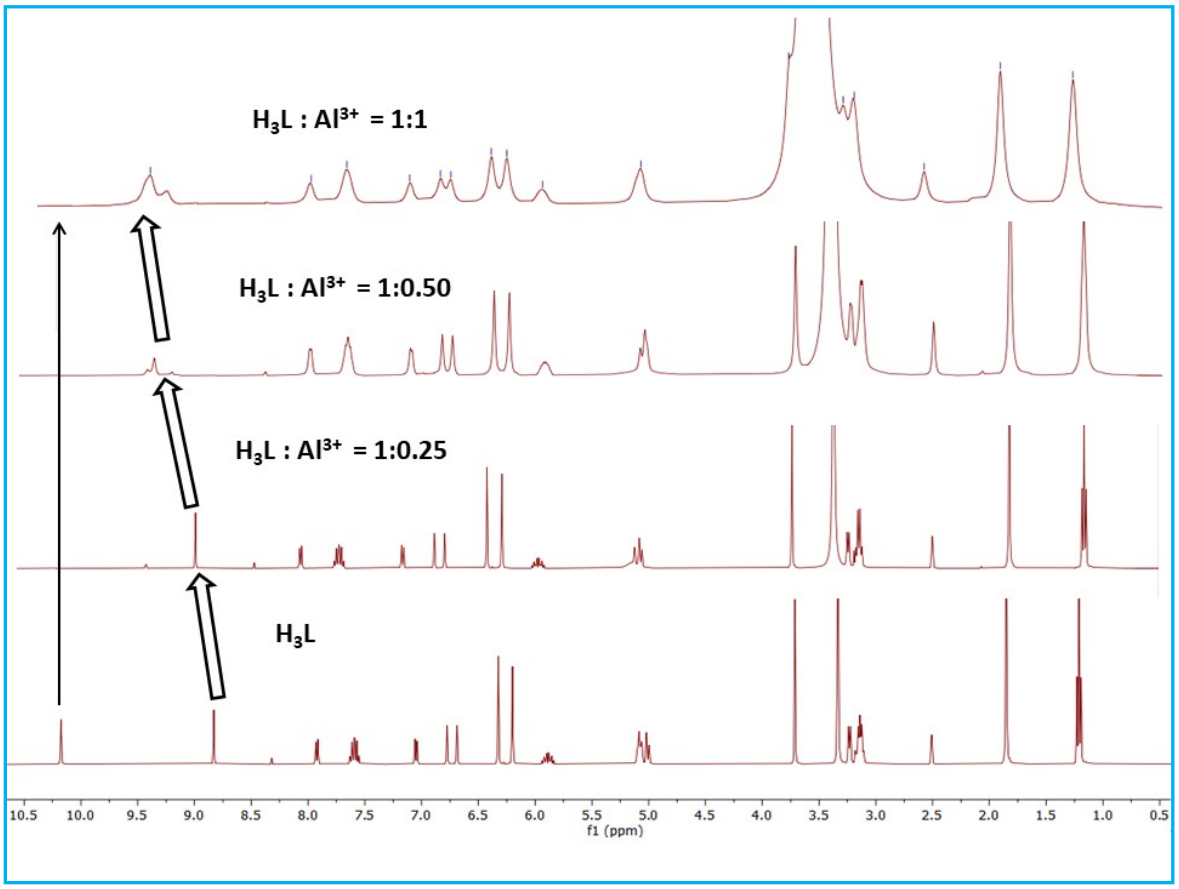


Fig. S9 ^{1}H NMR titration of the free ligand (**H_3L**) and with the addition of 0.25, 0.50 and 1 equivalent of Al^{3+} in DMSO-d_6 solvent.

