Supplementary information

A highly selective and dual responsive test paper sensor of Hg^{2+}/Cr^{3+} for naked eye detection in neutral water

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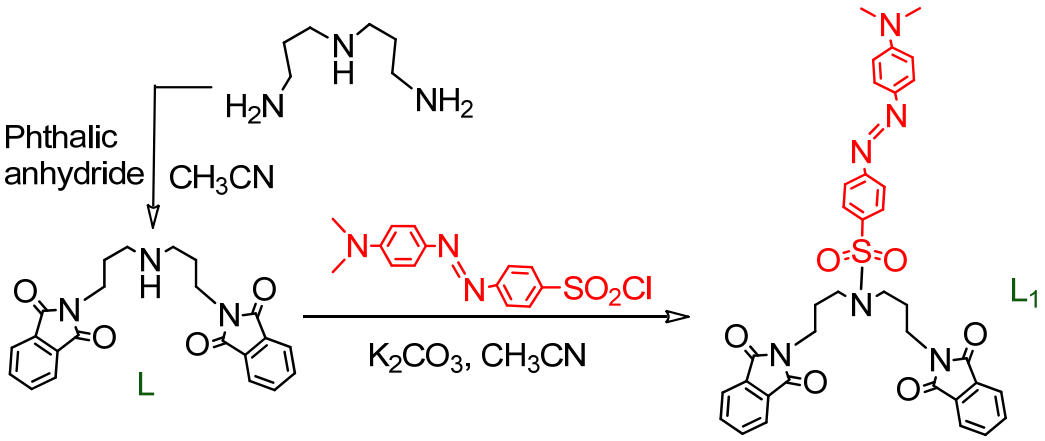
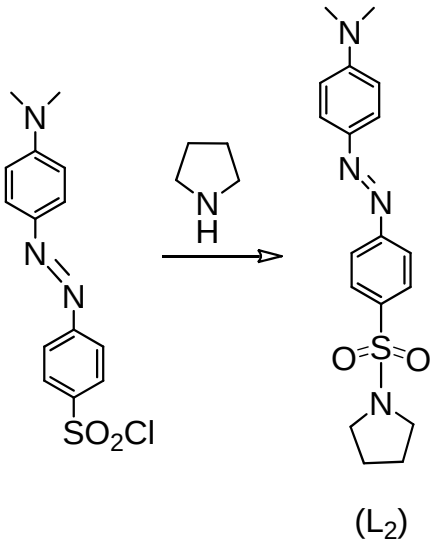
Synthetic Scheame-1

