Electronic supporting information (ESI)

A single probe for sensing both acetate and aluminum(III): Visible region detection, red fluorescence and human breast cancer cell imaging

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1. General method of UV-Vis and fluorescence titration

Path length of the cells used for absorption and emission studies is 1 cm. Stock solutions of **L** and AcO^- are prepared in DMSO while for Al^{3+}work, stock solutions of **L** and Al^{3+} are prepared in CH_3OH/ water (4/1, v/v). Working solutions of **L**, Al^{3+} and AcO^- are prepared from their respective stock solutions. Fluorescence measurements are performed using 10 nm x 5 nm slit width for AcO^- and 2.5 nm x 2.5 nm slit width for Al^{3+} work.

2. Job's plot from fluorescence experiments

A series of solutions containing **L**, Al^{3+} and AcO^- in respective solvents are prepared such that the total concentration of Al^{3+}+**L** or **L** + AcO^- remain constant (50 μM) in all the sets. The mole fraction (X) of **L** is varied from 0.1 to 0.8. The fluorescence intensities are plotted against the mole fraction of **L.**

3. Determination of binding constant

The binding constant of **L** for Al^{3+} and AcO^- are determined using modified Benesi–Hildebrand equation[1]: $(F_{max} - F_{min})/(F_x - F_{min}) = 1 + (1/K)\ (1/[C]^n)$ where F_{max}, F_{min} and F_x are emission

intensity values for **L** in the presence of Al^{3+} or AcO^- at saturation, in the absence of Al^{3+}/ AcO^- and at any intermediate Al^{3+}/ AcO^- concentration, respectively. A plot of $(F_{max} - F_{min})/(F_x - F_{min}) = 1 + (1/K)\ (1/[C]^n)$ (here n = 1, for both cases) allows to calculate the binding constant from the slope.

4. Determination of quantum yield

Fluorescence quantum yields (Φ) are estimated by integrating the area under the fluorescence curves using the equation,

$$\Phi_{sample} = \frac{OD_{standard} \times A_{sample}}{OD_{sample} \times A_{standard}} \times \Phi_{standard} \times \frac{\eta_{sample}^2}{\eta_{standard}^2}$$

where A is the area under the fluorescence spectra and OD is optical density of the compound at the excitation wavelength.[2] The area of the emission spectrum is integrated using the software available in the instrument. Φ_{sample} and Φ_{ref} are the fluorescence quantum yields of the sample and reference respectively. A_{sample} and A_{ref} are the area under the fluorescence spectra of the sample and the reference, respectively. OD_{sample} and OD_{ref} are the corresponding optical densities of the sample and the reference solution at the wavelength of excitation. η_{sample} and η_{ref} are the refractive indeces of the sample and reference, respectively. Anthracene is used as reference with a known Φ_{ref} value of 0.27 in EtOH[3] for measuring the quantum yields of ligand and its Al^{3+} complex and Rhodamine B is used as reference with a known Φ_{ref} value of 0.65 in basic EtOH[4] for measuring the quantum yields of **L** and its AcO^- adduct.

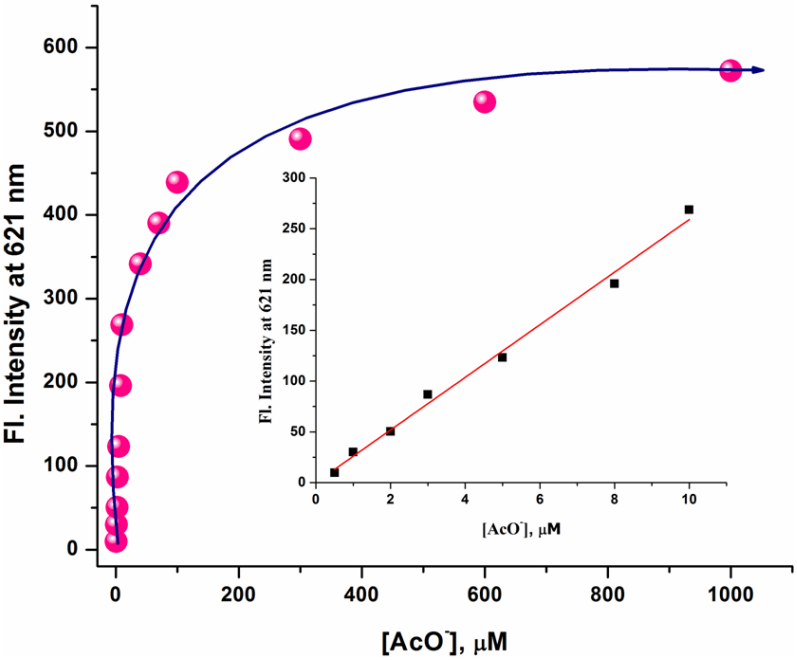

Fig.S1. Plot of emission intensities of **L** (10 μM, λ_{ex} = 532 nm, λ_{em} = 621 nm) as afunction of externally added AcO^{-} (0.5-1000 μM). Inset shows the linear region (0.5-10 μM AcO^{-})