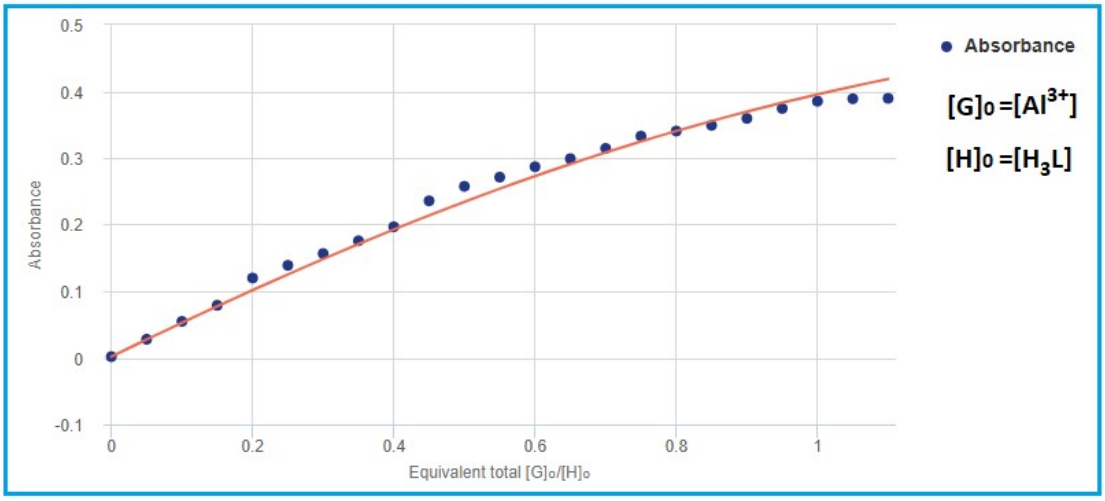


Fig. S10 Binding constant calculation for **H_3L** with Al^{3+} in HEPES buffer at pH 7.4 (MeOH:H_2O, 9:1, (v/v)). [http://supramolecular.org]. Binding constant = $2.01 \times 10^5\ M^{-1}$.

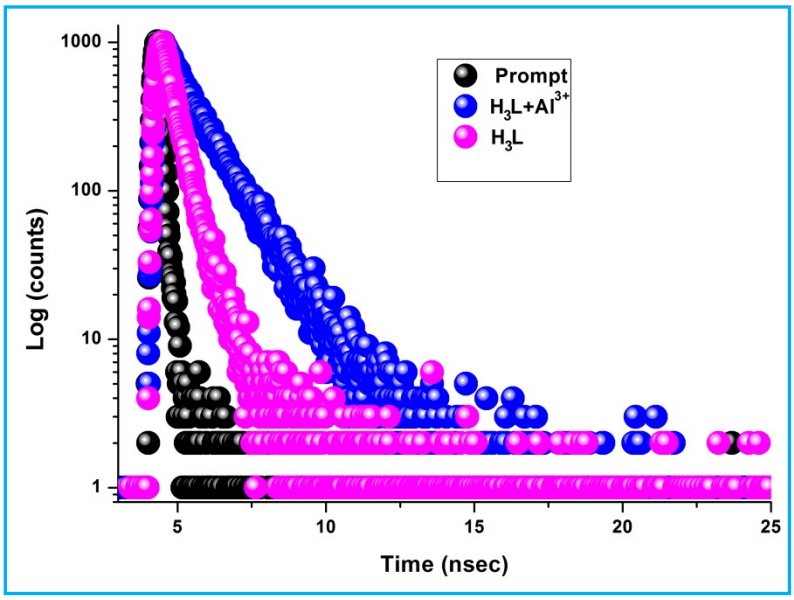


Fig. S11 Time-resolved fluorescence decay curves (logarithm of normalized intensity vs time in nS) of **H_3L** in the absence ( ) and presence ( ) of Al^{3+} ion, ( ) indicates decay curve for the scattered.

