Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A FRET based 'off-on' molecular switch: an effective design strategy for selective detection of nanomolar Al^{3+} ions in aqueous media†

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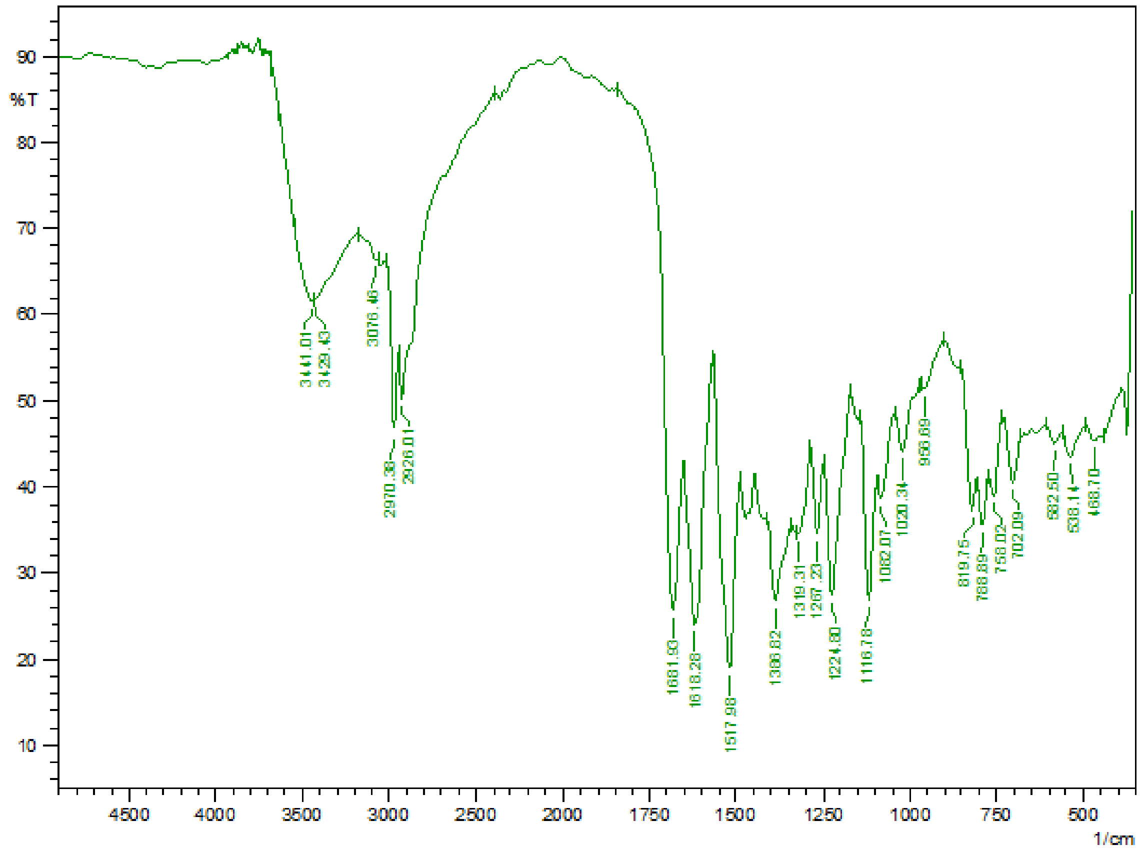


Fig. S1A FTIR spectrum of probe (**L**[1])

