Supporting Information

Rhodamine-azo based two fluorescent probes for recognition of trivalent metal ions: crystal structures elucidation and biological application

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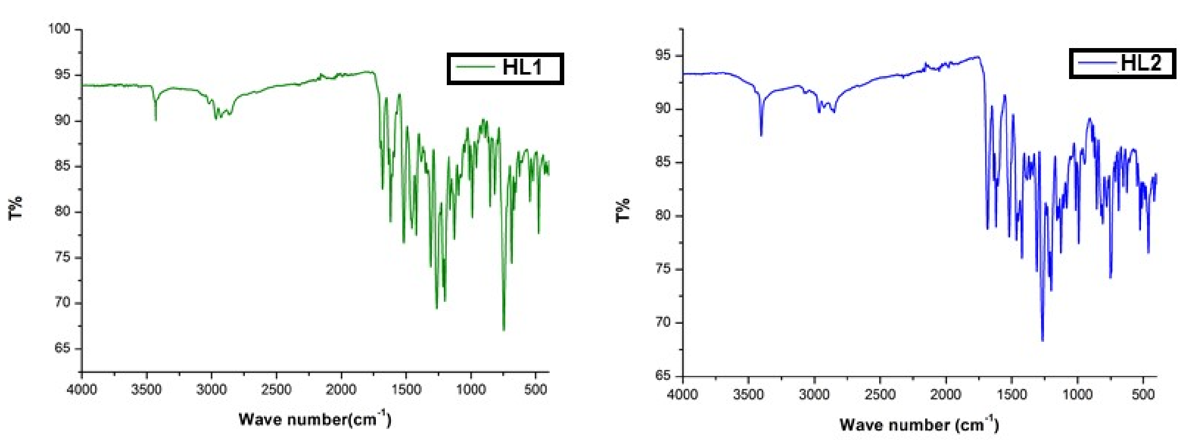

Fig. S1 FTIR spectra of chemosensor **HL1** and **HL2**.

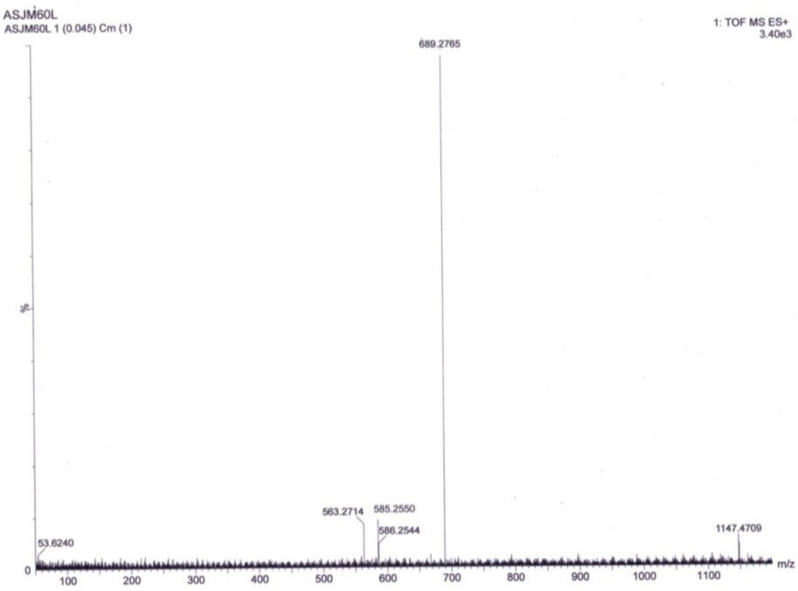

Fig. S2 ESI-mass spectrum of chemosensor **HL1**

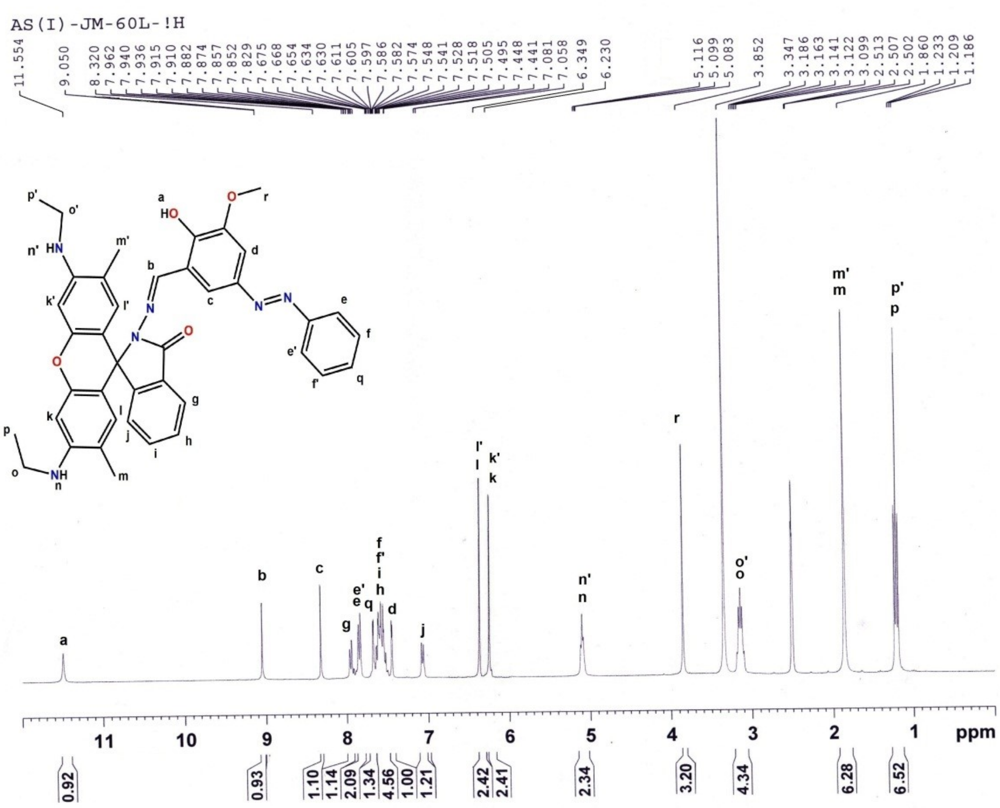

Fig. S3(a) ^{1}H-NMR spectrum of the chemosensor **HL1** in DMSO-d_6 recorded on a 300 MHz Bruker NMR spectrometer.

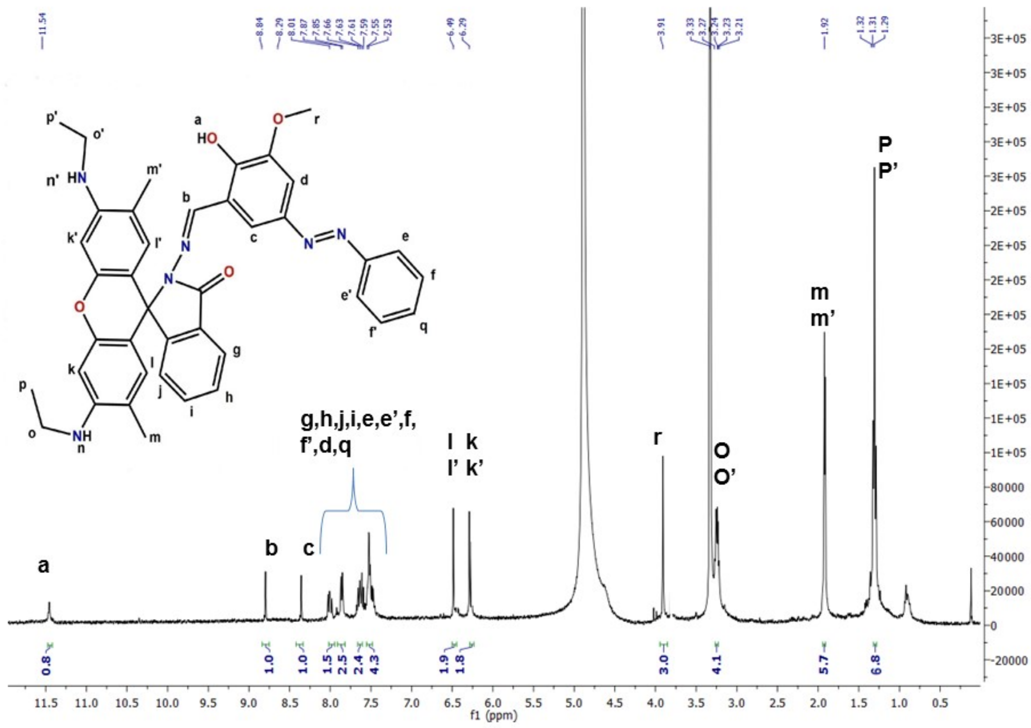

Fig. S3(b) [1]H-NMR spectrum of the chemosensor **HL1** in CD_3OD recorded on a 400 MHz Bruker NMR spectrometer.

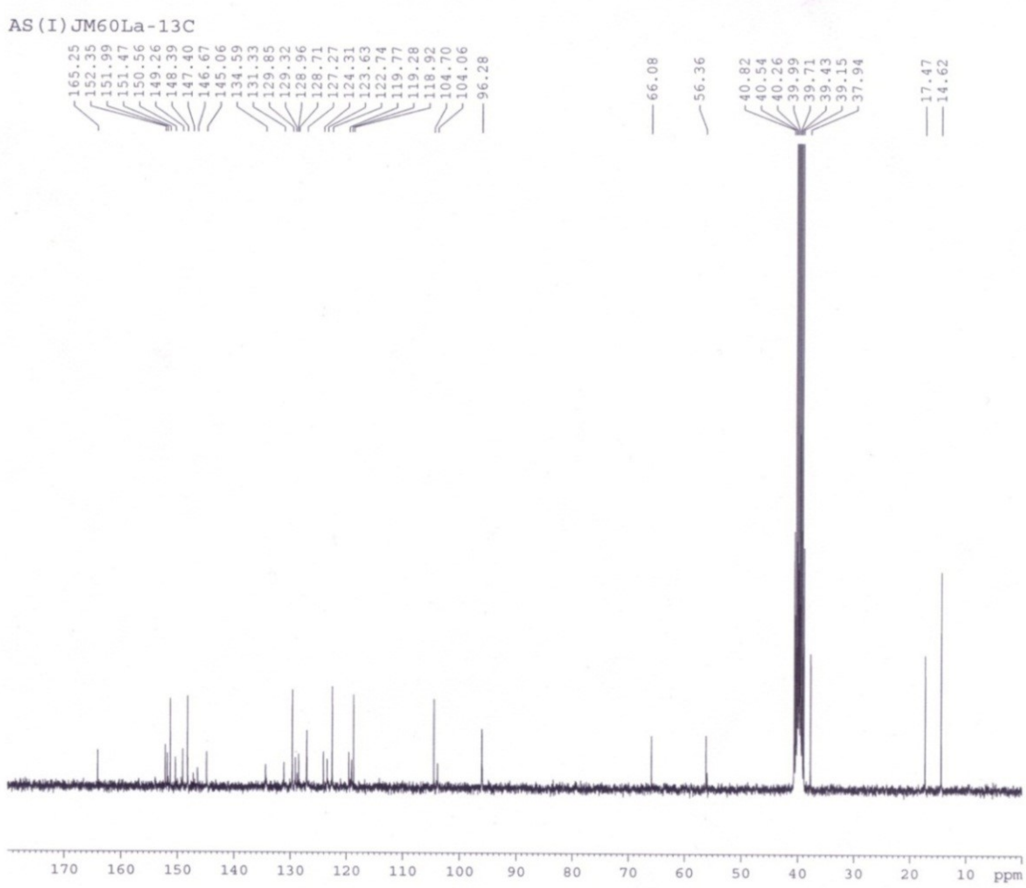

Fig. S4 [13]C NMR spectrum of **HL1** in DMSO-d_6.

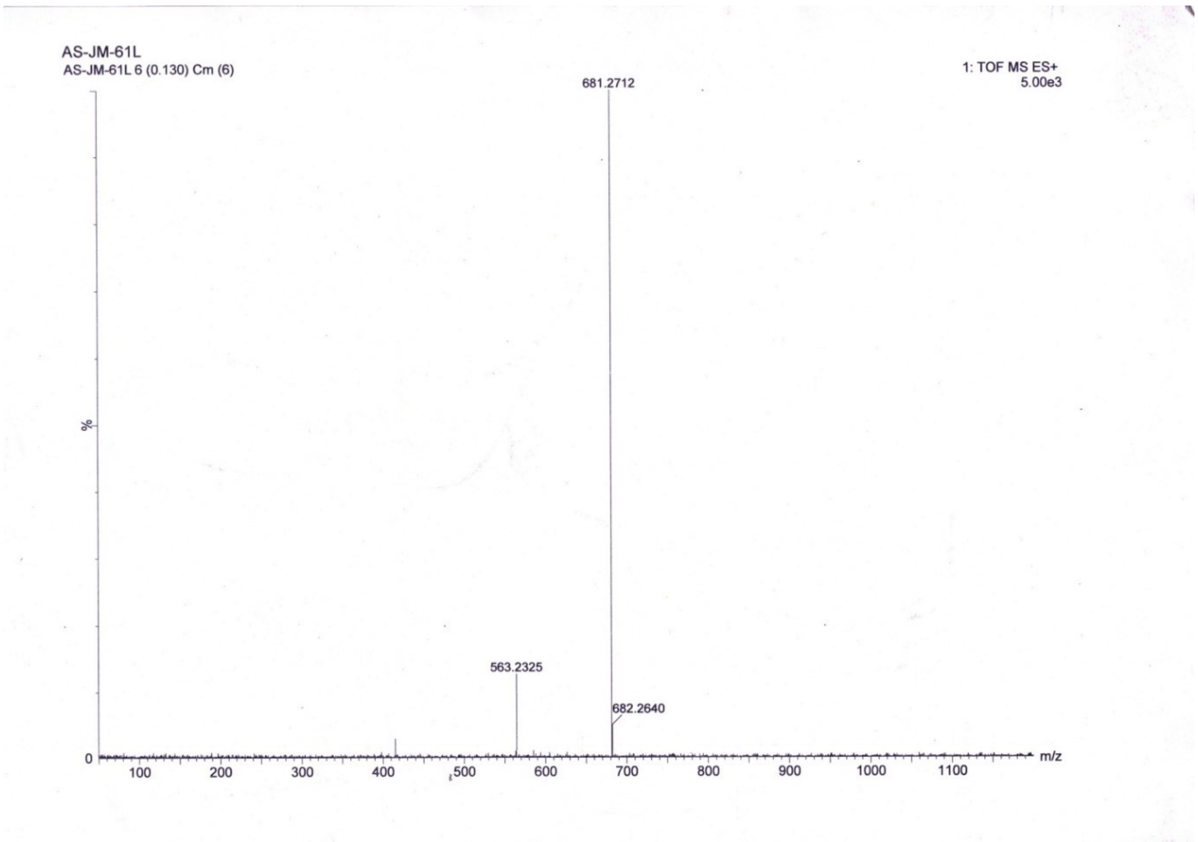

Fig. S5 ESI-mass spectrum of chemosensor **HL2**.

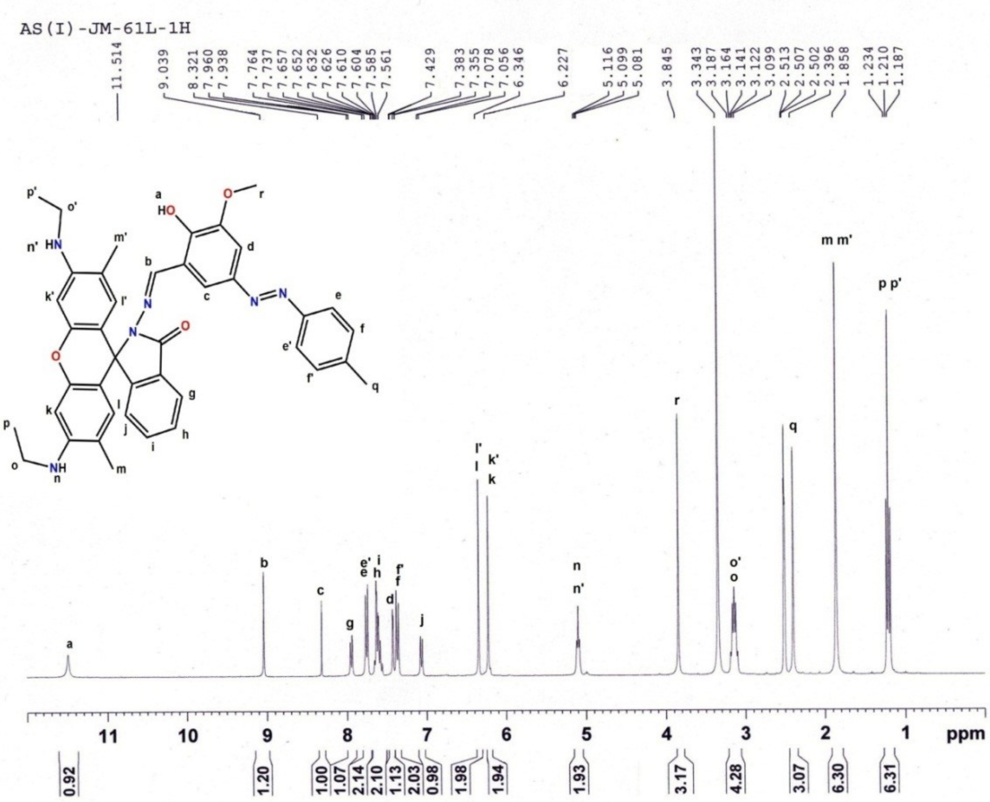

Fig. S6(a) ^{1}H-NMR spectrum of the chemosensor **HL2** in DMSO-d_6 recorded on a 300 MHz Bruker NMR spectrometer.

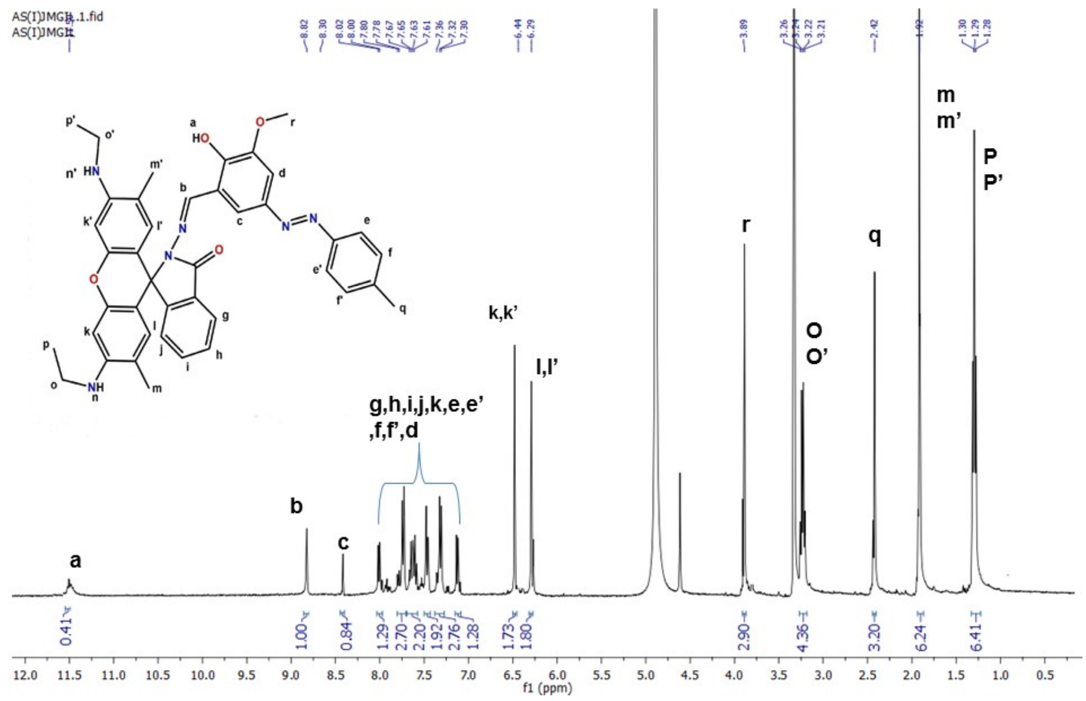

Fig. S6(b) ^{1}H-NMR spectrum of the chemosensor **HL2** in CD_3OD recorded on a 400 MHz Bruker NMR spectrometer.

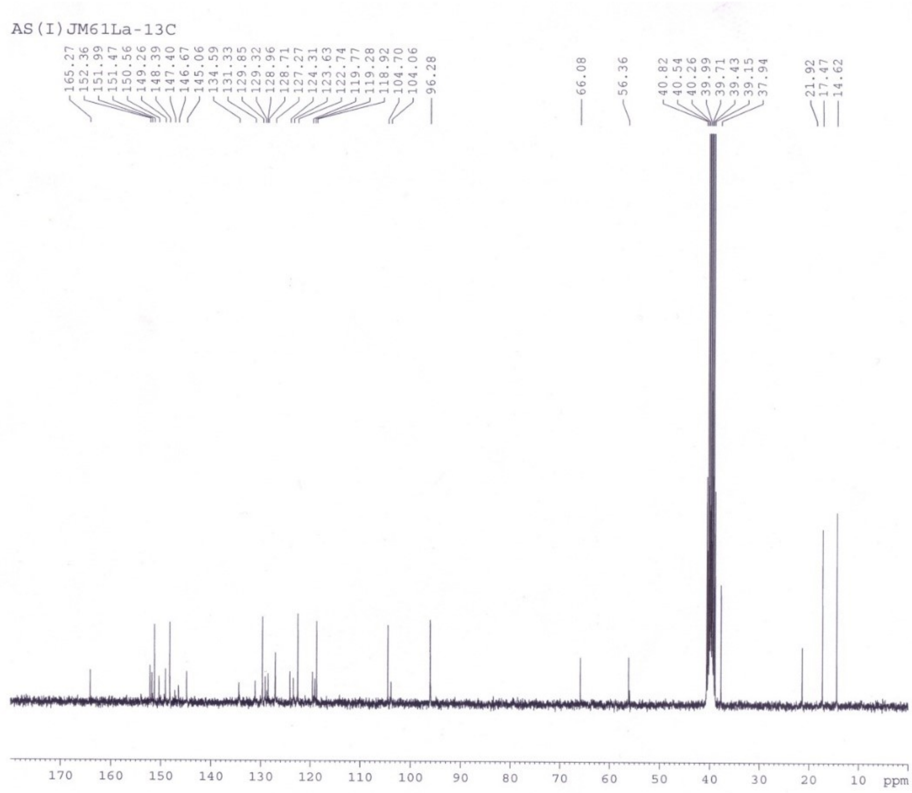

Fig. S7 ^{13}C NMR spectrum of **HL2** in DMSO-d_6.

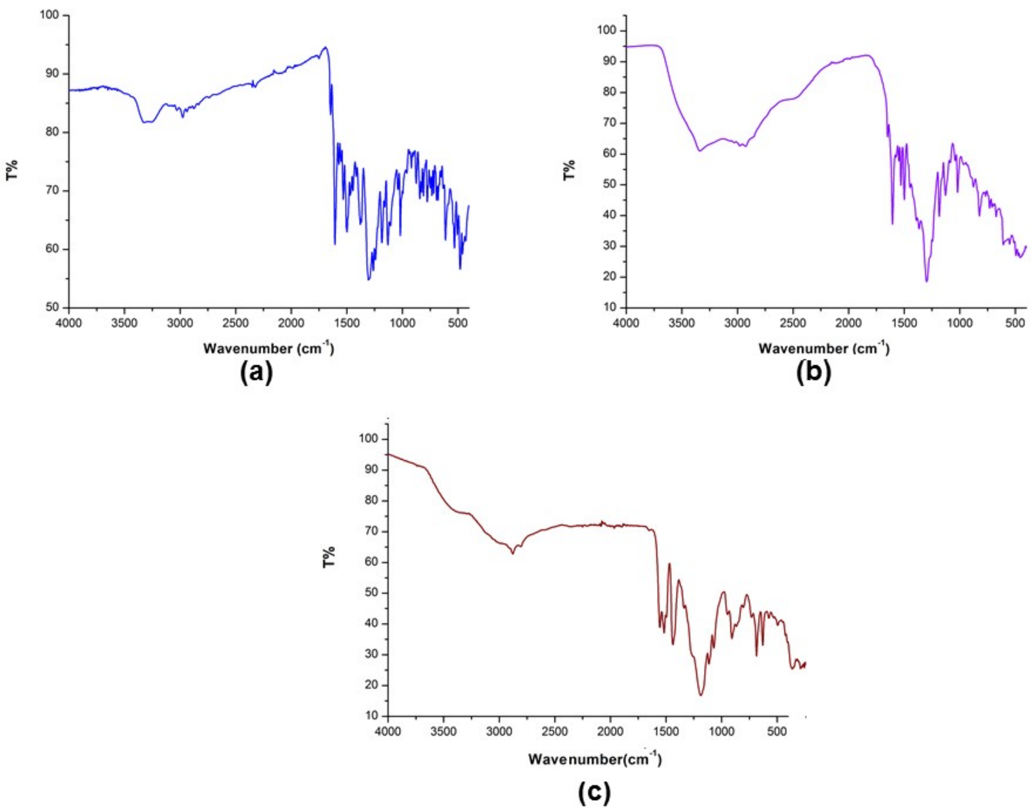

Fig. S8 FTIR spectra of (a) complex **1**, (b) complex **2** and (c) complex **3**.

