†Electronic Supplementary Information (ESI)

A naphthalene based Al^{3+} selective fluorescent sensor for living cell imaging

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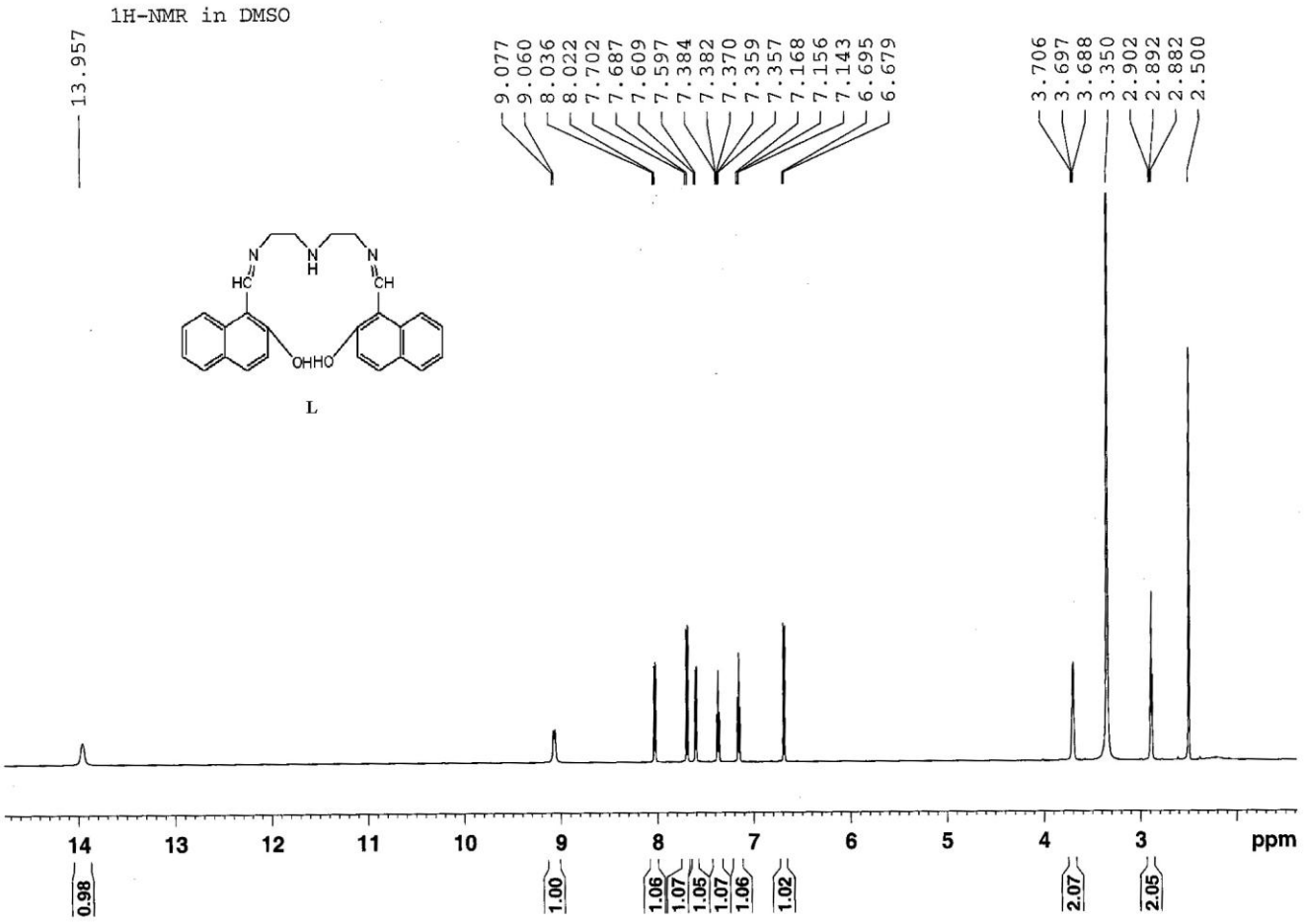