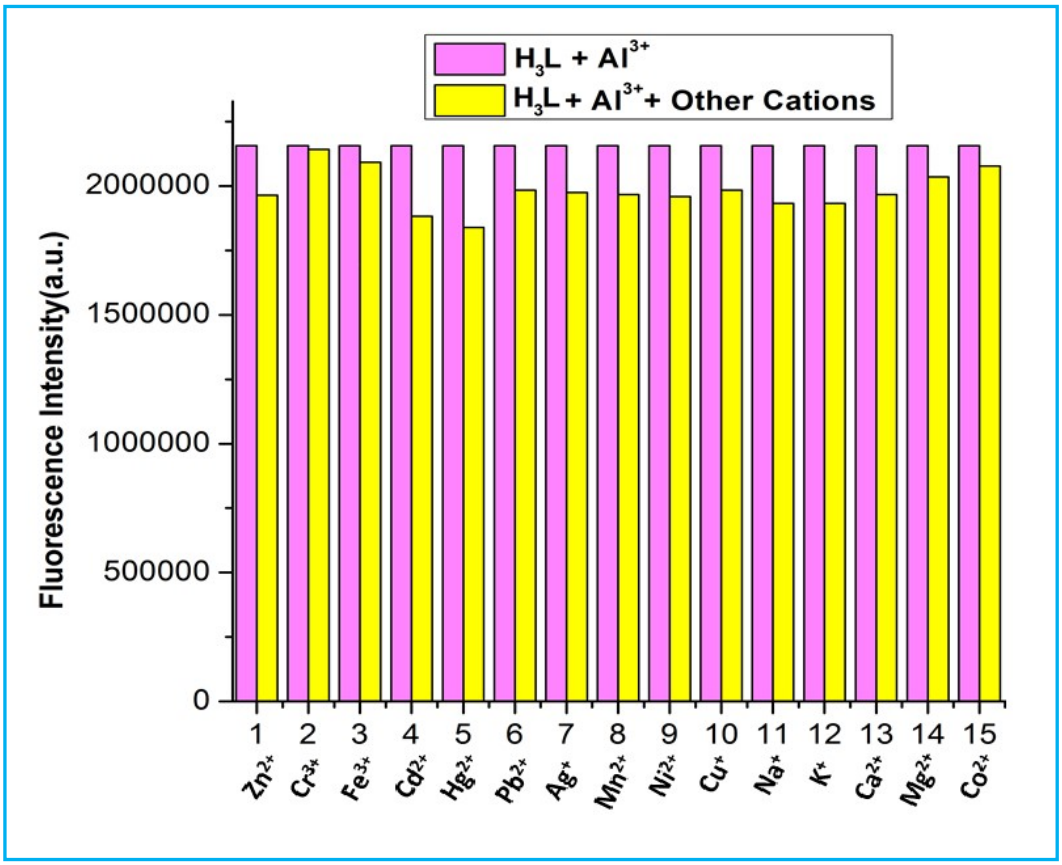


Fig. S12 Relative fluorescence intensity diagram of [**H_3L**–Al^{3+}] with different cations upon λ_{ex}= 500 nm in HEPES buffer at pH 7.4 (MeOH:H_2O, 9:1, (v/v)) where **H_3L** (20 μM) + Al^{3+} (20 μM) + M^{n+} (100 μM) and M^{n+}= (1-Zn^{2+}, 2-Cr^{3+}, 3-Fe^{3+}, 4-Cd^{2+}, 5-Hg^{2+}, 6-Pb^{2+}, 7-Ag^{+}, 8-Mn^{2+}, 9-Ni^{2+}, 10-Cu^{2+}, 11-Na^{+}, 12-K^{+}, 13-Ca^{2+}, 14-Mg^{2+} and 15-Co^{2+}, respectively).