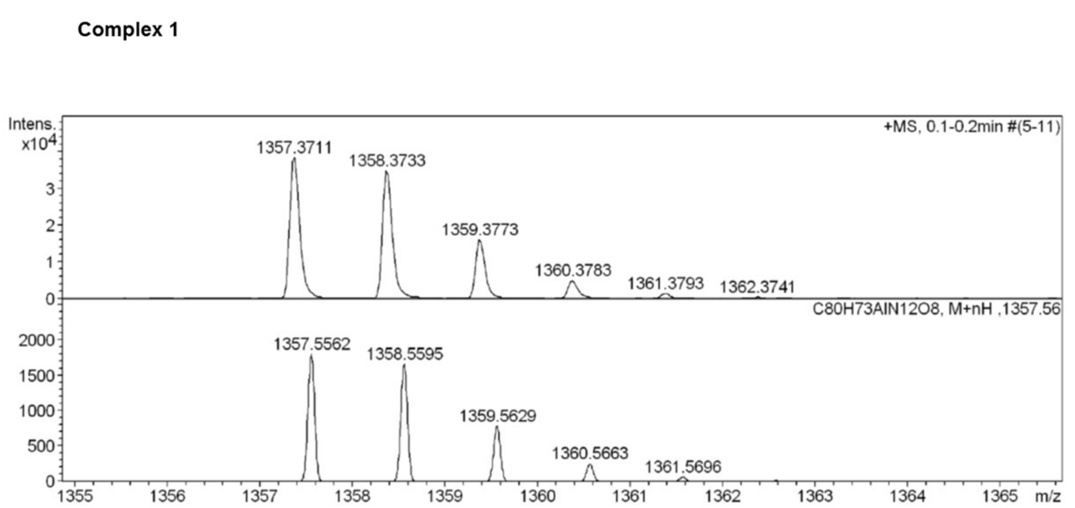

Fig. S9 (a) ESI-mass spectrum of $[Al(\mathbf{L1})_2]^+$ (complex **1**).

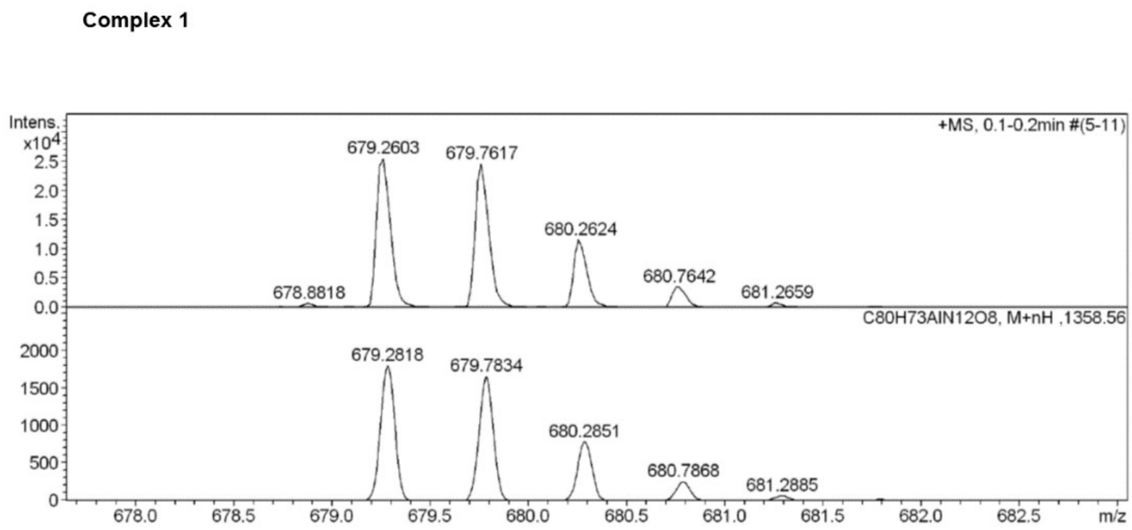

Fig. S9 (b) ESI-mass spectrum of $[Al(\mathbf{L1})_2 + H]^{2+}$ (complex **1**).

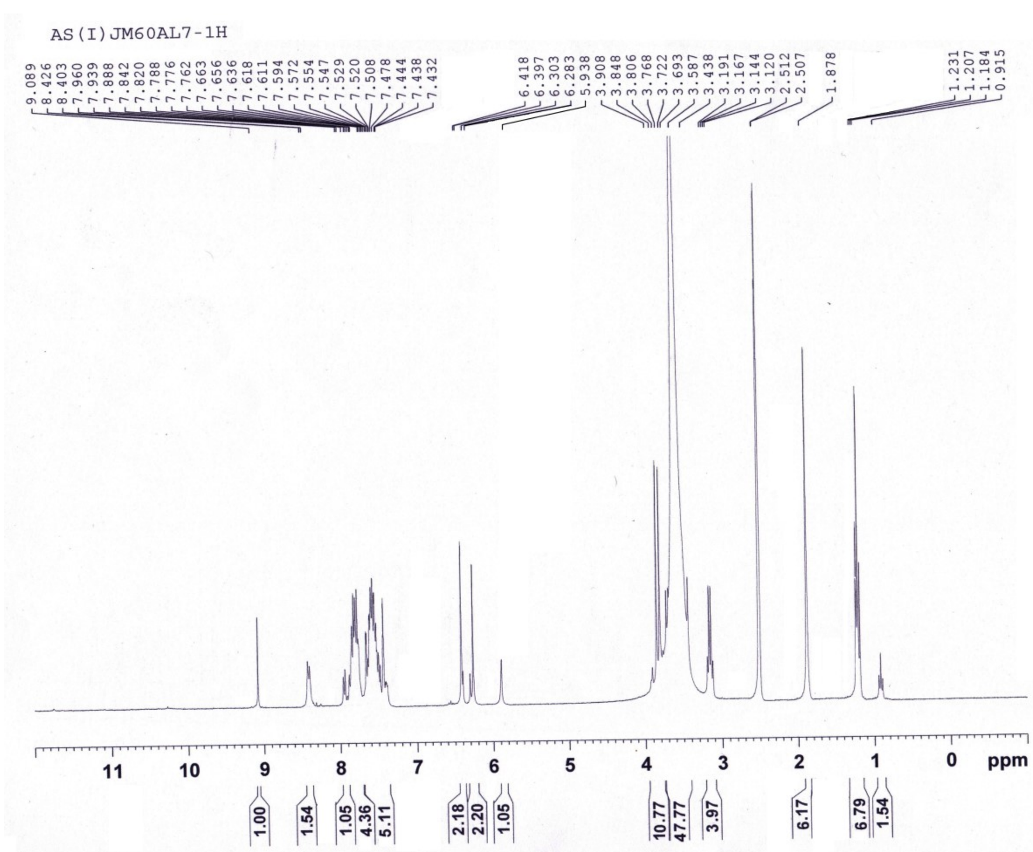

Fig. S10(a) ^{1}H-NMR spectrum of complex **1** in DMSO-d_6 recorded on a 300 MHz Bruker NMR spectrometer.

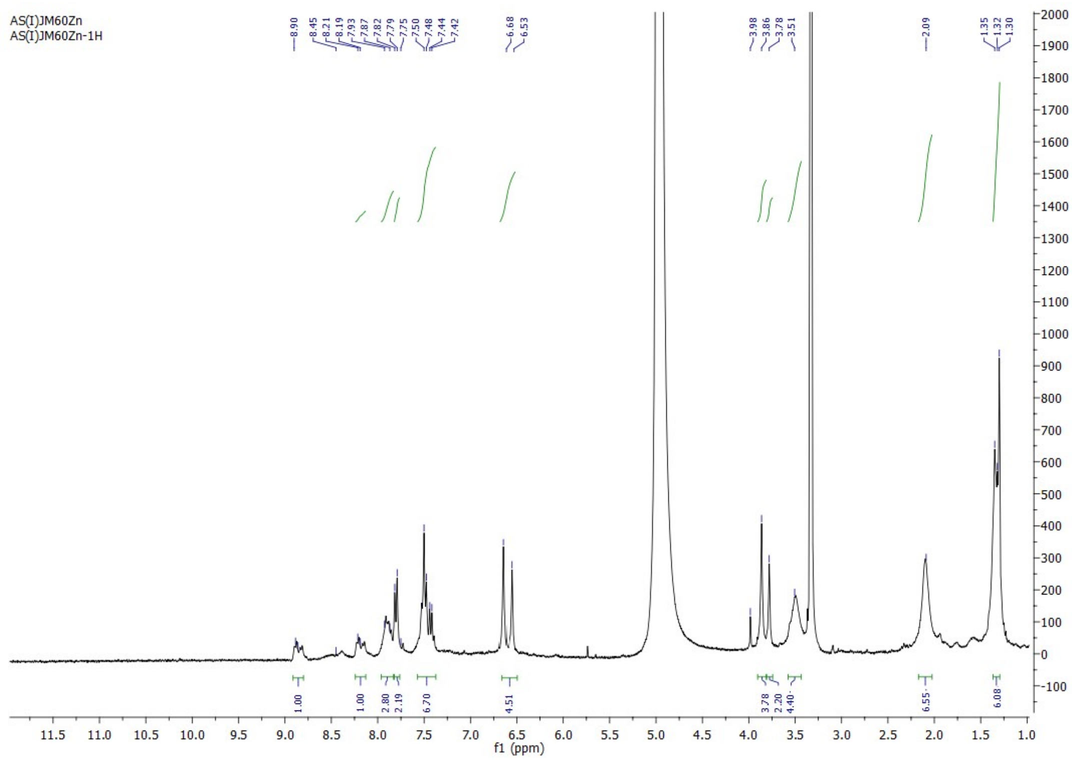

Fig. S10(b) ^{1}H-NMR spectrum of complex **1** in CD_3OD recorded on a 400 MHz Bruker NMR spectrometer.

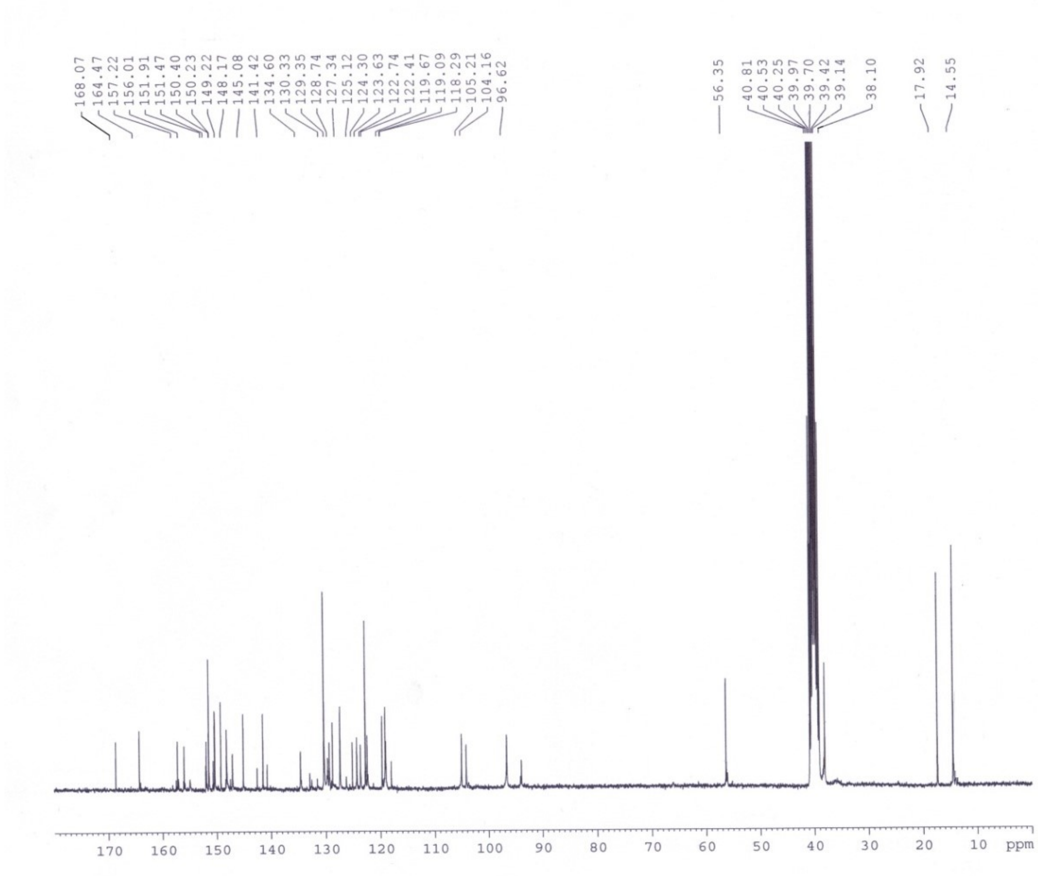

Fig. S11 ^{13}C NMR spectrum of complex **1** in DMSO-d_6

Complex 2

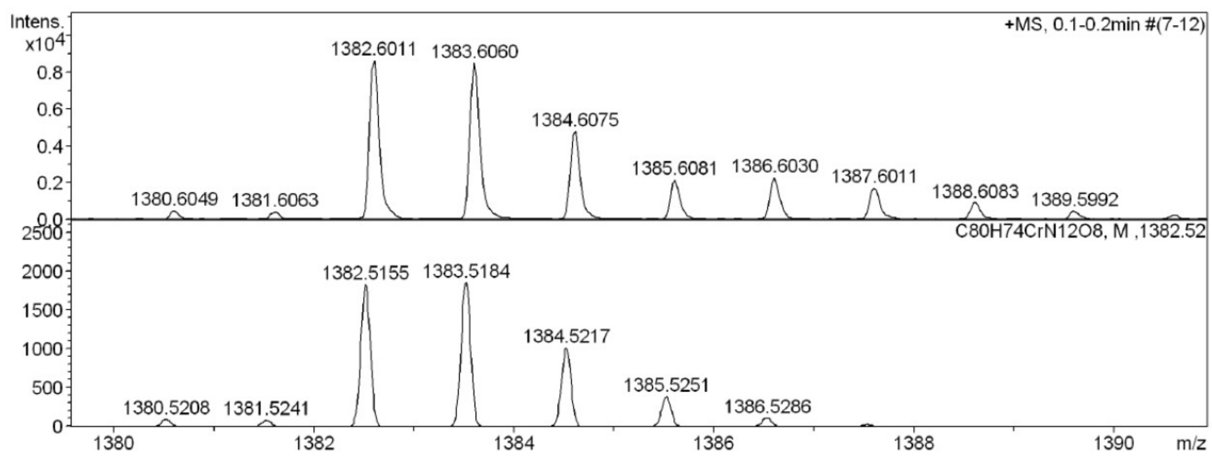

Fig. S12 (a) ESI-mass spectrum of $[Cr(\mathbf{L1})_2]^+$ (complex **2**).

Complex 2

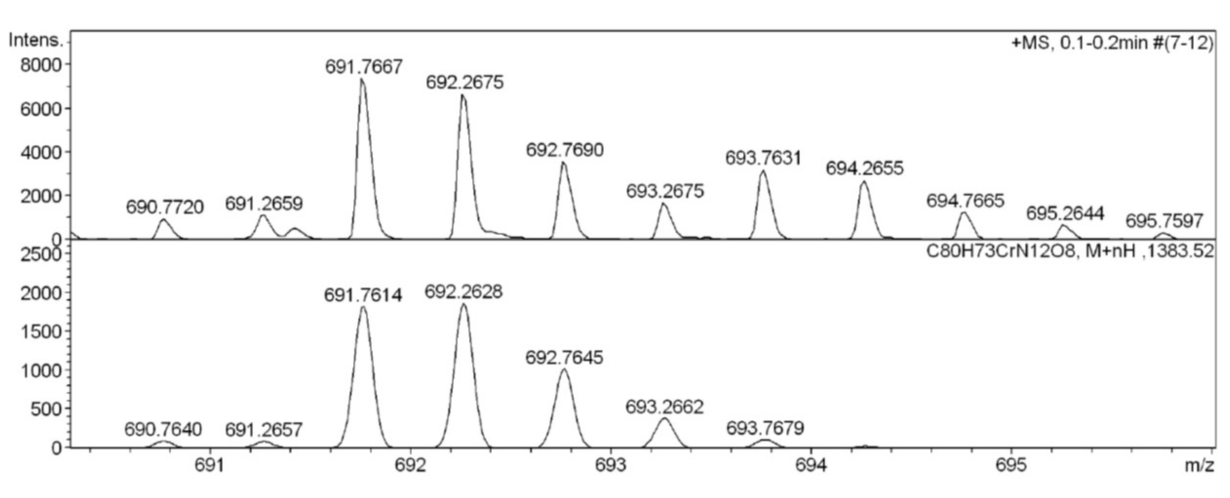

Fig. S12 (b) ESI-mass spectrum of $[Cr(\mathbf{L1})_2\text{+H}]^{2+}$ (complex **2**).

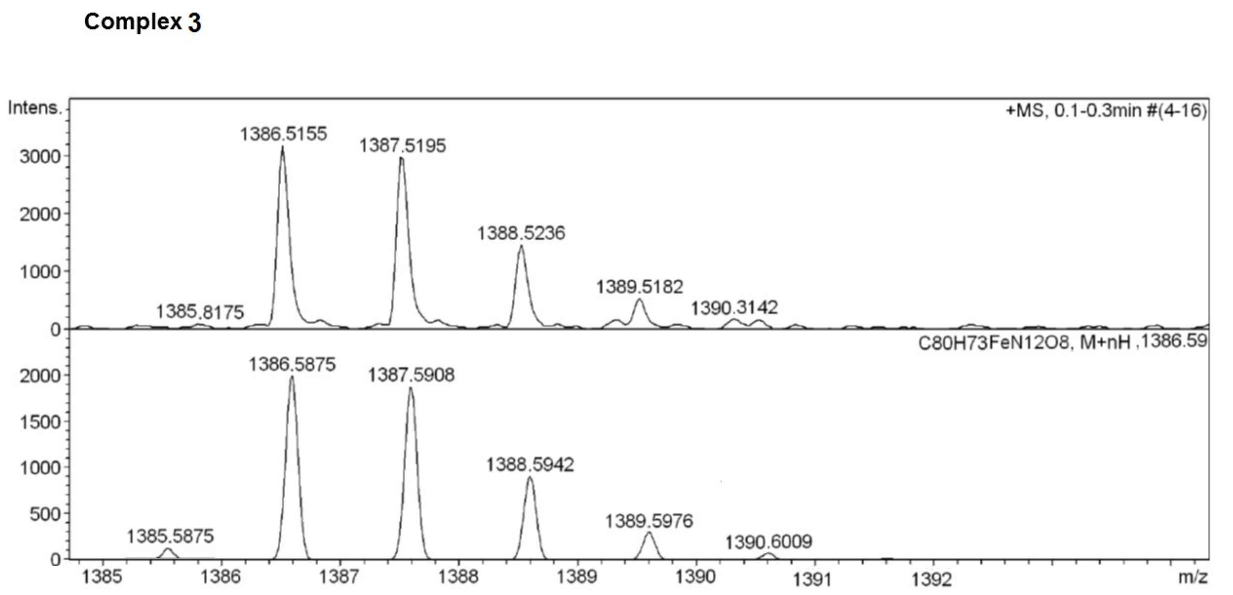

Fig. S13 (a) ESI-mass spectrum of $[Fe(\mathbf{L1})_2]^+$ (complex **3**).

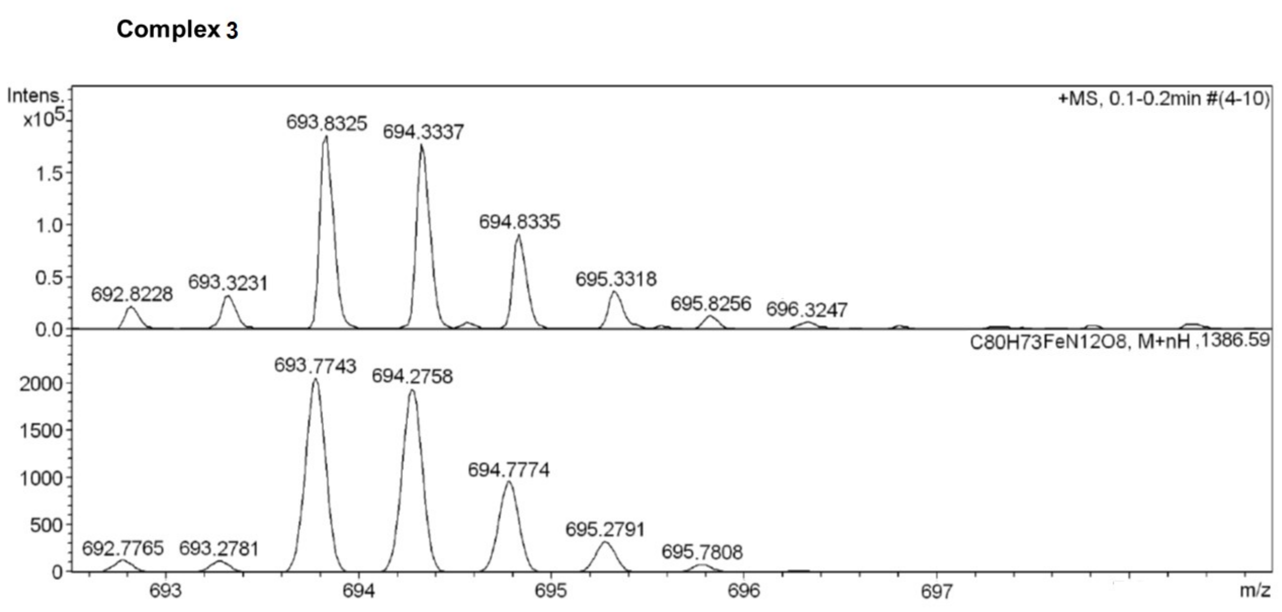

Fig. S13 (b) ESI-mass spectrum of $[Fe(\mathbf{L1})_2+H]^{2+}$ (complex **3**).

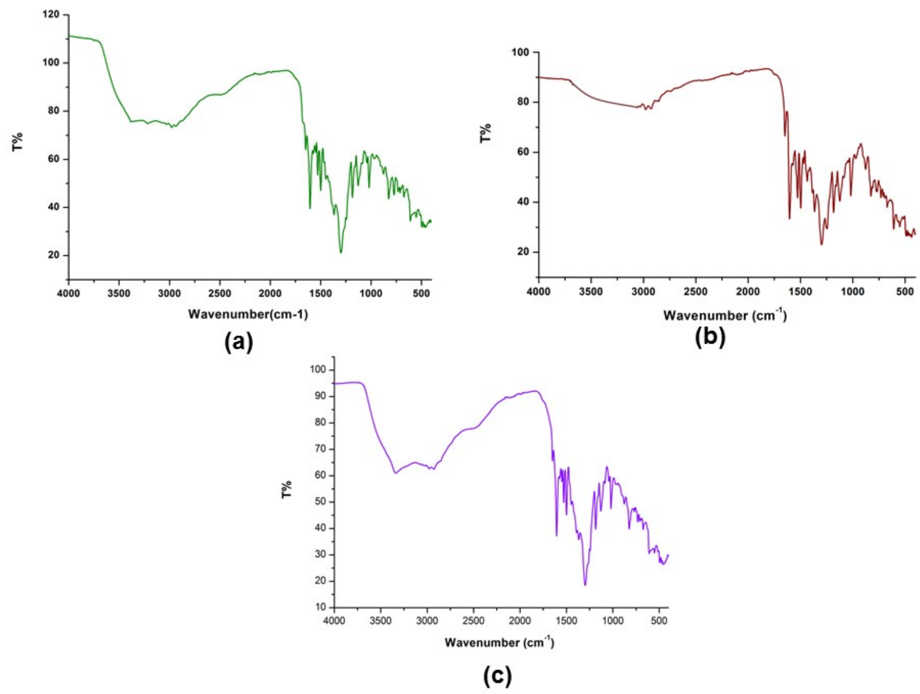

Fig. S14 FTIR spectra of (a) complex **4**, (b) complex **5** and (c) complex **6**.

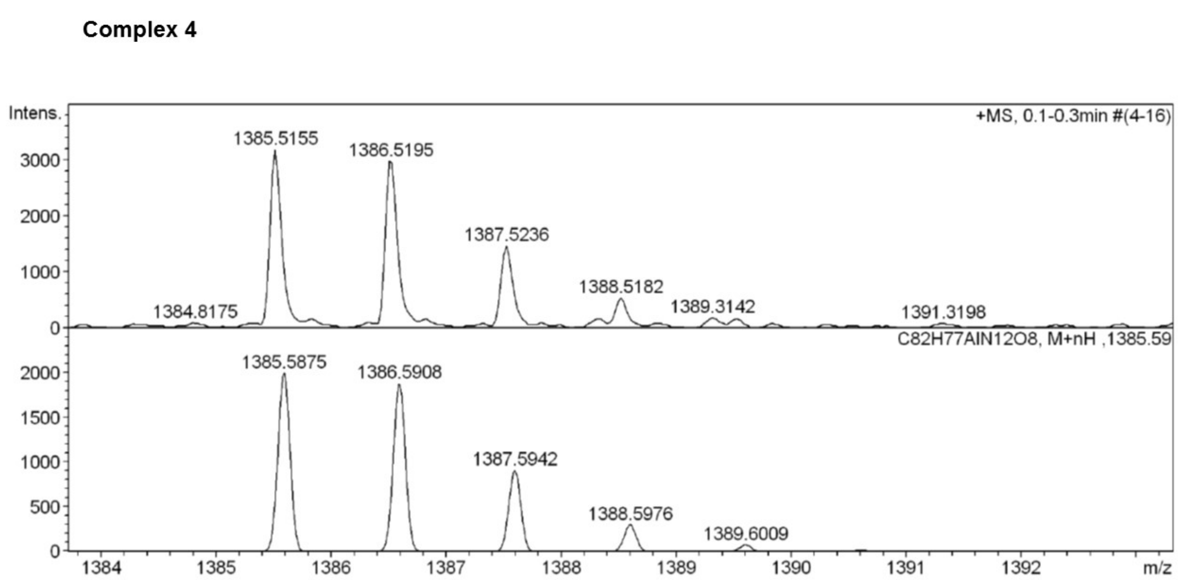

Fig. S15 (a) ESI-mass spectrum of $[Al(\mathbf{L2})_2]^+$ (complex **4**).