Fig. S1. ^{1}HNMR of **L** in DMSO-$d_{6.}$

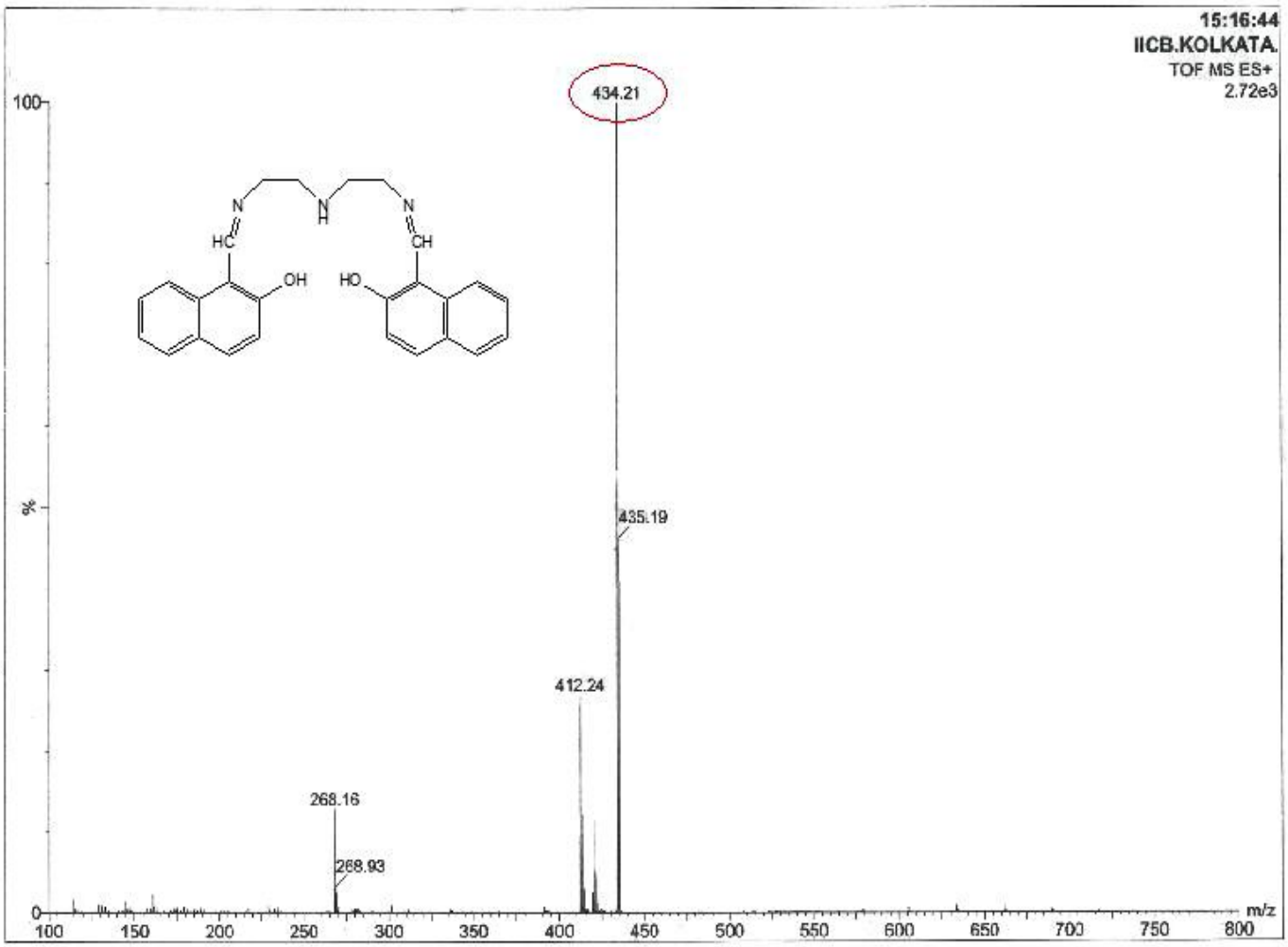


Fig.S2. QTOF-MS spectrum of **L**

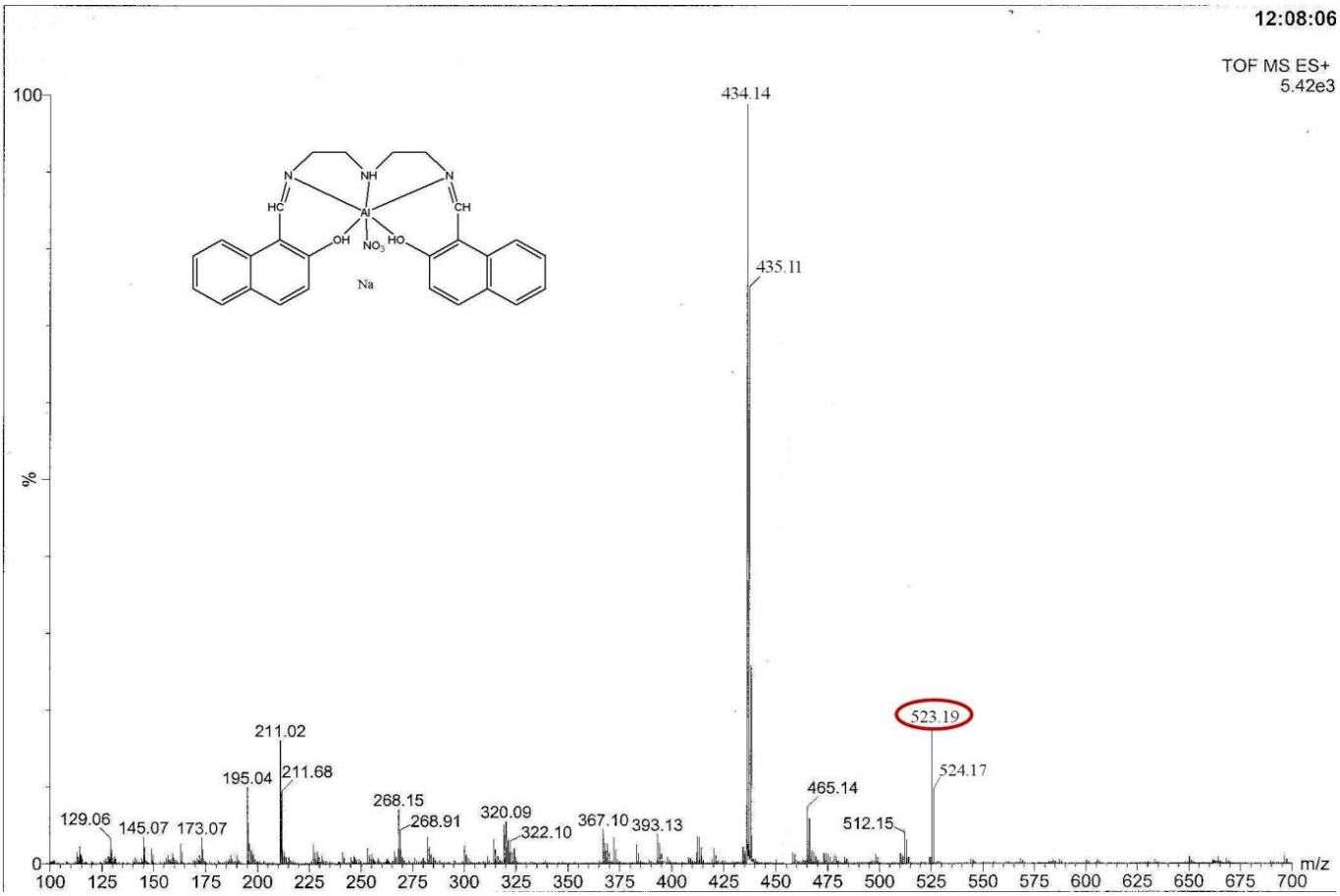


Fig. S3. QTOF-MS spectrum of complex $[\mathbf{L} + Al^{3+} + NO_3]Na^+$.