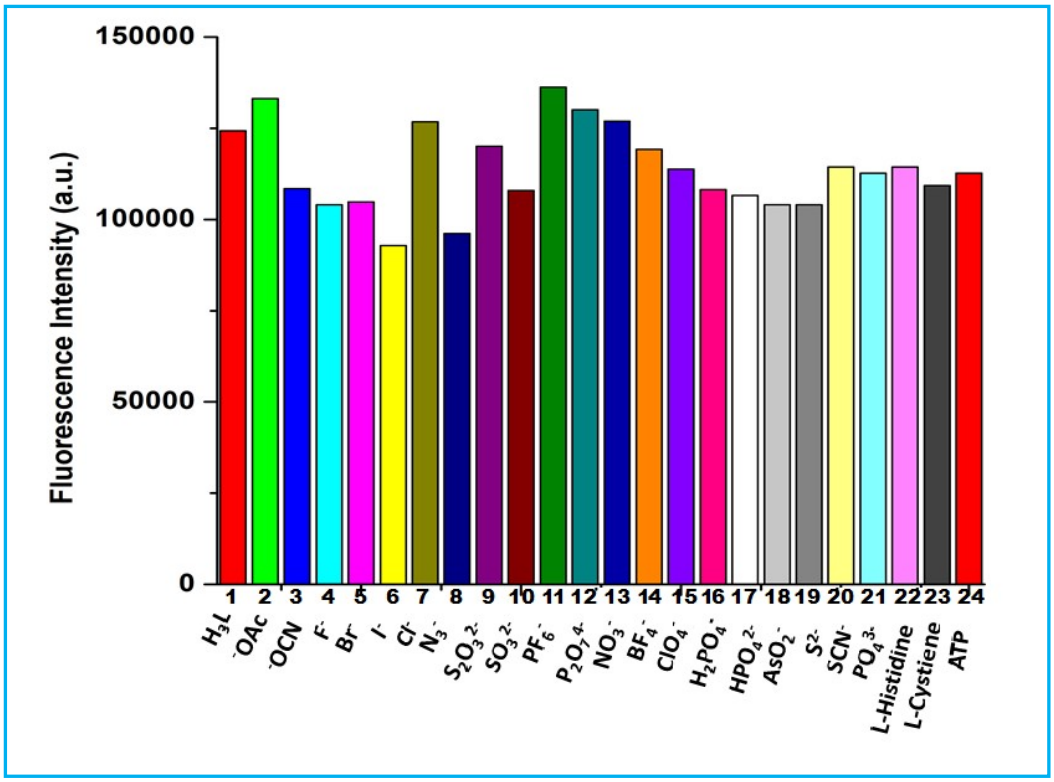


Fig. S13 Relative fluorescence intensity diagram of **H_3L** with of different anions upon λ_{ex}= 500 nm in HEPES buffer at pH 7.4 (MeOH:H_2O, 9:1, (v/v)). 1=only **H_3L** (20 μM); 2-24= **H_3L** (20 μM) + M^{n-}(100 μM), where M^{n-}= 2-AcO^-, 3-OCN^-, 4-F^-, 5-Br^-, 6-I^-, 7-Cl^-, 8-N_3^-, 9-$S_2O_3^{2-}$, 10-SO_3^{2-}, 11-PF_6^-, 12-$P_2O_7^{2-}$, 13-NO_3^-, 14-BF_4^-, 15-ClO_4^-, 16-$H_2PO_4^-$, 17-HPO_4^{2-}, 18-AsO_2^-, 19-S^{2-}, 20-SCN^-, 21-PO_4^{3-}, 22-L-Histidine, 23-L-Cystiene and 24-ATP, respectively.