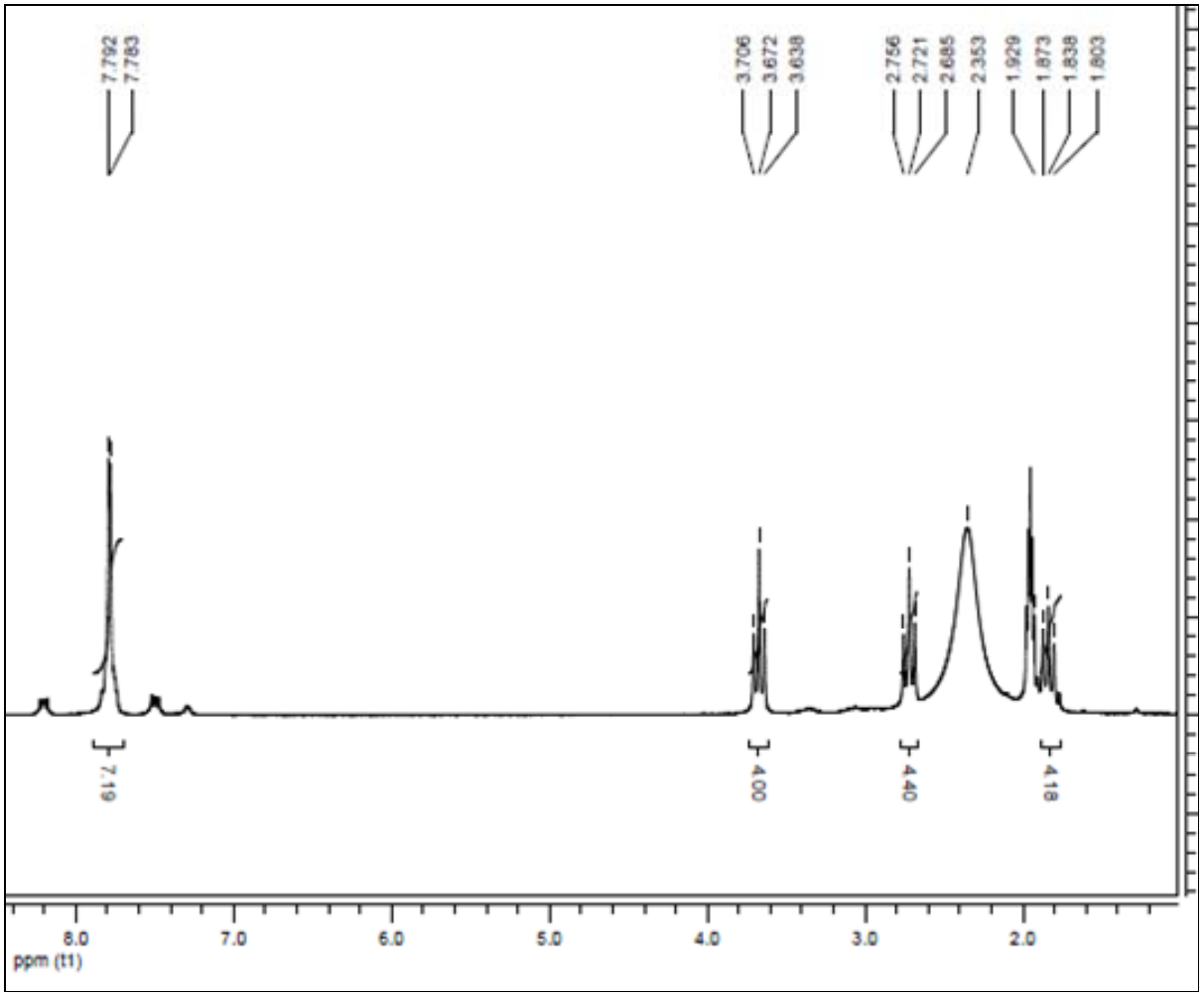


Synthetic Scheame-2



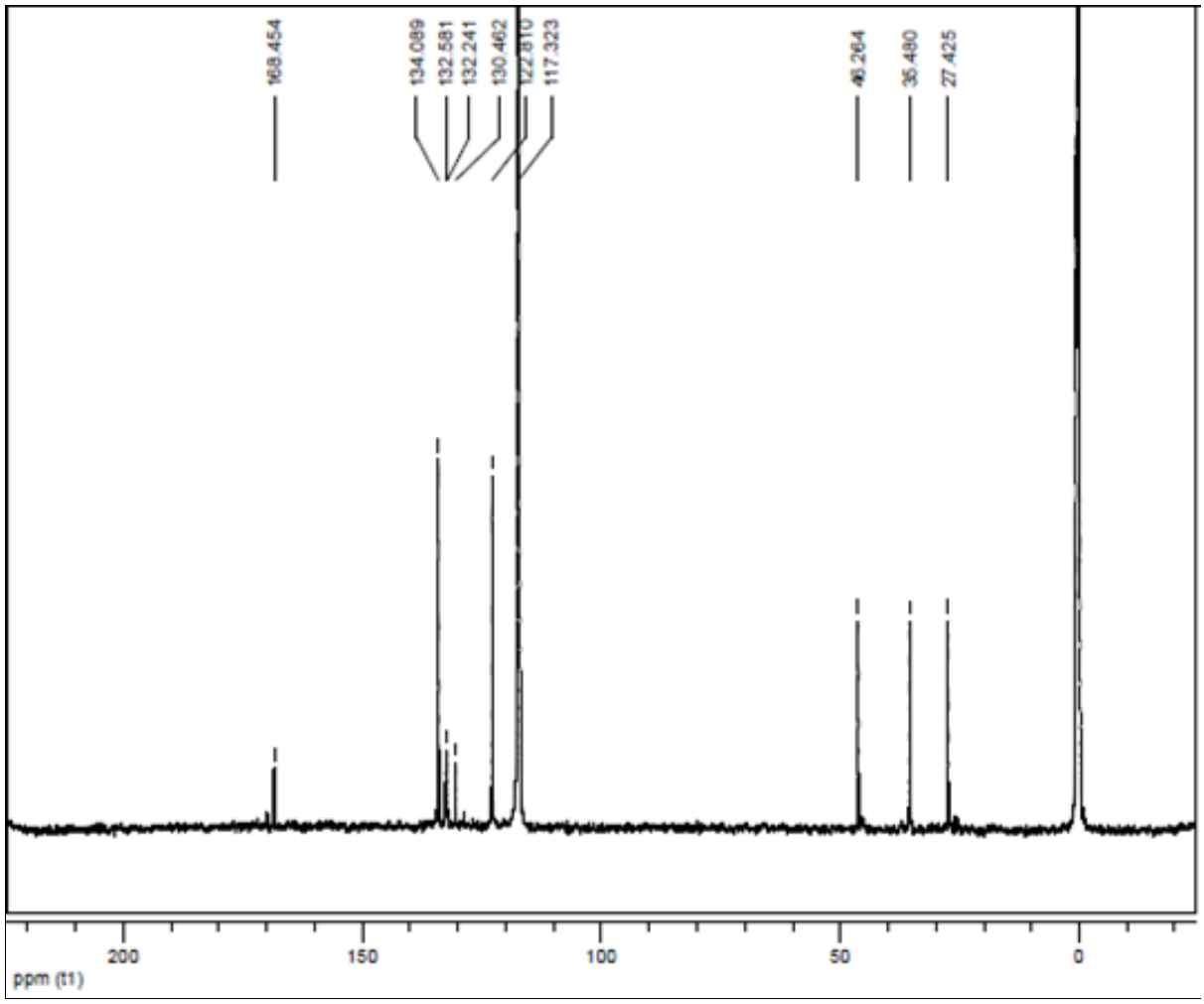
(L_2)

^{1}H NMR of L



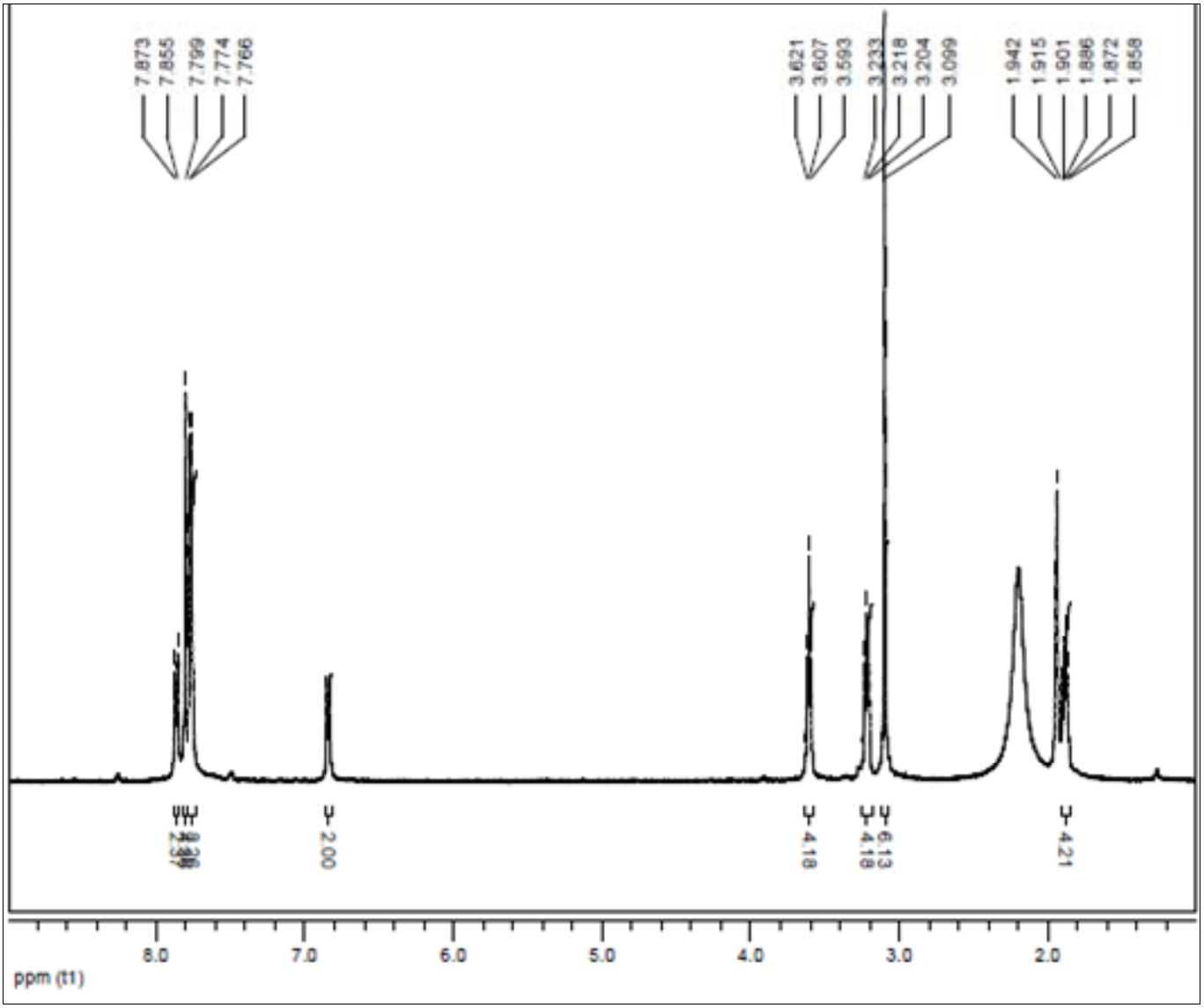
SI Figure 1: ^{1}H NMR spectra of L in CD_3CN.