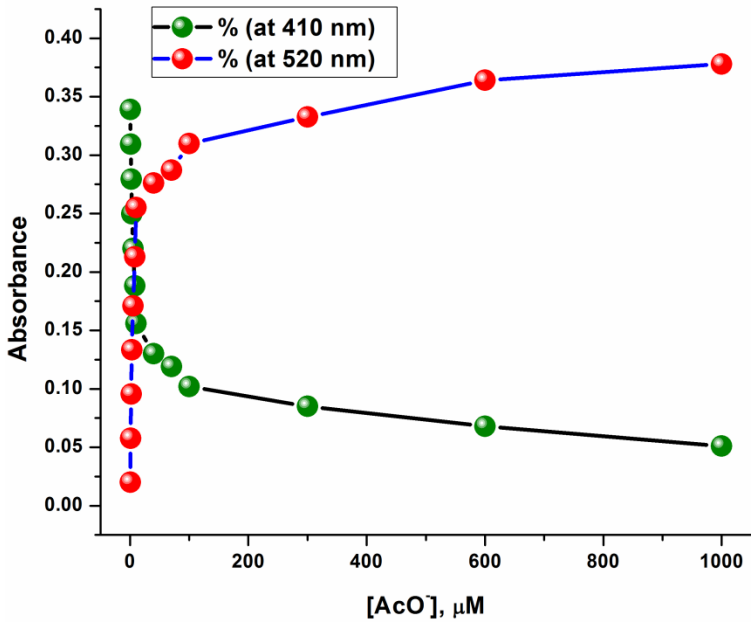

Fig.S2. Absorbance of **L** (10 μM) as a function of externally added AcO^{-} concentration (0.5-1000 μM)

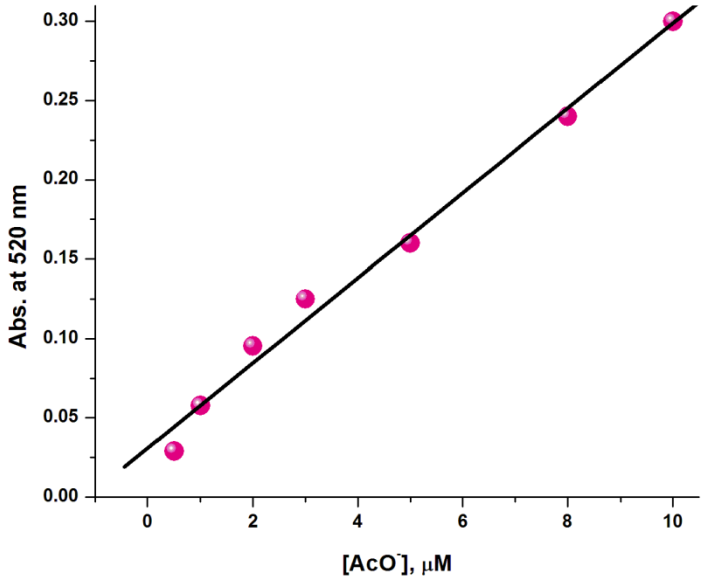

Fig.S3. Linear region of the plot of absorbance of **L** (10 μM, λ, 520 nm) as a function of externally added AcO^{-} concentration (0.5-10 μM)

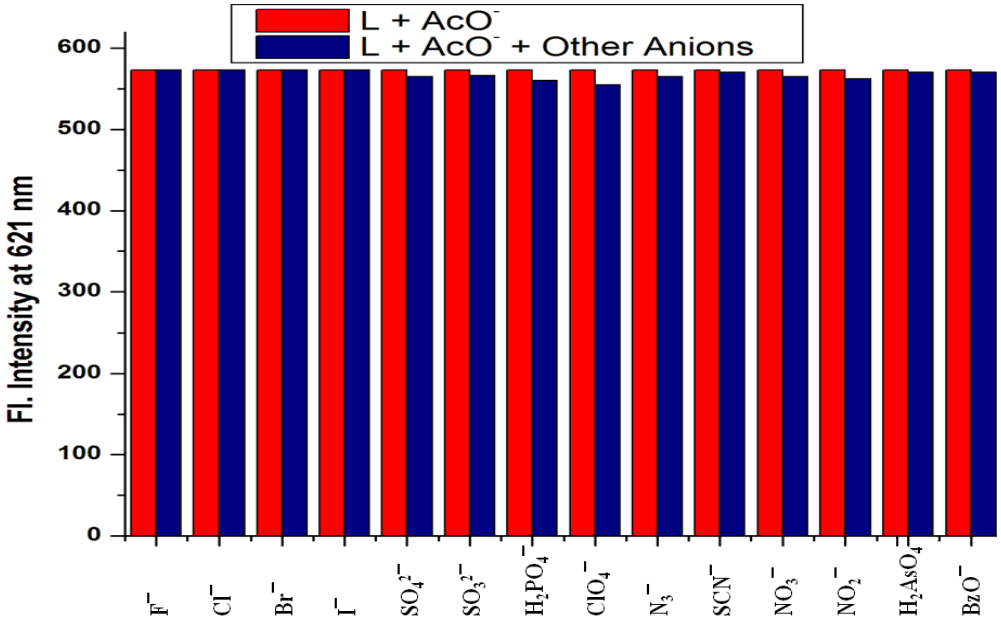

Fig.S4. Emission intensities of [**L** + AcO^{-}] system in presence of competing anions