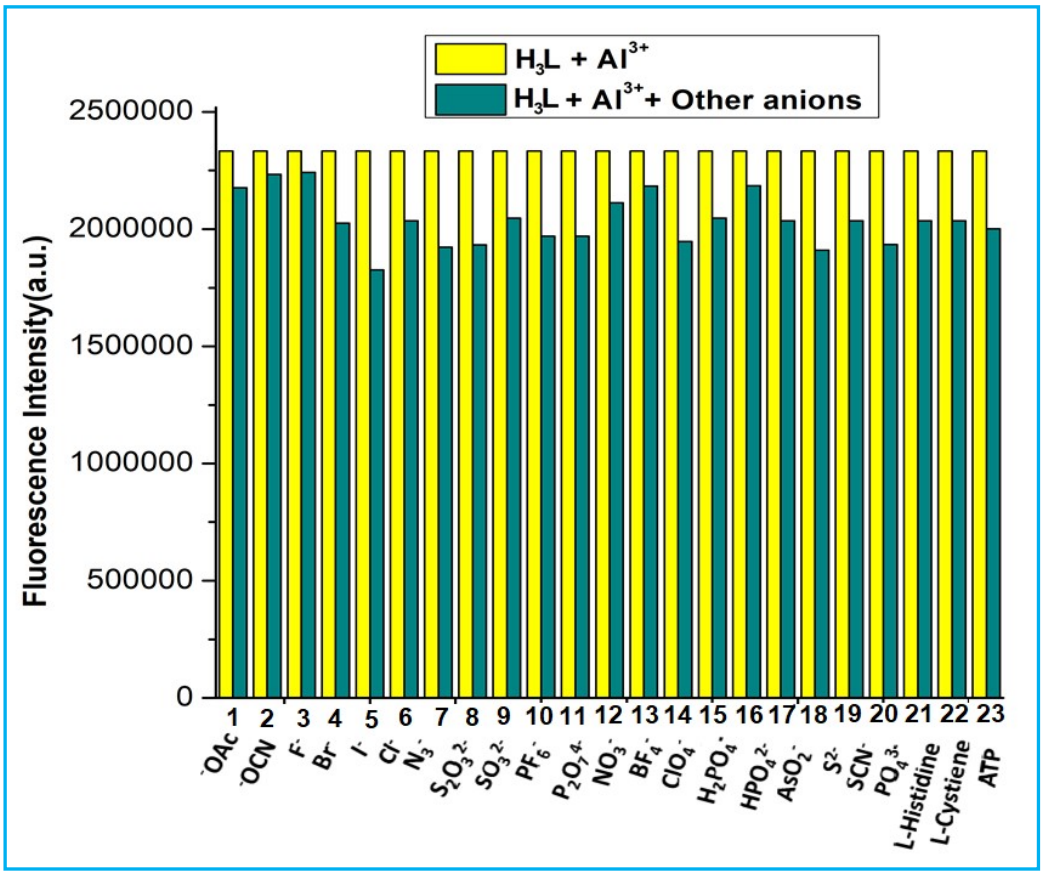


Fig. S14 Relative fluorescence intensity diagram of [**H_3L**–Al^{3+}] with different anions upon λ_{ex}= 500 nm in HEPES buffer at pH 7.4 (MeOH:H_2O, 9:1, (v/v)) where **H_3L** (20 μM) + Al^{3+} (20 μM) + M^{n-}(100 μM) and M^{n-}= 1-AcO^-, 2-OCN^-, 3-F^-, 4-Br^-, 5-I^-, 6-Cl^-, 7-N_3^-, 8-$S_2O_3^{2-}$, 9-SO_3^{2-}, 10-PF_6^-, 11-$P_2O_7^{2-}$, 12-NO_3^-, 13-BF_4^-, 14-ClO_4^-, 15-$H_2PO_4^-$, 16-HPO_4^{2-}, 17-AsO_2^-, 18-S^{2-}, 19-SCN^-, 20-PO_4^{3-}, 21-L-Histidine, 22-L-Cystiene and 23-ATP, respectively.

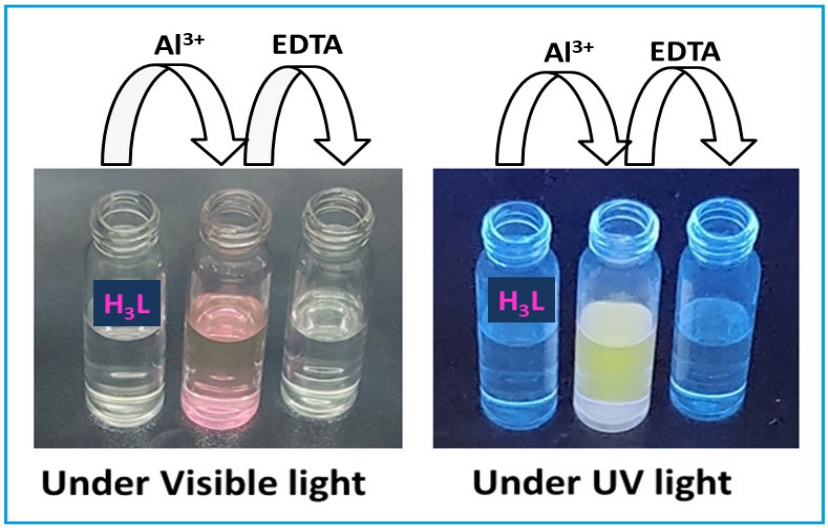


Fig. S15 Colour changes of chemosensor (**H_3L**) (20μM) under UV and Visible light in HEPES buffer at pH 7.4 (MeOH:H_2O, 9:1, (v/v)).