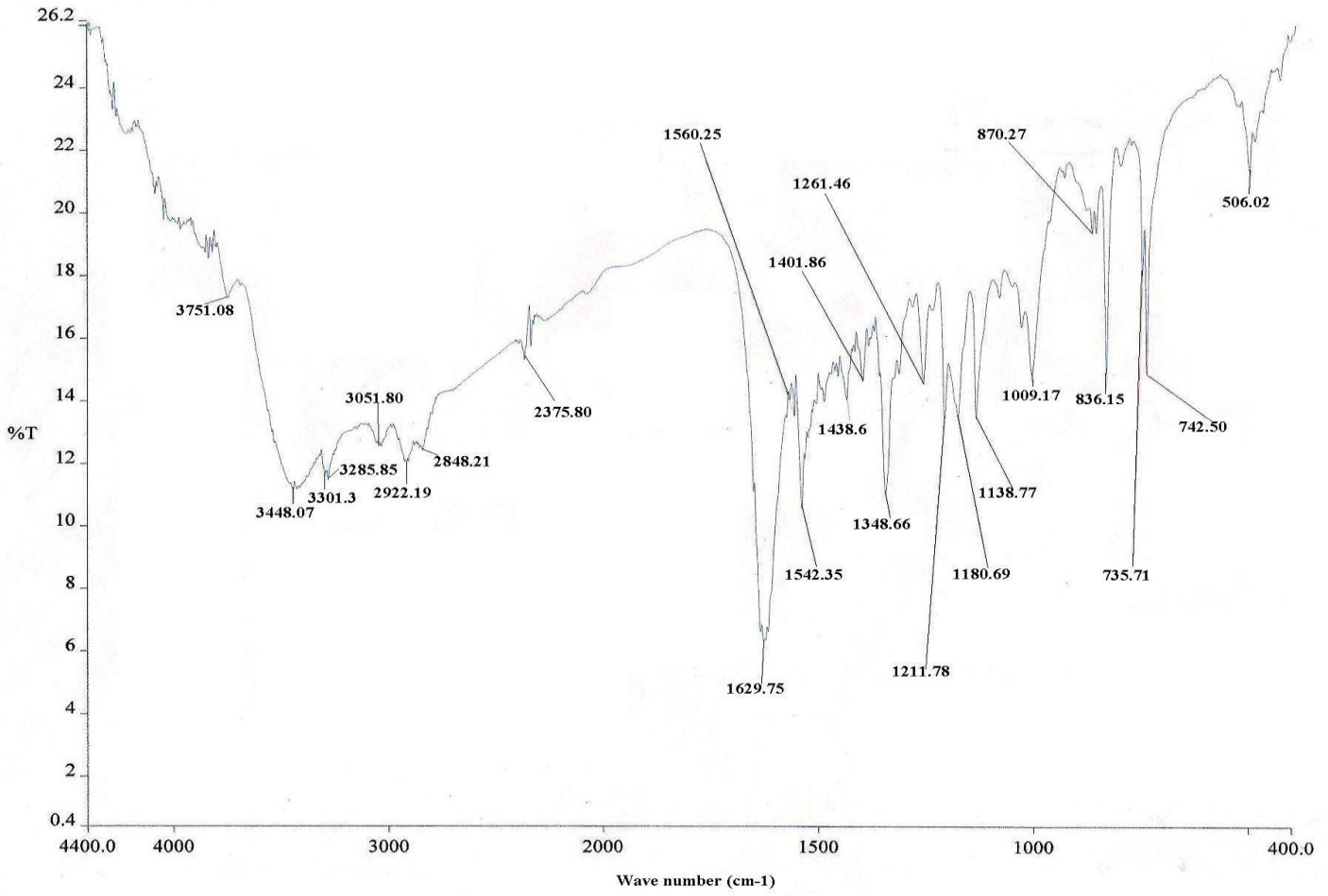


Fig.S4. FTIR spectra of **L**

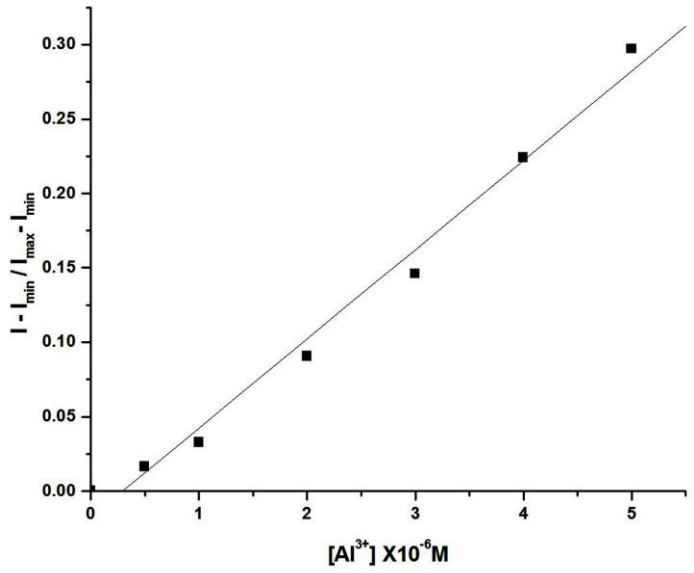


Fig.S5. Emission intensities of **L** (10 μM) as a function of externally added [Al^{3+}] in ethanol, λ_{em}: 445 nm, λ_{ex} : 355 nm. The detection limit is 3.0×10^{-7}.

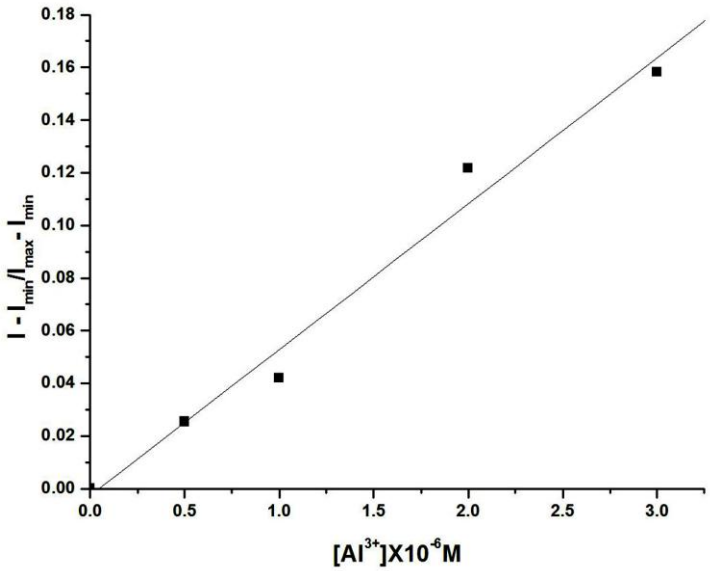