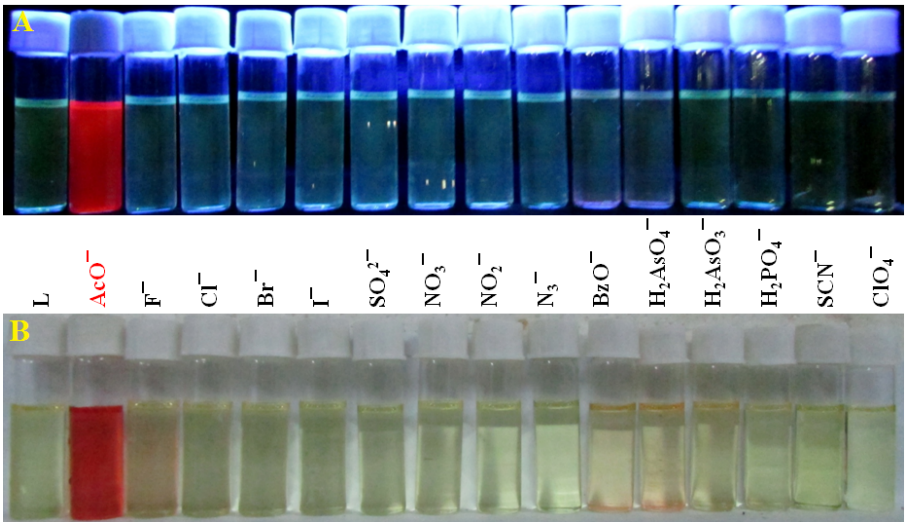

Fig.S5. Visual colour changes of **L** upon addition of equimolar amount of various cations under UV light (A) and visible light (B)

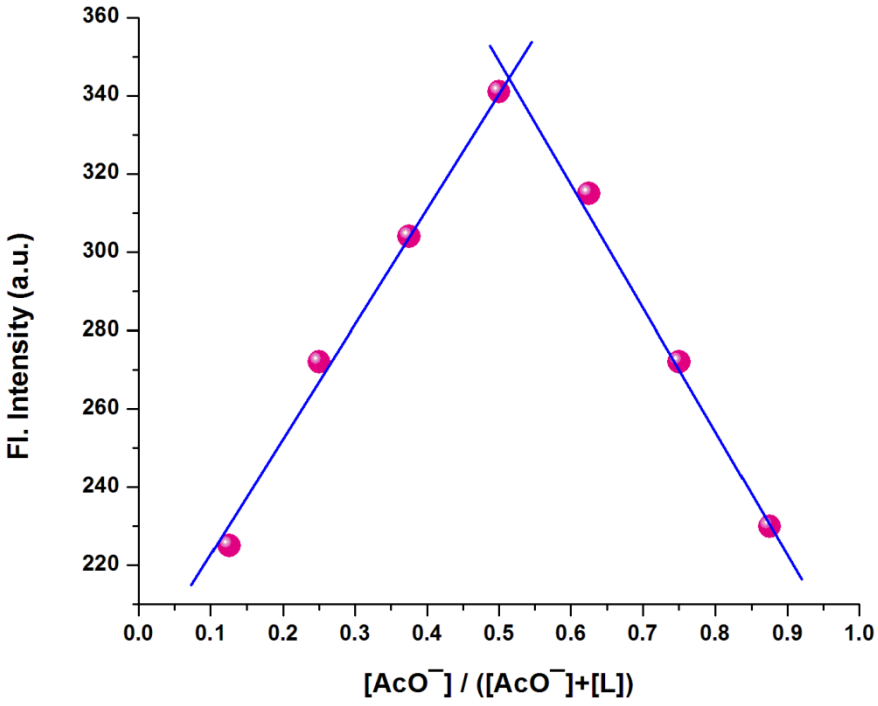

Fig.S6. Job's plot for determination of stoichiometry of the [**L** -AcO^-] adduct in DMSO (λ_{ex}, 532 nm, λ_{em}, 621 nm)

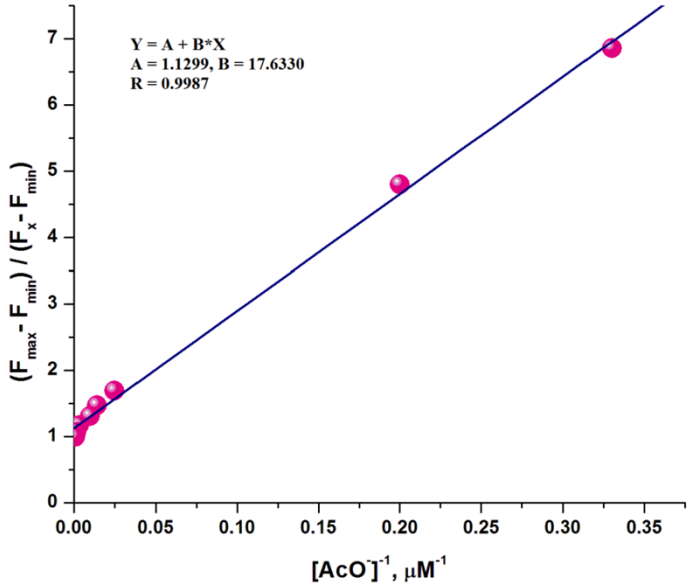

Fig.S7. Determination of binding constant of **L** for AcO^{-} in DMSO (λ_{ex}, 532 nm, λ_{em}, 621 nm) using fluorescence technique