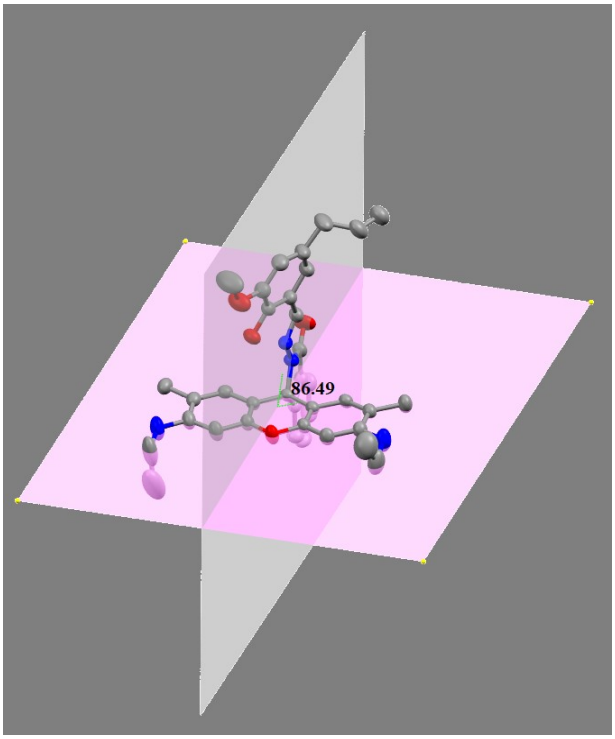


Fig. S16 Selected angle between two planes of chemosensor **H_3L**.

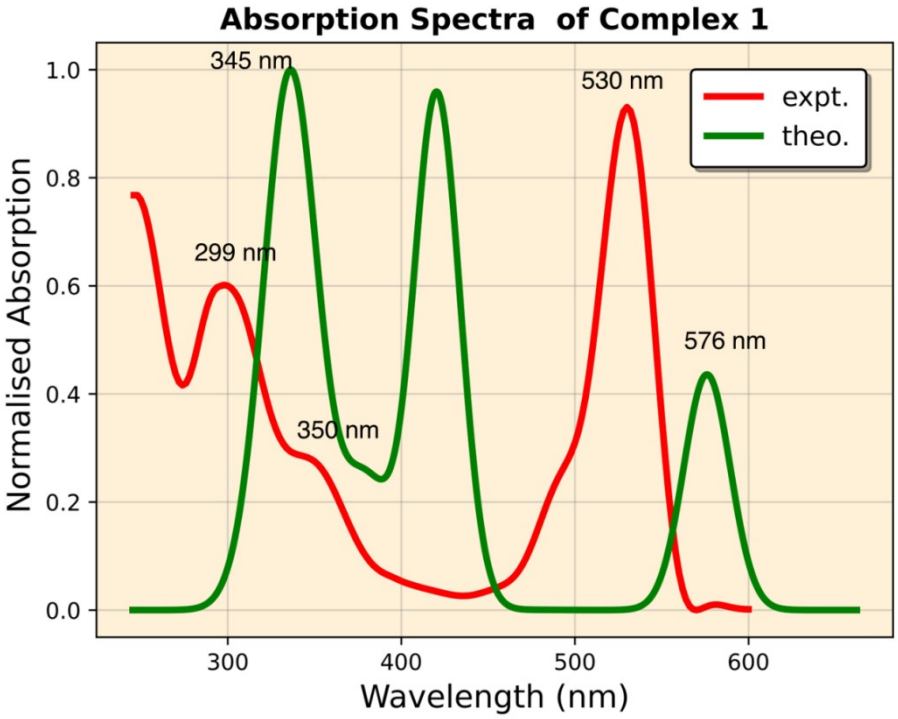
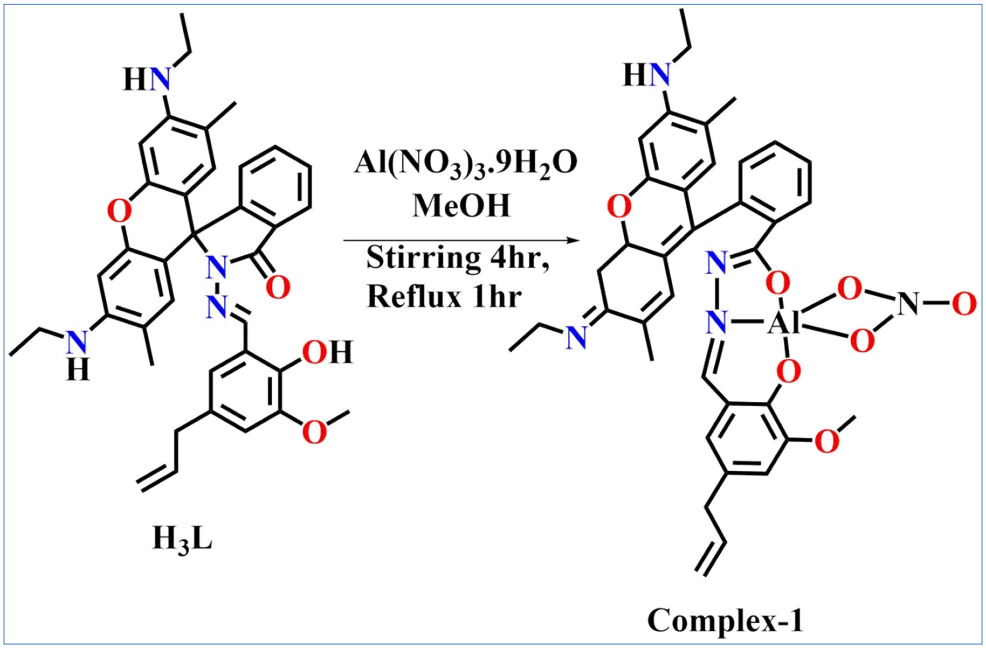
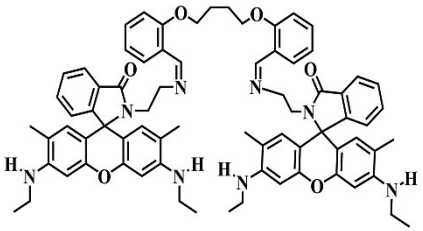
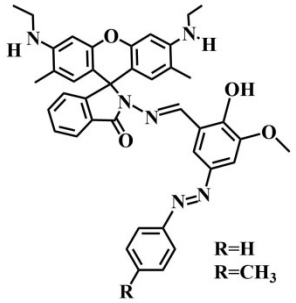
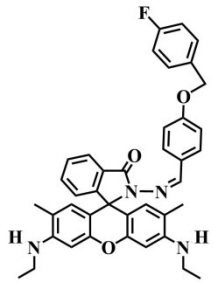