Fig.S6. Emission intensities of **L** (10 μM) as a function of externally added [Al^{3+}] in HEPES buffer (0.1 M in ethanol/water = 3/7, v/v, pH 7.4, λ_{em}: 445 nm, λ_{ex} : 355 nm). The detection limit is 1.0×10^{-7}.

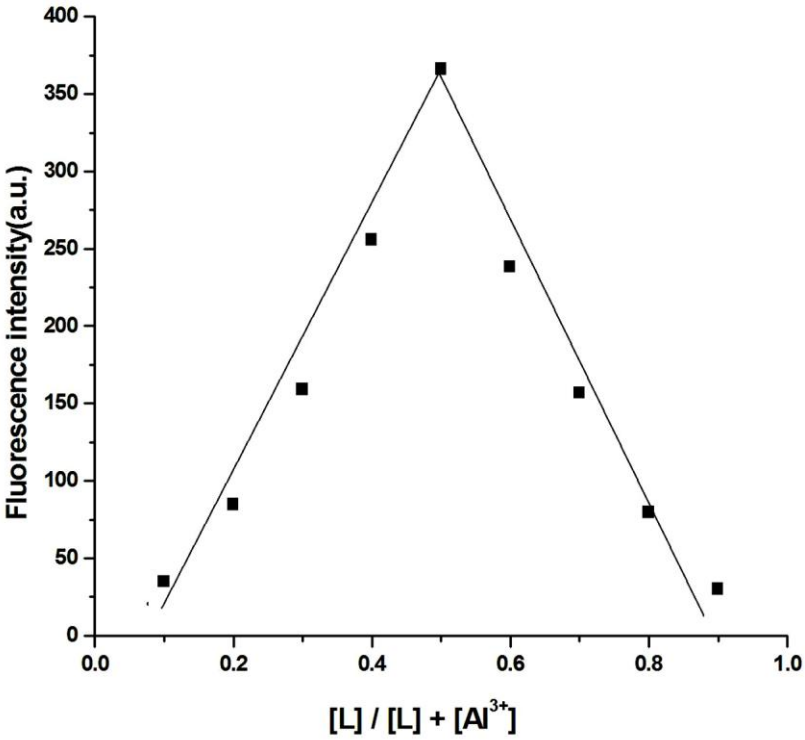


Fig. S7. Job's plot of the complexation reaction between **L** and Al^{3+} in HEPES buffer (0.1 M) solution (ethanol/water = 3/7, v/v, pH 7.4).