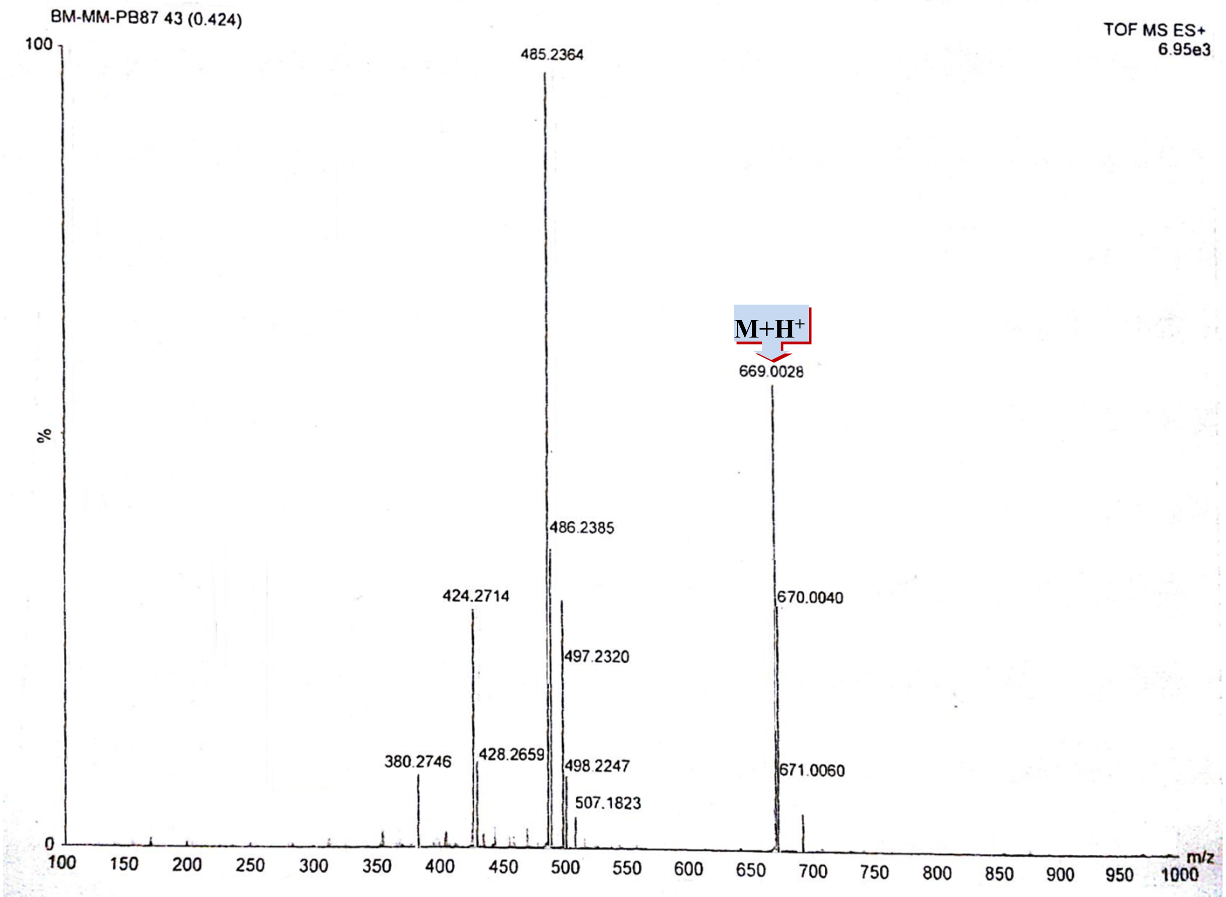


Fig. S1B ESI-MS spectrum of probe (**L¹**) in MeOH

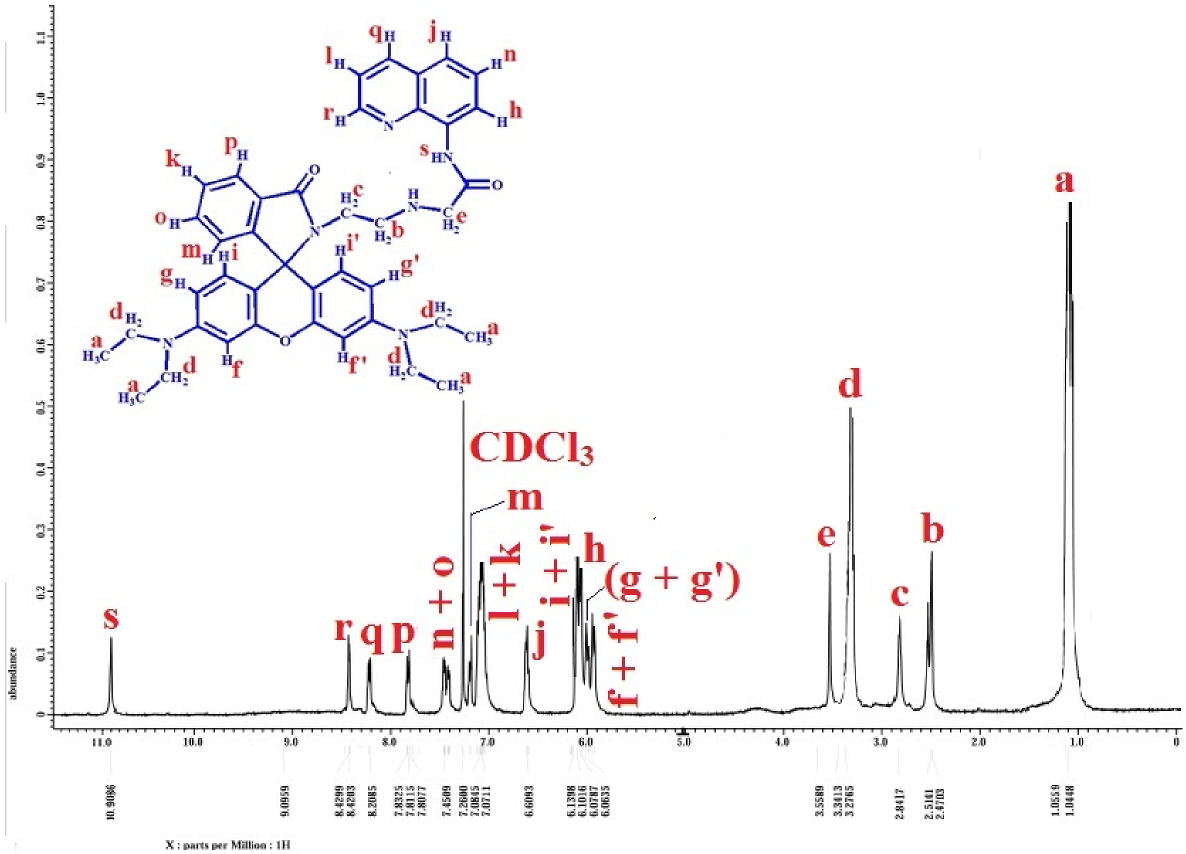


Fig. S1C ^{1}H NMR of the probe (**L^{1}**) in $CDCl_3$

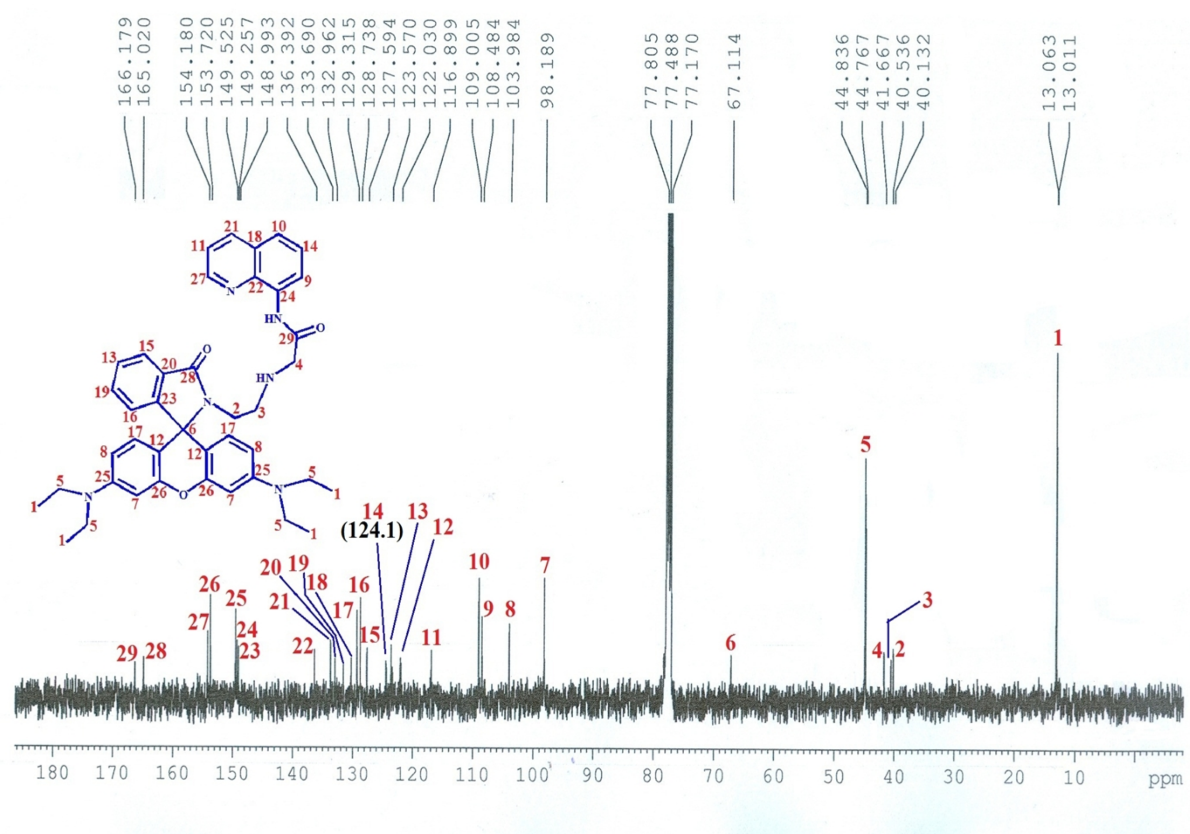


Fig. S1D ^{13}C NMR of the probe (**L^1**) in $CDCl_3$

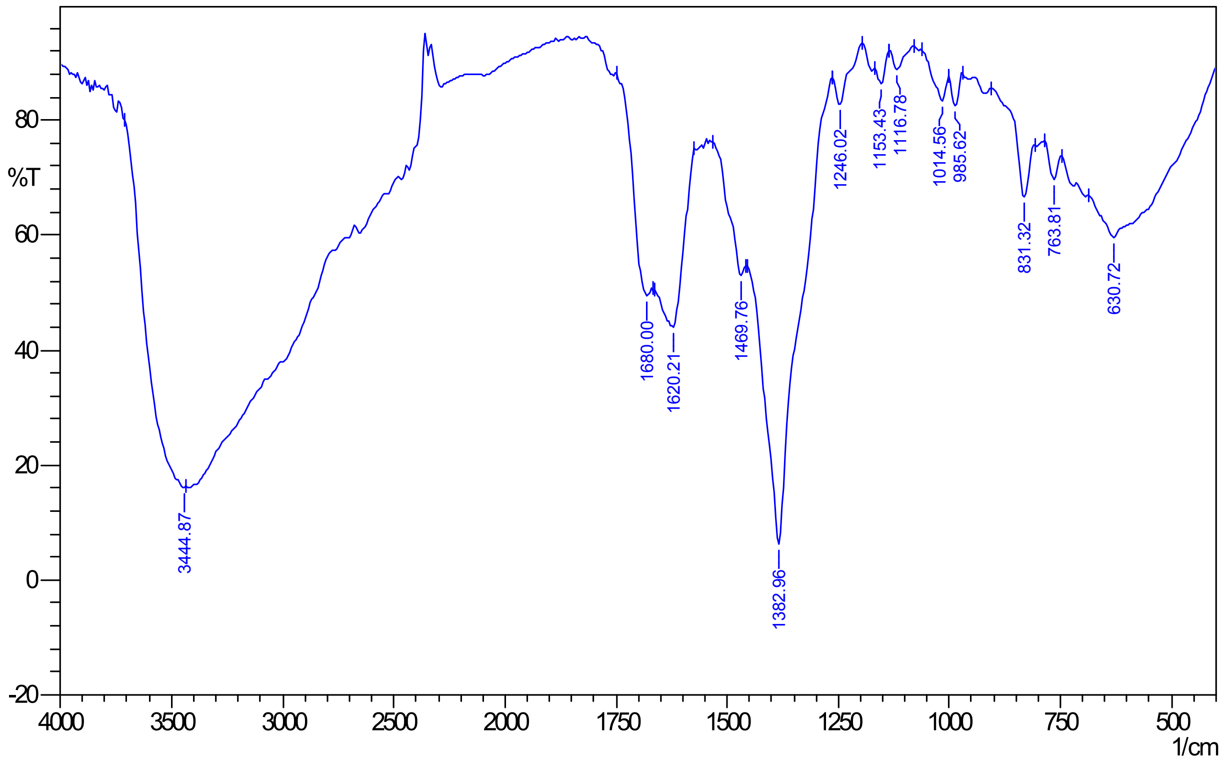


Fig. S2A FTIR spectrum of $[Al(L)(NO_3)_2]$

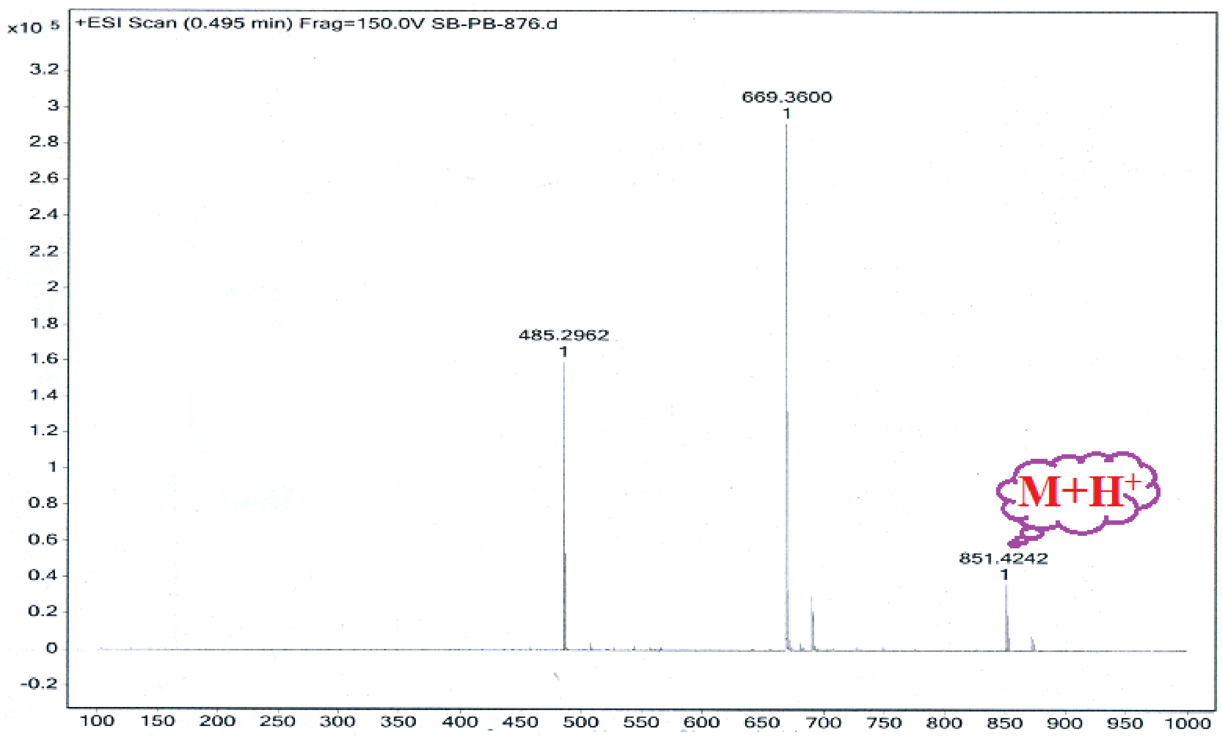


Fig. S2B ESI-MS spectrum of $[Al(L)(NO_3)_2]$ in MeOH

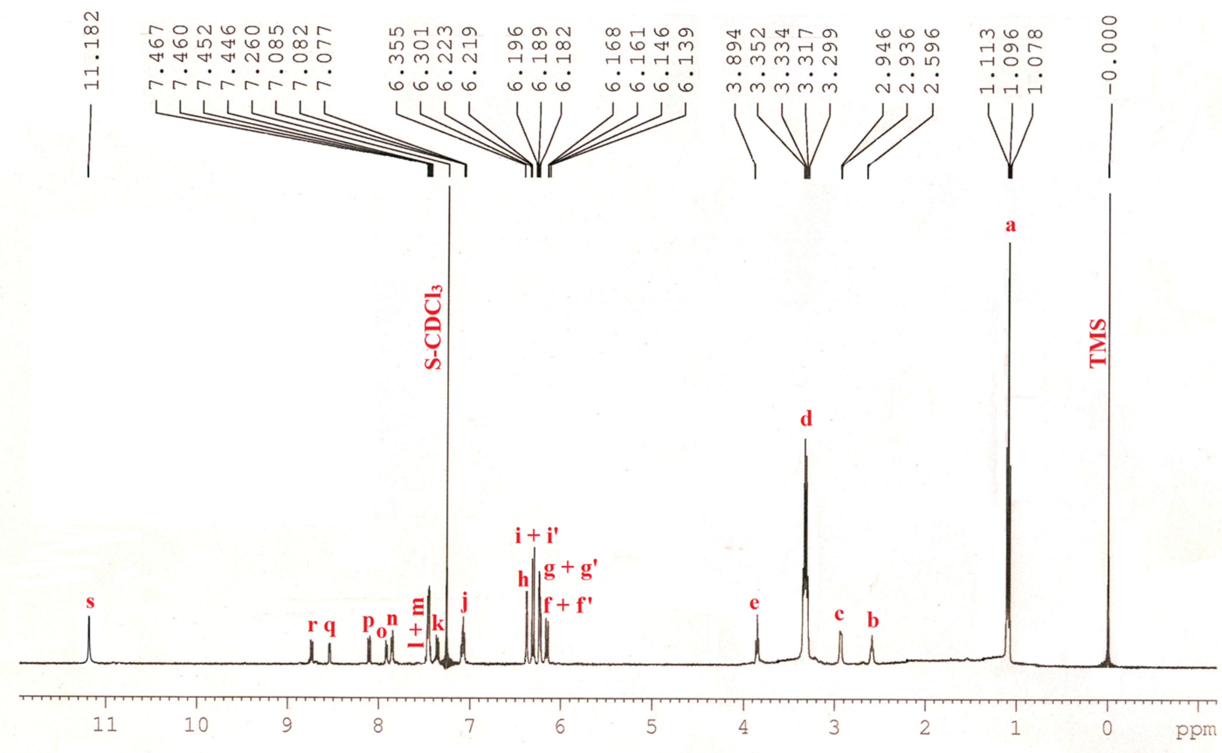


Fig. S2C ^{1}H NMR of $[Al(L)(NO_3)_2]$ in $CDCl_3$

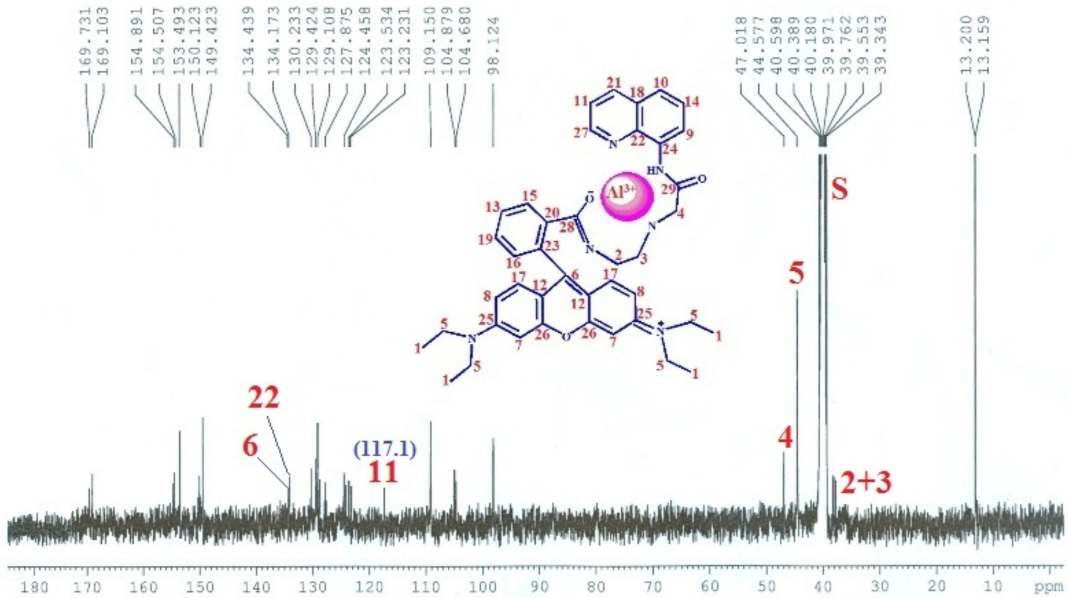
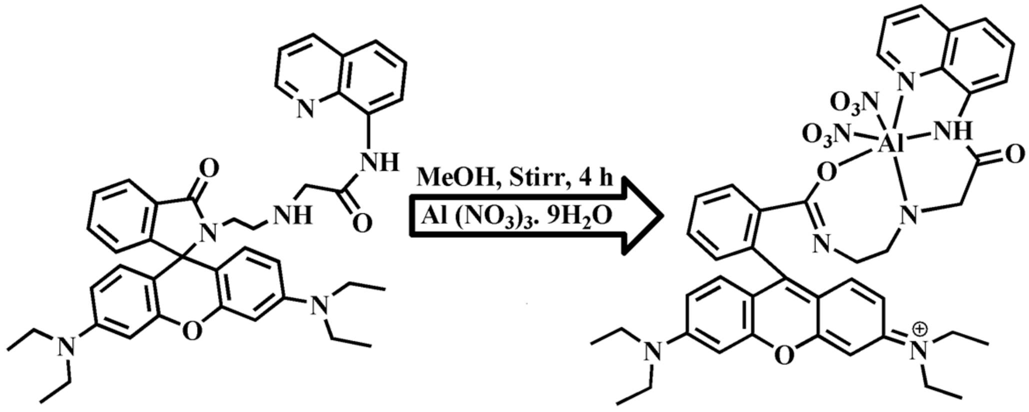


Fig. S2D ^{13}C NMR spectrum of $[Al(L)(NO_3)_2]$ in DMSO-d6



Scheme S1 Synthesis of L-Al Complex as [Al(L)$(NO_3)_2$]

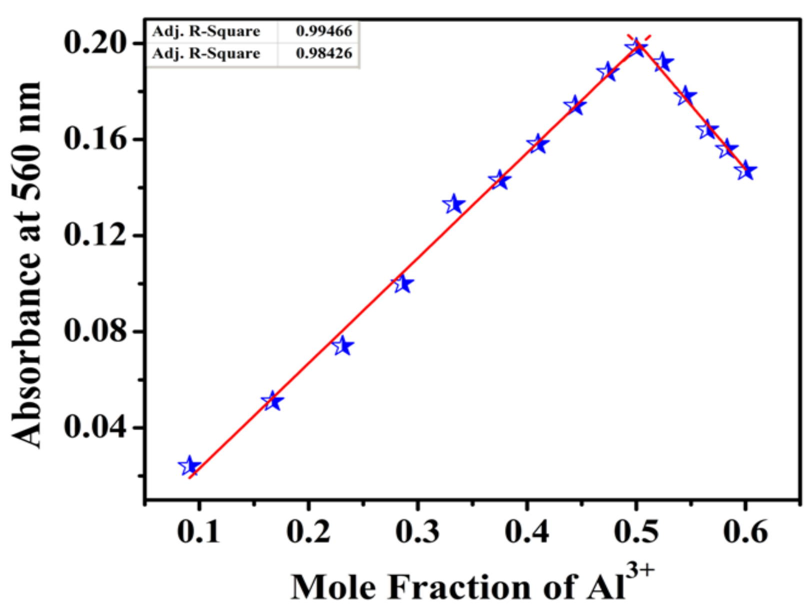


Fig. S3 Job's plot analysis from UV-vis data showing maximum absorption at 1:1 ratio [**L¹**: Al^{3+}] at λ_{em} = 588 nm

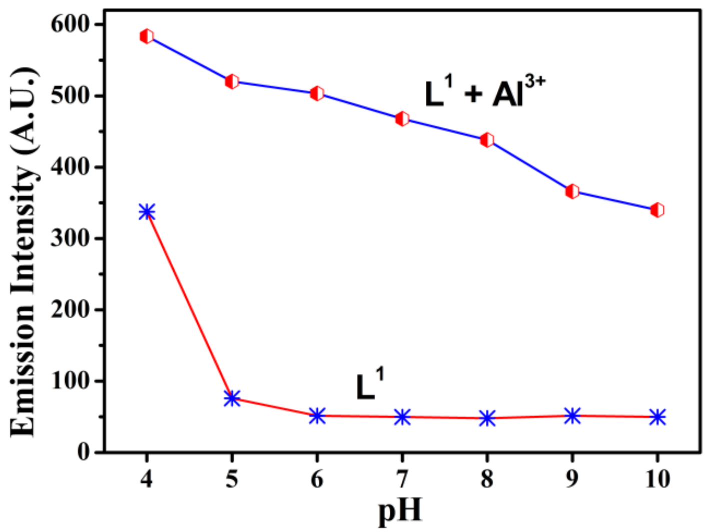


Fig. S4 Effect of pH in absence of Al^{3+} ions and in presence of Al^{3+} ions in HEPES buffer (1 mM, pH 7.4; 2% EtOH) at 25°C at λ_{em} = 588 nm

Detection Limit

The detection limit was determined from the fluorescence titration data at λ_{em} 588 nm using one earlier reported method by Veciana et. al.[1a] as well as by 3σ method.[1b] Results showed that both were comparable with each other.

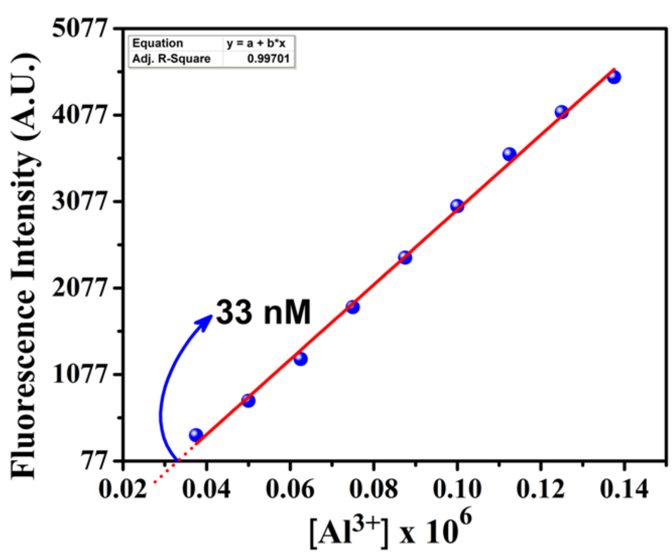


Fig. S5 Detection limit of Al^{3+} (33 x 10^{-9} M) in HEPES buffer (1 mM, pH 7.4; 2% EtOH) at λ_{em} = 588 nm

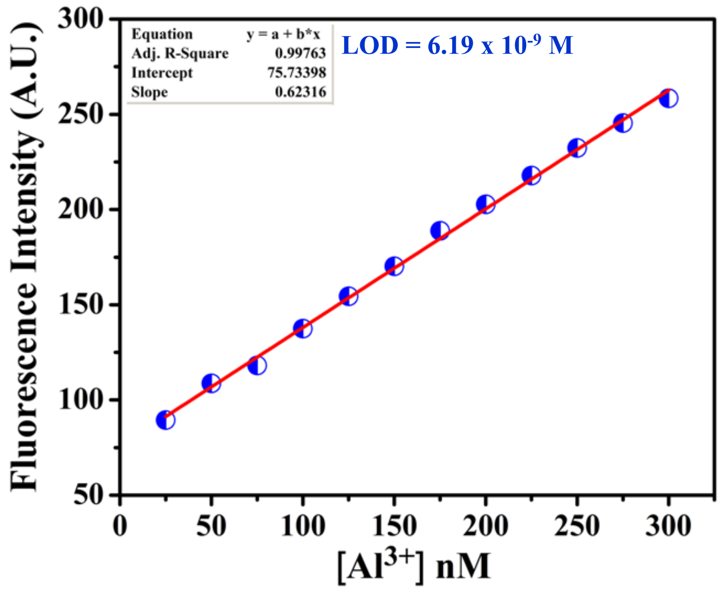


Fig. S6 Calibration curve in the nanomolar range (0-300 nM) for calculating the LOD of Al^{3+} by $\mathbf{L^1}$ in HEPES buffer (1 mM, pH 7.4; 2% EtOH) at 25 °C [Here, S = 0.62316, σ = 1.286, LOD (C_L) = 3σ/S = 6.19 nM]

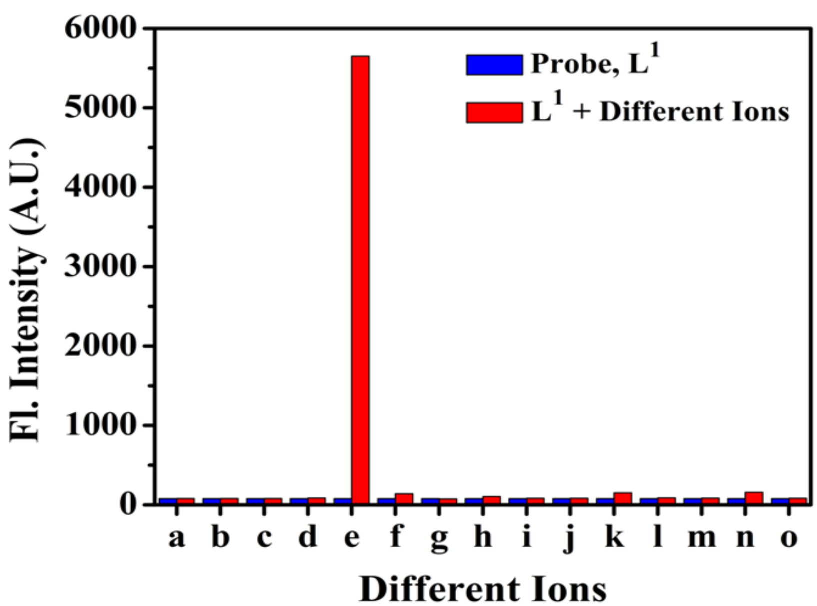


Fig. S7 Fluorescence intensity assay of $\mathbf{L^1}$ in presence of different metal ion salts in HEPES buffer (1 mM, pH 7.4; 2% EtOH) at 25 °C (λ_{ex} = 550 nm), a) Na^+, b) K^+, c) Ca^{2+}, d) Mg^{2+}, e) Al^{3+}, f) Cr^{3+}, g) Mn^{2+}, h) Fe^{3+}, i) Co^{2+}, j) Ni^{2+}, k) Cu^{2+}, l) Zn^{2+}, m) Cd^{2+}, n) Hg^{2+}, and o) Pb^{2+} at λ_{em} = 588 nm.

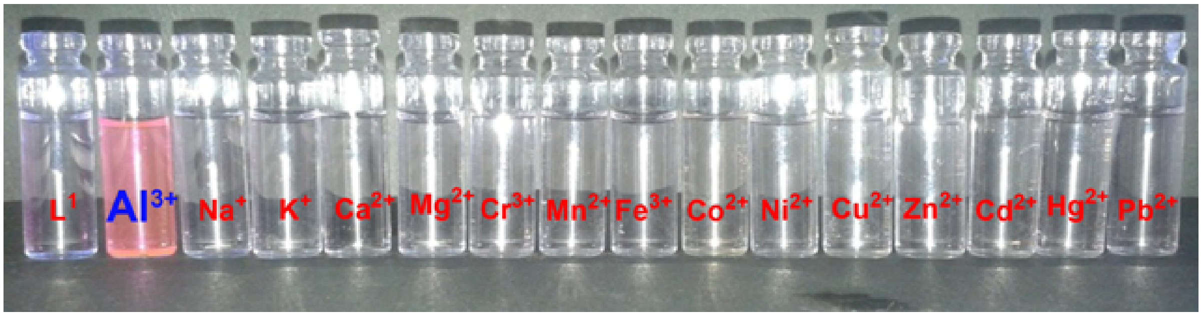


Fig. S8 Visual color change of the probe due to the addition of different cations in HEPES buffer (1 mM, pH 7.4; 2% EtOH)

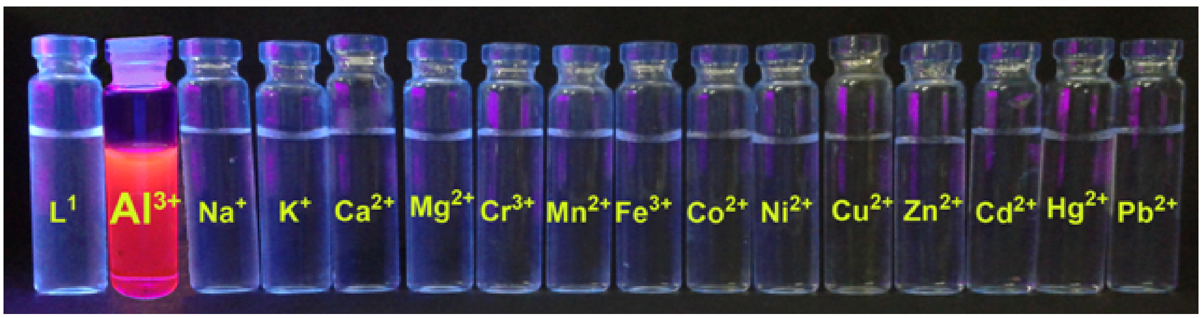


Fig. S9 Fluorescence color of the probe in absence and presence of different metal ions in HEPES buffer (1 mM, pH 7.4; 2% EtOH)

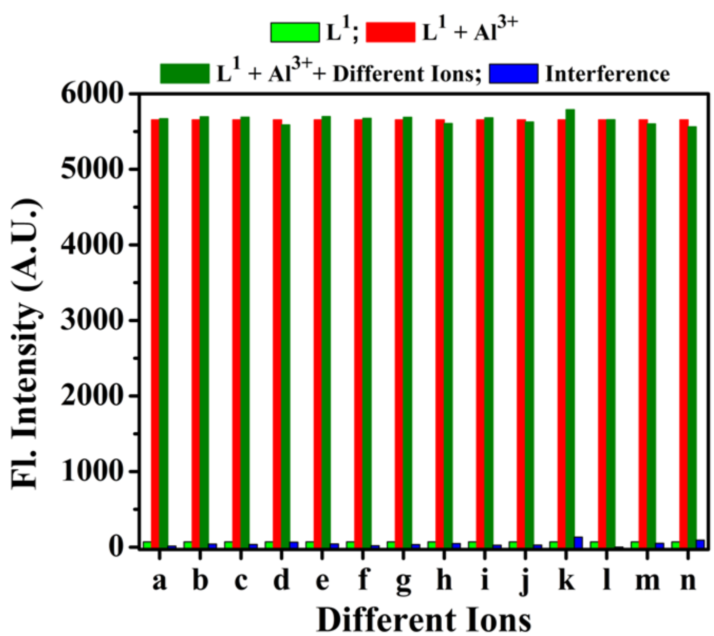


Fig. S10 Signaling of Al^{3+} ions by $\mathbf{L^1}$ in the presence of 10-50 eq. of competitive a) Na^+, b) K^+, c) Ca^{2+}, d) Mg^{2+}, e) Cr^{3+}, f) Mn^{2+}, g) Fe^{3+}, h) Co^{2+}, i) Ni^{2+}, j) Cu^{2+}, k) Zn^{2+}, l) Cd^{2+}, m) Hg^{2+}, and n) Pb^{2+} ions in HEPES buffer (1 mM, pH 7.4; 2% EtOH) at 25 °C at λ_{ex} = 550 nm