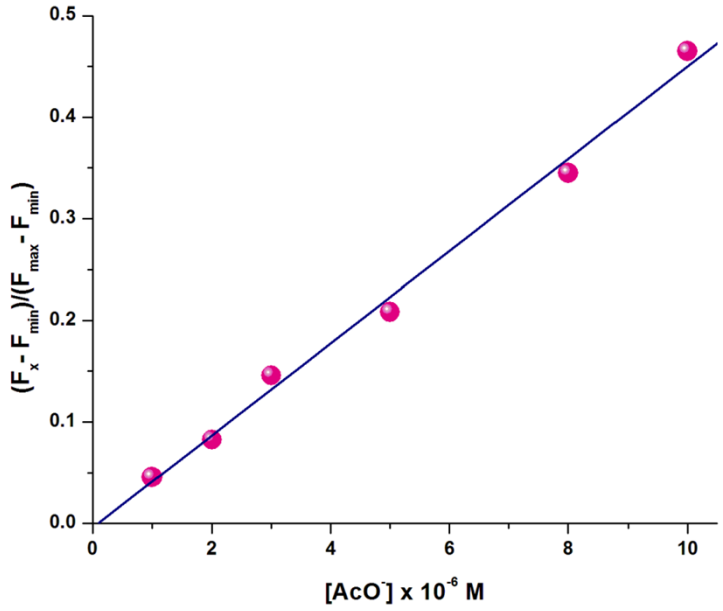

Fig.S8. Emission intensities of **L** (10 μM) as a function of externally added [AcO^{-}] in DMSO (λ_{ex}, 532 nm, λ_{em}, 621 nm) using fluorescence titration data in Fig.2

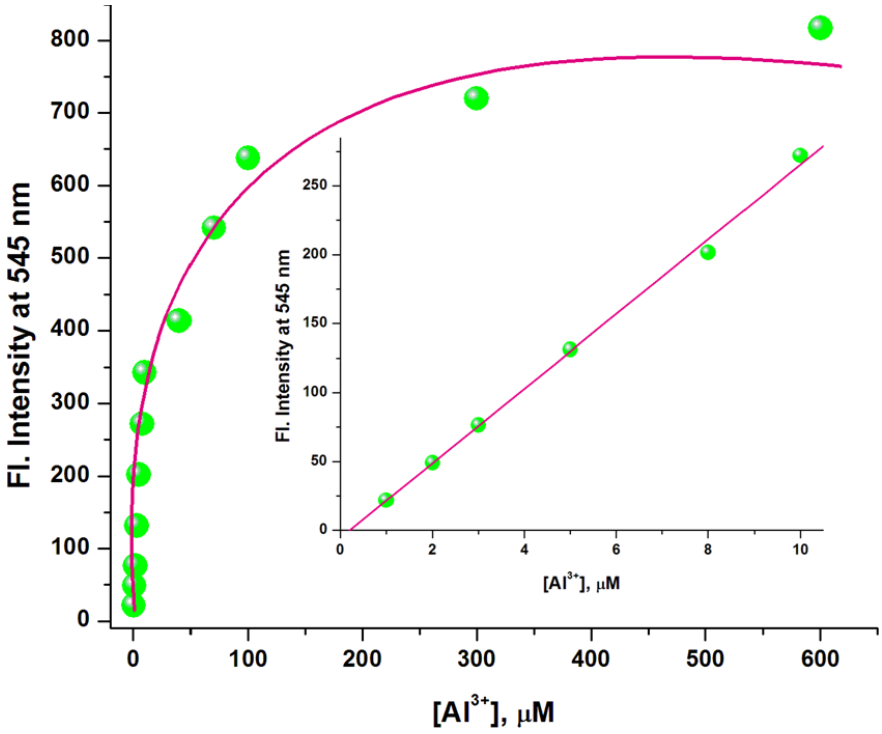

Fig.S9. Plot of emission intensities of **L** (15 μM, λ_{ex} = 432 nm, λ_{em} = 545 nm) as a function of externally added Al^{3+} (0.5-600 μM); Inset: linear region (0.5-10 μM Al^{3+})

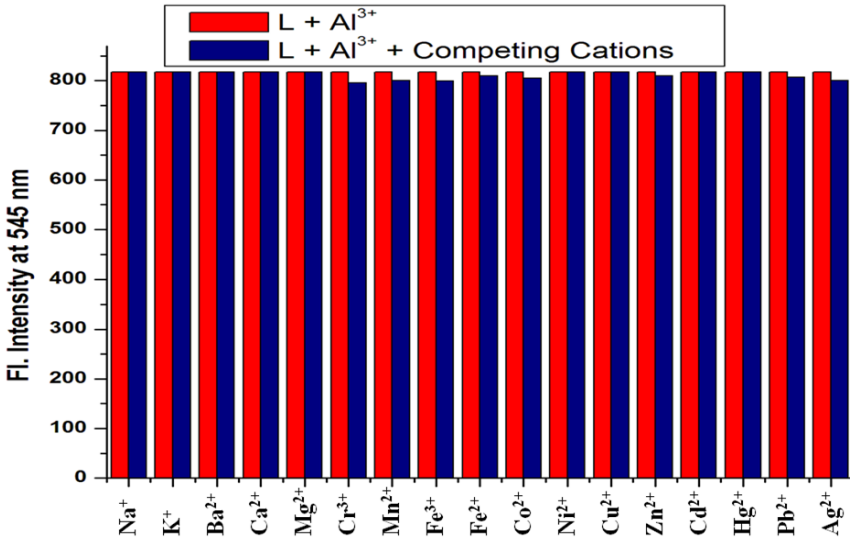

Fig.S10. Emission intensities of [**L**-Al^{3+}] system in presence of common cations

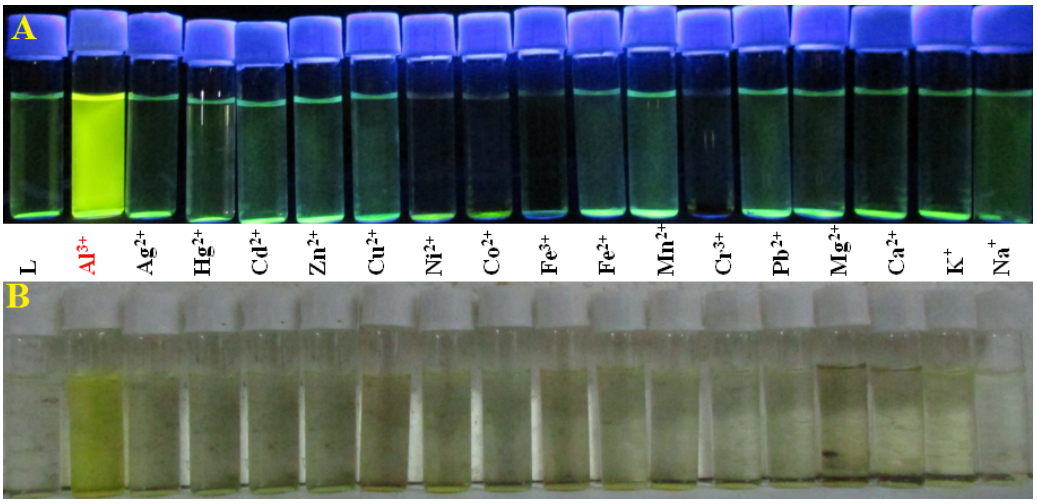

Fig.S11. Visual colour changes of **L** upon addition of equimolar amount of various cations under UV light (A) and visible light (B)

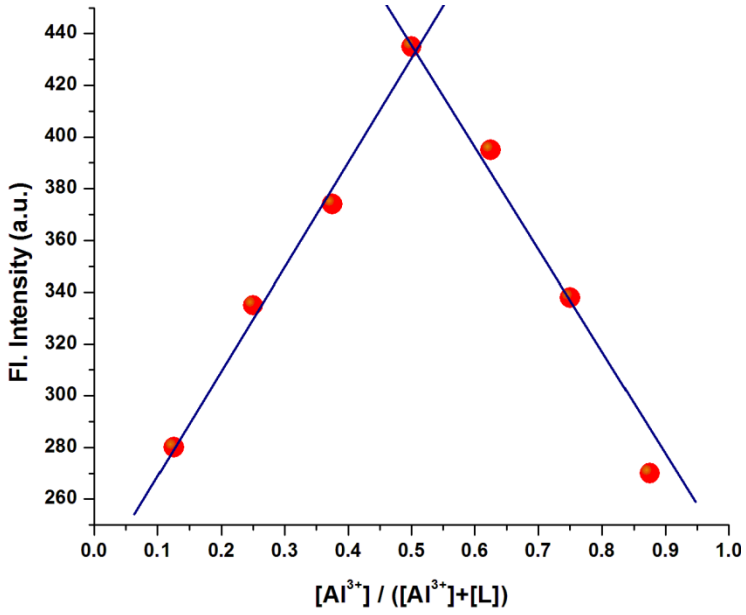

Fig.S12. Job's plot for determination of stoichiometry of the [**L**-Al^{3+}] adduct in aqueous-methanol (1:4, v/v, λ_{ex}, 532 nm, λ_{em}, 621 nm)

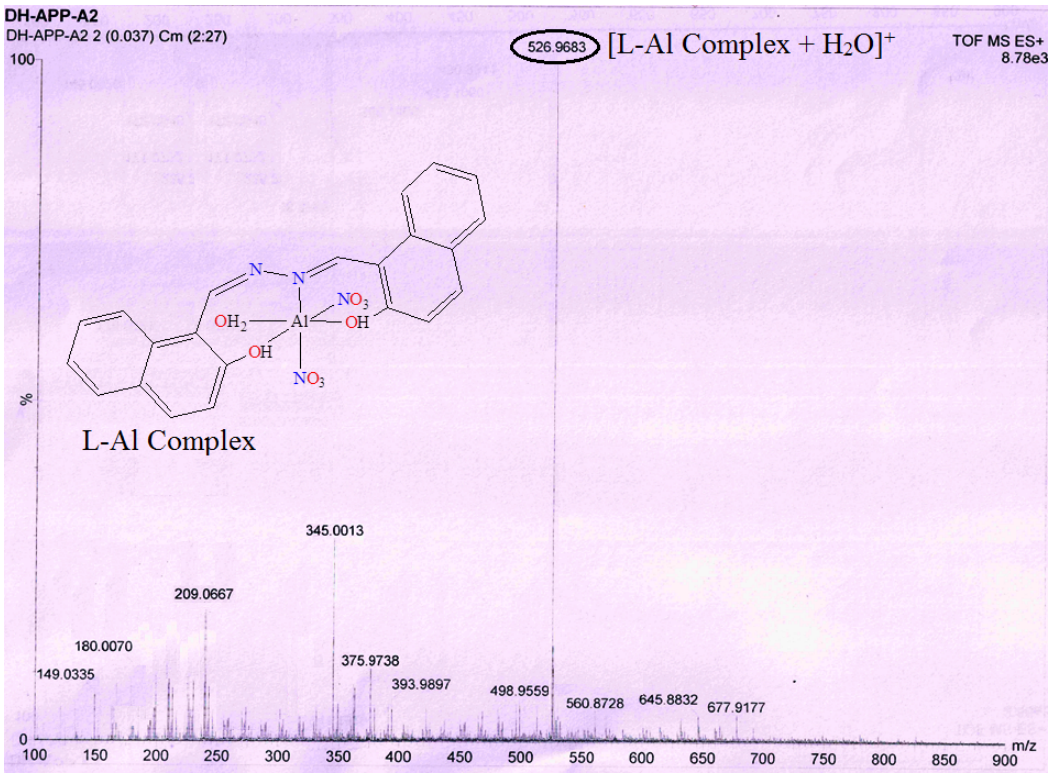

Fig.S13. QTOF-MS spectrum of [**L- Al^{3+}**] adduct.

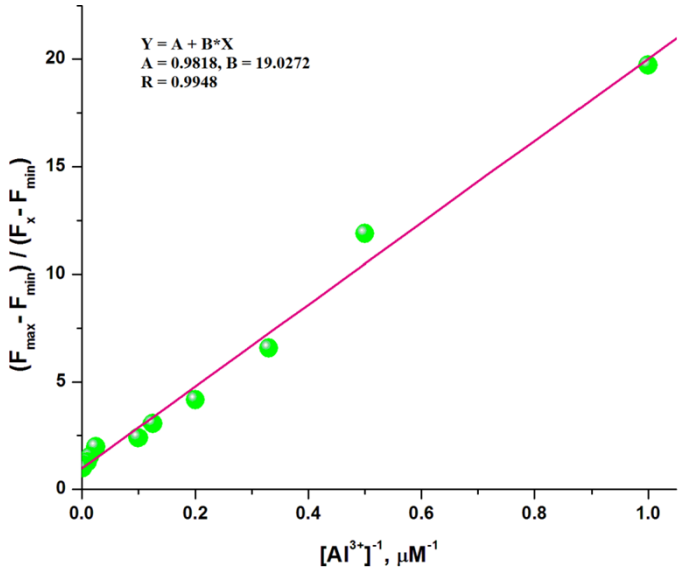

Fig.S14. Determination of binding constant of **L** for Al^{3+} in aqueous-methanol (1:4, v/v, λ_{ex}, 432 nm, λ_{em}, 545 nm) using fluorescence technique

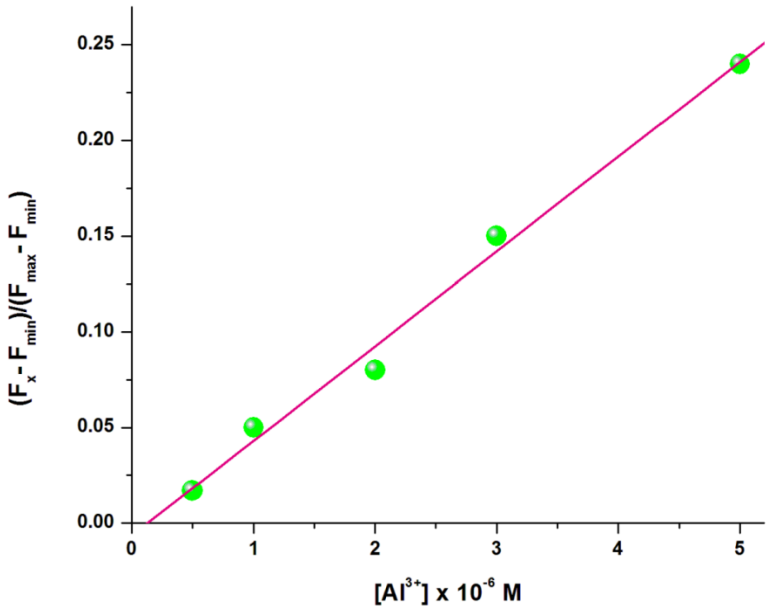

Fig.S15. Emission intensities of **L** (15 μM) as a function of externally added [Al^{3+}] in aqueous-methanol (1:4, v/v,λ_{ex}, 432 nm, λ_{em}, 545 nm for LOD determination (using fluorescence titration data of Fig.7)

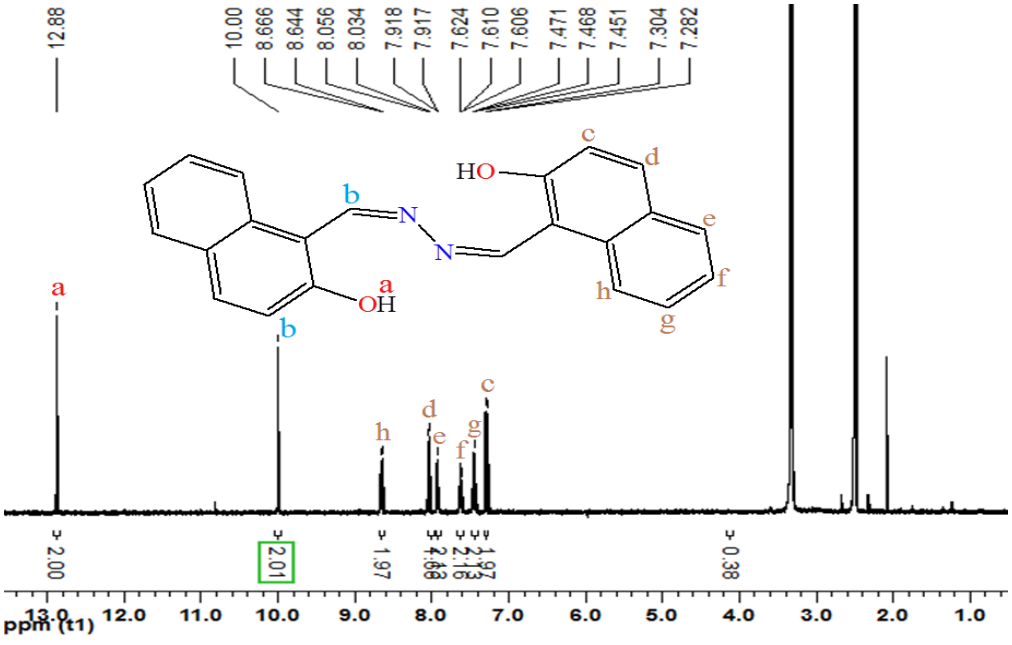

Fig.S16.^{1}H NMR spectrum of **L** in DMSO-d_6

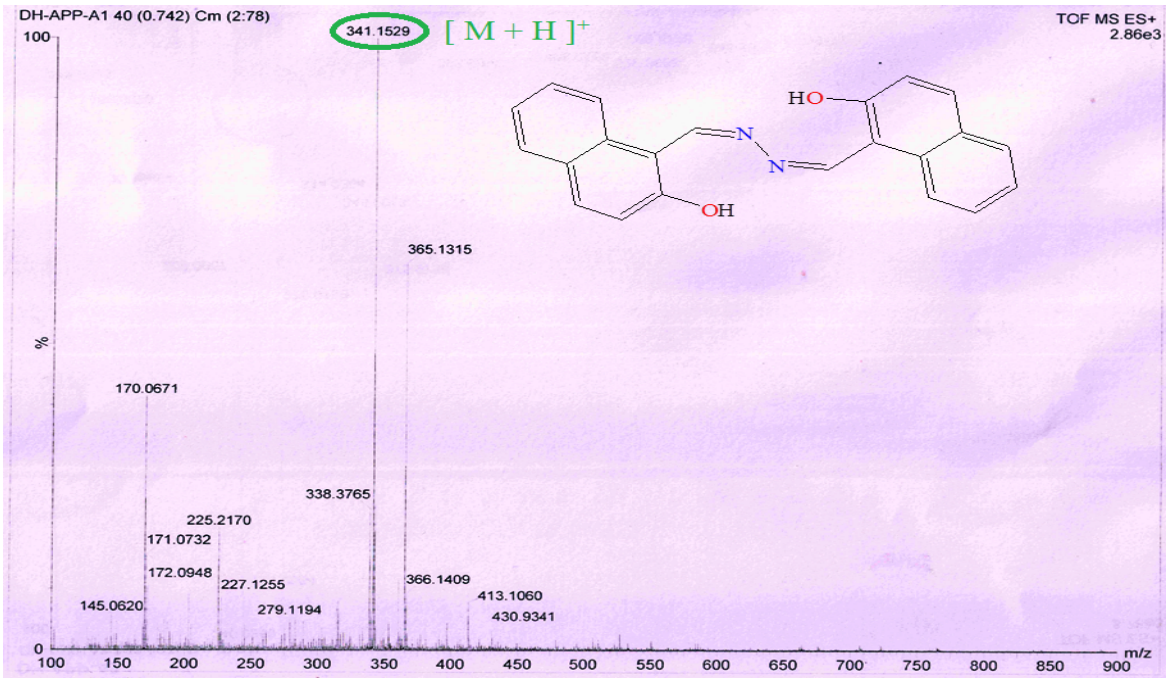

Fig.S17. QTOF-MS spectrum of **L**

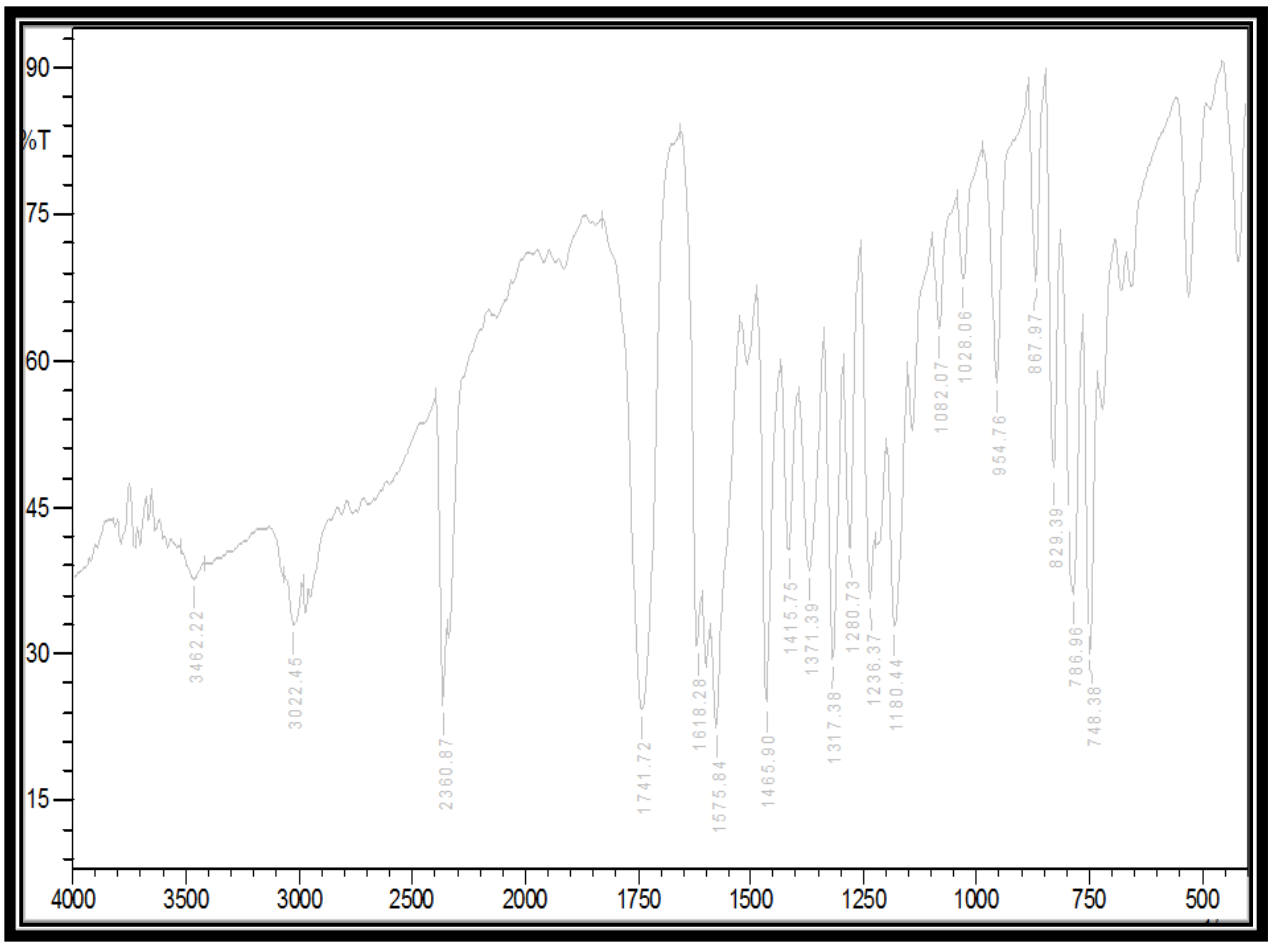

Fig.S18.FTIR spectrum of **L**

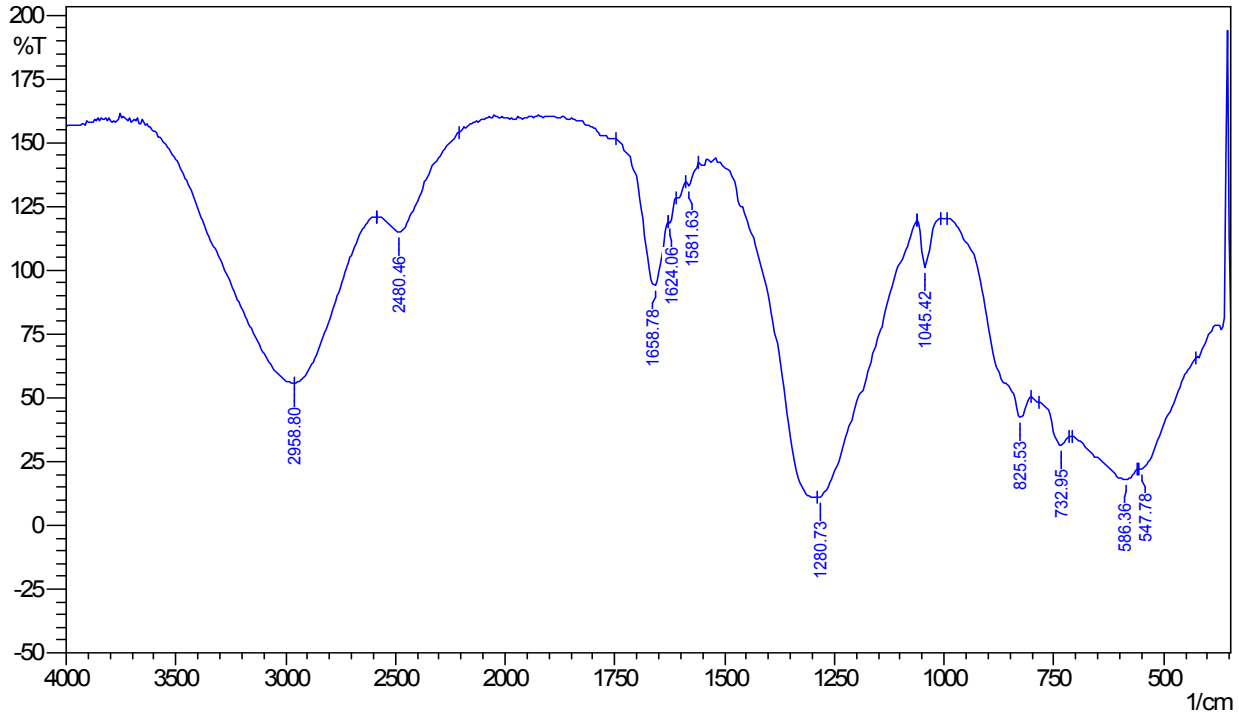

Fig.S19. FTIR spectrum of [**L- Al^{3+}**] adduct

Table S1. Comparison of the present probe with the existing probe[5]

Sensing parameters		Present probe	Reported probe[5] (S. Goswami et. al.)
Detection limits	Acetate	1.0×10^{-7} M	170×10^{-7} M
	Al^{3+}	1.2×10^{-7} M	15.4×10^{-7} M
Binding constants	Acetate	5.67×10^{4} M^{-1}	3.2×10^{4} M^{-1}
	Al^{3+}	5.25×10^{4} M^{-1}	4.0×10^{4} M^{-1}
Emission wavelengths	Acetate	621 nm	486 nm
	Al^{3+}	545 nm	450 nm

References

(1) H. A. Benesi and J. H. Hildebrand*, J. Am. Chem. Soc*., 1949, **71**, 2703-2707.

(2) E. Austin, M. Gouterman, *Bioinorg. Chem.*1978**, 9**, 281-298.

(3) W. H. Melhuish, *J. Phys. Chem.*1961, **65**, 229-235.

(4). R. Kubin and A. Fletcher, *J. Lumin.*, 1983, **27**, 455-462.

(5) S. Goswami, A.K. Das, K. Aich, A. Manna, H.K. Fun and C.K. Quah, *Supramol. Chem.*, 2014, **26**, 94-104.