^{13}C NMR of L



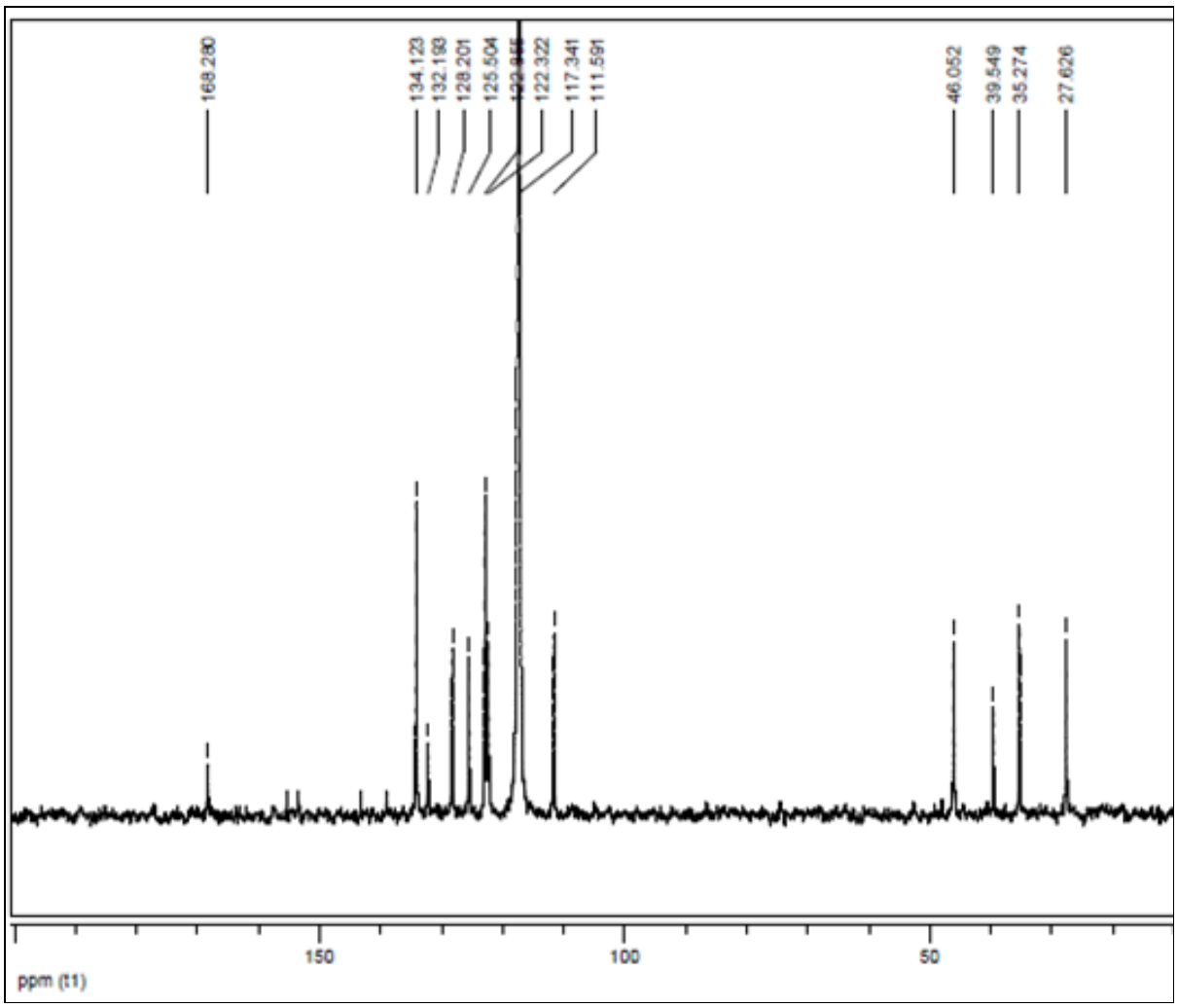
SI Figure 2: ^{13}C NMR spectra of L in CD_3CN.

^{1}H NMR of L_1



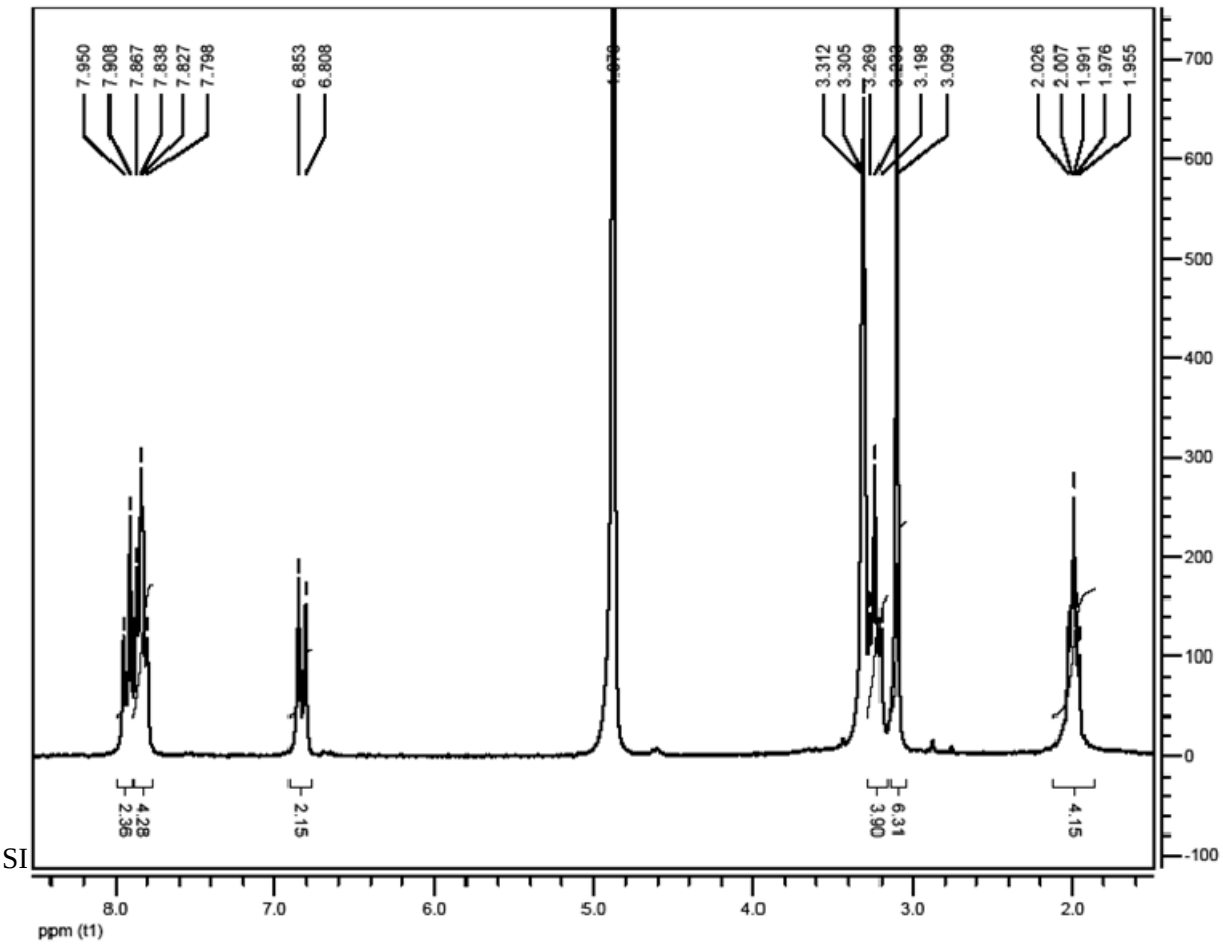
SI Figure 3: ^{1}H NMR spectra of L_1 in CD_3CN.