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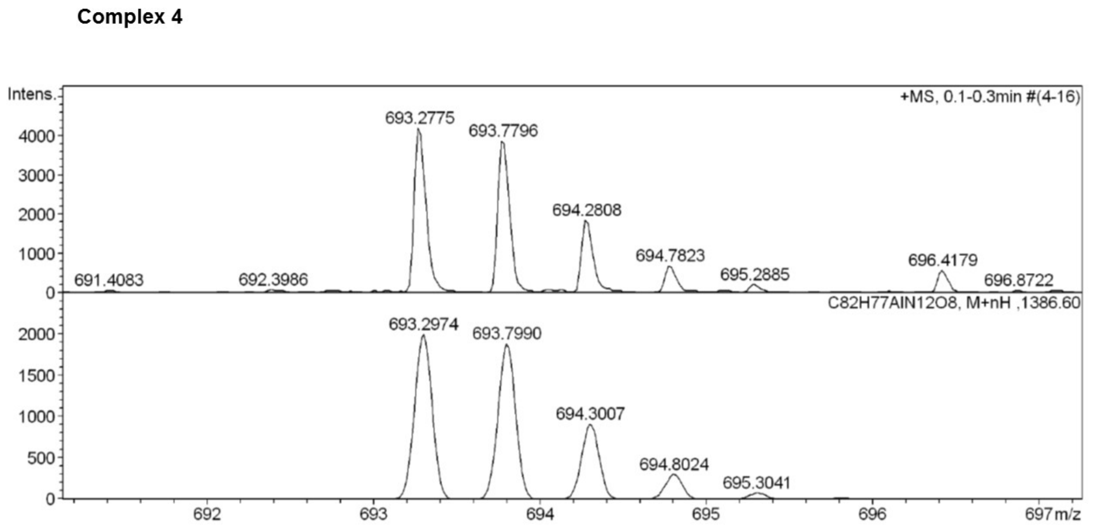

Fig. S15 (b) ESI-mass spectrum of $[Al(\mathbf{L2})_2+H]^+$ (complex **4**).

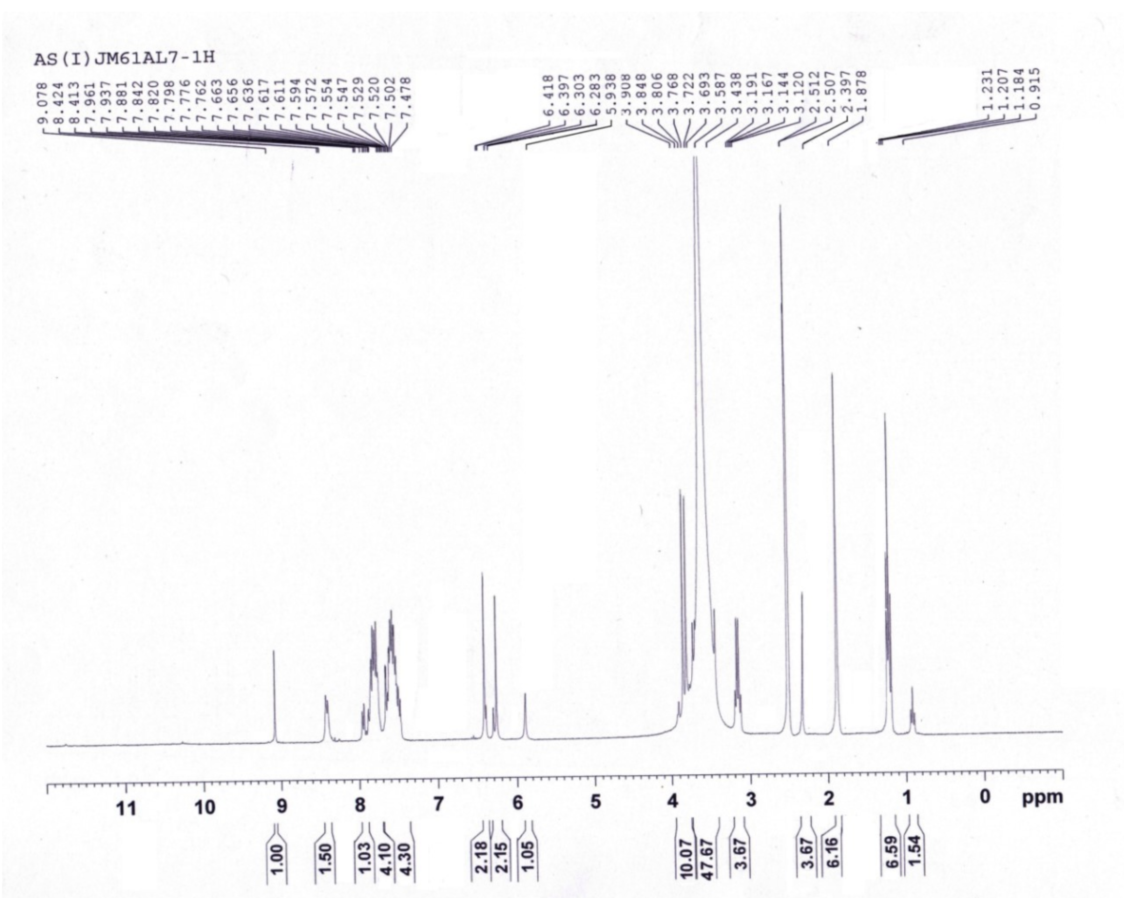

Fig. S16(a) ^{1}H-NMR spectrum of complex **4** in DMSO-d_6 recorded on a 300 MHz Bruker NMR spectrometer.

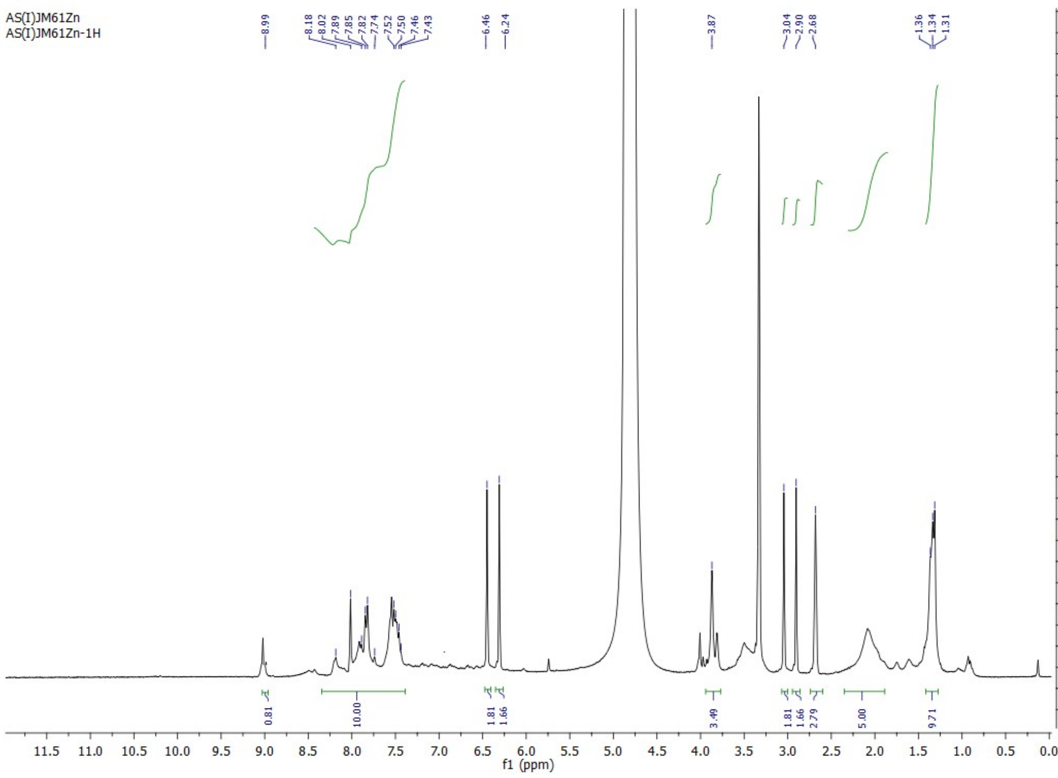

Fig. S16(b) ^{1}H-NMR spectrum of complex **4** in CD_3OD recorded on a 400 MHz Bruker NMR spectrometer.

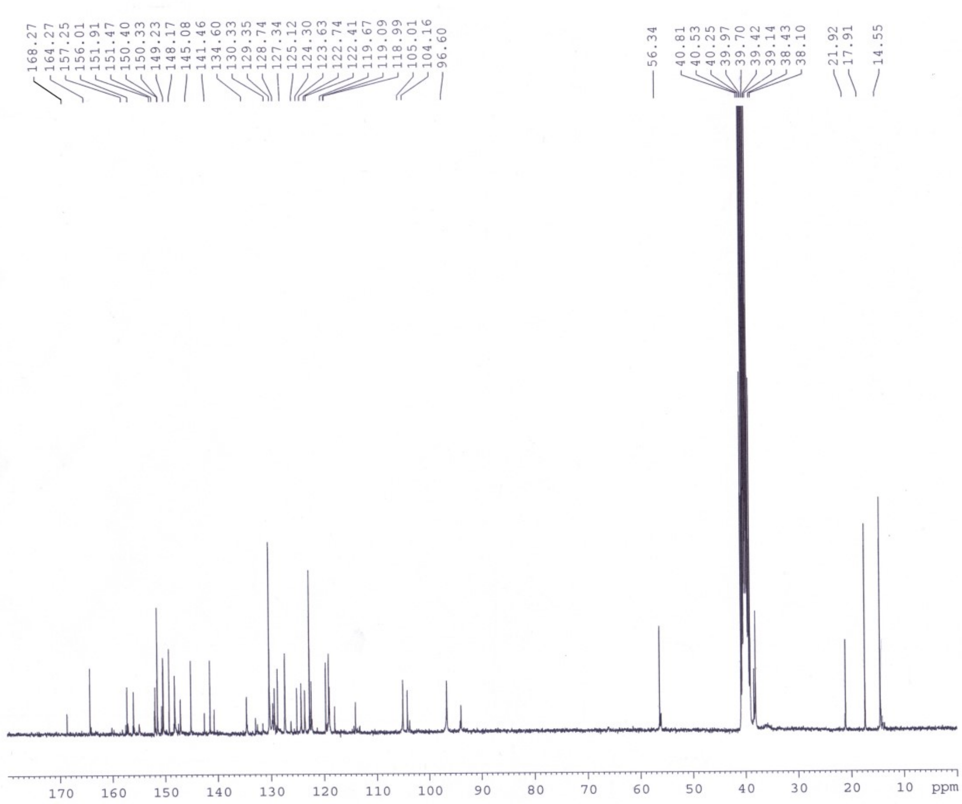

Fig. S17 ^{13}C NMR spectrum of complex **4** in DMSO-d_6

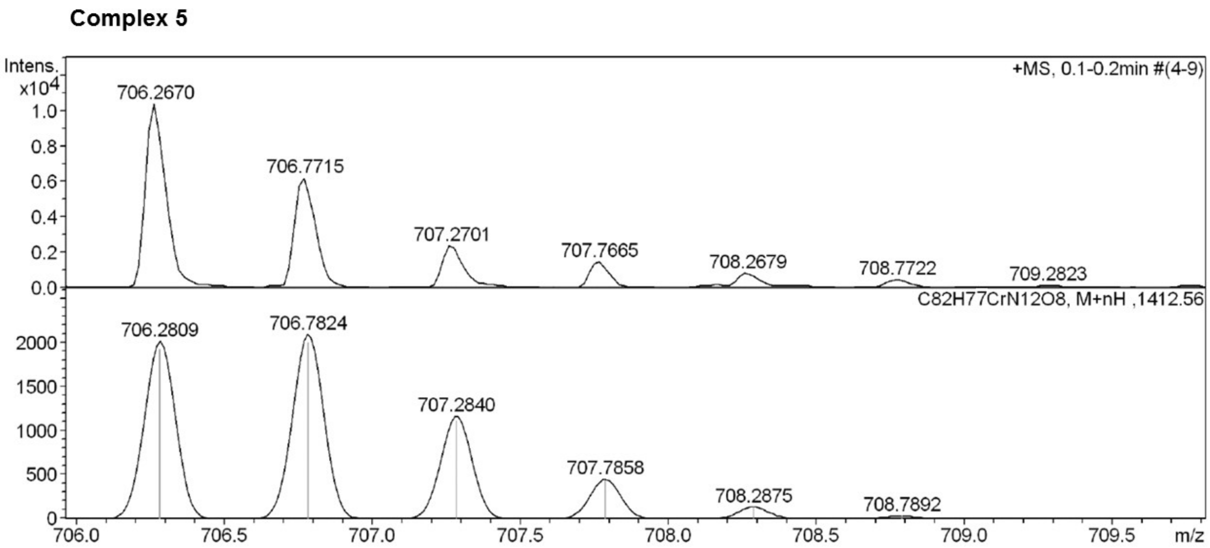

Fig. S18 (a) ESI-mass spectrum of $[Cr(\mathbf{L2})_2]^+$ (complex **5**).

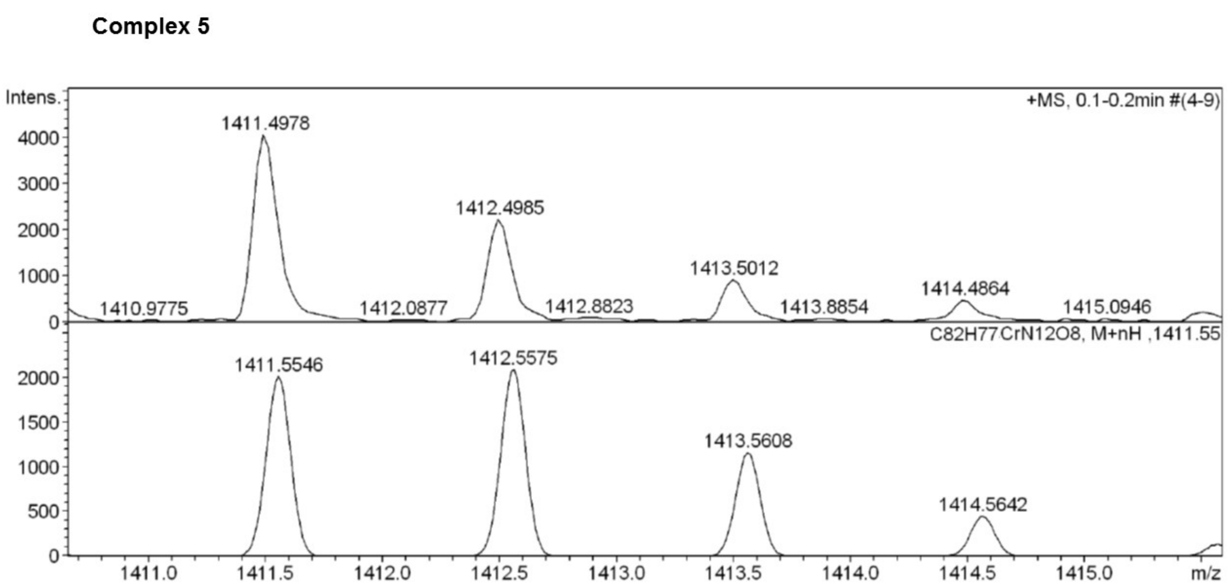

Fig. S18 (b) ESI-mass spectrum of $[Cr(\mathbf{L2})_2+H]^{2+}$ (complex **5**).

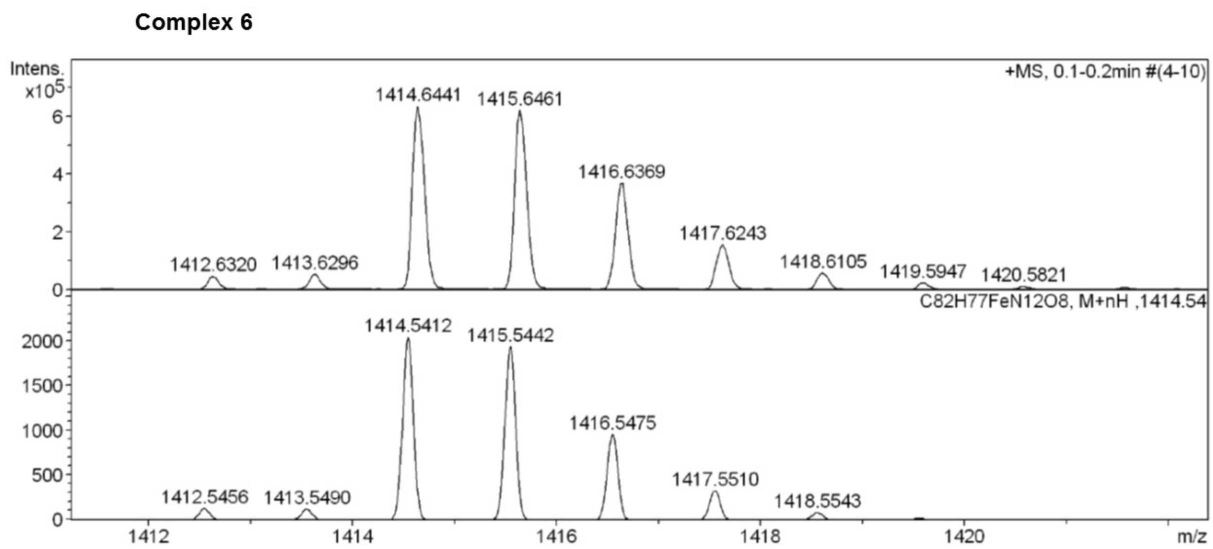

Fig. S19 (a) ESI-mass spectrum of $[Fe(\mathbf{L2})_2]^+$ (complex **6**).

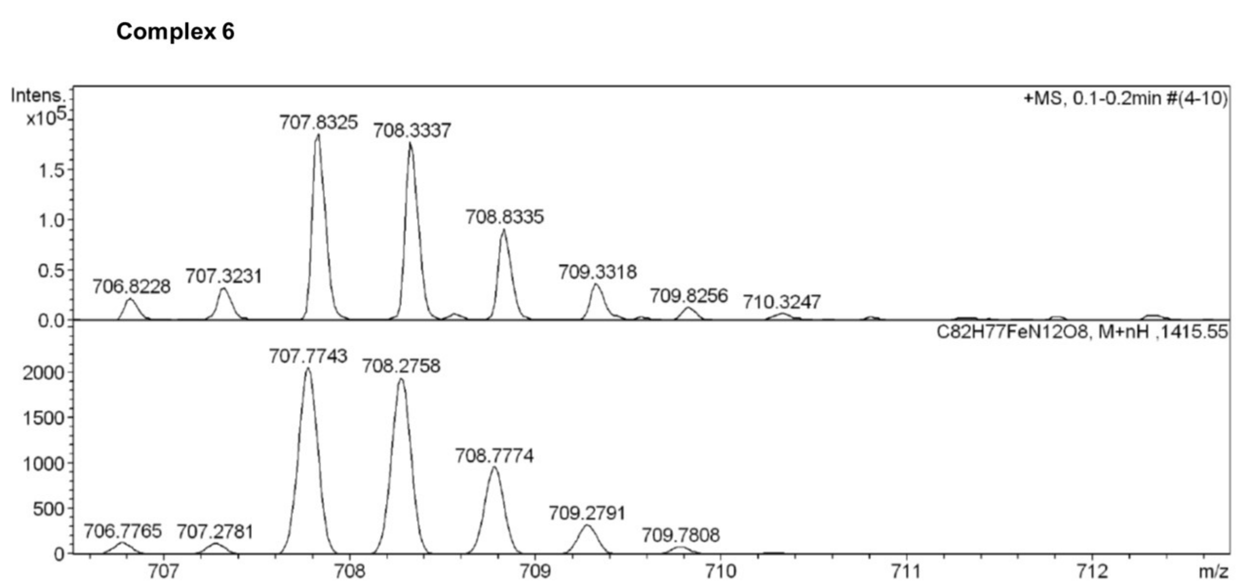

Fig. S19 (b) ESI-mass spectrum of $[Fe(\mathbf{L2})_2{+}H]^{2+}$ (complex **6**).

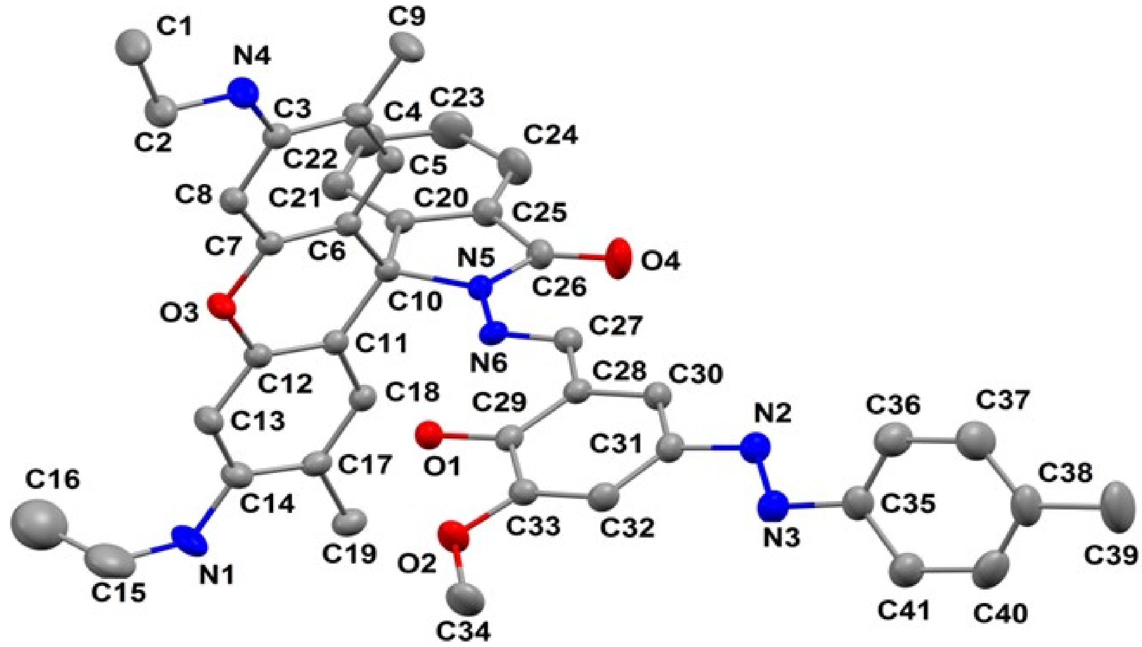

Fig. S20 Crystal structure of the chemosensor **HL2**. Atoms are shown as 30% thermal ellipsoids. Here, H and solvent molecule atoms are omitted for clarity.

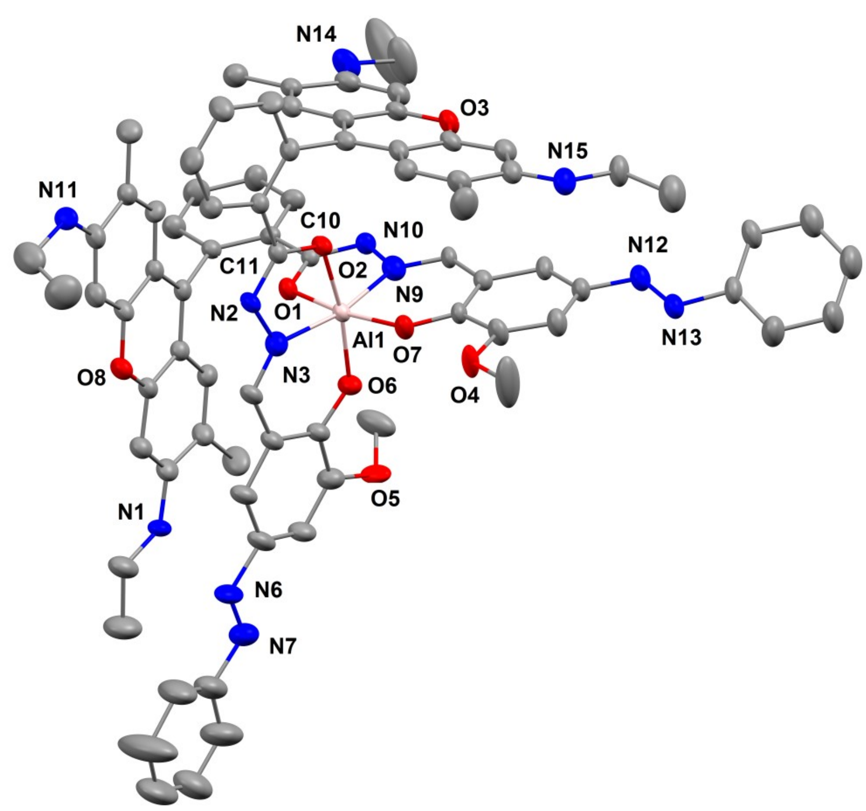

Fig. S21 Crystal structure of complex cation of **1**. Atoms are shown as 30% thermal ellipsoids. Here, H atoms are omitted for clarity.