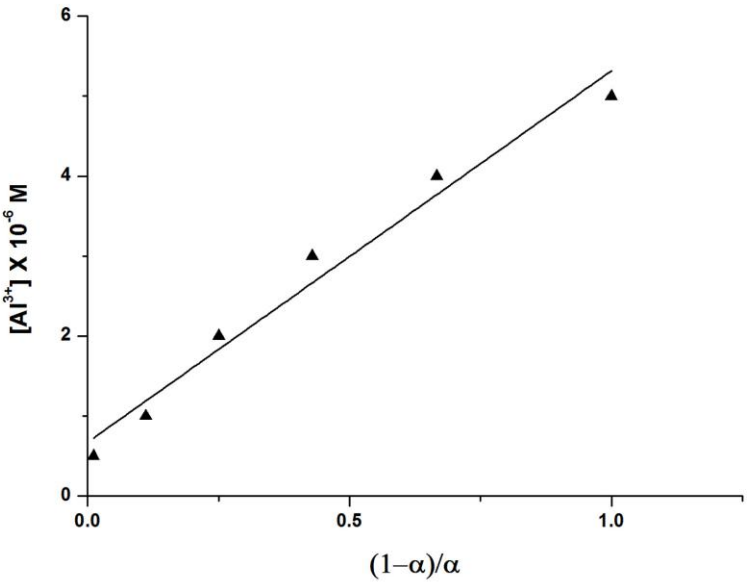


Fig. S8. The binding constant (K_a) of **L** for Al^{3+}

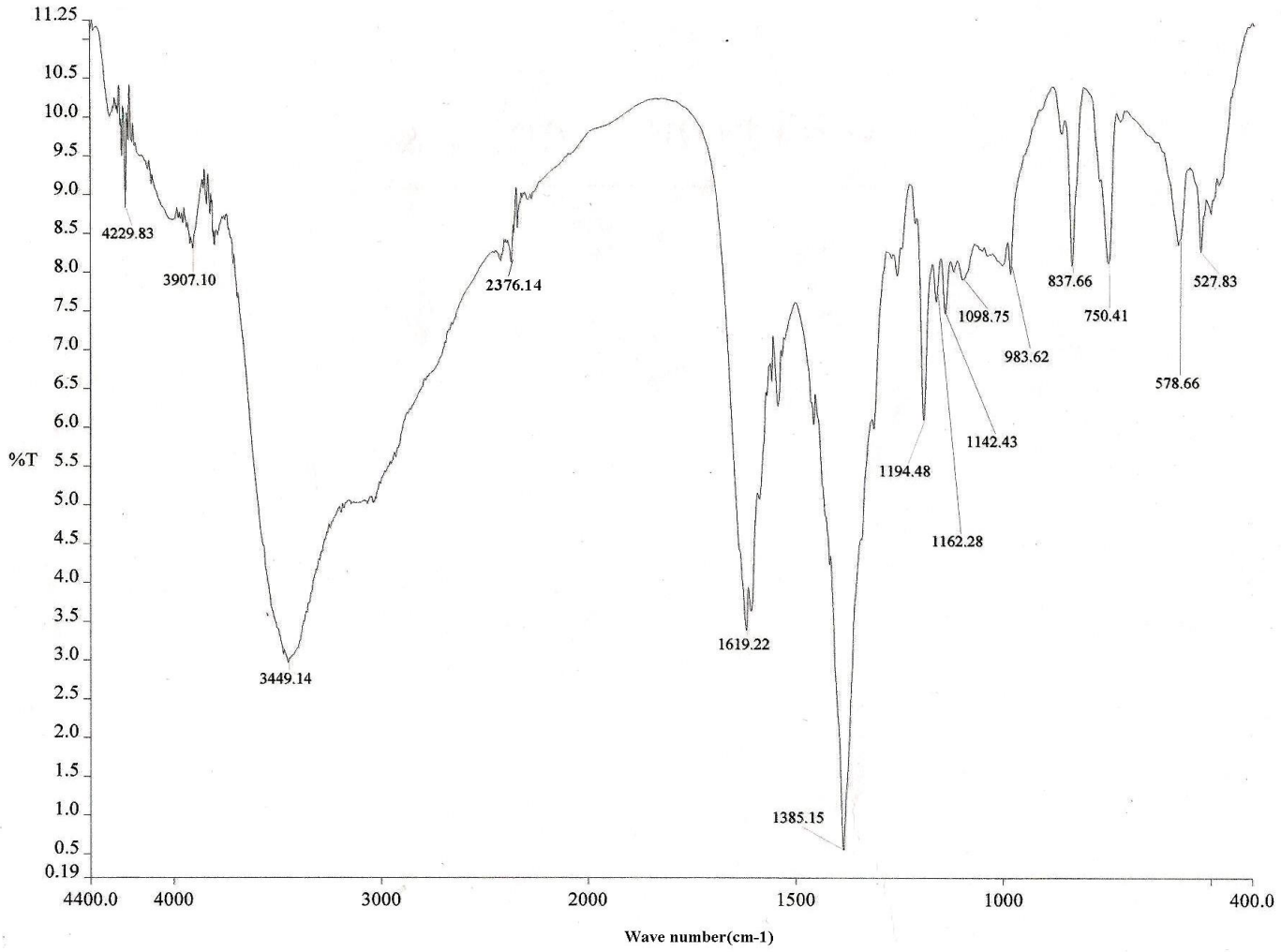


Fig. S9. FTIR spectra of [**L**-Al] $^{3+}$ NO_3 complex.