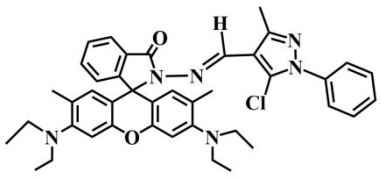
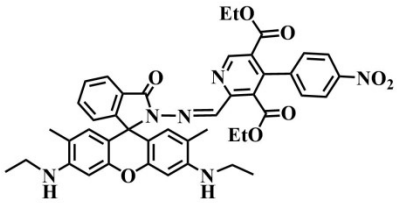
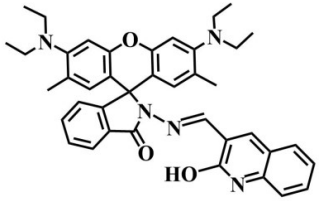
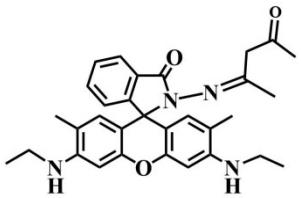
Fig. S17 Experimental and theoretical absorption spectra of complex **1**.

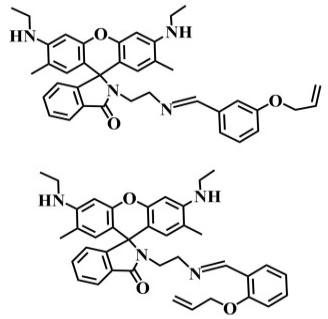
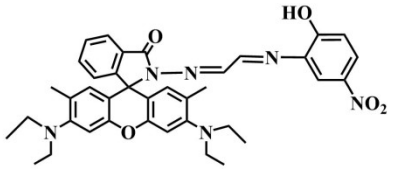
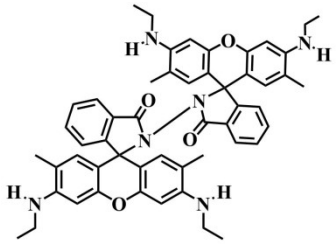
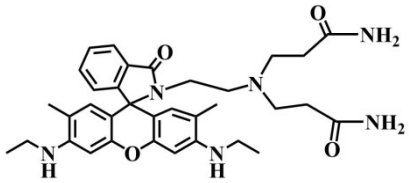


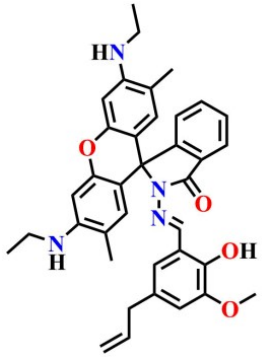
Scheme S1 Synthesis route of complex **1**.

Chart S1 Literature survey of rhodamine based metal ion sensors.

Sl. No.	**Probe**	Sensing metal	Solvent used	Excitation/ Emission (nm)	Limit of detection (LOD) (M)	Binding constant (M^{-1})	Fluorescent intensity enhancement	Crystal structure	Biological study	**Refs.**
1.		Fe^{3+} Al^{3+} Cr^{3+}	H_2O/CH_3CN (7 : 3, v/v, pH 7.2)	502/558	2.57× 10^{-6} 0.78 × 10^{-6} 0.47 × 10^{-6}	K_d= 1.94×10^{-5} 3.15×10^{-5} 2.26×10^{-5}	669 653 667	No	None	**31a**
2.		Al^{3+} Cr^{3+} Fe^{3+}	Britton–Robinson buffer solution (H_2O/MeOH 1 : 9 v/v; pH 7.4)	525/555	For R=H 2.86×10^{-8} 2.67×10^{-8} 5.62×10^{-6} For R=CH_3 2.78×10^{-8} 2.61×10^{-8} 6.14×10^{-6}	For R=H (M^{-2}) 5.14 ×10^5 4.91× 10^5 3.37 × 10^4 For R=CH_3 5.03 × 10^5 4.86 × 10^5 3.95 × 10^4	400 400 100	Yes	Cell imaging	**31b**
3.		Al^{3+} Ga^{3+} In^{3+} Tl^{3+}	10 mM HEPES buffer in (1:9, v/v) H_2O:EtOH (pH =7.4)	530/555 530/553 530/553 530/558	2.66 ×10^{-8} 10.40 ×10^{-8} 8.19×10^{-8} 3.10 ×10^{-8}	5.01 ×10^4 4.79 ×10^4 4.57 ×10^4 5.75 ×10^4	96 26 32 80	No	None	**31c**

4.		Al^{3+} Fe^{3+} Cr^{3+}	HEPES buffer at pH 7.4 in H_2O/ MeOH (9:1, v/v)	510/575	1.74×10^{-5} 1.86×10^{-5} 3.45×10^{-5}	1.44×10^{6} 1.52×10^{6} 4.01×10^{7}	~10 ~8 ~4	Yes	Cell imaging	**31d**
5.		Cr^{3+}	10 mM, CH_3CN–PBS (9 : 1 v/v, pH = 7.4)	531/558	0.21×10^{-6}	1.56×10^{4}	~7	Yes	None	**31e**
6.		Al^{3+} Cr^{3+} HSO_4^-	H_2O-CH_3CN (1:9, v/v)	500/585 500/583 500/587	2.20×10^{-8} 2.12×10^{-8} 8.63×10^{-7}	1.79×10^{5} 1.79×10^{4}	341 292 136	No	Cell imaging	**31f**
7.		Cu^{2+}	1 mM PBS buffer in an CH_3CN /PBS (v/v, 1 :1%) at pH = 7.4	510/550	3.58×10^{-8}	0.2×10^{-5}	28	No	Cell imaging	**31g**

8.		Al^{3+}	10 mM HEPES buffer in H_2O/EtOH = 1:9 (v/v) (pH 7.4)	530/553	1.11×10^{-9} 1.05×10^{-9}	3.98×10^4 1.09×10^4	145 52	No	Cell imaging	**31h**
9.		Fe^{3+} Al^{3+} Cr^{3+} and Hg^{2+}	EtOH/H_2O (4/1, v/v HEPES, pH = 7.4)	559/582 559/582 559/582 and 555/578	10.20×10^{-9} 14.66×10^{-9} 58.78×10^{-9} and 73.33×10^{-9}	5.78×10^5 7.07×10^5 4.10×10^5 3.97×10^5	~15	No	Cell imaging	**31i**
10.		Al^{3+} Fe^{3+}	EtOH	530/560	0.76×10^{-9} 0.49×10^{-9}	---	>900	Yes	Cell imaging	**31j**
11.		Fe^{3+}	H_2O (pH 7.2, 10 mM HEPES buffer)	510/551	4.184×10^{-6}	$(1.16 \pm 0.04)\times10^4$	14	No	Cell imaging	**31k**

12.		Al^{3+}	**HEPES buffer (9:1, MeOH: H_2O, v/v, pH 7.4)**	**500/552**	**2.82×10^{-6}**	**2.01×10^{5}**	**138**	**Yes**	**Cell imaging**	**This wok**