^{13}C NMR of L_1



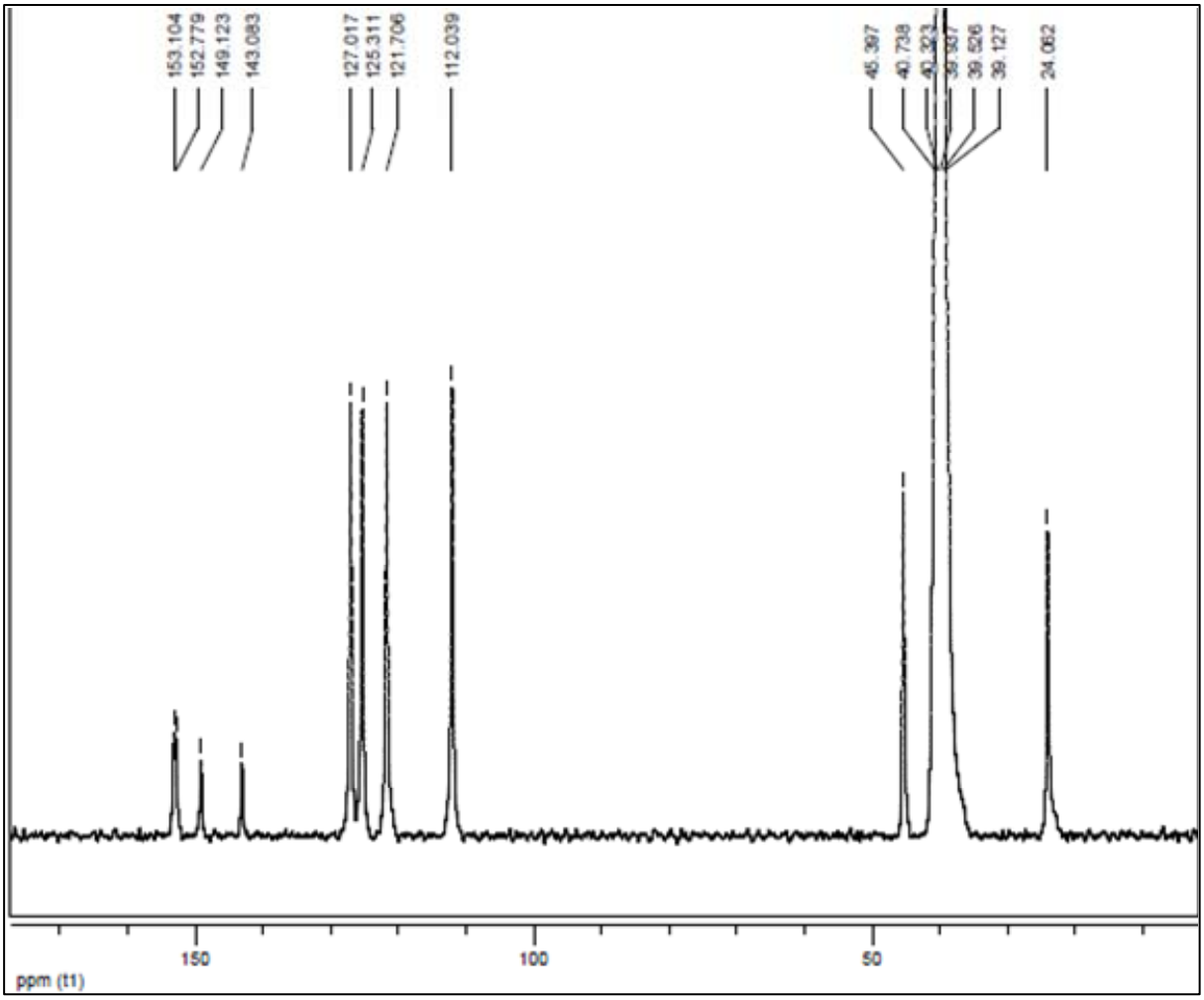
SI Figure 4: ^{13}C NMR spectra of L_1 in CD_3CN.

^{1}H NMR of L_2



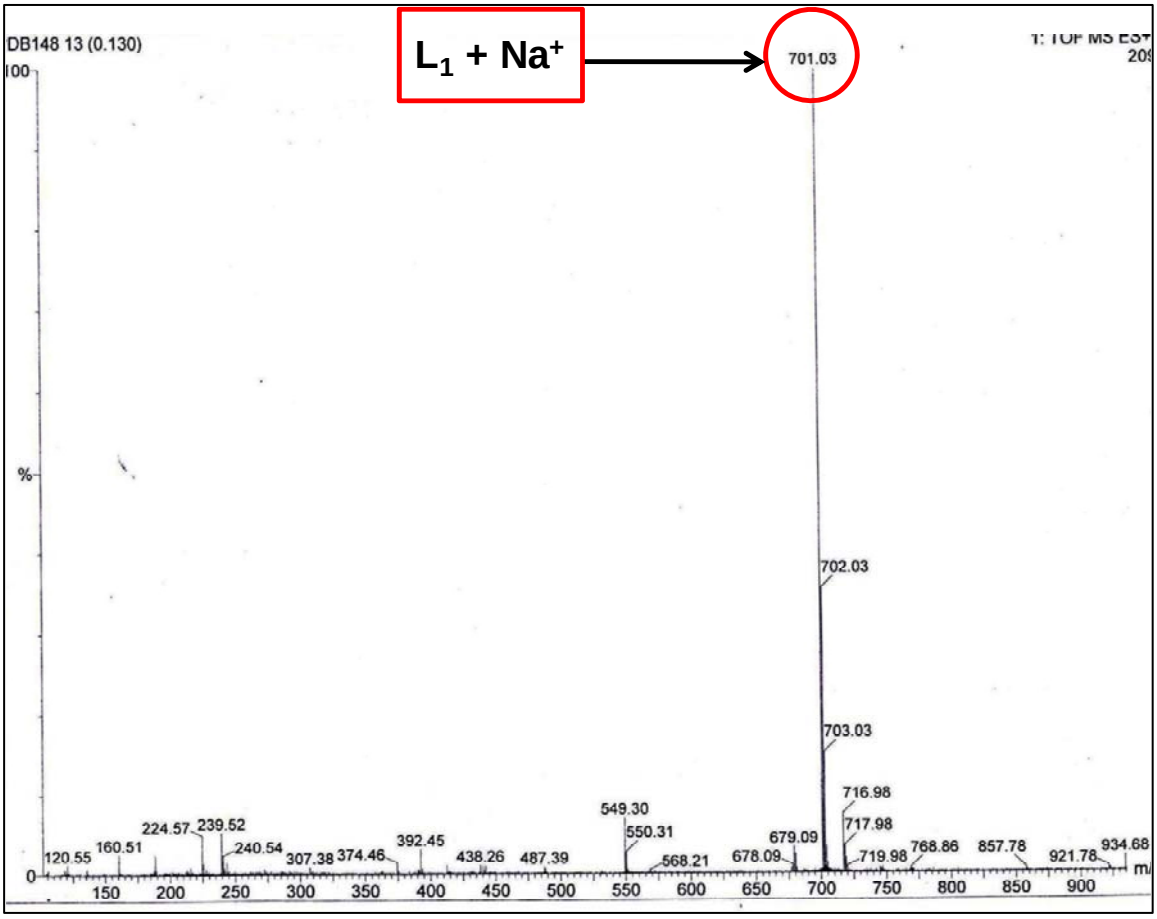
SI Figure 5: ^{1}H NMR spectra of L_2 in CD_3OD.

^{13}C NMR of L_2



SI Figure 6: ^{13}C NMR spectra of L_2 in CD_3OD.

ESI-Mass Spectra of L_1



SI Figure 7: ESI-Mass spectra of L_1 in CH_3CN.

Calculation of Binding constants:

Spectrophotometric titration:

The equilibrium of complexation between **L_1** and $Cr(ClO_4)_2$, $Hg(ClO_4)_2$was evaluated using non-linear least square equation (Eq. 4-6) for the following reaction.

$L_1 + nM^{n+} \rightarrow [M^{n+}]_nL_1$

The stability constant of the complex could be define as

$K_n = [M_nL_1]/[L_1][M]^n$ (SIEq. 1)

Where, M_nL_1 and M stands for **$[Cr^{3+}]_nL_1$** , **$[Hg^{2+}]_nL_1$** and Cr^{3+}, Hg^{2+} respectively. **L_1** and M^{n+} do not have any absorption maxima above 440 nm, so the new absorbance maxima that developed at around 509 nm on addition of M^{n+} was attributed to the formation of a coordination complex (Eq. a). We have selected these two wavelengths for our studies. Thus we have

$A_{440} = \varepsilon_{\{L_1\}_{440}}.l.[L_1] + \varepsilon_{\{M_nL_1\}_{440}}.l.[M_nL_1]$ (SIEq. 2)

$A_{509} = \varepsilon_{\{L_1\}_{509}}.l.[L_1] + \varepsilon_{\{M_nL_1\}_{509}}.l.[M_nL_1]$ (SIEq. 3)

$\varepsilon_{\{L_1\}_{440}}$ and $\varepsilon_{\{L_1\}_{509}}$ are the respective molar extinction coefficient of **L_1** at 440 and 509 nm; while $\varepsilon_{\{M_nL_1\}_{440}}$ and $\varepsilon_{\{M_nL_1\}_{509}}$ are the molar extinction coefficients of $[M^{n+}]_nL_1$ at 440 and 509 nm respectively. For optical path length (l) of 1cm, as used for the present study and the ratio A_{440}/A_{509} could be expressed by SI Equation 4.

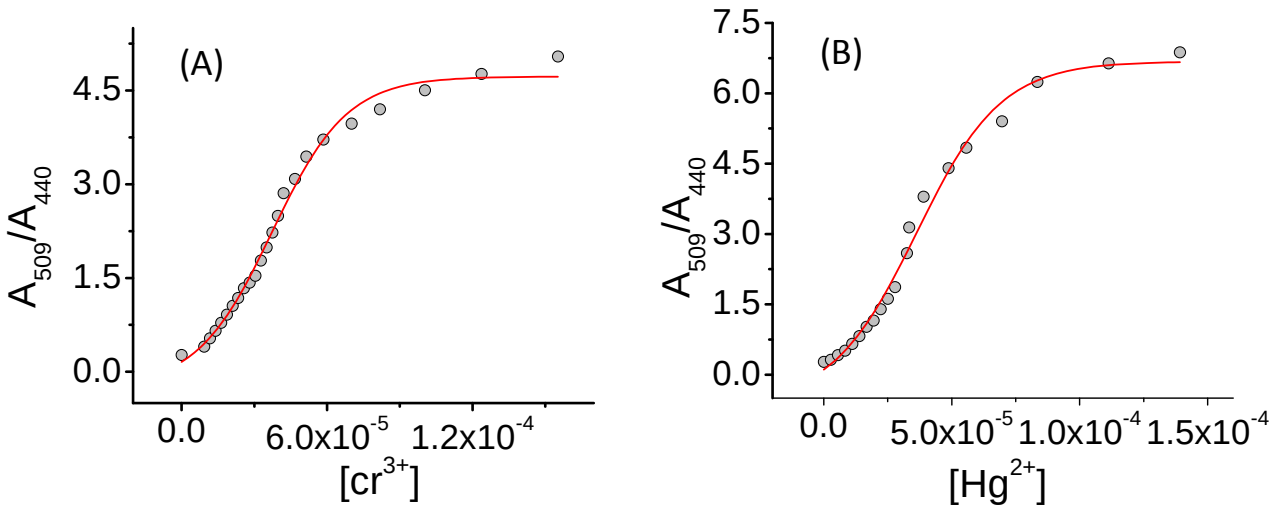
$A_{440}/A_{509} = (K_n\varepsilon_{\{M_nL_1\}_{440}}[M]^n + \varepsilon_{\{L_1\}_{440}})/(K_n\varepsilon_{\{M_nL_1\}_{509}}[M]^n + \varepsilon_{\{L_1\}_{509}})$ (SIEq. 4)

The overall concentration in Cation is $C_M = [M] + n[M_nL_1]$ (SIEq. 5)

Thus $[M] = C_M - n[M_nL_1] = (C_M - nA_{440})/\varepsilon_{\{M_nL_1\}_{440}}$ (SIEq. 6)

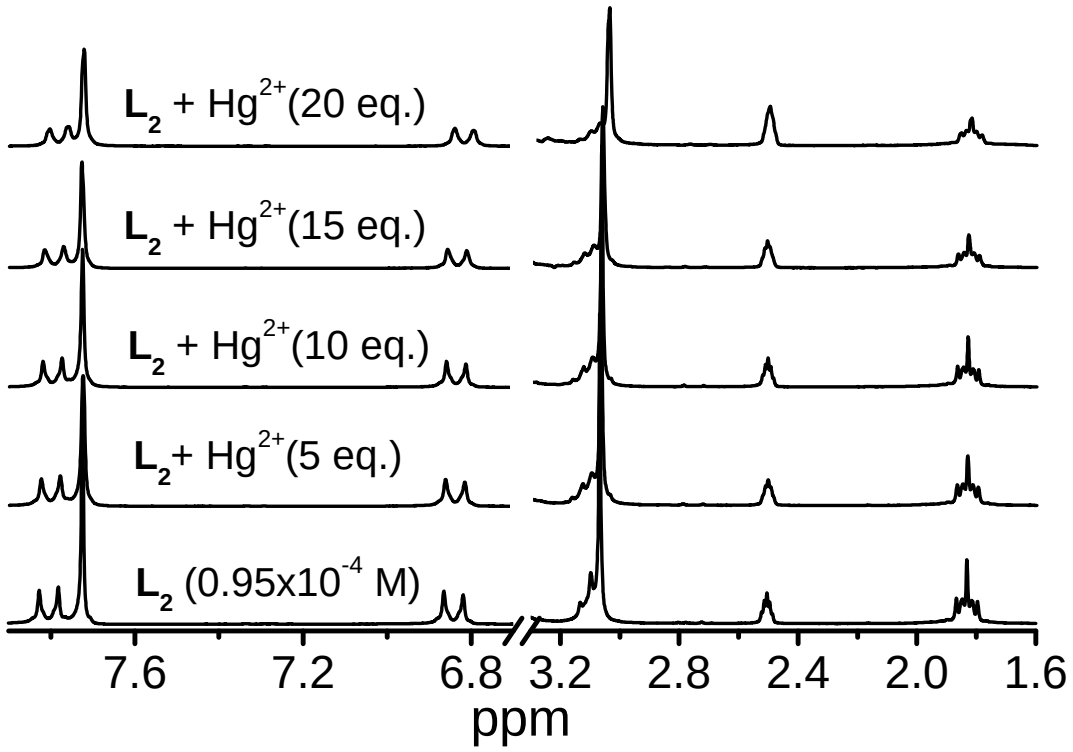
The absorbance data were analysed by using a nonlinear least squares method [Valeur, B.; Pouget, J.; Bouson, J. *J. Phys. Chem.* **1992**, *96*, 654]. Appropriate substitution and approximation was used for evaluation of the stochiometry and affinity constant (n and K_n, respectively).

The absorbance data obtained from the spectroscopic titration of L_1 with $Hg(ClO_4)2$ and $Cr(ClO_4)_3$ were analyzed by using the nonlinear least square method (previously mentioned) for n and K_n. The analysis provided the stoichiometry of the complex formed between **L_1** and Cr^{3+} (SI Figure-8A) was 1:1 (L_1:Cr^{3+}) and the association constant K_{ass} = (6.54 ± 0.07) $x10^{-4}M^{-1}$ with a correlation coefficient 0.987. For the complex of **L_1** and Hg^{2+} (SI Figure-8B) the stoichiometric assembly was 1:1 (L_1:Hg^{2+}) and the association K_{ass} = (4.31 ± 0.04) $x10^{-4}M^{-1}$ with the correlation coefficient 0.9935. These results of receptor **L_1** with $Cr3^{+}$ and Hg^{2+} are consistent and therefore verify the proposed coordinating process (as shown in Figure 9).



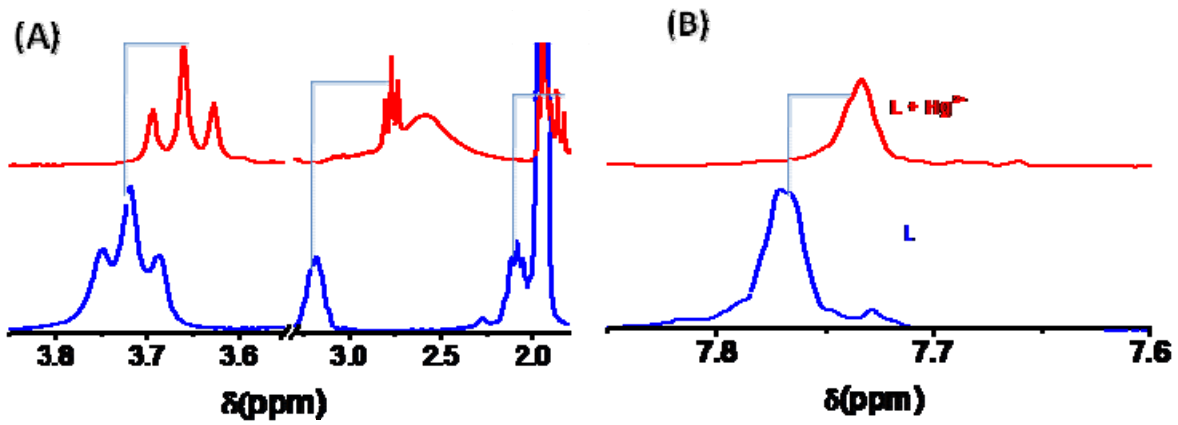
SI Figure 8: variations in absorbance of A_{509} / A_{440} of a solution receptor **L_1** in acetonitrile (2 x 10^{-5}M) as a function of concentration of (A) $Cr(ClO_4)_3$ and (B) $Hg(ClO_4)_2$. The solid lines represent the best fit with the equation SIEq. 4.

^{1}H NMR Spectra of L_2 with $Hg(ClO_4)_2$



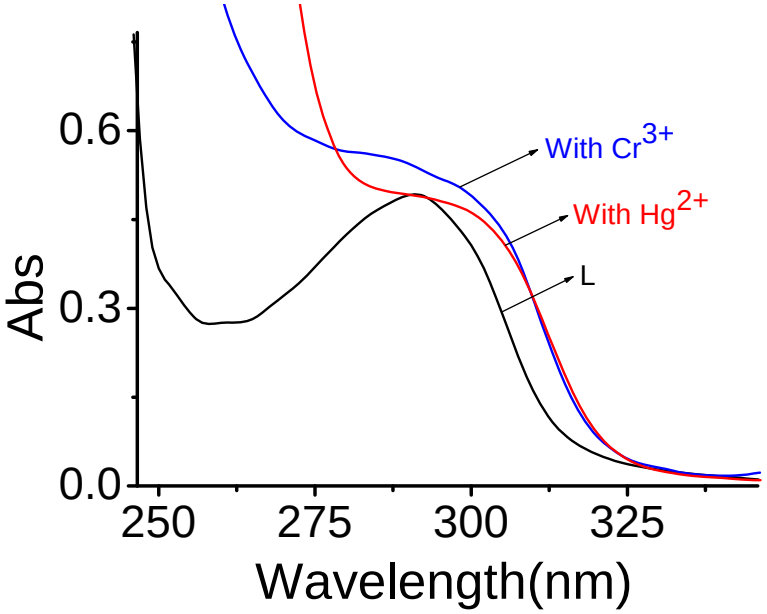
SI Figure 9: ^{1}H NMR spectra of **L_2** in presence of different concentration of $Hg(ClO_4)_2$ in dmso(d_6) medium.

^{1}H NMR Spectra of L with $Hg(ClO_4$



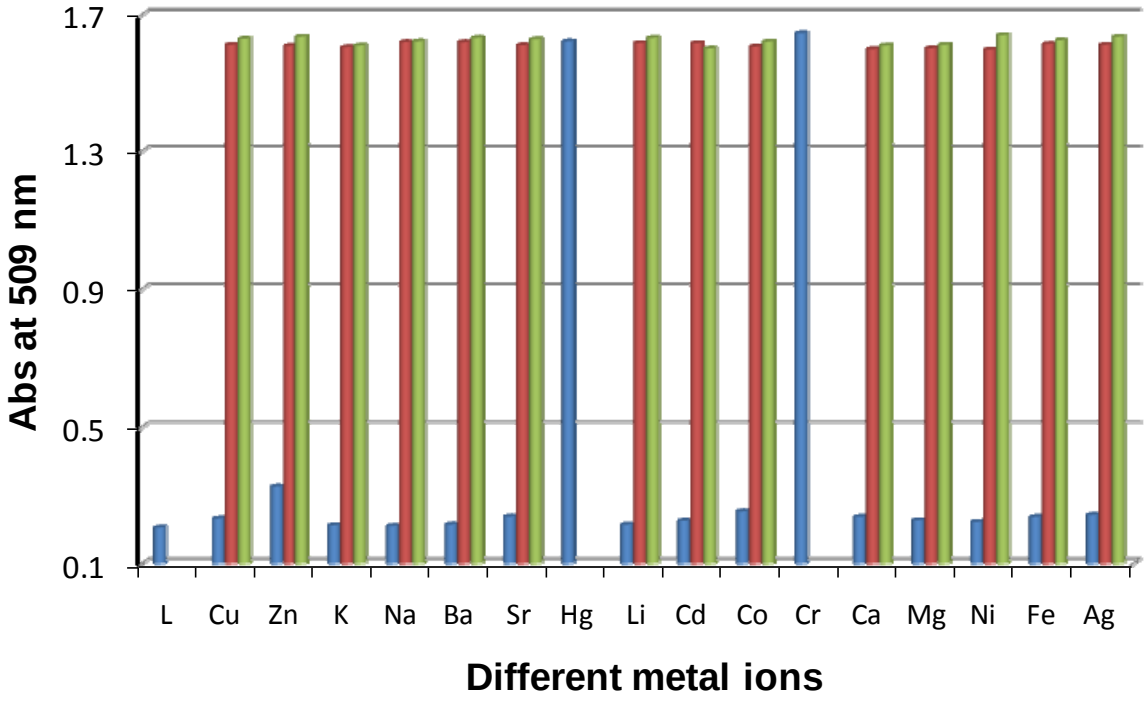
SI Figure 10: ^{1}H NMR spectra of **L** in presence of 20 mol eq concentration of $Hg(ClO_4)_2$ in CD_3CN medium.

Absorption Spectra Of L with $Cr(ClO_4)_3$ and $Hg(ClO_4)_2$



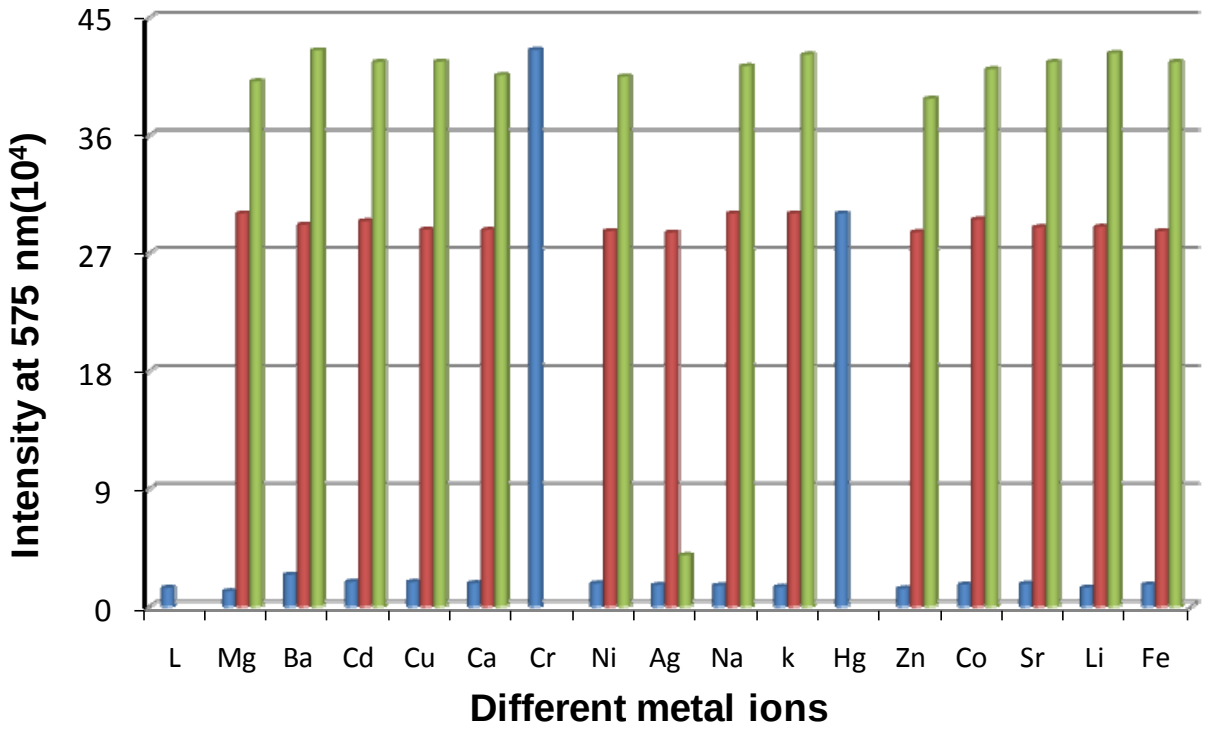
SI Figure11: Absorption spectra of **L** (2.0 X 10^{-5}M) in absence and presence of $Cr(ClO_4)_3$ and $Hg(ClO_4)_2$ in CH_3CN medium.

UV response of L_1 in presence of different metal ion and interference study or competitive effect



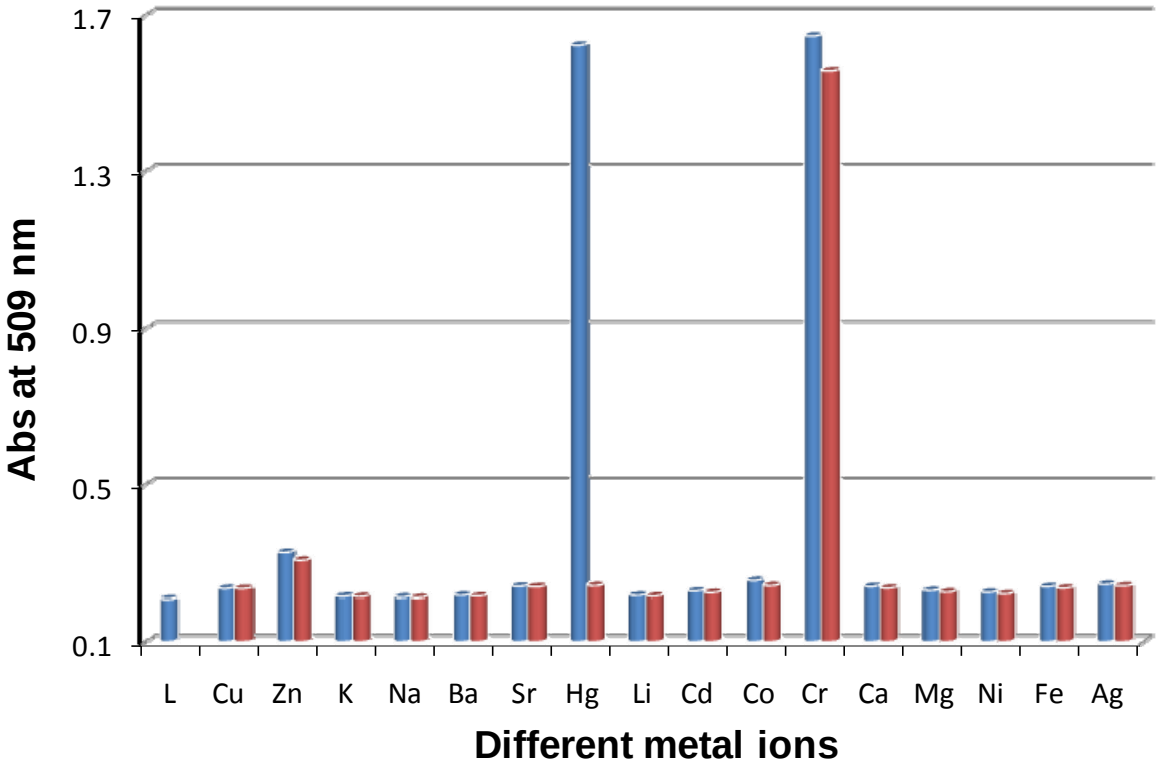
SI Figure12: Absorbance of L_1 (20 μM) at 509 nm in presence of 10 mole equivalent different metal ions (Cu^{2+}, Zn^{2+}, K^{+}, Na^{+}, Ba^{2+}, Sr^{2+}, Hg^{2+}, Li^{+}, Cd^{2+}, Co^{3+}, Cr^{3+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Ag^{+})(blue bars). The red and green bars show the absorbance of $\mathbf{L_1\text{-}Hg^{2+}}$ and $\mathbf{L_1\text{-}Cr^{3+}}$ respectively (at 509 nm) in presence of the above mentioned metal ions in actonitrile medium.

Luminescence response of L_1 in presence of different metal ion and interference study or competitive effect



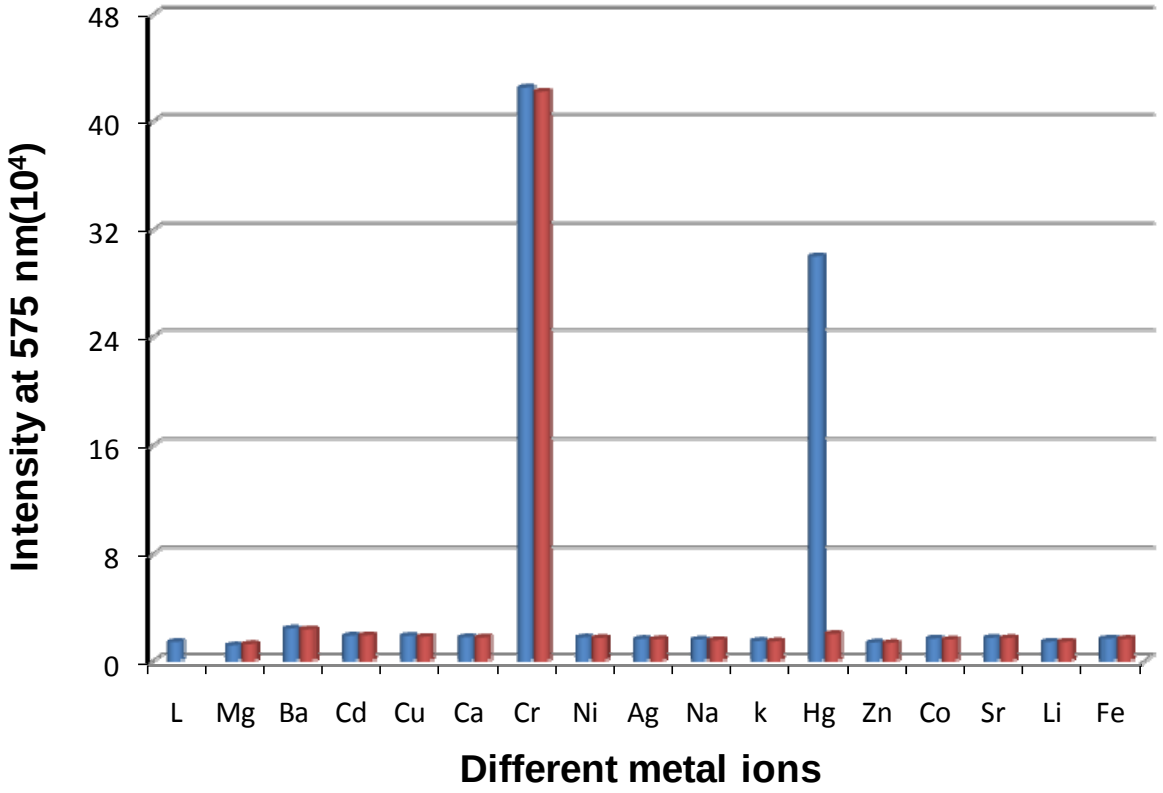
SI Figure13: Emission intensity of L_1 (20 μM) at 575 nm in presence of 10 mole equivalent different metal ions (Cu^{2+}, Zn^{2+}, K^{+}, Na^{+}, Ba^{2+}, Sr^{2+}, Hg^{2+}, Li^{+}, Cd^{2+}, Co^{3+}, Cr^{3+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Fe^{2+}, Ag^{+})(blue bars). The red and green bars show the emission intensity of **L_1-Hg^{2+}** and **L_1-Cr^{3+}** respectively (at 575 nm) in presence of the above mentioned metal ions in acetonitrile medium.

UV response of L_1 with different metal ions in absence and presence of $[Bu_4N]I$



SI Figure14: Absorbance of L_1 (20 μM) at 509 nm with 10 mole equivalent different metal ions in absence of $[Bu_4N]I$ (blue bars) and in presence of $[Bu_4N]I$ (5mM) (red bars) in actonitrile medium.

Emission response of L_1 with different metal ions in absence and presence of $[Bu_4N]I$



SI Figure15: Emission intensity of L_1 (20 μM) at 575 nm with 10 mole equivalent different metal ions in absence of $[Bu_4N]I$ (blue bars) and in presence of $[Bu_4N]I$ (5mM) (red bars) in actonitrile medium.