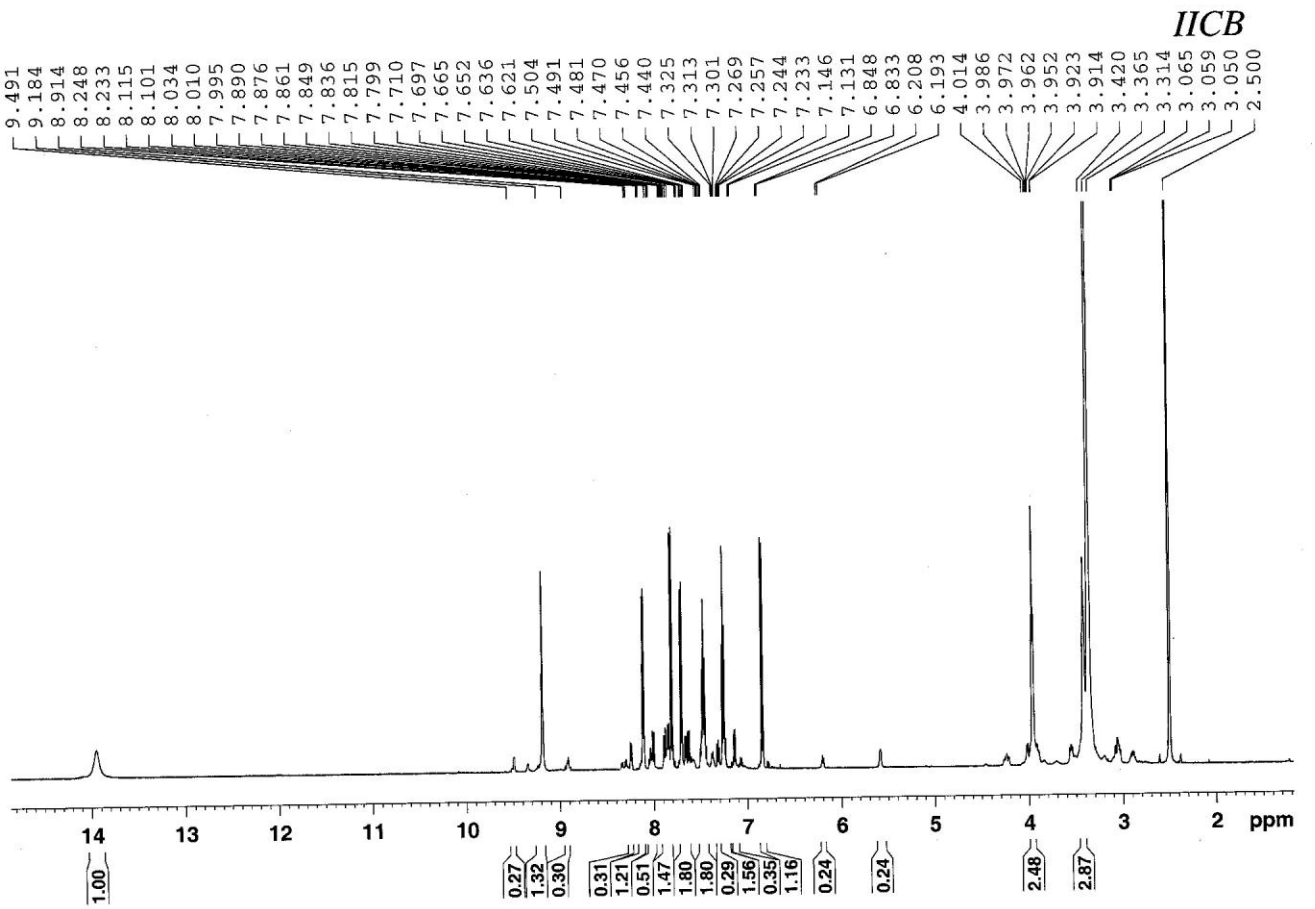


Fig. S10. ^{1}HNMR spectra of [**L**-Al] $^{3+}$ NO_3 complex. in DMSO-d_6.