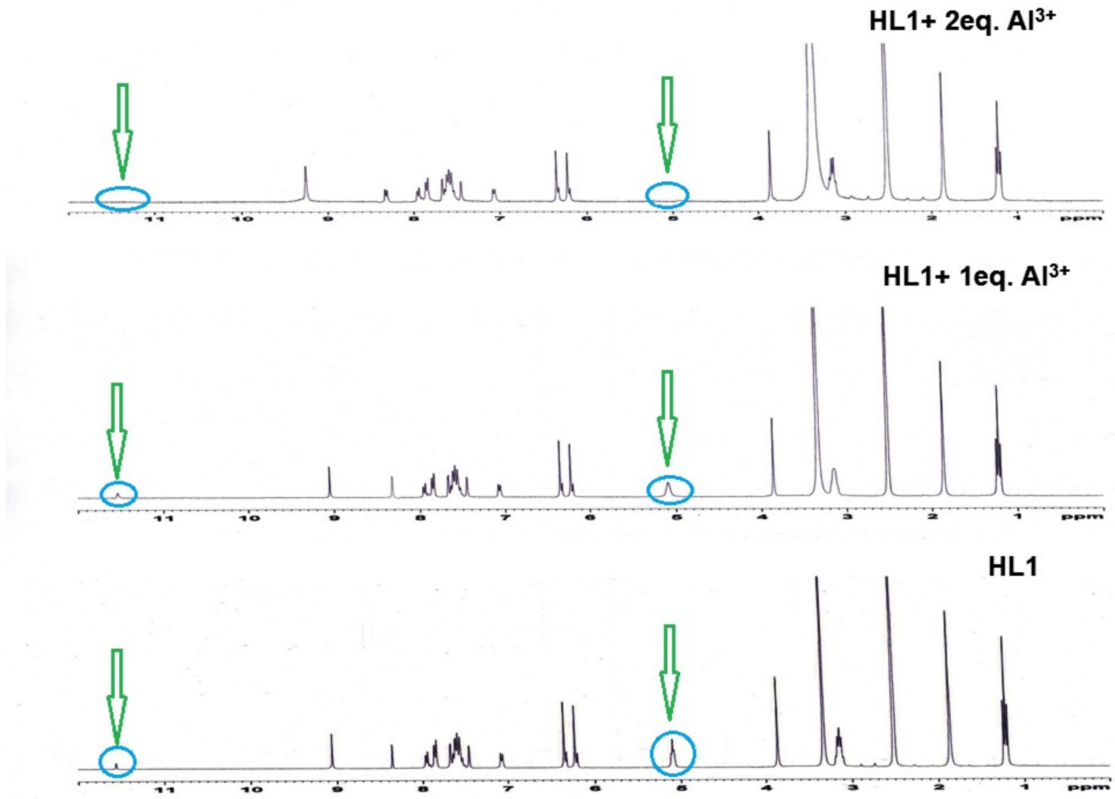

Fig. S22 ^{1}H-NMR titration of the free ligand (**HL1**) and with the addition of 1 and 2 equivalent of Al^{3+} in DMSO-d_6 recorded on a 300 MHz Bruker NMR spectrometer.

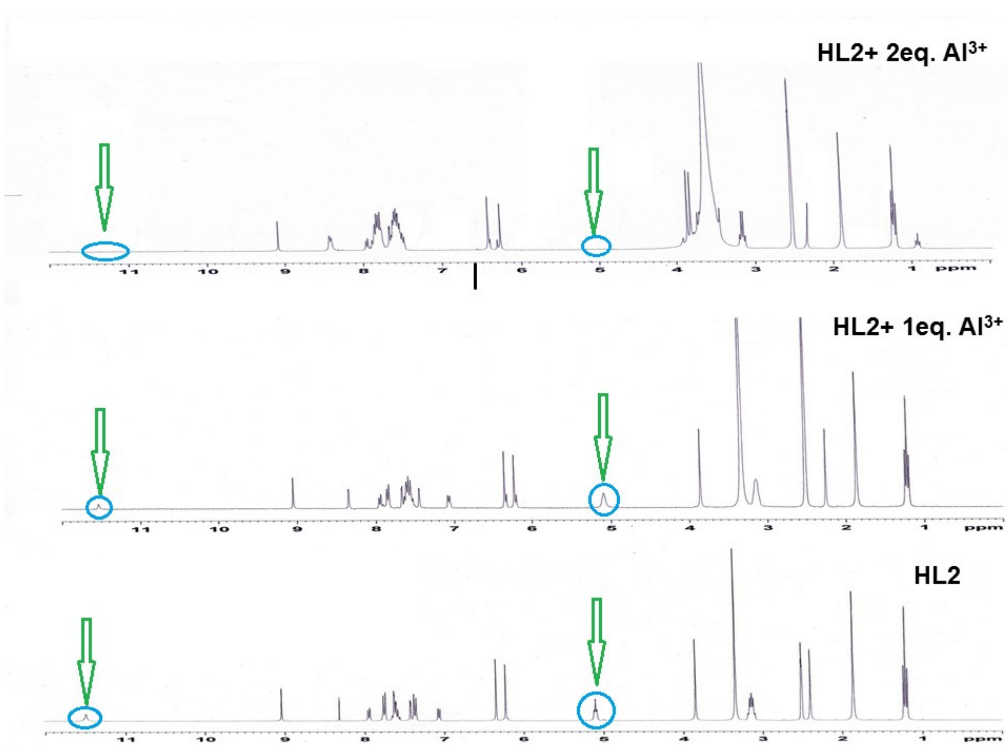

Fig. 23 ^{1}H-NMR titration of the free ligand (**HL2**) and with the addition of 1 and 2 equivalent of Al^{3+} in DMSO-d_6 recorded on a 300 MHz Bruker NMR spectrometer.

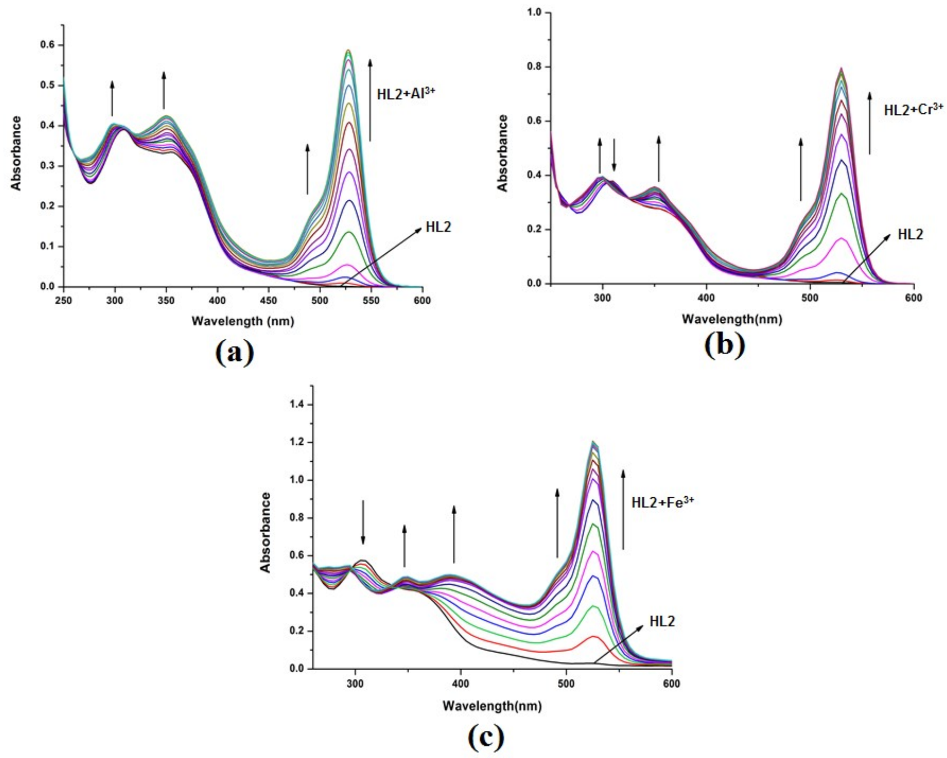

Fig. S24 Absorption titration study of **HL2** (10 μM) with gradual addition of metal ions (Al^{3+}, Cr^{3+} and Fe^{3+}) (a-c) 0-6 μM in 10 mM Britton Robinson buffer at pH 7.4.

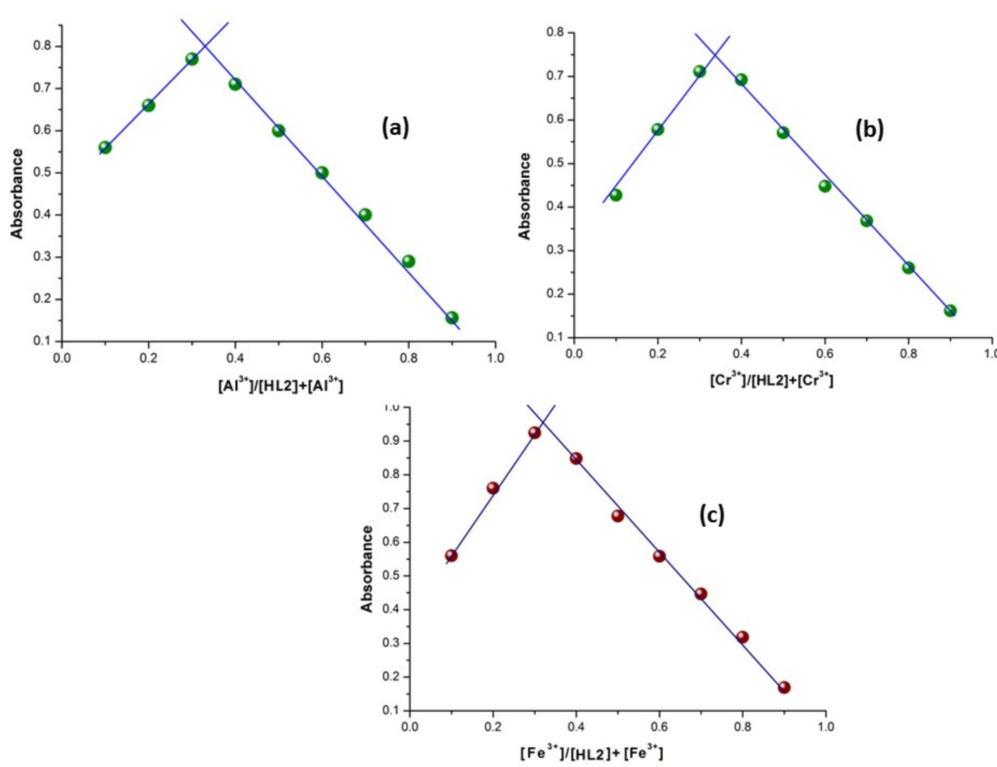

Fig. S25 2:1 (Ligand:Metal) binding stoichiometry has shown by Job's plot of complex **4-6**(a-c)(at λ= 525 nm). Symbols and solid lines represent the experimental and simulated profiles, respectively.

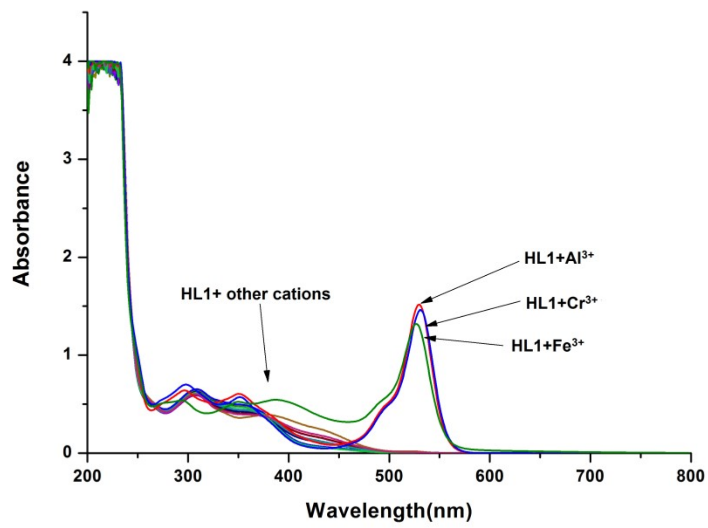

Fig. S26 Absorption spectra of **HL1** in presence of different metal ions in 10 mM Britton Robinson buffer at pH 7.4.

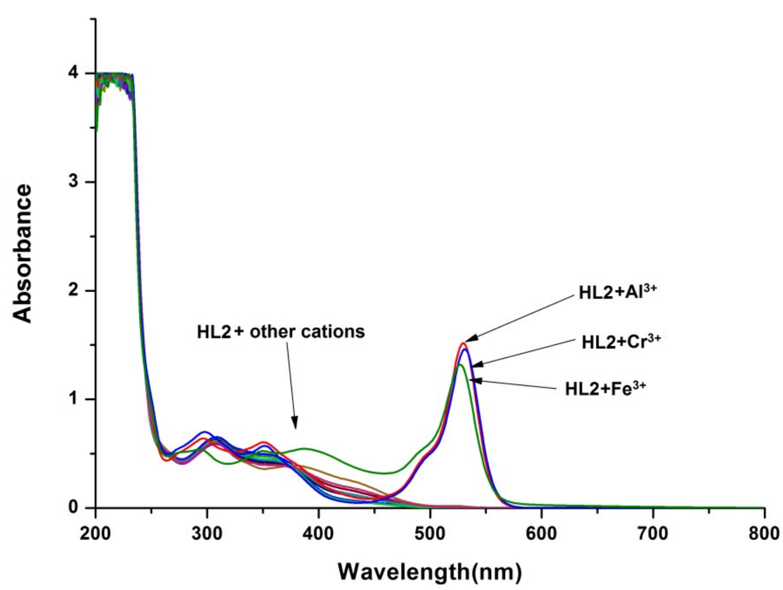

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Fig. S27 Absorption spectra of **HL2** in presence of different metal ions in 10 mM Britton Robinson buffer at pH 7.4.

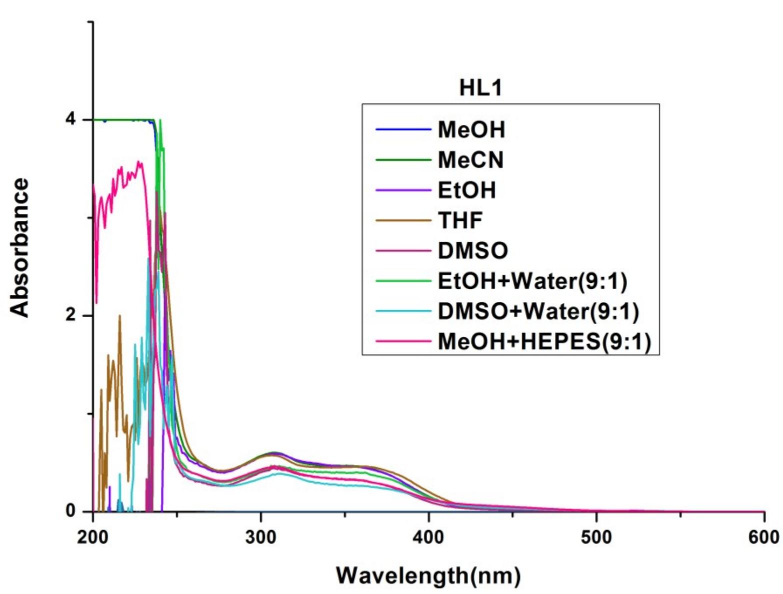

Fig. S28(a) Absorption spectra of **HL1** in presence of different solvent.

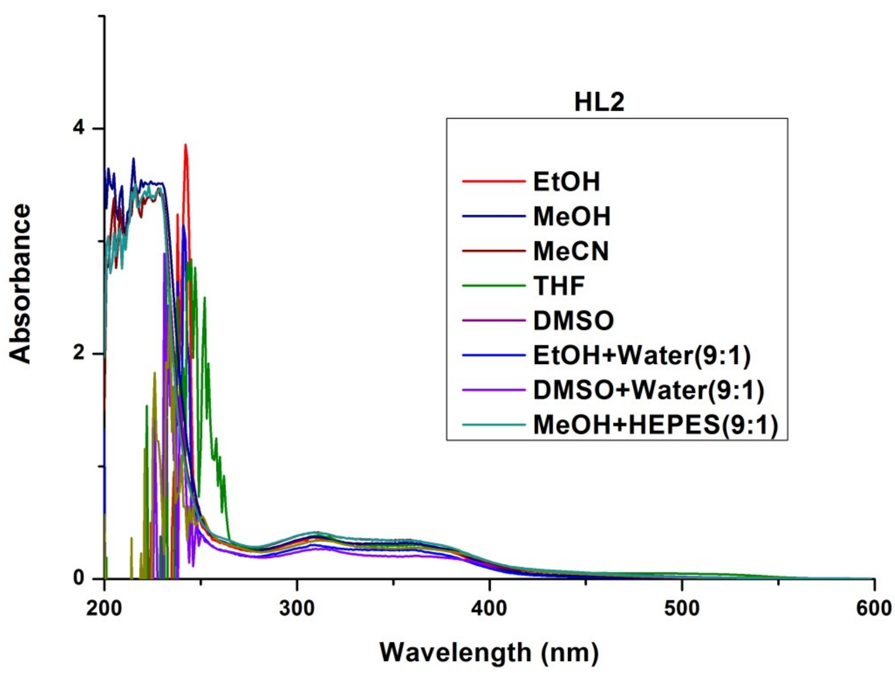

Fig. S28(b) Absorption spectra of **HL2** in presence of different solvent.

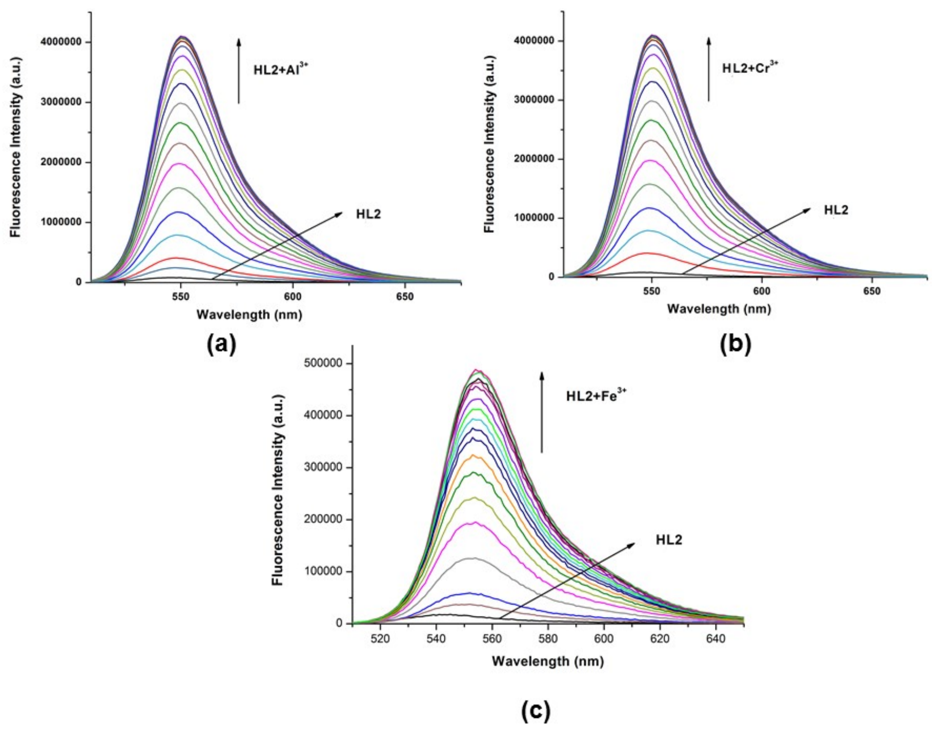

Fig. S29 Fluorescence titration of **HL2** (10 μM) in 10 mM Britton Robinson buffer at pH =7.4 by successive addition of metal ions (Al^{3+}, Cr^{3+} and Fe^{3+}) (0–6 μM) with λ_{em}= 555 nm.

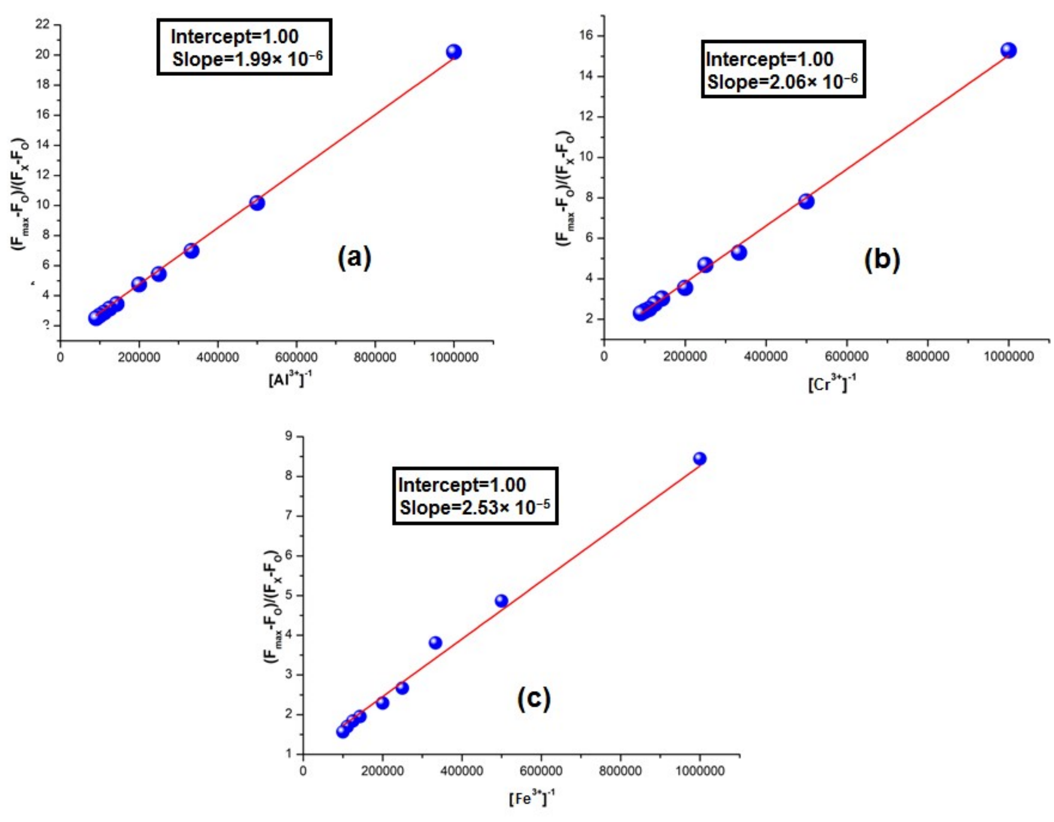

Fig. S30 Benesi-Hildebrand plot for complex **4-6** (a-c). The plot is obtained after adding 5 μM Al^{3+}, Cr^{3+} and Fe^{3+} solution to the **HL2** solution (10 μM) (in 10 mM HEPES buffer medium, pH 7.4).

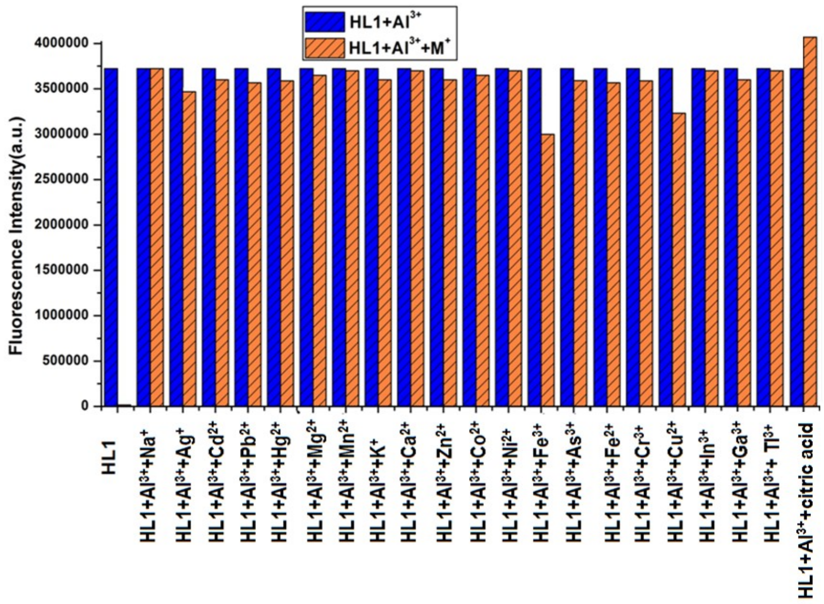

Fig. S31 Relative fluorescence intensity diagram of [**HL1**-Cr^{3+}] system in the presence of different cations in 10 mM Britton Robinson buffer at pH 7.4.

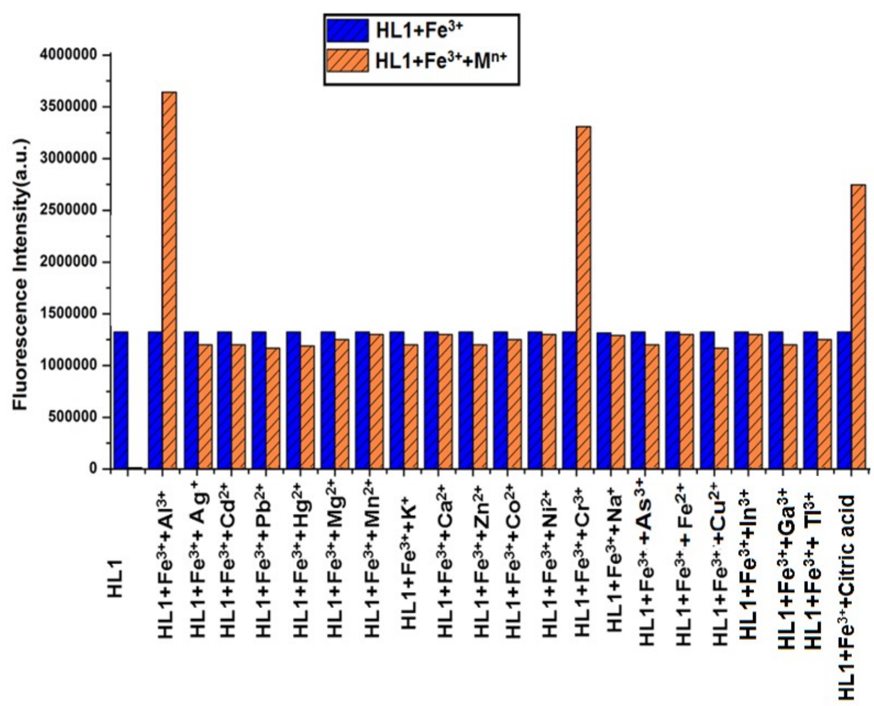

Fig. S32 Relative fluorescence intensity diagram of [**HL1**-Fe^{3+}] system in the presence of different cations in 10 mM Britton Robinson buffer at pH 7.4.