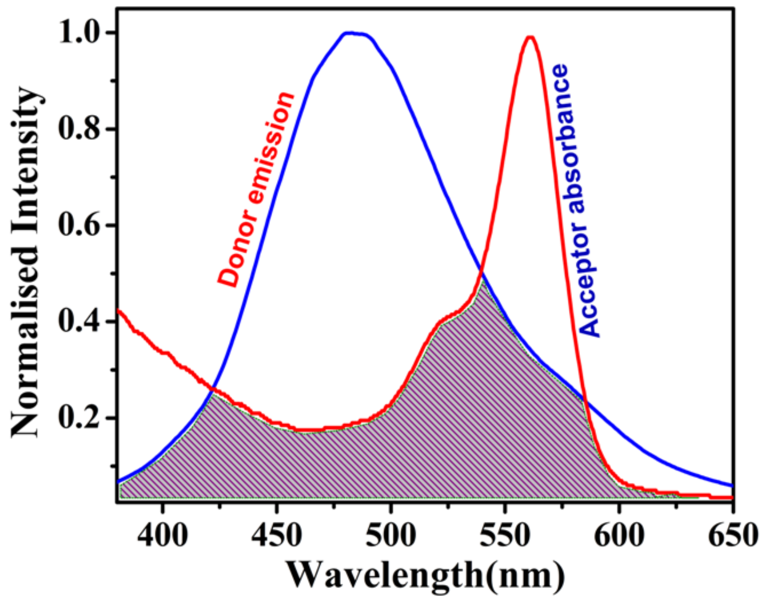


Fig. S11 Overlap spectra of donor emission and acceptor absorbance of **L¹** (10 µM) in HEPES buffer (1 mM, pH 7.4; 2% EtOH)

Binding Constant: The binding constant value was determined from the emission intensity data following the modified Benesi-Hildebrand equation.[2]

$$1/\Delta F = 1/\Delta F_{max} + (1/K[C])(1/\Delta F_{max}),\ \Delta F = F_x - F_0,\ \Delta F_{max} = F_\infty - F_0$$
$$\text{i.e. } (F_\infty - F_0)/(F_x - F_0) = 1 + 1/K[C]$$

where F_0, F_x, and F_∞ are the emission intensities of organic moiety considered in the absence of Al^{3+} ions, at an intermediate Al^{3+} concentration, and at a concentration of complete interaction, respectively, and where K is the association constant and [C] is the Al^{3+} concentration. K value ($5.81 \times 10^6\ M^{-1}$) was calculated from the intercept/slope using the plot of $(F_\infty - F_0)/(F_x - F_0)$ against $[C]^{-1}$.

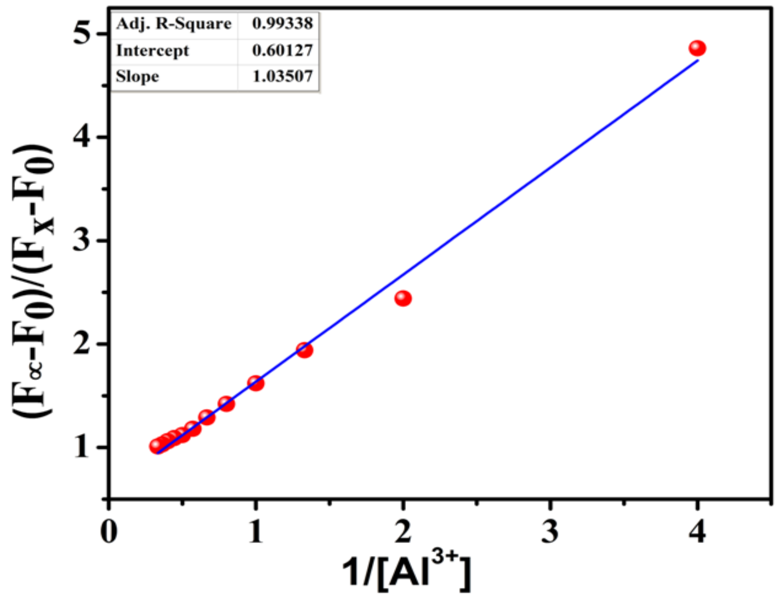


Fig. S12 Binding constant (K) value 5.81 x 10^6 M^{-1} determined from the determined from the intercept/slope of the plots resulting in the interactions of $\mathbf{L^1}$ with Al^{3+}

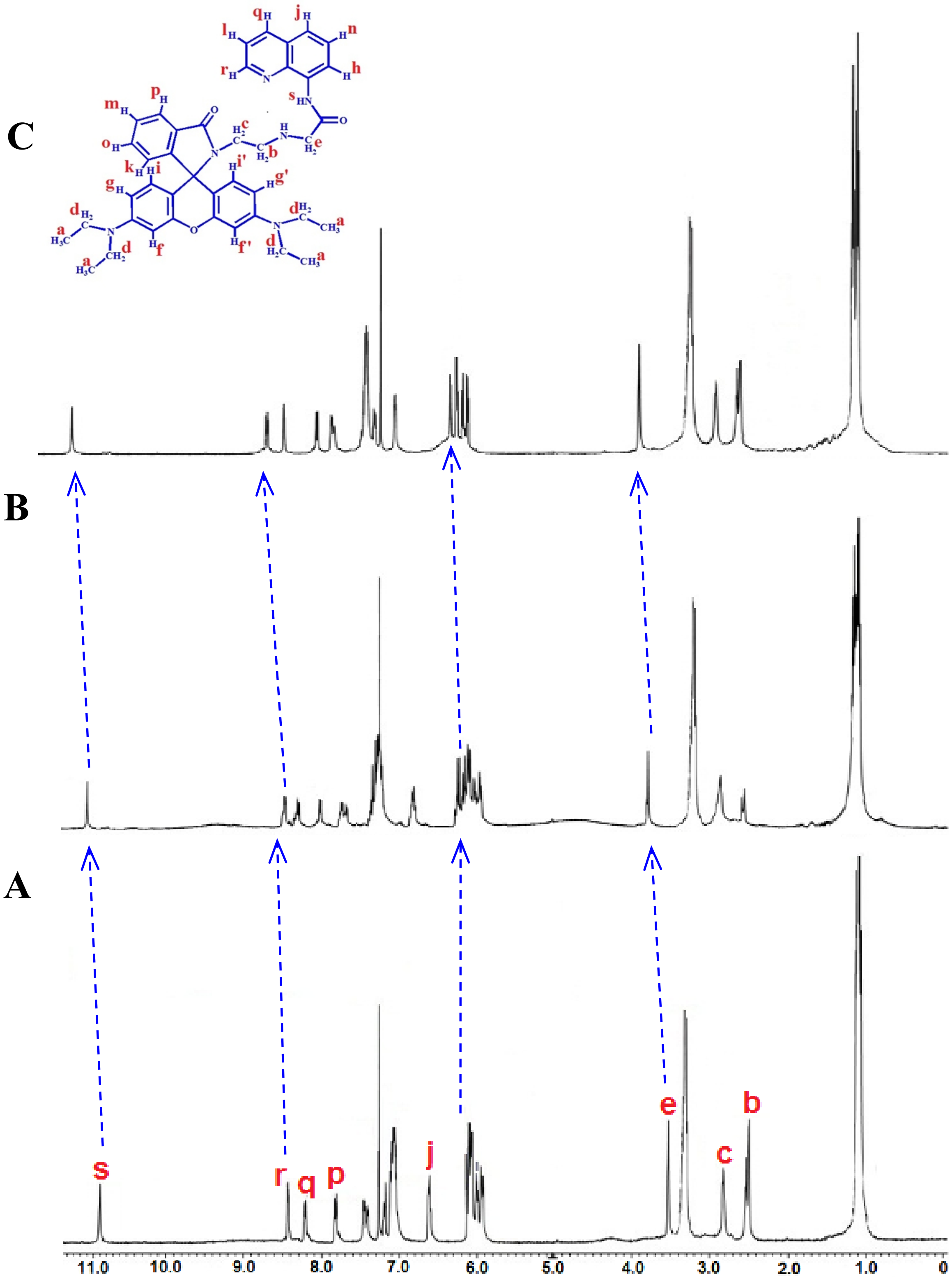


Fig. S13 Partial ^{1}H NMR spectra for $\mathbf{L^1}$ (10 mM) in presence of varying [Al^{3+}] [A) 0 mM, B) 5 mM, and C) 10 mM] in $CDCl_3$

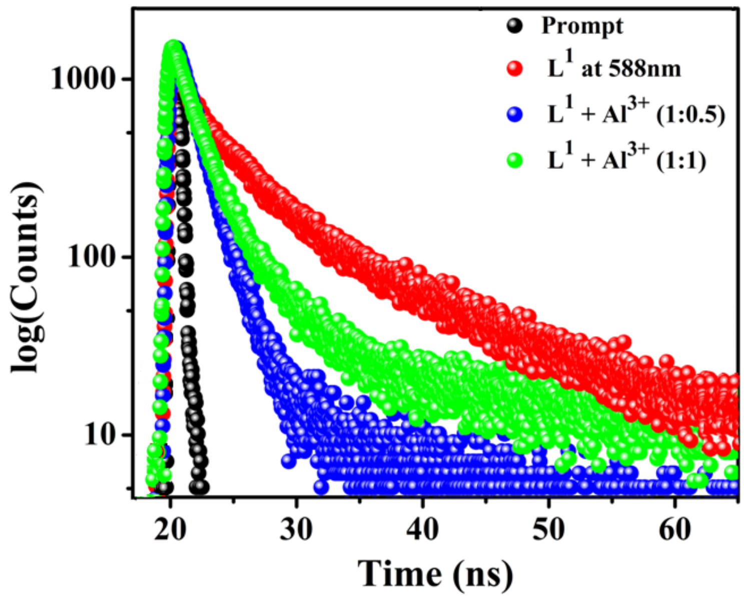


Fig. S14 Time resolved fluorescence decay of **L^1** (10μM) in absence and presence of added Al^{3+} in HEPES buffer (1 mM, pH 7.4; 2% EtOH) at 25 °C using a nano LED of 377 nm as the light source at λ_{em} = 588nm

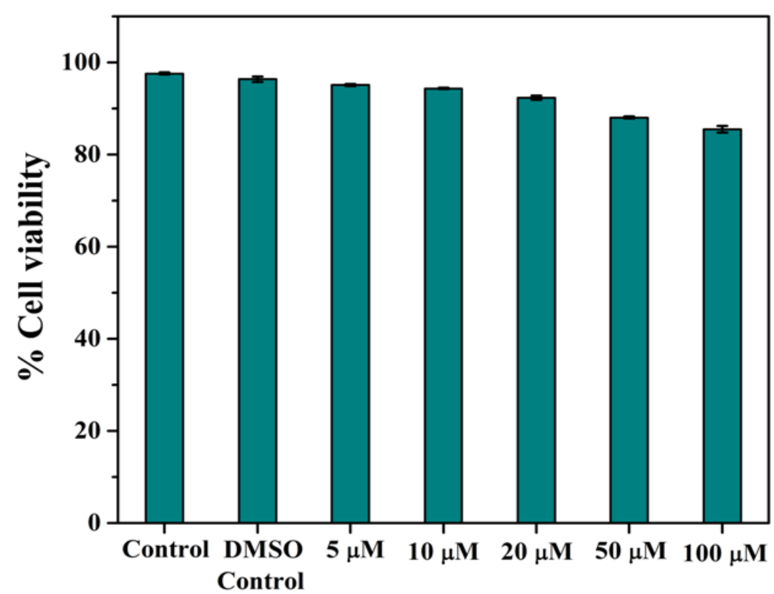


Fig. S15 Cytotoxic effect of **L^1** (5, 10, 20, 50 and 100 μM) in HeLa cells incubated for 6 h

Reference

(1) (a) A. Caballero, R. Martinez, V. Lloveras, I. Ratera, J. V. Gancedo, K. Wurst, A. Tarraga, P. Molina, J. Veciana, *J. Am. Chem. Soc.,* 2005, **127**, 15666; (b) A. Hakonen, *Anal. Chem.*, 2009, **81**, 4555.

(2) H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.