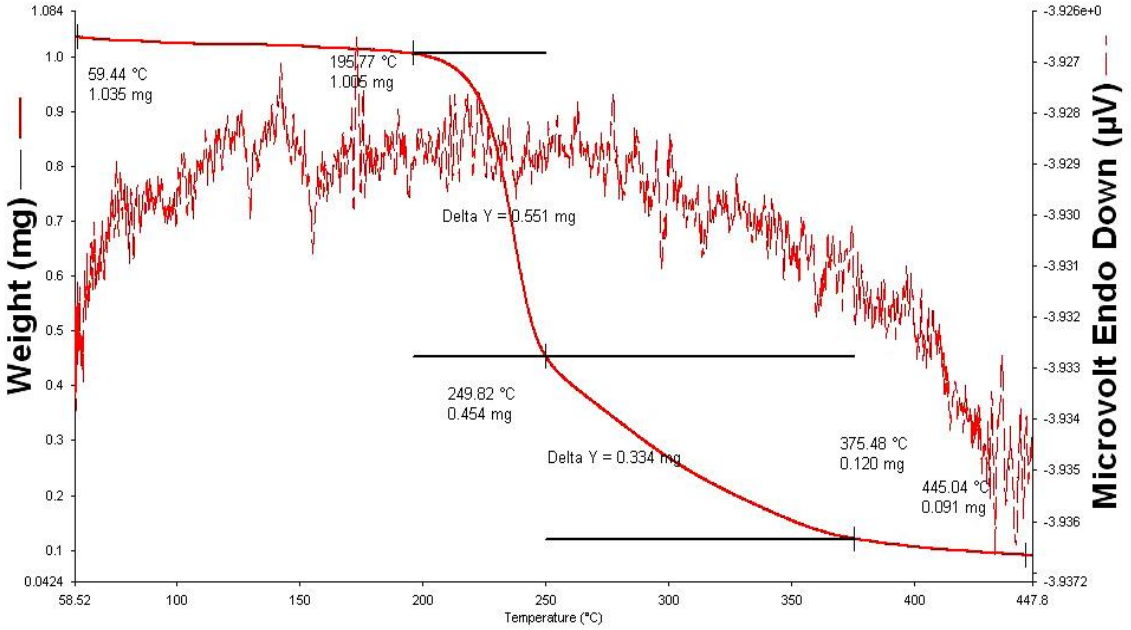


Fig. S11. Thermogravimetric analysis of **L**.

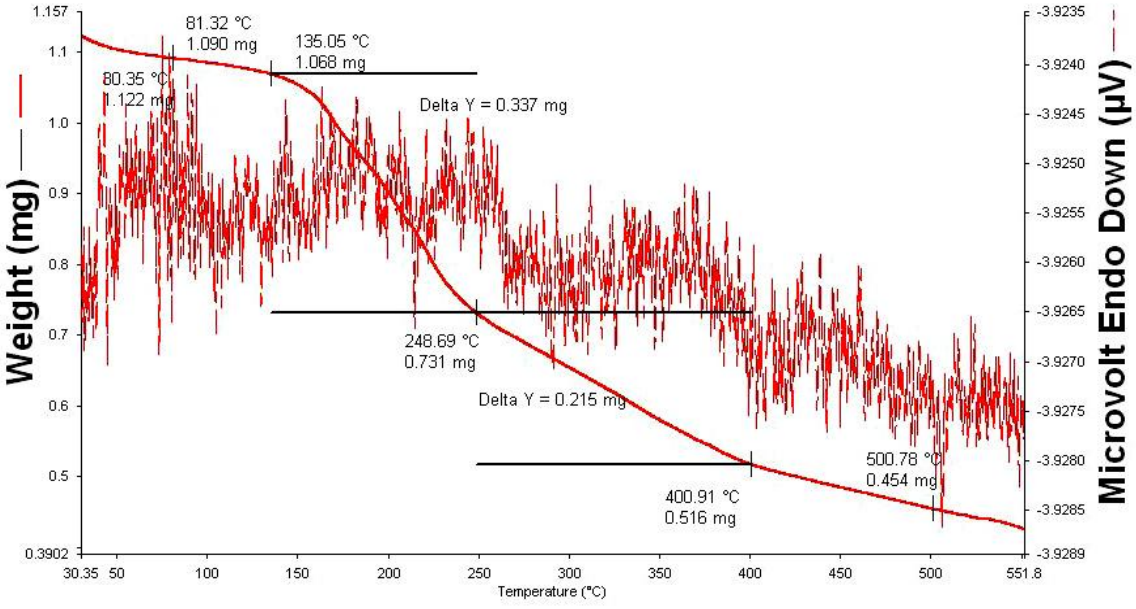


Fig. S 12. Thermogravimetric analysis of [**L** -Al^{3+}]NO_3 complex.

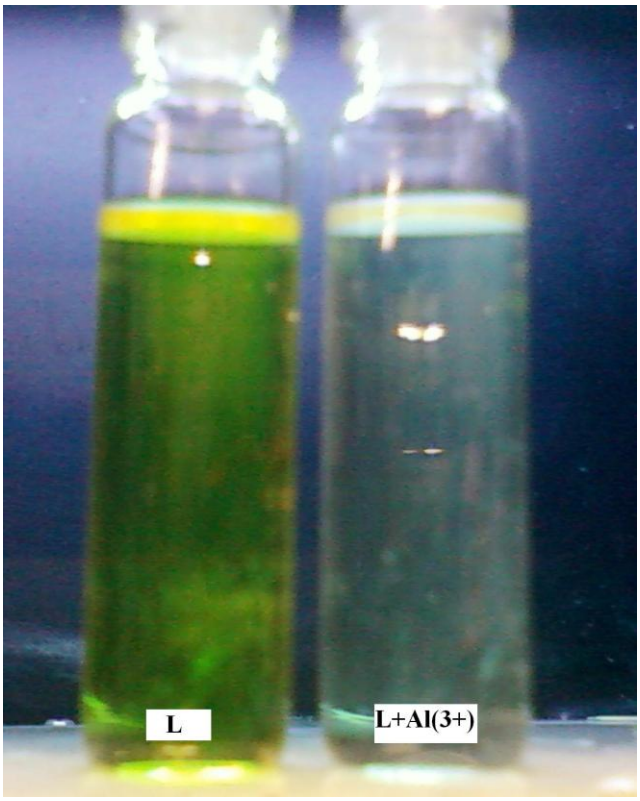


Fig. S 13. Colour change of the Ligand solution after adding equivalent quantity of Al^{3+} (under UV light).