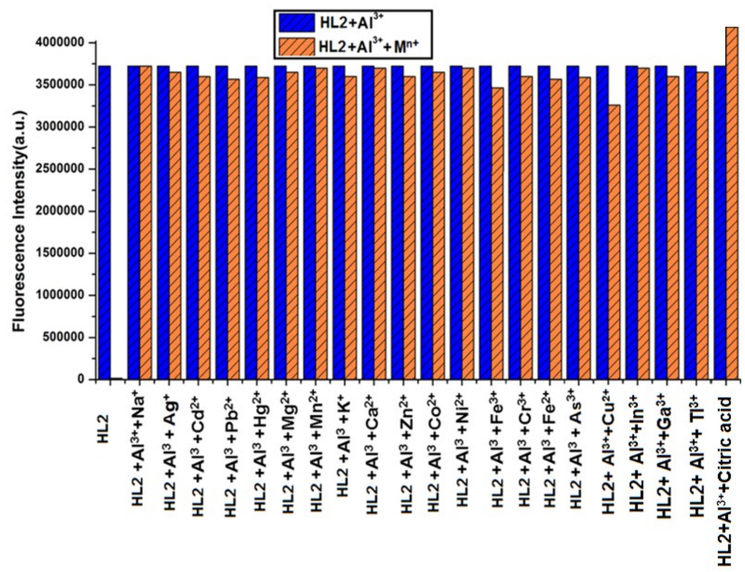

Fig. S33 Relative fluorescence intensity diagram of [**HL2**-Al^{3+}] system in the presence of different cations in 10 mM Britton Robinson buffer at pH 7.4

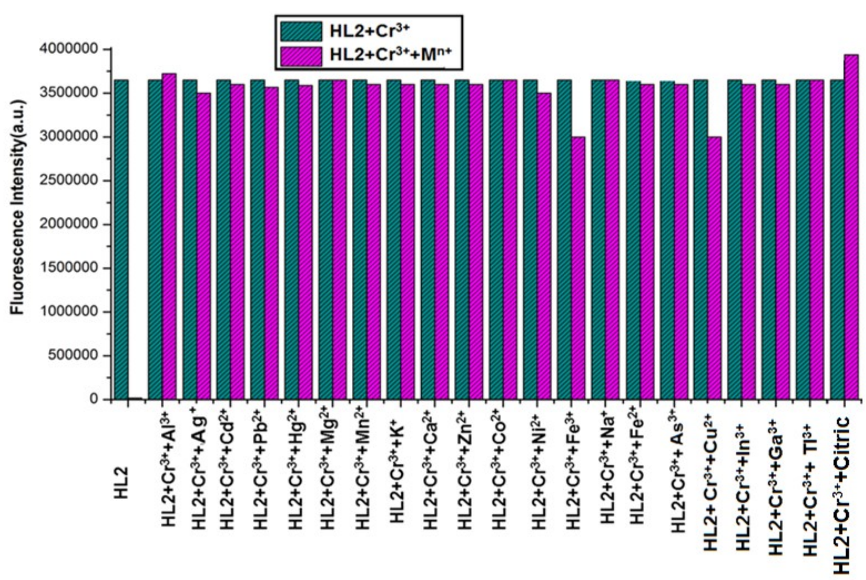

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Fig. S34 Relative fluorescence intensity diagram of [**HL2**-Cr^{3+}] system in the presence of different cations in 10 mM Britton Robinson buffer at pH 7.4.

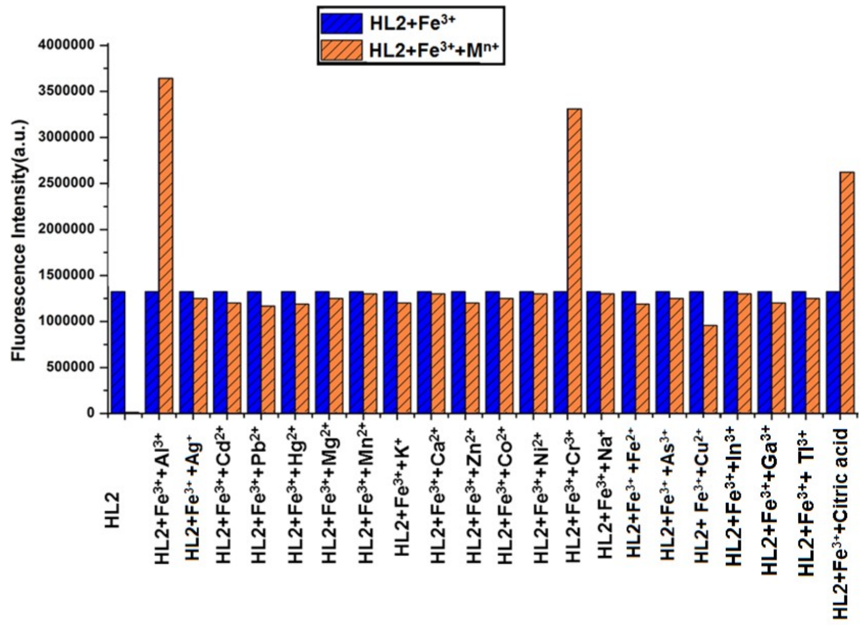

Fig. S35 Relative fluorescence intensity diagram of [**HL2**-Fe^{3+}] system in the presence of different cations in 10 mM Britton Robinson buffer at pH 7.4.

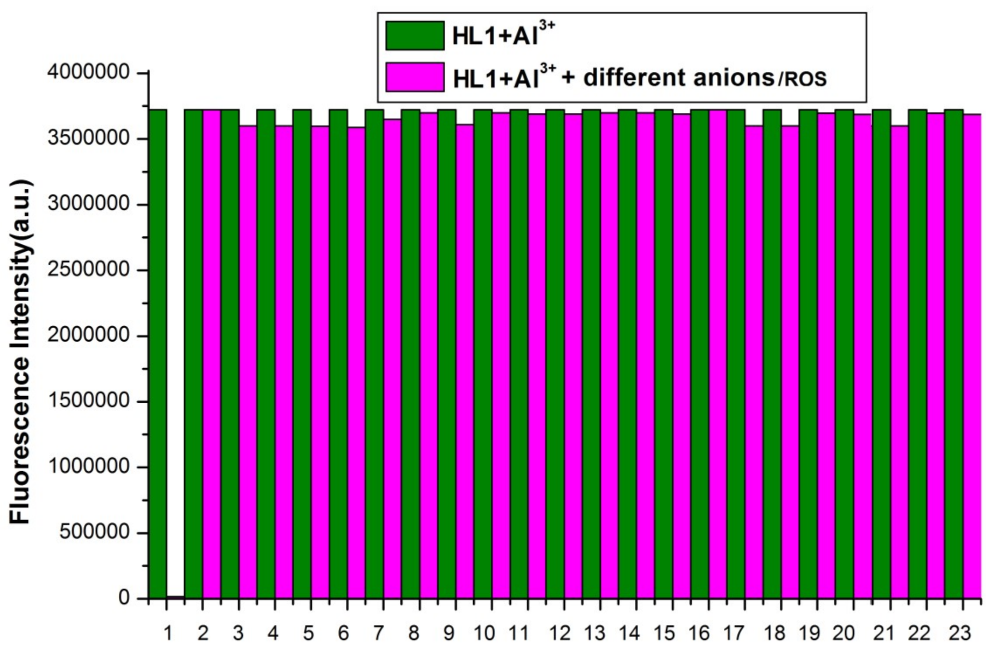

Fig. S36 Relative fluorescence intensity diagram of [**HL1**-Al^{3+}] system in the presence of different anions in Britton Robinson buffer medium (10 mM) at pH 7.4. 1=only **HL1** (10 μM) and (2-20)= **HL1** (10 μM) + Al^{3+}(5 μM) + Anions (50 μM), Anions = 2-$S_2O_3^{2-}$, 3-S^{2-}, 4-SO_3^{2-}, 5-HSO_4^-, 6-SO_4^{2-}, 7-SCN^-, 8-N_3^-, 9-OCN^-, 10-AsO_4^{3-}, 11-$H_2PO_4^-$, 12-HPO_4^{2-}, 13-PO_4^{3-}, 14-ClO_4^-, 15-AcO^-, 16-NO_3^-, 17-F^-, 18-Cl^-, 19-PF_6^-, 20-$P_2O_7^{4-}$, 21NaOCl, 22KO_2, 23H_2O_2.

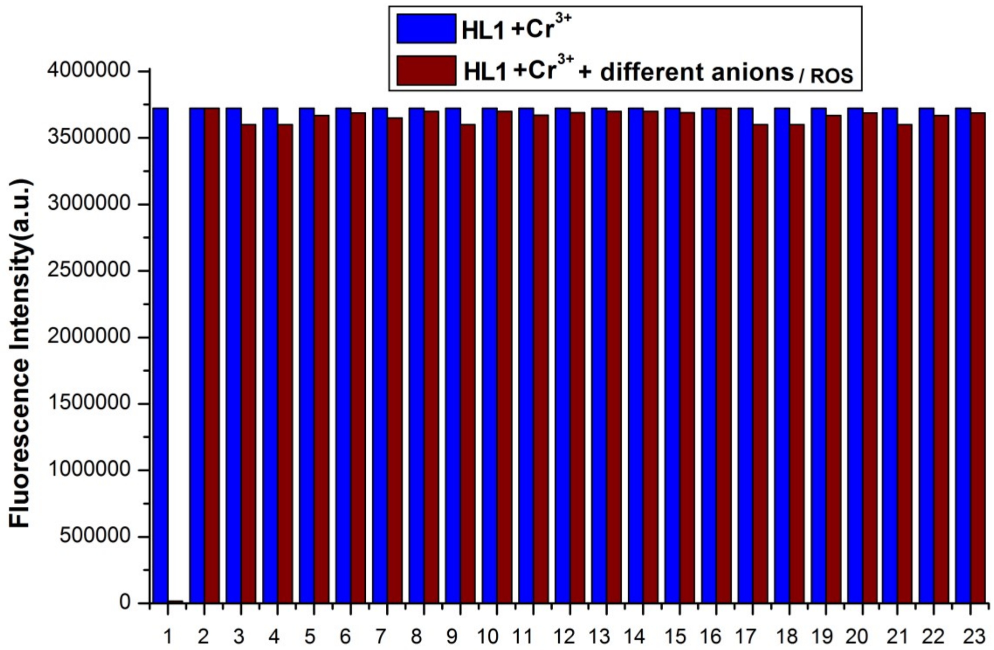

Fig. S37 Relative fluorescence intensity diagram of [**HL1**-Cr^{3+}] system in the presence of different anions in Britton Robinson buffer medium (10 mM) at pH 7.4. 1=only **HL1** (10 μM) and (2-20)= **HL1** (10 μM) + Cr^{3+}(5 μM) + Anions (50 μM), Anions = 2-$S_2O_3^{2-}$, 3-S^{2-}, 4-SO_3^{2-}, 5-HSO_4^-, 6-SO_4^{2-}, 7-SCN^-, 8-N_3^-, 9-OCN^-, 10-AsO_4^{3-}, 11-$H_2PO_4^-$, 12-HPO_4^{2-}, 13-PO_4^{3-}, 14-ClO_4^-, 15-AcO^-, 16-NO_3^-, 17-F^-, 18-Cl^-, 19-PF_6^-, 20-$P_2O_7^{4-}$, 21NaOCl, 22KO_2, 23H_2O_2.

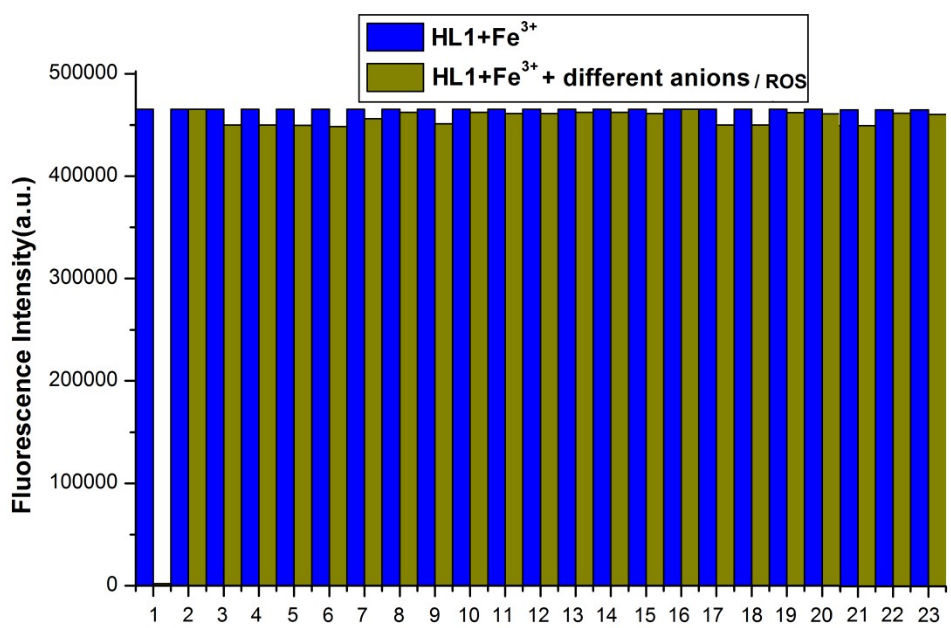

Fig. S38 Relative fluorescence intensity diagram of [**HL1**-Fe^{3+}] system in the presence of different anions in Britton Robinson buffer medium (10 mM) at pH 7.4. 1=only **HL1** (10 μM) and (2-20)= **HL1** (10 μM) + Fe^{3+}(5 μM) + Anions (50 μM), Anions = 2-$S_2O_3^{2-}$, 3-S^{2-}, 4-SO_3^{2-}, 5-HSO_4^-, 6-SO_4^{2-}, 7-SCN^-, 8-N_3^-, 9-OCN^-, 10-AsO_4^{3-}, 11-$H_2PO_4^-$, 12-HPO_4^{2-}, 13-PO_4^{3-}, 14-ClO_4^-, 15-AcO^-, 16-NO_3^-, 17-F^-, 18-Cl^-, 19-PF_6^-, 20-$P_2O_7^{4-}$, 21NaOCl, 22KO_2, 23H_2O_2.

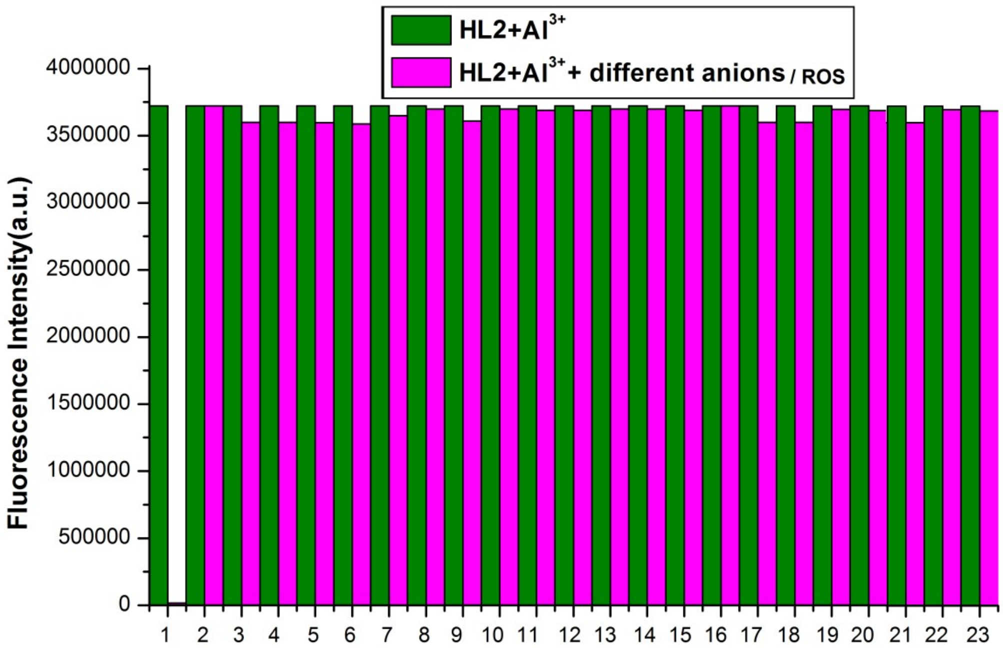

Fig. S39 Relative fluorescence intensity diagram of [**HL2**-Al^{3+}] system in the presence of different anions in Britton Robinson buffer medium (10 mM) at pH 7.4. 1=only **HL2** (10 μM) and (2-20)= **HL2** (10 μM) + Al^{3+}(5 μM) + Anions (50 μM), Anions = 2-$S_2O_3^{2-}$, 3-S^{2-}, 4-SO_3^{2-}, 5-HSO_4^-, 6-SO_4^{2-}, 7-SCN^-, 8-N_3^-, 9-OCN^-, 10-AsO_4^{3-}, 11-$H_2PO_4^-$, 12-HPO_4^{2-}, 13-PO_4^{3-}, 14-ClO_4^-, 15-AcO^-, 16-NO_3^-, 17-F^-, 18-Cl^-, 19-PF_6^-, 20-$P_2O_7^{4-}$, 21NaOCl, 22KO_2, 23H_2O_2.

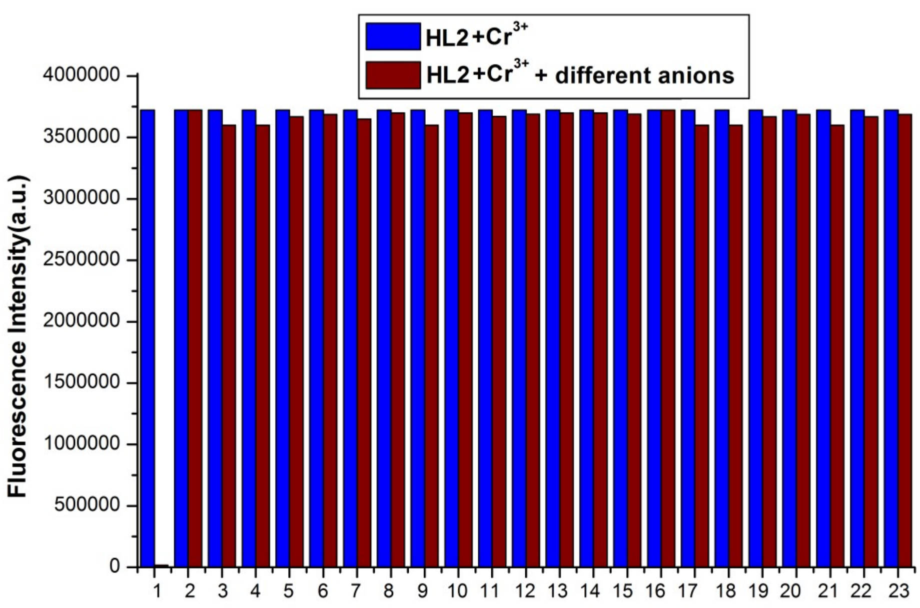

Fig. S40 Relative fluorescence intensity diagram of [**HL2**-Cr^{3+}] system in the presence of different anions in Britton Robinson buffer medium (10 mM) at pH 7.4. 1=only **HL2** (10 μM) and (2-20)= **HL2** (10 μM) + Fe^{3+}(5 μM) + Anions (50 μM), Anions = 2-$S_2O_3^{2-}$, 3-S^{2-}, 4-SO_3^{2-}, 5-HSO_4^-, 6-SO_4^{2-}, 7-SCN^-, 8-N_3^-, 9-OCN^-, 10-AsO_4^{3-}, 11-$H_2PO_4^-$, 12-HPO_4^{2-}, 13-PO_4^{3-}, 14-ClO_4^-, 15-AcO^-, 16-NO_3^-, 17-F^-, 18-Cl^-, 19-PF_6^-, 20-$P_2O_7^{4-}$, 21NaOCl, 22KO_2, 23H_2O_2.

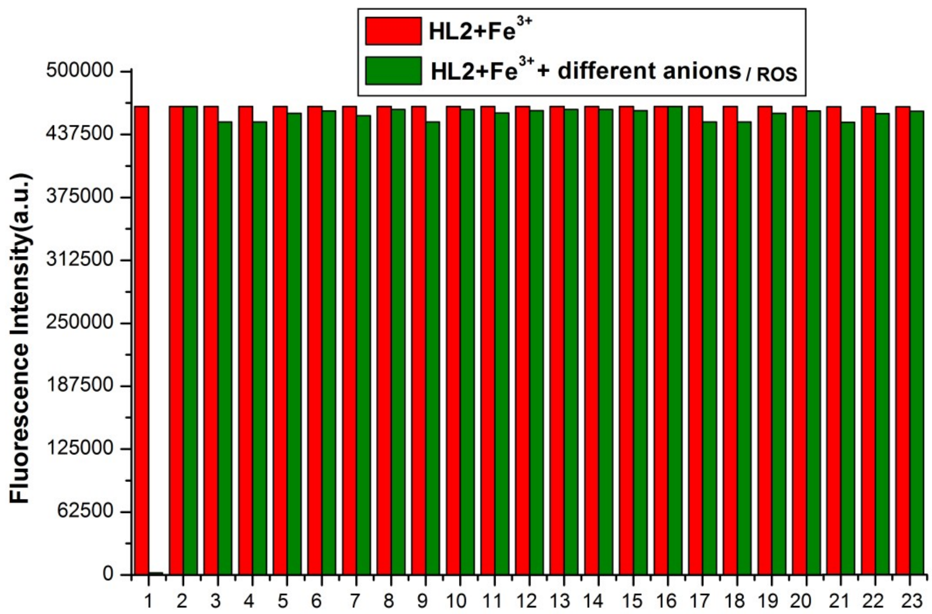

Fig. S41 Relative fluorescence intensity diagram of [**HL2**-Fe^{3+}] system in the presence of different anions in Britton Robinson buffer medium (10 mM) at pH 7.4. 1=only **HL2** (10 μM) and (2-20)= **HL2** (10 μM) + Fe^{3+}(5 μM) + Anions (50 μM), Anions = 2-$S_2O_3^{2-}$, 3-S^{2-}, 4-SO_3^{2-}, 5-HSO_4^-, 6-SO_4^{2-}, 7-SCN^-, 8-N_3^-, 9-OCN^-, 10-AsO_4^{3-}, 11-$H_2PO_4^-$, 12-HPO_4^{2-}, 13-PO_4^{3-}, 14-ClO_4^-, 15-AcO^-, 16-NO_3^-, 17-F^-, 18-Cl^-, 19-PF_6^-, 20-$P_2O_7^{4-}$, 21NaOCl, 22-KO_2, 23H_2O_2.

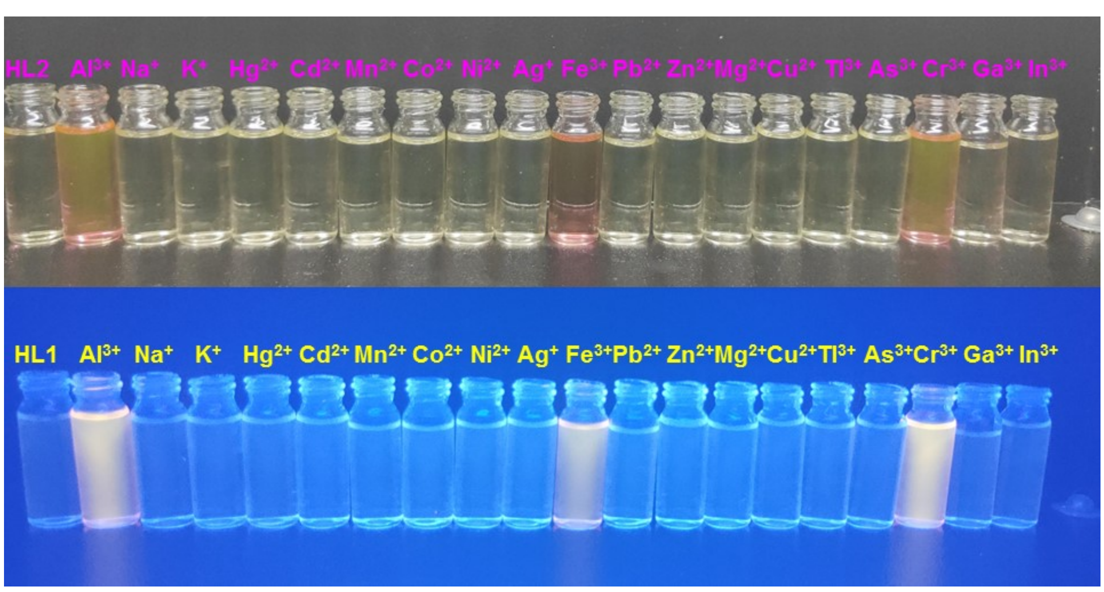

Fig. S42 Visual colour changes of chemosensor **HL2** (10μM) in presence of common metal ions (0.5 equivalent) in 10 mM Britton Robinson buffer (pH 7.4). The images in above row and below row were taken under visible light and UV light respectively.

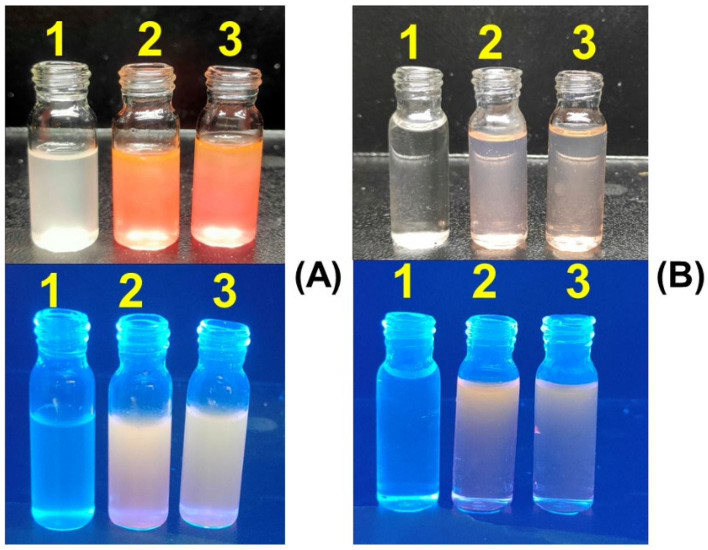

Fig. S43 Visual colour changes of real samples under normal light (above) and UV light (below) in presence of chemosensors (**HL1** and **HL2**). (A) Saloon waste water, (1= Only saloon waste water, 2 and 3= Saloon waste water + **HL1/HL2**). (B) Laboratory tap water (1= Only laboratory tap water, 2 and 3=laboratory tap water + **HL1/HL2**).

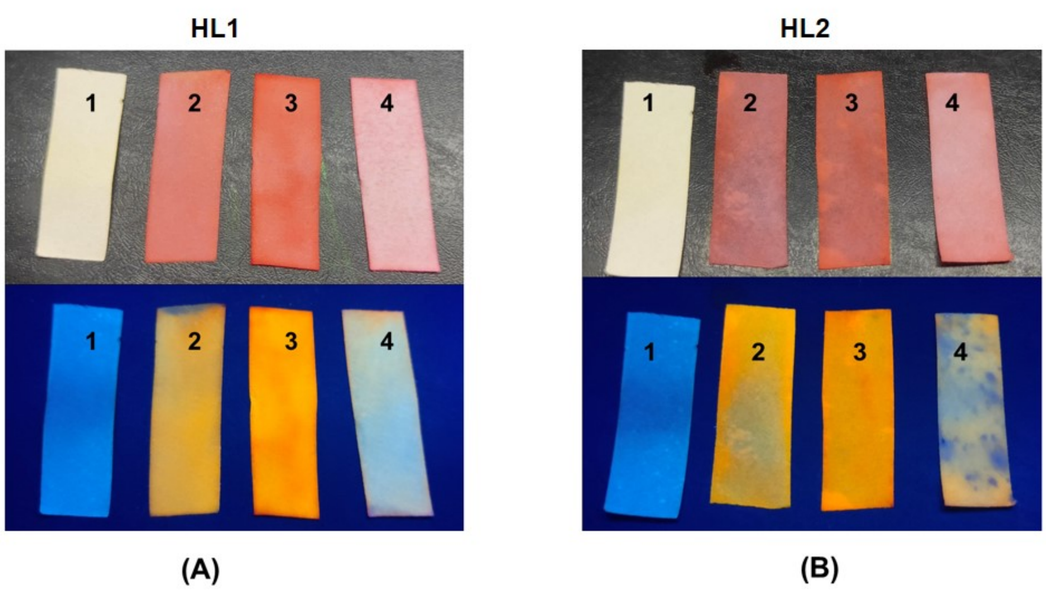

Fig. S44 Colour changes of paper strip under normal light (above) and UV light (below) in presence of chemosensors **HL1** (A) and **HL2** (B) [1=only **HL1**/ **HL2**; 2-4= **HL1**/ **HL2** + Cr^{3+}, Al^{3+} and Fe^{3+}, respectively].

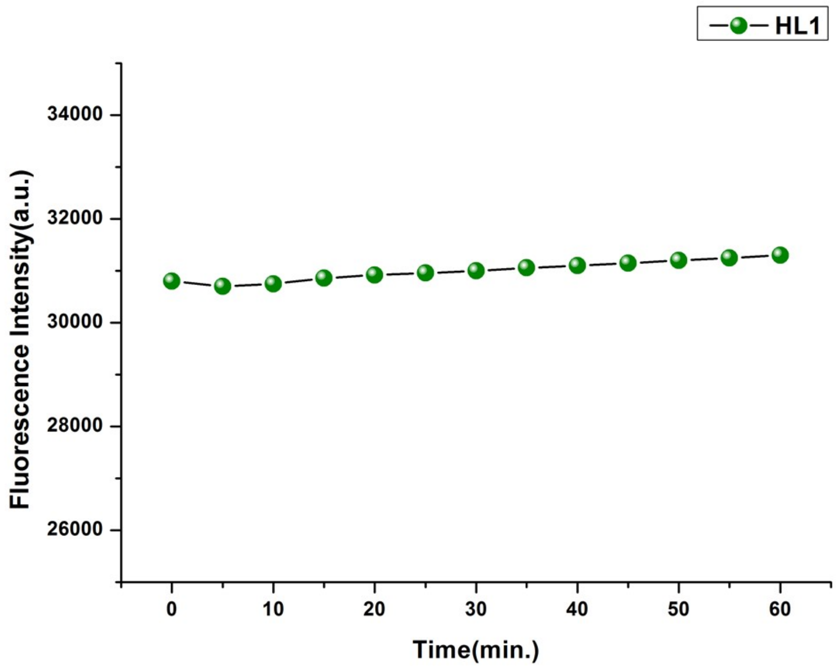

Fig. S45 The photostability of **HL1** (10 μM) in 10 mM Britton Robinson buffer at pH 7.4.(λex = 450 nm. Slit 1/1).

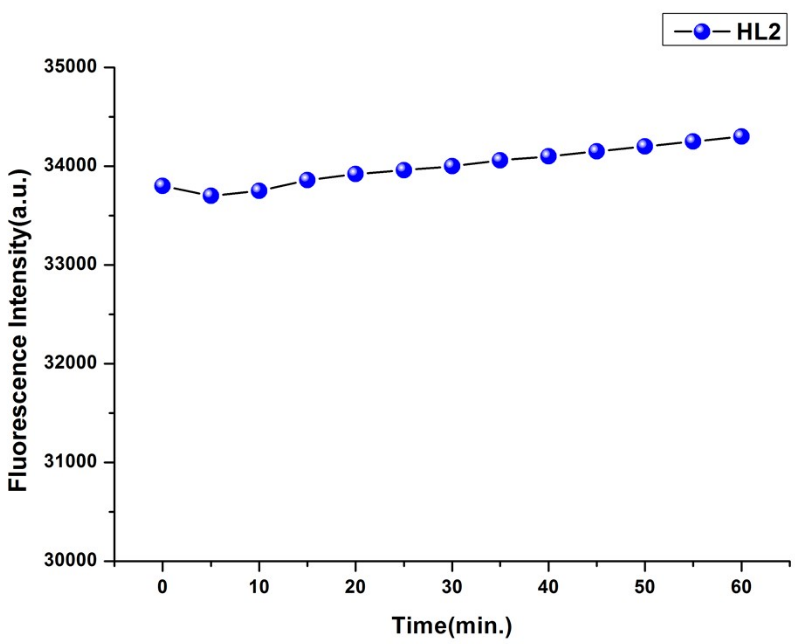

Fig. S46 The photostability of **HL2** (10 μM) in 10 mM Britton Robinson buffer at pH 7.4.(λex = 450 nm. Slit 1/1).

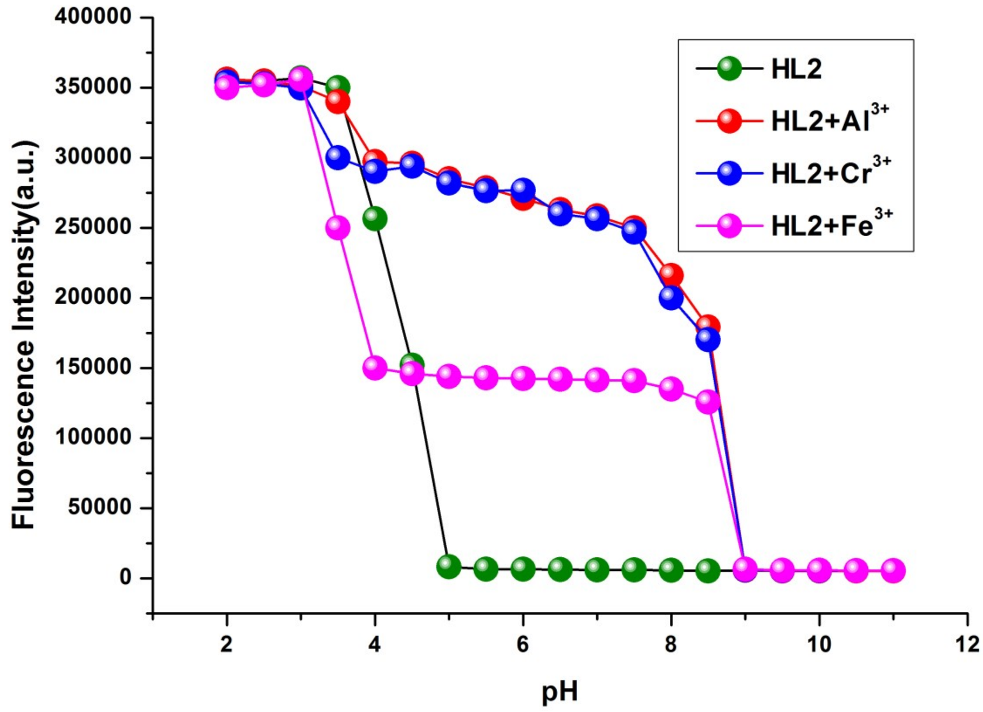

Fig. S47 Fluorescence intensity of **HL2** (10 μM) in the absence and presence of metal ions (Al^{3+}, Cr^{3+} and Fe^{3+}) (5 μM) at different pH values in 10 mM Britton Robinson buffer.

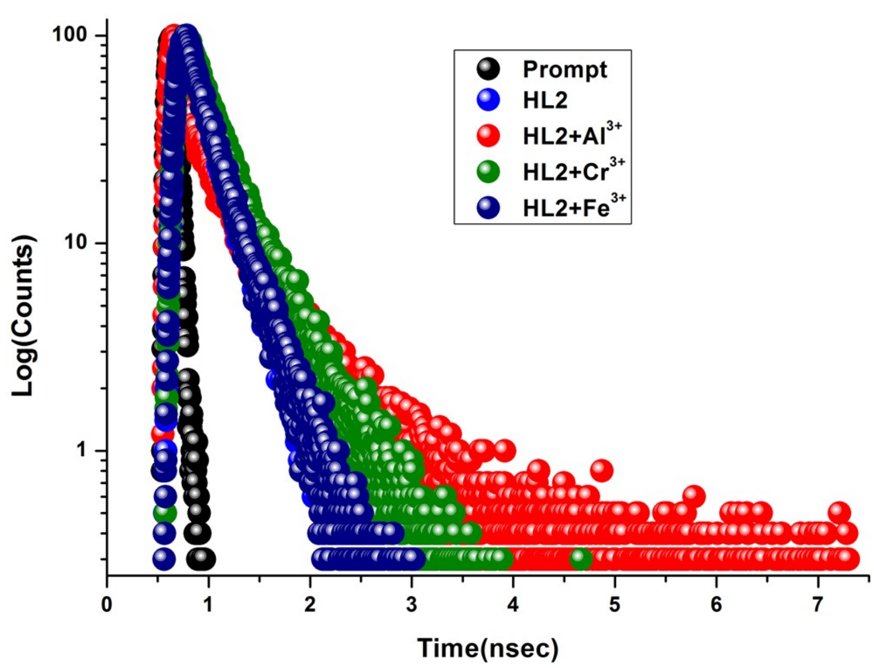

Fig. S48 Time-resolved fluorescence decay curves (logarithm of normalized intensity vs time in ns) of **HL2.**

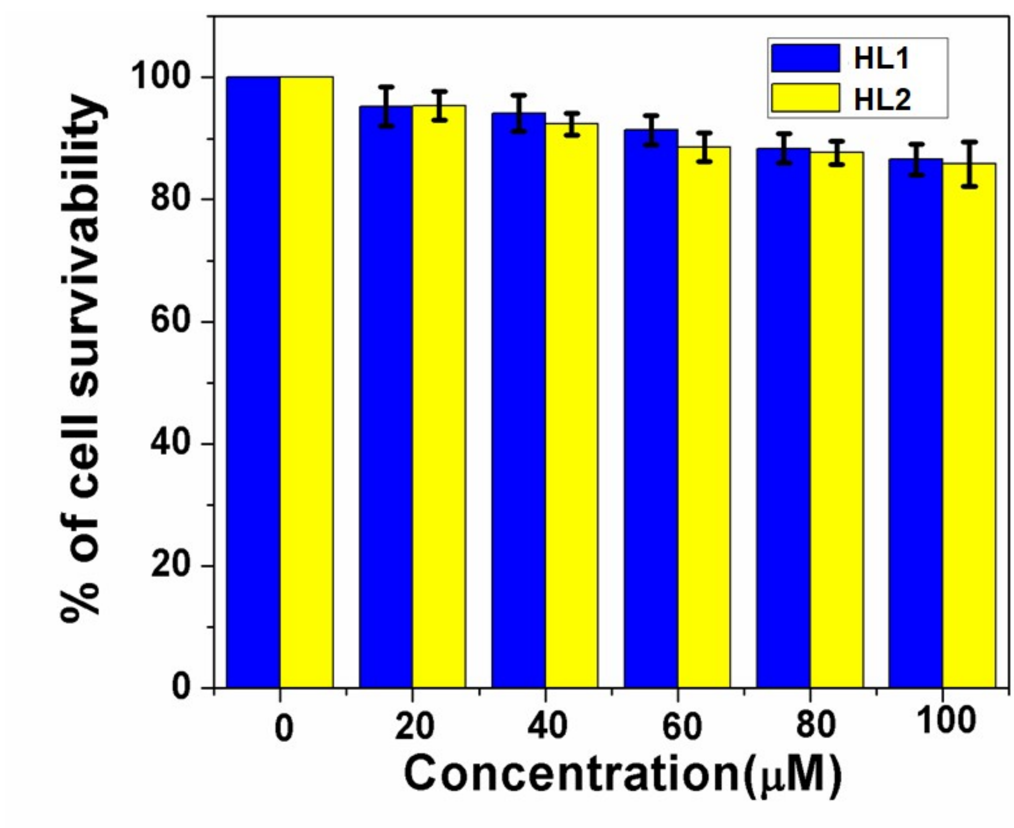

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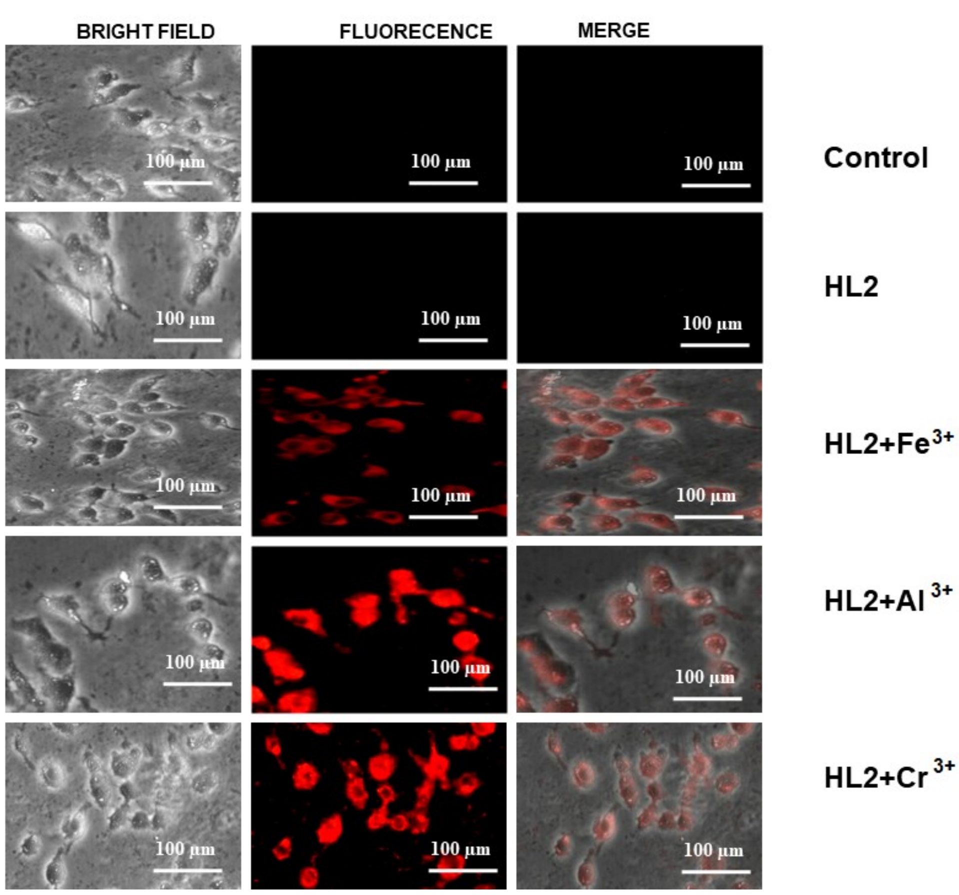
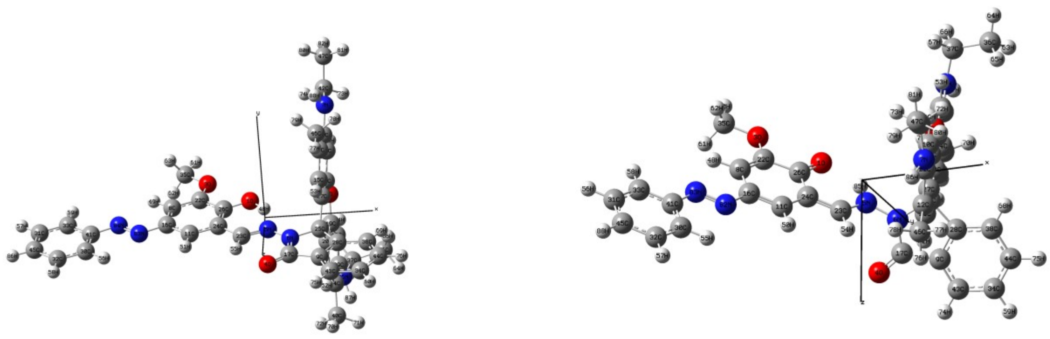
Fig. S49 Survivability of WI38 cells exposed to **HL1** and **HL2.**

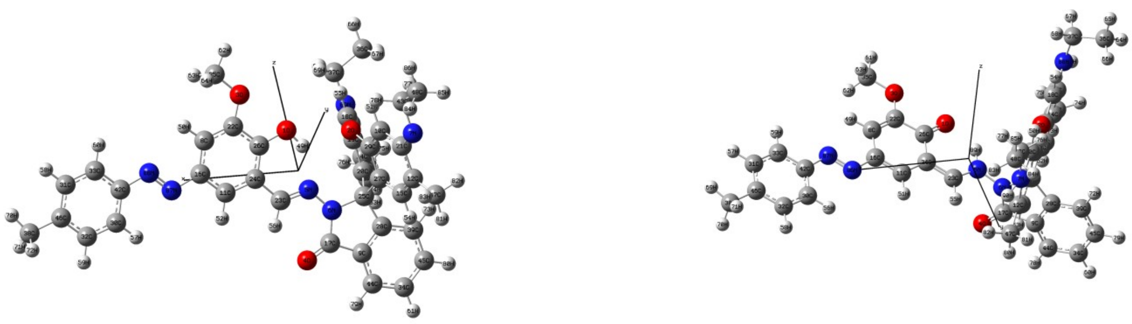


. **Fig. S50** Bright field, fluorescence and merged microscopic images of untreated HeLa (Control), cells in presence of chemosensor (**HL2**) (10μM) + M^{3+} (Al^{3+}, Cr^{3+} and Fe^{3+}) (5μM).



(Enol) (Keto)

Fig. S51(a) DFT optimized structure of **HL1 (Enol and Keto form)**



(Enol) (Keto)

Fig. S51(b) DFT optimized structure of **HL2 (Enol and Keto form)**

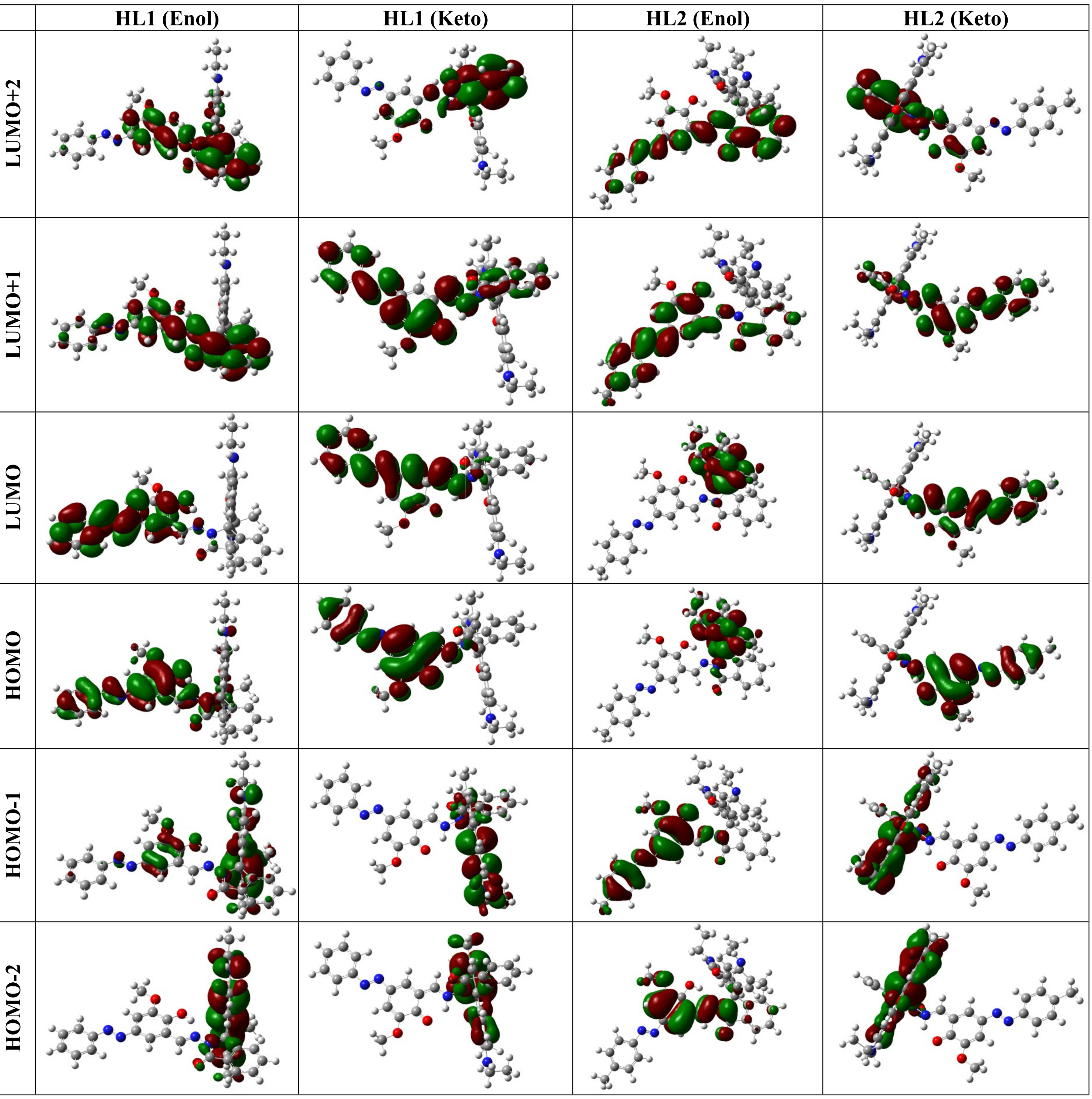
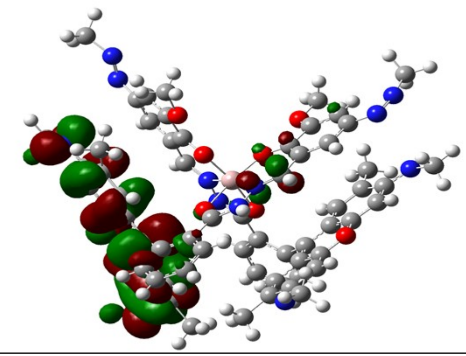
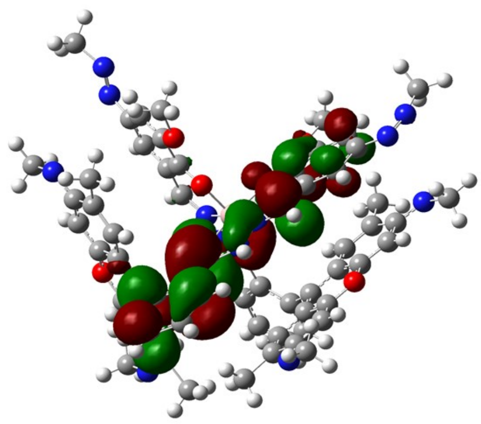
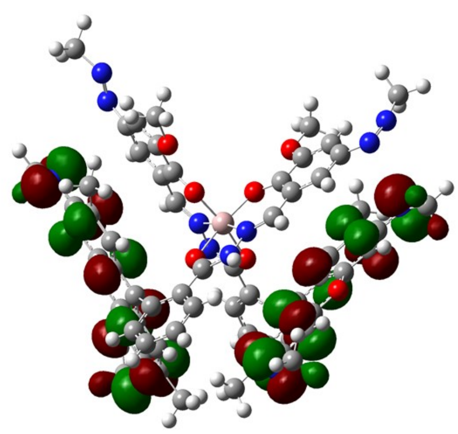
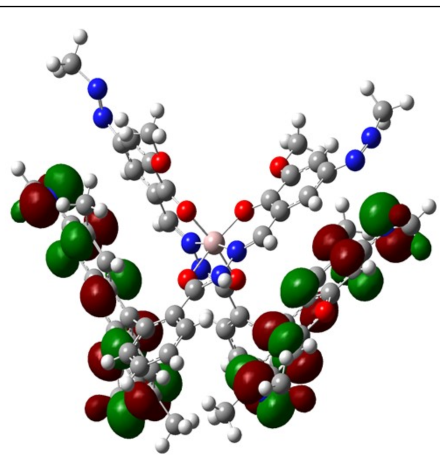


Fig. S52(b) Selected contour plots of molecular orbitals of **HL1** and **HL2**.

	Al-bound
LUMO+2	
LUMO+1	
LUMO	
HOMO	

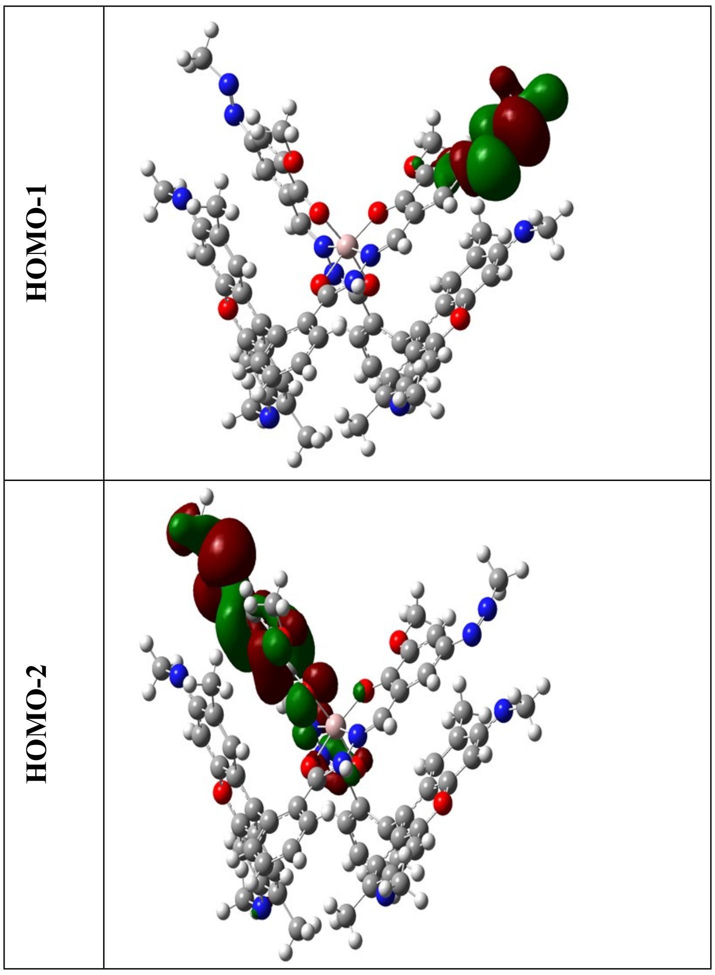


Fig. S52 (b) Selected contour plots of molecular orbitals of **Al-bound** chemosensor.

Table S1. Lifetime, quantum yield, LOD and binding constant values of chemosensors (**HL1** and **HL2**) and complexes (**1-6**).

	Lifetime (ns) ($\tau_{av.}$)	Quantum Yield (Φ)	LOD (M)	Binding Constant (M^{-1})
HL1	2.26	0.005	-	-
HL2	2.21	0.006	-	-
complex **1**	4.56	0.26	2.86×10^{-8} M	5.14×10^{5}
complex **2**	3.77	0.24	2.67×10^{-8} M	4.91×10^{5}
complex **3**	2.14	0.027	5.62×10^{-6} M	3.37×10^{4}
complex **4**	4.24	0.25	2.78×10^{-8} M	5.03×10^{5}
complex **5**	3.59	0.23	2.61×10^{-8} M	4.86×10^{5}
complex **6**	2.12	0.022	6.14×10^{-6} M	3.95×10^{4}

Table S2. Crystal parameters and selected refinement details for **HL1**, **HL2**, complex **1** and complex **4**.

sample	**HL 1**	**HL2**	complex **1**	complex **4**
CCDC	2051844	2051845	2051846	2051847
Empirical formula	$C_{42}H_{38}Cl_6N_6O_4$	$C_{42}H_{38}Cl_3N_6O_4$	$C_{89}H_{97}AlN_{17}O_{15}$	$C_{164}H_{150}Al_2N_{28}O_{36}$
Formula weight	903.48	797.13	1671.81	3143.07
Temperature (K)	273(2)	273(2)	273(2)	293(2)
Crystal system	monoclinic	triclinic	Monoclinic	triclinic
Space group	*P21/c*	*P-1*	*P21/c*	*P-1*
a (Å)	23.1315(19)	9.2184(7)	13.9132(12)	16.651(16)
b (Å)	11.7069(10)	13.4158(10)	16.3851(14)	20.317(19)
c (Å)	17.5826(15)	17.3821(13)	19.9383(17)	28.03(3)
α(°)	90	84.617(3)	92.089(3)	106.557(14)
β(°)	110.173(3)	78.146(3)	106.005(3)	94.278(18)
γ(°)	90	76.103(3)	90.341(3)	114.051(14)
Volume (Å^3)	4469.3(7)	2040.0(3)	4365.6(7)	8101(13)
Z	4	2	2	2
D_{calc} (g cm^{-3})	1.343	1.298	1.272	1.288
Absorption coefficient (mm^{-1})	0.432	0.273	0.098	0.103
F(000)	1864	830	1766	3288
θ Range for data collection (°)	1.97-27.11	1.92- 27.15	1.66-27.19	1.61-27.12
Reflections collected	9827	9010	19326	35653
Independent reflection / R_{int}	4996/0.1022	5171/0.0898	12734/0.0695	14083/0.1302
Data / restraints / parameters	9827/0/581	9010/0/500	19326/0/1072	35653/0/2132
Goodness-of-fit on F^2	1.026	1.022	1.036	1.024
Final indices[I>2σ(I)]	R1= 0.0936 wR1= 0.2212	R1= 0.1062 wR1= 0.0761	R1=0.0812 wR1= 0.2388	R1=0.0941 wR1= 0.2572
R indices (all data)	R1= 0.1700 wR2= 0.2707	R1= 0.1062 wR2= 0.3072	R1= 0.1190 wR2= 0.2844	R1= 0.2280 wR2= 0.3493
Largest diff. peak / deepest hole (e Å^{-3})	0.297/-0.369	0.957/-0.663	0.858/-0.828	1.163/-0.328

Table S3. Selected Bond lengths (Å) and Bond angles (°) for **HL1**, **HL2**, complex **1** and complex **4**.

HL1		HL2		complex **1**		complex **4**	
N4-C9	1.282(4)	**C27-N6**	1.221(4)	**Al1-O1**	1.889(2)	**Al1-O2**	1.863(4)
N4-N3	1.370(4)	**N6-N5**	1.361(5)	**Al1-O2**	1.893(2)	**Al1-O3**	1.811(4)
O2-C19	1.229(4)	**C26-N5**	1.367(2)	**Al1-O6**	1.850(2)	**Al1-O6**	1.929(4)
O3-C31	1.356(4)	**C10-N5**	1.489(3)	**Al1-O7**	1.840(2)	**Al1-O7**	1.807(4)
O5-C40	1.371(4)	**C26-O4**	1.230(4)	**Al1-N3**	1.985(2)	**Al1-N3**	1.957(4)
O5-C32	1.375(4)	**C29-O1**	1.335(4)	**Al1-N9**	1.992(2)	**Al1-N10**	2.000(4)
N3-C19	1.374(4)	**C10-C11**	1.511(5)	**O2-C11**	1.291(3)	**O6 -C67**	1.251(5)
N3-C8	1.510(4)	**C10-C6**	1.512(4)	**O1-C10**	1.290(3)	**O2- C26**	1.294(5)
N5-N6	1.241(4	**C27-N6**	1.282(6)	**N2-C11**	1.307(3)	**N9-C67**	1.334(6)
N5-C12	1.446(5)	**C14-N1**	1.382(3)	**N10-C10**	1.312(3)	**N3-C26**	1.322(5)
O7-C29	1.375(5)	**C3-N4**	1.361(4)	**N6-N7**	1.265(4)	**N11–N12**	1.265(6)
O7-C30	1.436(6)	**N4-C3**	1.371(5)	**N2-N3**	1.401(3)	**N5–N6**	1.277(6)
N1-C4	1.392(5)	**N4-C2**	1.454(6)	**O7-Al1-O1**	168.75(9	**O2–Al–O3**	170.38(15)
N6-C14	1.434(5)	**N2-N3**	1.261(5)	**O6-Al1-O2**	169.39(9)	**N4–Al–N10**	170.19(17)
N2-C36	1.446(7)	**N1-C15**	1.489(9)	**N3-Al1-N9**	167.36(10)	**O7–Al–O6**	168.23(14)
N3-C8-C100	109.9(3)	**N5-C10-C20**	99.6(3)	**O7-Al1-O6**	91.10(10)	**N4-Al1-O2**	80.43(15)
N3-C8-C7	110.5(3)	**N5-C10-C6**	109.6(3)	**O2-Al1-N9**	90.24(9)	**N4-Al1- O3**	92.43(17)
C100- C8-C7	110.6(3)	**C20-C10-C6**	111.4(3)	**O6-Al1-O1**	90.21(10)	**N10-Al1-O3**	92.15(15)
N3-C8-C25	98.7(2)	**N5-C10-C11**	111.3(3)	**O7-Al1-N3**	97.59(9)	**N10-Al1-O2**	94.01(14)
C100-C8-C25	113.8(3)	**C20-C10-C11**	114.1(3)	**O6-Al1-N3**	90.13(9)	**N10-Al1-O6**	78.87(15)
C7-C8-C25	112.7(3)	**C6-C10-C11**	110.4(3)	**O1-Al1-N3**	93.58(9)	**N10-Al1-O6**	89.78(14)
				O2-Al1-N3	79.29(9)	**N4-Al1-O6**	92.69(15)
				O7-Al1-N9	89.60(9)	**N4-Al1-O7**	98.38(17)

Electrochemical study

The electrochemical behavior of the metal bound chemosensor complexes (**1-6**) was studied in acetonitrile medium containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte in a conventional three-electrode configuration using a Pt disk working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode. All electrochemical data are collected in Table S4. Interestingly we are only able to collect data for Fe^{3+} and Cr^{3+} bound chemosensor complexes (**2**, **3**, **5** and **6**) and all the peaks are irreversible in nature. The reductive response at -0,44 V and the oxidative response at 1.26 V may be assigned to FeIII/FeII and FeIII/FeIV couple. The lowest potential cathodic response occurs near -0.59 V has been assigned to the Cr(III)/Cr(II) couple. Rest of the oxidative peaks appears in all the compounds are probably due to ligand based oxidations.

Table S4. Electrochemical Data for complexes **2**, **3**, **5** and **6**.

Complex	E_p(V)
HL1	0.33, 0.90, 1.33
HL2	0.31, 1.16, 1.33
2	0.33, 0.92, -0.59
3	0.877, 1.48, 1.26, -0.44
5	0.33, 0.95, 1.15, 1.51, -0.58
6	0.32, 0.90, 1.28, 1.49, -0.44

Table S5. Energy (eV) and composition (%) of selected M.O.s of **HL1** and **HL2**.

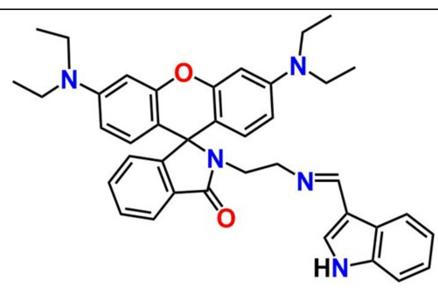
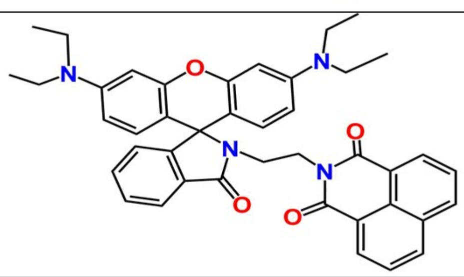
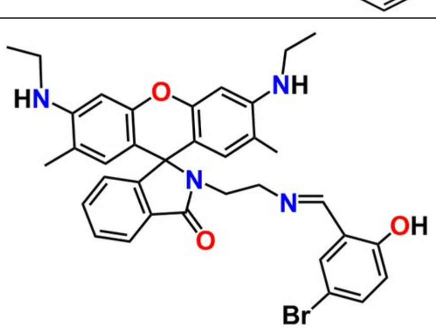
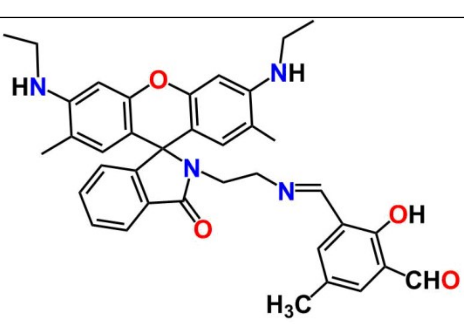
M.O.s	**HL1** Energy(eV)		**HL2** Energy(eV)	
	Enol	Keto	Enol	Keto
LUMO+5	1.48	1.35	1.12	1.37
LUMO+4	1.2	1.02	0.66	1.03
LUMO+3	1.05	0.84	0.43	0.86
LUMO+2	0.79	0.21	-0.37	0.23
LUMO+1	-0.12	-0.04	-0.6	0
LUMO	-0.53	-0.5	-3.19	-0.45
HOMO	-6.43	-6.06	-5.68	-6
HOMO-1	-6.57	-6.67	-6.55	-6.66
HOMO-2	-6.64	-6.79	-7.35	-6.78
HOMO-3	-7.18	-7.32	-7.61	-7.31
HOMO-4	-7.2	-7.42	-7.83	-7.37
HOMO-5	-7.55	-7.59	-7.84	-7.49

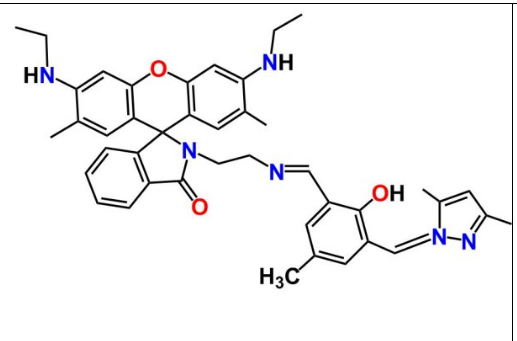
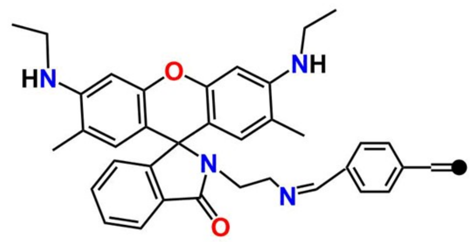
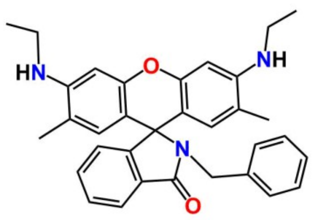
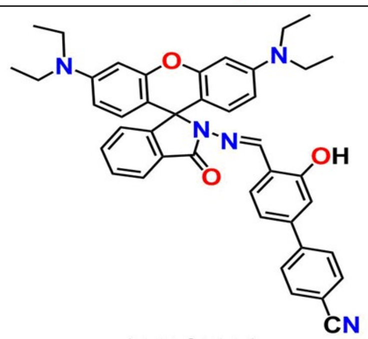
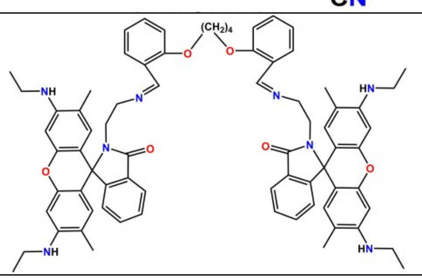
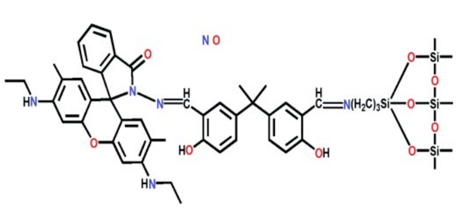
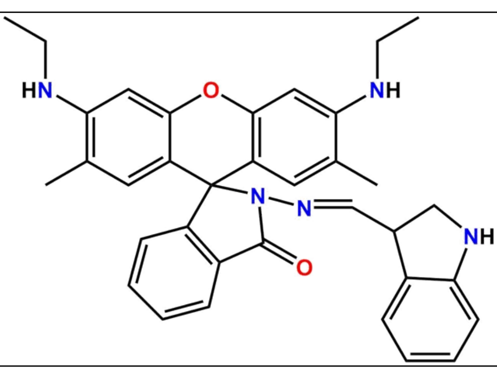
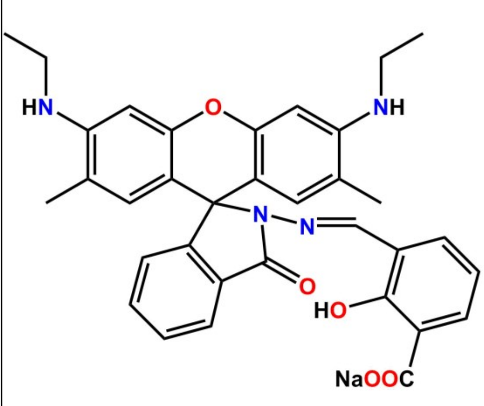
Table S6. Electronic transition calculated by TDDFT using CAM-B3LYP/CPCM method in methanol solvent of chemosensors enol form (**HL1** and **HL2**) (Used number of states = 20).

Probe	$E_{excitation}$ (ev)	$\lambda_{excitation}$ (nm)	Osc. frequency	Key transation	Experimental
HL1 (enol)	29575.75	338.1149	0.9577	HOMO-2→LUMO (89%)	360
	32361.61	309.0081	0.6827	HOMO-2→LUMO+1 (56%), HOMO→LUMO+1 (12%)	310
HL2 (enol)	29370.08	340.4826	1.0739	HOMO-2→LUMO (89%)	360
	32192.23	310.634	0.6948	HOMO-2→LUMO+1 (53%) HOMO→LUMO+1(14 %)	310
HL1 (Keto)	26710.04	374.391	0.728	HOMO-2→LUMO (83%), HOMO→LUMO+1 (10%)	360
				HOMO→LUMO (10%), HOMO→LUMO+1	360

				(80%)	
	32425.33	308.4009	0.0104	HOMO-11→LUMO+1 (11%), HOMO-9→LUMO (10%), HOMO-9→LUMO+1 (27%)	310
HL2 (Keto)	26624.55	375.5933	0.7514	HOMO→LUMO (86%)	360
	29166.02	342.8648	0.7536	HOMO→LUMO+1 (84%)	360
	32407.58	308.5698	0.0097	HOMO-11→LUMO+1 (11%) HOMO-9→LUMO (15%), HOMO-9→LUMO+1 (32%), HOMO-6→LUMO+1 (10%)	310

Chart. S1 Literature survey of rhodamine based derivatives used in sensing of Al^{3+}, Cr^{3+} and Fe^{3+} ions.

Sl. No.	Probe	Crystal structure of metal-bound chemosensor(L)	Sensing Medium	Limit of detection (LOD)	Biological study	Fluorescence intensity enhancement	Refs.
1.		No	$CH_3CN:H_2O$ (1:1, v/v)	12×10^{-6} M(Al^{3+}), 15×10^{-6} M(Cr^{3+}), 20×10^{-6} M (Fe^{3+})	No	--	**24a**
2.		No	MeOH–H_2O (6:4, v/v)	1.74×10^{-9} M (Al^{3+}), 2.36×10^{-6} M (Cr^{3+}), 2.90×10^{-6}M(Fe^{3+})	No	62 (Al^{3+}), 1.7 (Cr^{3+}), 1.47 (Fe^{3+})	**24b**
3.		No	H_2O:methanol (3:7, v/v)	1.18×10^{-9} M(Al^{3+}), 1.80×10^{-6} M (Cr^{3+}), 4.04×10^{-6}M (Fe^{3+})	No	98 (Al^{3+}), 50 (Cr^{3+}), 38 (Fe^{3+})	**24c**
4.		No	CH_3OH–H_2O, (9:1, v/v)	6.87×10^{-9} M (Al^{3+}), 15.8×10^{-6} M (Cr^{3+}), 14.0×10^{-6} M (Fe^{3+})	Yes	1465 (Al^{3+}), 588 (Cr^{3+}), 800 (Fe^{3+})	**24d**

5.		No	methanol/H_2O (1 : 1, v/v, pH 7.2)	0.34×10^{-6} M (Al^{3+}), 0.29×10^{-6} M (Cr^{3+}), 0.31×10^{-6} M (Fe^{3+})	Yes	14 (Al^{3+}), 10 (Cr^{3+}), 21 (Fe^{3+})	**24e**
6.		No	water/ethanol (14:1, v/v)	23.5×10^{-9} M (Al^{3+}), 13.4×10^{-9} M (Cr^{3+}), 69.7×10^{-9} M (Fe^{3+})	NO	145 (Al^{3+}), 174 (Cr^{3+}), 30 (Fe^{3+})	**24f**
7.		No	H2O/CH_3CN (4:1),v/v	1.34×10^{-6} M (Al^{3+}), 2.28×10^{-6} M (Cr^{3+}), 1.28×10^{-6} M (Fe^{3+})	Yes	31 (Al^{3+}), 26 (Cr^{3+}), 41 (Fe^{3+})	**24g**
8.		No	HEPES-buffered MeOH/H_2O	1.61×10^{-7} M (Al^{3+}), 8.91×10^{-8} M (Cr^{3+}), 8.74×10^{-8} M (Fe^{3+})	No	**--**	**24h**
9.		No	H_2O/CH_3CN (7:3, v/v, pH 7.2, 20 mM HEPES buffer)	0.74×10^{-6} M (Al^{3+}), 0.47×10^{-6} M (Cr^{3+}), 2.57×10^{-6} M (Fe^{3+})	No	653 (Al^{3+}), 667 (Cr^{3+}), 669 (Fe^{3+})	**24i**
10.		No	EtOH water/acetonitrile (14 : 1, v/v) (pH 7.2, 10 mM HEPES buffer)	3.79×10^{-7} M (Al^{3+}), 14.8×10^{-7} M (Cr^{3+}), 3.29×10^{-7} M (Fe^{3+}) 0.74×10^{-7} M (Cu^{2+})	No	36 (Al^{3+}), 17 (Cr^{3+}), 40 (Fe^{3+}), 89 (Cu^{2+})	**24j**
11		No	aqueous medium	24×10^{-9} M (Al^{3+}), 27×10^{-9} M (Cr^{3+}),	No	--	**24k**
12.		Yes	H_2O–EtOH (4 : 1, v/v)	3.26×10^{-6} M(Al^{3+})	Yes	--	**24l**

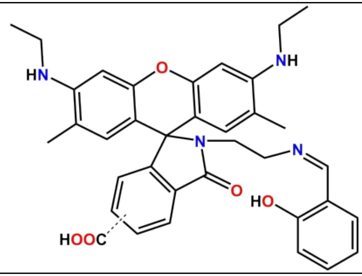
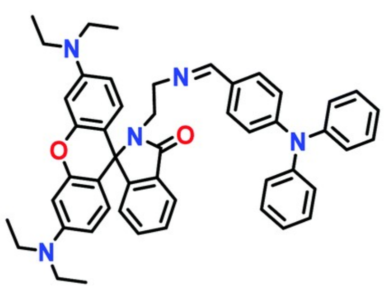
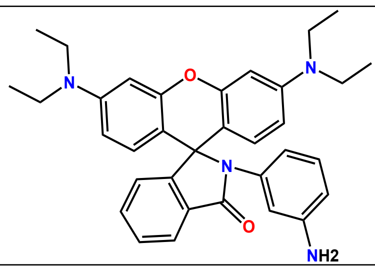
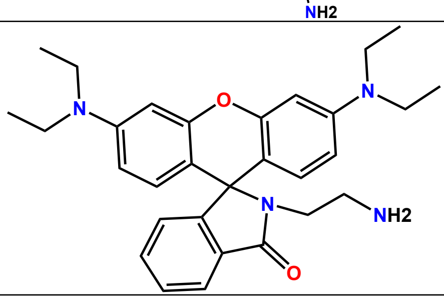
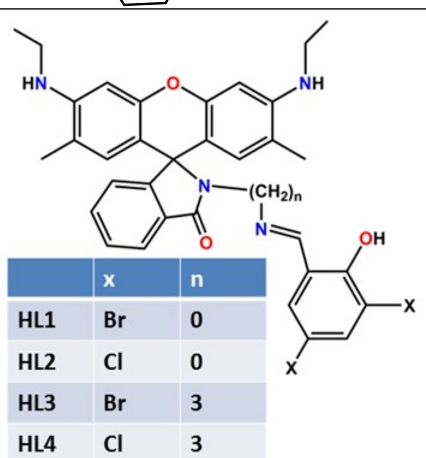
13.		No	Water, 10 mM with Tris–HCl buffer solution (pH = 7.4).	5.2×10^{-6} M (Fe^{3+})	Yes	>200 (Fe^{3+})	**24m**
14.		No	MeOH/H_2O (1/4, v/v), HEPES buffer (10 mM), pH 7.2	6.7×10^{-8} M (Al^{3+}),	Yes	--	**24n**
15.		No	MeOH/H2O (1 : 1, v/v, HEPES, 0.5 mM, pH = 7.35	0.314×10^{-6} M (Al^{3+})	Yes	---	**24o**
16.		No	Ethanol	40×10^{-6} M (Fe^{3+})	No	--	**24p**
17.		No	water:methanol (9:1, v/v)	~10^{-9} M(Al^{3+})	Yes	780(HL1)(Al^{3+}) 725(HL2)(Al^{3+}) 425(HL3)(Al^{3+}) 391(HL4)(Al^{3+})	**24q**
18.	**HL1**	Yes	water:methanol (1:9, v/v)	2.86×10^{-8} M (Al^{3+}), 2.67×10^{-8} M (Cr^{3+}), 5.62×10^{-6} M (Fe^{3+})	Yes	400 (Al^{3+}), 380 (Cr^{3+}), 100 (Fe^{3+})	**This work**
19.	**HL2**	Yes	water:methanol (1:9, v/v)	2.78×10^{-8} M (Al^{3+}), 2.61×10^{-8} M (Cr^{3+}), 6.14×10^{-6} M (Fe^{3+})	Yes	396 (Al^{3+}), 390 (Cr^{3+}), 100 (Fe^{3+})	**This work**

Table S7 Cartesian Coordinates of the optimized species

Keto form of HL1

8	-0.588775000	-2.798812000	0.192668000
8	2.763804000	0.528391000	-1.963802000
8	-2.678875000	-4.190594000	-0.648359000
8	0.847358000	-0.263225000	4.000223000
7	0.445381000	-0.651282000	1.216528000
7	1.470673000	0.044889000	1.790706000
7	0.677508000	4.769993000	-2.414346000
6	-4.134003000	-2.332722000	-0.154429000
6	2.931707000	0.821945000	3.338158000
6	1.721259000	2.599925000	-2.152542000
6	-3.185990000	-0.300321000	0.786124000
6	1.028186000	3.862045000	-0.201955000
6	3.792681000	-1.657929000	0.783442000
6	4.352748000	-2.709849000	0.088996000
6	1.516615000	2.839026000	0.584078000
6	-4.275245000	-0.990283000	0.346244000
6	1.631487000	0.130956000	3.165097000
6	3.835985000	-1.535795000	-1.967284000
6	3.267902000	-0.504614000	-1.225185000
6	3.237069000	-0.531984000	0.161266000
6	1.132330000	3.739342000	-1.612780000
6	-2.921317000	-2.938966000	-0.201119000
6	-0.794700000	-0.180475000	1.218398000
6	-1.891840000	-0.892664000	0.752680000
6	2.596495000	0.574848000	0.971114000
6	-1.701948000	-2.247110000	0.247922000
6	2.113479000	1.683505000	0.061686000
6	3.492643000	1.079858000	2.095237000
6	2.204350000	1.593164000	-1.318879000
6	-7.881450000	1.015664000	0.593604000

6	-10.101850000	-0.386320000	-0.348240000
6	-9.139274000	1.597210000	0.625735000
6	-8.843133000	-0.973501000	-0.381940000
6	4.789811000	1.826841000	4.429260000
6	-3.783874000	-4.938110000	-1.099077000
6	6.377796000	-2.850097000	-3.861074000
6	5.163629000	-3.688505000	-3.460153000
6	4.717477000	1.722320000	2.000859000
6	4.375622000	-2.651268000	-1.330379000
6	4.910671000	-3.907270000	0.809014000
6	-7.729807000	-0.278066000	0.086220000
6	0.548610000	4.623592000	-3.851065000
6	3.560720000	1.185535000	4.520202000
6	5.358878000	2.091279000	3.179974000
6	-10.252485000	0.900816000	0.155798000
6	0.411305000	5.091369000	0.408001000
6	-0.052623000	5.882104000	-4.457498000
1	-5.038043000	-2.825863000	-0.485662000
1	1.816460000	2.457316000	-3.220989000
1	-3.320823000	0.708325000	1.164494000
1	3.776898000	-1.708308000	1.869208000
1	1.440034000	2.935569000	1.664298000
1	3.827647000	-1.439281000	-3.045089000
1	-0.913514000	0.823137000	1.616324000
1	-7.004673000	1.539570000	0.954623000
1	-10.964935000	-0.933555000	-0.714573000
1	-9.257445000	2.601870000	1.020840000
1	-8.694974000	-1.976310000	-0.768629000
1	5.313864000	2.126354000	5.331194000
1	-3.390627000	-5.906463000	-1.409986000
1	-4.522460000	-5.082557000	-0.300472000

1	-4.275528000	-4.452310000	-1.951498000
1	7.289444000	-3.244003000	-3.400338000
1	6.514525000	-2.861719000	-4.947242000
1	6.261920000	-1.810841000	-3.541502000
1	5.304041000	-4.725219000	-3.781482000
1	4.266011000	-3.333415000	-3.975866000
1	5.164162000	1.931071000	1.033968000
1	4.777789000	-3.807533000	1.888580000
1	5.986344000	-4.037885000	0.626691000
1	4.411138000	-4.832927000	0.498141000
1	1.543845000	4.451570000	-4.276556000
1	-0.064251000	3.746614000	-4.112995000
1	3.094034000	0.967674000	5.475205000
1	6.319732000	2.594163000	3.128736000
1	0.468862000	5.055709000	1.498375000
1	0.920159000	6.003916000	0.075077000
1	-0.650232000	5.197931000	0.144759000
1	-1.061495000	6.063983000	-4.070195000
1	0.565020000	6.755769000	-4.229862000
1	-0.127941000	5.786705000	-5.543701000
7	-5.504957000	-0.320611000	0.416776000
7	-6.493437000	-0.971048000	0.005454000
7	4.894742000	-3.716788000	-2.036111000
1	0.564982000	-1.620265000	0.882833000
1	-0.028109000	5.355560000	-1.991657000
1	5.465633000	-4.352620000	-1.501842000
1	-11.234447000	1.363145000	0.184854000

Enol form of HL1

8	-0.698463000	0.297496000	-1.533754000
8	2.980093000	0.353667000	-1.632892000

8	-2.674739000	0.651882000	-3.179687000
8	0.146769000	-0.901287000	3.798452000
7	0.144458000	-0.253306000	0.904930000
7	1.178416000	-0.434072000	1.765415000
7	3.139943000	5.033678000	-0.836766000
6	-4.309726000	0.232852000	-1.437998000
6	2.559744000	-0.800649000	3.532945000
6	3.036076000	2.642248000	-1.213947000
6	-3.485985000	-0.268195000	0.776757000
6	2.821966000	3.531796000	1.030548000
6	2.805262000	-2.681359000	0.398300000
6	2.968007000	-3.654846000	-0.565847000
6	2.704586000	2.236965000	1.491310000
6	-4.547497000	-0.080960000	-0.085776000
6	1.141266000	-0.732433000	3.112207000
6	3.137543000	-1.892113000	-2.218784000
6	2.961041000	-0.945712000	-1.213030000
6	2.795965000	-1.310186000	0.114681000
6	2.990089000	3.741901000	-0.363022000
6	-3.019565000	0.354243000	-1.902699000
6	-1.081580000	-0.355620000	1.282870000
6	-2.163364000	-0.149589000	0.326875000
6	2.555348000	-0.282630000	1.198963000
6	-1.921541000	0.164278000	-1.021633000
6	2.748265000	1.115545000	0.652860000
6	3.381192000	-0.544094000	2.446626000
6	2.917556000	1.351801000	-0.702684000
6	-8.308004000	-0.506818000	1.594957000
6	-10.450158000	-0.114428000	-0.150185000
6	-9.611090000	-0.623750000	2.052236000
6	-9.145452000	0.003809000	-0.613385000

6	4.449709000	-1.080618000	4.946872000
6	-3.718779000	0.844604000	-4.105518000
6	5.131679000	-3.583801000	-4.429396000
6	3.653610000	-3.936678000	-4.259954000
6	4.759550000	-0.551357000	2.593740000
6	3.135880000	-3.251549000	-1.917039000
6	2.948467000	-5.115890000	-0.205834000
6	-8.072661000	-0.190989000	0.253943000
6	3.082667000	5.337352000	-2.253393000
6	3.068793000	-1.072036000	4.795068000
6	5.283677000	-0.822228000	3.854668000
6	-10.684909000	-0.428499000	1.183719000
6	2.781786000	4.703239000	1.973885000
6	3.182010000	6.838742000	-2.474928000
1	-0.048643000	0.135849000	-0.806037000
1	-5.166614000	0.371902000	-2.082782000
1	3.154819000	2.750676000	-2.283977000
1	-3.692231000	-0.509320000	1.814350000
1	2.669988000	-2.996145000	1.429693000
1	2.570748000	2.079260000	2.558248000
1	3.266003000	-1.528223000	-3.229804000
1	-1.343227000	-0.593262000	2.309509000
1	-7.460106000	-0.654509000	2.252843000
1	-11.282634000	0.038437000	-0.829910000
1	-9.795733000	-0.869079000	3.093777000
1	-8.930481000	0.247668000	-1.648465000
1	4.887707000	-1.288518000	5.917908000
1	-3.239572000	1.065712000	-5.059724000
1	-4.336699000	-0.056031000	-4.209186000
1	-4.362177000	1.685737000	-3.818451000
1	5.767635000	-4.414301000	-4.105902000

1	5.361000000	-3.370437000	-5.478458000
1	5.397796000	-2.705389000	-3.835173000
1	3.411163000	-4.821421000	-4.857083000
1	3.021304000	-3.131336000	-4.646019000
1	5.410964000	-0.350931000	1.749157000
1	2.764194000	-5.249558000	0.862575000
1	3.901650000	-5.613341000	-0.433011000
1	2.162596000	-5.655516000	-0.748525000
1	3.920681000	4.838142000	-2.753047000
1	2.161157000	4.946229000	-2.712876000
1	2.396095000	-1.268415000	5.623383000
1	6.360461000	-0.832831000	3.993197000
1	2.712898000	4.365489000	3.010501000
1	3.679990000	5.325685000	1.881906000
1	1.915581000	5.353879000	1.789922000
1	2.340199000	7.363227000	-2.008710000
1	4.109440000	7.233157000	-2.049502000
1	3.165887000	7.071618000	-3.542777000
7	-5.834493000	-0.222313000	0.472913000
7	-6.782418000	-0.046037000	-0.322407000
7	3.252270000	-4.220868000	-2.895885000
1	-11.702720000	-0.521951000	1.549912000
1	3.508198000	-5.136572000	-2.560264000
1	2.737667000	5.746682000	-0.245441000

Enol form of HL2

8	-0.349098000	0.316519000	-1.523356000
8	3.128755000	0.350253000	-1.613203000
8	-2.275985000	0.708991000	-3.223801000
8	0.385547000	-0.927651000	3.800485000

7	0.412940000	-0.256317000	0.918738000
7	1.437275000	-0.452679000	1.783308000
7	3.462836000	5.013402000	-0.768225000
6	-3.967735000	0.297992000	-1.532992000
6	2.804659000	-0.855141000	3.552104000
6	3.267500000	2.633827000	-1.170099000
6	-3.212337000	-0.227868000	0.702128000
6	3.181342000	3.499348000	1.095140000
6	3.089697000	-2.705420000	0.398874000
6	3.232877000	-3.669668000	-0.578159000
6	3.051921000	2.201253000	1.544354000
6	-4.246526000	-0.022017000	-0.190651000
6	1.392109000	-0.764319000	3.123991000
6	3.306275000	-1.890715000	-2.224375000
6	3.153219000	-0.955860000	-1.204098000
6	3.045910000	-1.331002000	0.126699000
6	3.292515000	3.725867000	-0.304007000
6	-2.661767000	0.406724000	-1.960096000
6	-0.820740000	-0.348591000	1.272487000
6	-1.876411000	-0.122723000	0.289945000
6	2.822197000	-0.312620000	1.222477000
6	-1.595261000	0.196395000	-1.048483000
6	3.028731000	1.088601000	0.690708000
6	3.635853000	-0.598429000	2.471706000
6	3.139536000	1.340488000	-0.668233000
6	-8.077008000	-0.412539000	1.376426000
6	-10.149197000	0.003875000	-0.434380000
6	-9.394959000	-0.514833000	1.784457000
6	-8.828254000	0.109266000	-0.854962000
6	4.685093000	-1.174855000	4.972288000
6	-3.293563000	0.934031000	-4.183602000

6	5.272530000	-3.544874000	-4.494176000
6	3.802057000	-3.910817000	-4.297146000
6	-11.880959000	-0.432765000	1.355321000
6	5.013395000	-0.625650000	2.625103000
6	3.341683000	-3.254986000	-1.934396000
6	3.261006000	-5.132785000	-0.226225000
6	-7.785321000	-0.097383000	0.044126000
6	3.354075000	5.341922000	-2.179011000
6	3.304862000	-1.146285000	4.814322000
6	5.527850000	-0.916571000	3.886285000
6	-10.454604000	-0.309759000	0.889108000
6	3.217005000	4.658064000	2.054571000
6	3.500132000	6.841394000	-2.384993000
1	-4.799613000	0.453197000	-2.206015000
1	3.346481000	2.756735000	-2.242578000
1	-3.447549000	-0.472998000	1.732526000
1	3.001598000	-3.031656000	1.431729000
1	2.964530000	2.034764000	2.614635000
1	3.397151000	-1.520070000	-3.237302000
1	-1.109293000	-0.591220000	2.290040000
1	-7.262186000	-0.571786000	2.072547000
1	-10.953651000	0.168211000	-1.145242000
1	-9.615984000	-0.758628000	2.820167000
1	-8.586036000	0.353615000	-1.884131000
1	5.115198000	-1.398550000	5.942869000
1	-2.781300000	1.158903000	-5.118702000
1	-3.919792000	0.044820000	-4.315724000
1	-3.926245000	1.782757000	-3.901179000
1	5.919533000	-4.370737000	-4.182240000
1	5.475750000	-3.331859000	-5.548378000
1	5.543822000	-2.661360000	-3.909307000

1	3.557264000	-4.795387000	-4.891747000
1	3.154941000	-3.108700000	-4.664667000
1	-12.584351000	-0.174776000	0.559866000
1	-12.101874000	-1.454912000	1.681683000
1	-12.076347000	0.225254000	2.208405000
1	5.673902000	-0.426212000	1.787497000
1	3.121043000	-5.275036000	0.847686000
1	4.215178000	-5.603852000	-0.496200000
1	2.469815000	-5.689116000	-0.743295000
1	4.146219000	4.817722000	-2.725294000
1	2.396761000	4.994038000	-2.596626000
1	2.631850000	-1.343379000	5.642106000
1	6.603316000	-0.943362000	4.029505000
1	3.174385000	4.307792000	3.088331000
1	4.132283000	5.250229000	1.936608000
1	2.370976000	5.341908000	1.906529000
1	2.702479000	7.389201000	-1.871823000
1	4.461428000	7.195062000	-2.000729000
1	3.443180000	7.085673000	-3.448743000
7	-5.551871000	-0.153230000	0.333646000
7	-6.476847000	0.035039000	-0.486399000
7	3.434631000	-4.211586000	-2.923331000
1	3.131971000	5.738088000	-0.146604000
1	3.719617000	-5.127033000	-2.607495000
1	0.270713000	0.141921000	-0.769091000

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8	-0.251303000	-2.842351000	0.192796000
8	3.025778000	0.572006000	-1.959496000
8	-2.301150000	-4.289584000	-0.653587000
8	1.105694000	-0.263589000	3.999671000

7	0.722668000	-0.666752000	1.215023000
7	1.727485000	0.056897000	1.791416000
7	0.825605000	4.754341000	-2.424252000
6	-3.806301000	-2.469619000	-0.167653000
6	3.162166000	0.875894000	3.342040000
6	1.927252000	2.613802000	-2.155407000
6	-2.915907000	-0.411458000	0.771966000
6	1.188107000	3.856878000	-0.209526000
6	4.094185000	-1.586443000	0.794643000
6	4.683713000	-2.624599000	0.103858000
6	1.700213000	2.848118000	0.579862000
6	-3.984932000	-1.130488000	0.330039000
6	1.881472000	0.149899000	3.166052000
6	4.149113000	-1.464729000	-1.955845000
6	3.551533000	-0.447653000	-1.217429000
6	3.513932000	-0.475054000	0.168825000
6	1.303936000	3.736649000	-1.619611000
6	-2.577941000	-3.043895000	-0.209096000
6	-0.529642000	-0.228322000	1.211758000
6	-1.606014000	-0.969726000	0.744173000
6	2.841189000	0.615590000	0.974562000
6	-1.378816000	-2.319658000	0.242994000
6	2.331926000	1.709462000	0.061526000
6	3.719934000	1.146524000	2.100437000
6	2.433301000	1.621138000	-1.318423000
6	-7.651088000	0.775565000	0.556782000
6	-9.825265000	-0.684868000	-0.375944000
6	-8.923246000	1.318221000	0.583088000
6	-8.551445000	-1.239623000	-0.406475000
6	4.988892000	1.932891000	4.436984000
6	-3.384331000	-5.065825000	-1.108334000

6	6.729904000	-2.719531000	-3.837881000
6	5.534519000	-3.586241000	-3.440676000
6	-11.410352000	1.209037000	0.164953000
6	4.927229000	1.821720000	2.008615000
6	4.712475000	-2.566348000	-1.315402000
6	5.267048000	-3.807592000	0.827558000
6	-7.456663000	-0.516725000	0.057554000
6	0.709750000	4.604149000	-3.861659000
6	3.777292000	1.258743000	4.525310000
6	5.554625000	2.210226000	3.188985000
6	-10.033114000	0.600510000	0.119038000
6	0.533718000	5.068782000	0.396187000
6	0.080734000	5.846735000	-4.472711000
1	-4.696017000	-2.986847000	-0.501010000
1	2.032221000	2.473342000	-3.223221000
1	-3.078402000	0.594039000	1.147889000
1	4.073832000	-1.636696000	1.880343000
1	1.614835000	2.942886000	1.659578000
1	4.144239000	-1.368867000	-3.033732000
1	-0.675821000	0.772765000	1.606957000
1	-6.792767000	1.330371000	0.916278000
1	-10.671168000	-1.260186000	-0.741913000
1	-9.067494000	2.323107000	0.972526000
1	-8.381502000	-2.240313000	-0.789887000
1	5.501712000	2.248248000	5.339979000
1	-2.964715000	-6.023803000	-1.417004000
1	-4.122343000	-5.229190000	-0.312820000
1	-3.884992000	-4.593542000	-1.963120000
1	7.648924000	-3.091157000	-3.373298000
1	6.870996000	-2.728862000	-4.923519000
1	6.588041000	-1.683062000	-3.519769000

1	5.700781000	-4.619625000	-3.760415000
1	4.630678000	-3.253003000	-3.960120000
1	-12.152535000	0.551642000	-0.295581000
1	-11.727362000	1.397961000	1.196770000
1	-11.439966000	2.169197000	-0.361383000
1	5.371175000	2.040660000	1.042706000
1	5.125844000	-3.710733000	1.906327000
1	6.346583000	-3.911735000	0.651114000
1	4.792099000	-4.745351000	0.514446000
1	1.711823000	4.457423000	-4.280494000
1	0.121212000	3.711732000	-4.127271000
1	3.313547000	1.030235000	5.479260000
1	6.501638000	2.738912000	3.139756000
1	0.586225000	5.035291000	1.486886000
1	1.018674000	5.995026000	0.065431000
1	-0.528926000	5.145440000	0.127056000
1	-0.934890000	6.003246000	-4.091995000
1	0.674582000	6.735853000	-4.241624000
1	0.014797000	5.748954000	-5.559319000
7	-5.233220000	-0.494024000	0.395349000
7	-6.201933000	-1.172904000	-0.017433000
7	5.260871000	-3.619441000	-2.017698000
1	0.868173000	-1.633268000	0.884523000
1	0.100635000	5.319288000	-2.006230000
1	5.844530000	-4.240882000	-1.480303000

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13	0.175007000	0.571681000	-0.219133000
8	-0.988574000	-0.892804000	0.637186000
8	1.271814000	-0.853452000	-0.862249000
8	1.479004000	1.873363000	-0.525252000

8	-1.157555000	1.792728000	0.205411000
8	4.938979000	-1.011506000	1.240823000
7	0.901543000	0.459738000	1.698317000
7	-0.623286000	0.319021000	-2.018819000
8	-5.141738000	-0.863994000	-0.927831000
7	0.248520000	-0.495938000	2.473785000
7	-0.008081000	-0.684334000	-2.798430000
8	-2.633831000	3.650722000	1.413860000
8	3.008807000	3.679610000	-1.760378000
7	5.395370000	4.446376000	2.538508000
7	5.737465000	5.665072000	2.558542000
6	-0.740512000	-1.193805000	1.848304000
7	7.005517000	2.260271000	-1.637306000
6	1.851205000	1.180945000	2.249418000
1	2.100568000	1.000954000	3.297198000
6	2.600500000	2.192299000	1.579493000
7	2.662024000	-4.027750000	4.234141000
6	0.969807000	-1.245618000	-2.094979000
6	3.628766000	-2.190798000	-0.982268000
6	-1.458978000	-2.239050000	2.602240000
7	-5.336136000	4.050906000	-2.711535000
6	3.447364000	-2.719082000	0.311316000
6	4.491279000	-1.080634000	-1.167800000
6	2.957257000	-2.819809000	-2.165722000
6	1.729836000	-2.358827000	-2.704030000
6	4.345671000	3.884341000	1.721778000
6	5.152089000	-0.494852000	-0.039246000
6	-2.131374000	2.336008000	-0.502451000
6	2.380581000	2.489951000	0.193813000
6	-2.403026000	1.966129000	-1.858850000
6	-1.638023000	0.956283000	-2.540952000

1	-1.928537000	0.686340000	-3.555402000
6	2.611082000	-3.846855000	0.601569000
1	2.140826000	-4.352004000	-0.233981000
6	2.384792000	-4.301660000	1.876182000
6	4.087867000	-2.095942000	1.436649000
6	-0.796956000	-2.914766000	3.648165000
1	0.256186000	-2.738850000	3.842801000
6	4.159246000	4.174062000	0.338979000
1	4.795432000	4.906800000	-0.137700000
6	1.203678000	-2.986794000	-3.850519000
1	0.264837000	-2.618307000	-4.245080000
7	-6.152518000	4.818451000	-2.104996000
6	-2.798266000	-2.582967000	2.281125000
6	2.993607000	-3.606555000	3.017361000
7	-6.747109000	2.598455000	2.023005000
6	3.605036000	2.876391000	2.311041000
1	3.805697000	2.616442000	3.345282000
6	3.220691000	3.488378000	-0.411029000
6	-3.577835000	-1.959847000	1.161769000
6	1.863815000	-4.055743000	-4.454527000
1	1.436382000	-4.527403000	-5.333128000
6	6.234118000	1.192863000	-1.429437000
7	-3.433911000	-4.166130000	-4.002926000
6	4.751238000	-0.481133000	-2.440418000
1	4.266135000	-0.907552000	-3.310246000
6	-2.963270000	3.336798000	0.105587000
6	3.884213000	-2.507775000	2.726000000
1	4.401166000	-1.984909000	3.520236000
6	-4.384924000	-0.826808000	1.404294000
6	-4.268859000	3.527318000	-1.934059000
6	5.994524000	0.578728000	-0.147885000

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6	3.072593000	-4.518024000	-3.920668000
1	3.594404000	-5.350910000	-4.380797000
6	-3.471780000	2.577058000	-2.553327000
1	-3.693712000	2.299995000	-3.578313000
6	3.610268000	-3.899181000	-2.789533000
1	4.553220000	-4.247150000	-2.379536000
6	-2.751663000	-3.684721000	-0.467086000
1	-2.143312000	-4.132832000	0.309972000
6	-1.448842000	-3.895304000	4.395517000
1	-0.908731000	-4.416725000	5.177543000
6	-5.172348000	-0.273886000	0.336348000
6	-4.001983000	3.916603000	-0.596023000
1	-4.636959000	4.672640000	-0.155084000
6	1.535367000	-5.516302000	2.136501000
1	1.150680000	-5.932688000	1.200437000
1	0.691892000	-5.280654000	2.792897000
1	2.114087000	-6.289495000	2.654872000
6	-2.779395000	-4.212980000	4.106387000
1	-3.298538000	-4.972260000	4.681595000
6	-2.712450000	-4.215047000	-1.733512000
6	-4.478002000	-0.164609000	2.672292000
1	-3.905702000	-0.567280000	3.500559000
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6	-3.517865000	-3.612011000	-2.798320000
6	7.741073000	2.845398000	-0.511838000
1	8.439409000	2.125551000	-0.058002000
1	7.077815000	3.200322000	0.291196000
6	-5.251873000	0.950720000	2.876722000

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1	-4.946328000	-1.982835000	-3.200084000
6	3.283718000	-3.393898000	5.401340000
1	3.085176000	-2.310029000	5.459433000
1	2.885453000	-3.858329000	6.306284000
6	-1.845495000	-5.398713000	-2.064138000
1	-1.352336000	-5.787390000	-1.167684000
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1	-7.003947000	3.679329000	0.198698000
6	5.823971000	1.209610000	-3.954158000
1	5.310287000	0.640782000	-4.734609000
1	6.895311000	1.240163000	-4.178849000
1	5.475661000	2.247384000	-3.993097000
6	3.908074000	4.565951000	-2.482431000
1	3.829960000	5.596680000	-2.114592000
1	3.571182000	4.522476000	-3.517053000
1	4.944420000	4.215477000	-2.407831000
6	-5.325921000	1.617505000	4.223143000
1	-4.722082000	1.080950000	4.961528000

1	-6.360837000	1.669172000	4.577609000
1	-4.974778000	2.653371000	4.166697000
6	-4.210189000	-3.603213000	-5.110085000
1	-5.293833000	-3.624184000	-4.914437000
1	-3.936306000	-2.557501000	-5.320184000
1	0.477694000	-0.605232000	3.452706000
6	4.991569000	6.723199000	1.800298000
1	5.551367000	6.974232000	0.891681000
1	3.962396000	6.457258000	1.536493000
1	4.999847000	7.604306000	2.445483000
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1	-7.171160000	6.429402000	-2.975260000
1	-8.245791000	3.926441000	1.438960000
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1	4.377716000	-3.518684000	5.408697000
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