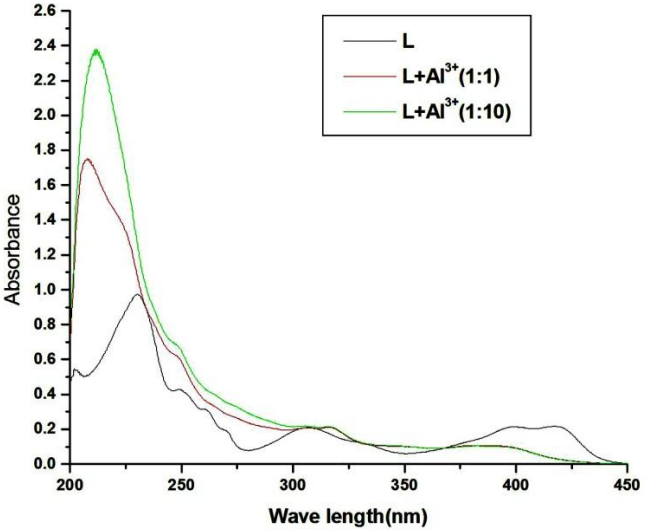


Fig. S 14. Absorbance spectra of **L** (10 μM), **L** + Al^{3+} (1:1, mole ratio) and **L** + Al^{3+} (1:10, mole ratio) in HEPES buffer (0.1 M) solution (ethanol/water = 3/7, v/v, pH 7.4).

1. General method of UV-vis. and fluorescence titration

Path length of the cells used for absorption and emission studies was 1 cm. For UV-vis and fluorescence titrations, stock solution of **L** was prepared (C = 10 μM) in ethanol and ethanol/water (3/7, v/v) HEPES (0.1M) buffer. Working solutions of **L** and Al^{3+} were prepared from their respective stock solutions. Fluorescence measurements were performed using 5 nm x 5 nm slit width.

2. Calculation of Quantum Yield

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

$$\phi_{\text{sample}} = \frac{\text{OD}_{\text{standard}} \times A_{\text{sample}}}{\text{OD}_{\text{sample}} \times A_{\text{standard}}} \times \phi_{\text{standard}}$$

where A was the area under the fluorescence spectral curve and OD was optical density of the compound at the excitation wavelength[1]. Anthracene was used as quantum yield standard (quantum yield is 0.27 in ethanol)[2] for measuring the quantum yields of ligand and its Al^{3+} complex.

3. Job's plot from fluorescence experiments

A series of solutions containing **L** and $Al(NO_3)_3$ were prepared such that the total concentration of Al^{3+} and **L** remained constant (10 μM) in all the sets. The mole fraction (X) of **L** was varied from 0.1 to 0.9. The fluorescence intensity at 445 nm was plotted against the mole fraction of the ligand (**L**) in solution.

4. Determination of Binding Constant

Li *et al*. derived the following Tsein equation[3] that can be used to find out the stoichiometric ratio between the ligand and metal ion.

$$[M^{n+}]^m = \frac{1}{n \cdot K} \cdot \frac{1}{[L]_T^{n-1}} \cdot \frac{1-\alpha}{\alpha^n}$$

Where K is complex equilibrium constant, M_mL_n is the complex species, L is ligand and M is the metal ion. Third bracket is used to denote their concentration. α is the ratio between free ligand concentration [L], and its initial concentration $[L]_T$. In our case, the stoichiometric ratio of the Al^{3+}: **L** was 1:1. So, this equation can be written as $[Al^{3+}] = 1/K.(1-\alpha)/\alpha$. The curve fitting of the experimental data points using this equation yielded, $K_a = (2.12 \pm 0.05) \times 10^5\ M^{-1}$.

Table 1: Changes in Chemical shifts (δ ppm) of **L** during ^{1}HNMR titration experiment upon concomitant additions of Al^{3+}.

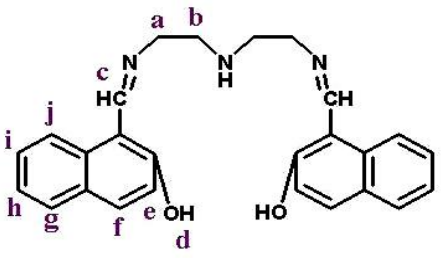
$[Al^{3+}]$ Equiv.	-OH	-CH=N-	-N-H	$-CH_2$ (a)	$-CH_2$ (b)	Ar-H (e)	Ar-H (f)	Ar-H (g)	Ar-H (h)	Ar-H (i)	Ar-H (j)
0.00	13.9	9.1	------	2.9	3.7	6.7	8.0	7.6	7.15	7.4	7.7
1.00	13.9	9.2	5.6	3.4	4.0	6.85	8.1	7.7	7.3	7.5	7.8
2.00	13.9	9.2	5.6	3.4	4.0	6.85	8.1	7.7	7.3	7.5	7.8

References

1 E. Austin, M. Gouterman, *Bioinorg. Chem.*, 1978, **9**, 281.

2 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.

3 G. Grynkiewcz, M. Poenie and R. Y. Tsein, *J. Biol.Chem.* 1985, **260**, 3440.



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Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry