

SUPPORTING INFORMATION

Hydrazinopyrimidine derived novel Al^{3+} chemosensor: molecular logic gate and biological applications

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Experimental

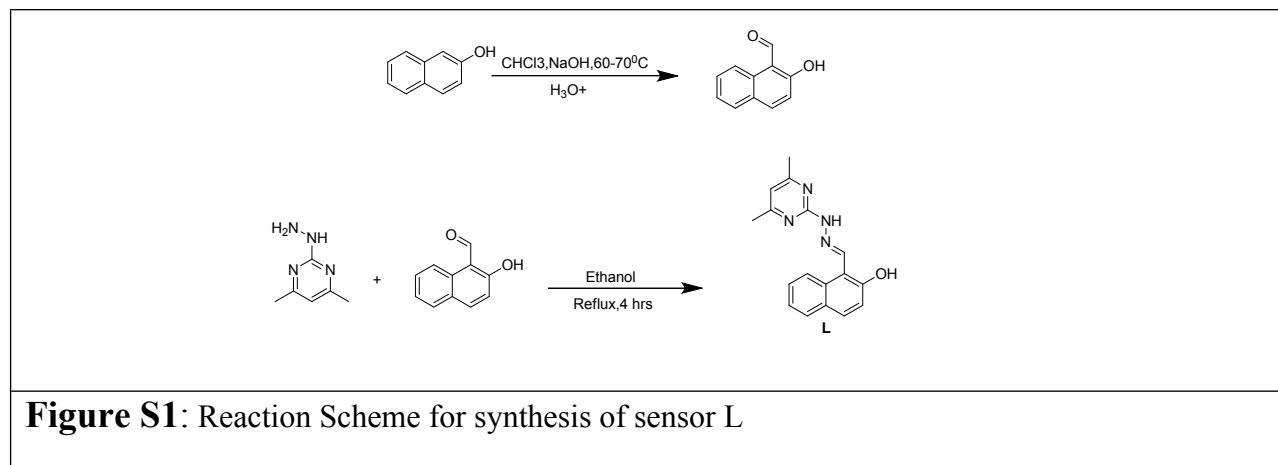
Materials and instruments

2-Naphthol ($\geq 99.0\%$) (a/a), chloroform ($\geq 99.0\%$), NaOH ($\geq 97.0\%$), ethyl acetate (98.0 %), silica gel (60-120 mesh), methanol ($\geq 99.0\%$), high-purity HEPES (99.0 %), Na₂EDTA (98.0 %), metal perchlorate salts and related solvent were purchased from Merck (India)Ltd. and were used without further purifications. 2-hydroxy-naphthaldehyde and 2,6-dimethyl pyrimidine hydrazine were prepared by using literature method described elsewhere. Solvents used were of spectroscopic grade for spectral measurements. Other chemicals were of analytical reagent grade and have been used without further purification except when specified. ¹H NMR was recorded on Bruker 400 MHz instruments using TMS as internal standard. Chemical shifts δ are expressed in ppm unit and ¹H–¹H coupling constants in Hz. Mass spectrum were recorded on Qtof Micro YA263 mass spectrometer. Absorbance data obtained from a UV-Visible spectrometer (model-evolution 201).Fluorescence data were recorded using a xenoflash(PTI) fluorescence spectrophotometer with excitation wavelength 380 nm for ligand and complex. Anthracene ($\phi = 0.27$ in ethanol) had been taken as reference compound to measure the fluorescence quantum yield.

Synthesis

(E)-1-((2-(4,6-dimethylpyrimidin-2-yl)hydrazono)methyl)naphthalen-2-ol

2-hydroxy-1-naphthaldehyde was prepared according to literature method using Reimer-Tiemann reaction. A solution of 4,6-dimethyl-2-hydrazinopyrimidine (100mg, 0.72mmol) in ethanol (~15 ml) was added drop wise to a solution containing 2-hydroxy-1-naphthaldehyde (125 mg, 0.72 mmol) in ethanol (~15 ml) with stirring. The resulting solution was then refluxed for 4 hours. After that volume of the solution was reduced to one-third of its initial volume to get a faint-yellow precipitate which was collected by filtration followed by washing thoroughly with cold methanol. The product was purified by column chromatography separation using ethyl acetate: petroleum ether (8:2; v/v) as eluent (**Scheme 1**). The yield of the product was found to be 76%.m.pt: 196-198°C, ¹H NMR (**ESI-Fig. S2**) [400 MHz, DMSO-*d*₆] δ(ppm): 13.16 (1H, s), 11.49 (1H, s), 9.15 (1H, s), 8.06 (1H, d, *J* = 8.4 Hz), 7.84-7.88 (2H, m), 7.57 (1H, d, *J* = 7.6 Hz), 7.40 (1H, d, *J* = 7.2 Hz), 7.21 (1H, d, *J* = 8.8 Hz), 6.69 (1H, s), 2.33 (6H, s). MS (**ESI-Fig. S3**): *m/z*=292.13 (calculated), 293.13[M+H]⁺ (observed). IR(KBr,cm⁻¹): (**ESI-Fig. S4**) 3350, 2921, 2851, 1620, 1598, 1566, 1483, 1401, 1383, 1364, 1315, 1282, 1187, 1158, 1125, 1028.



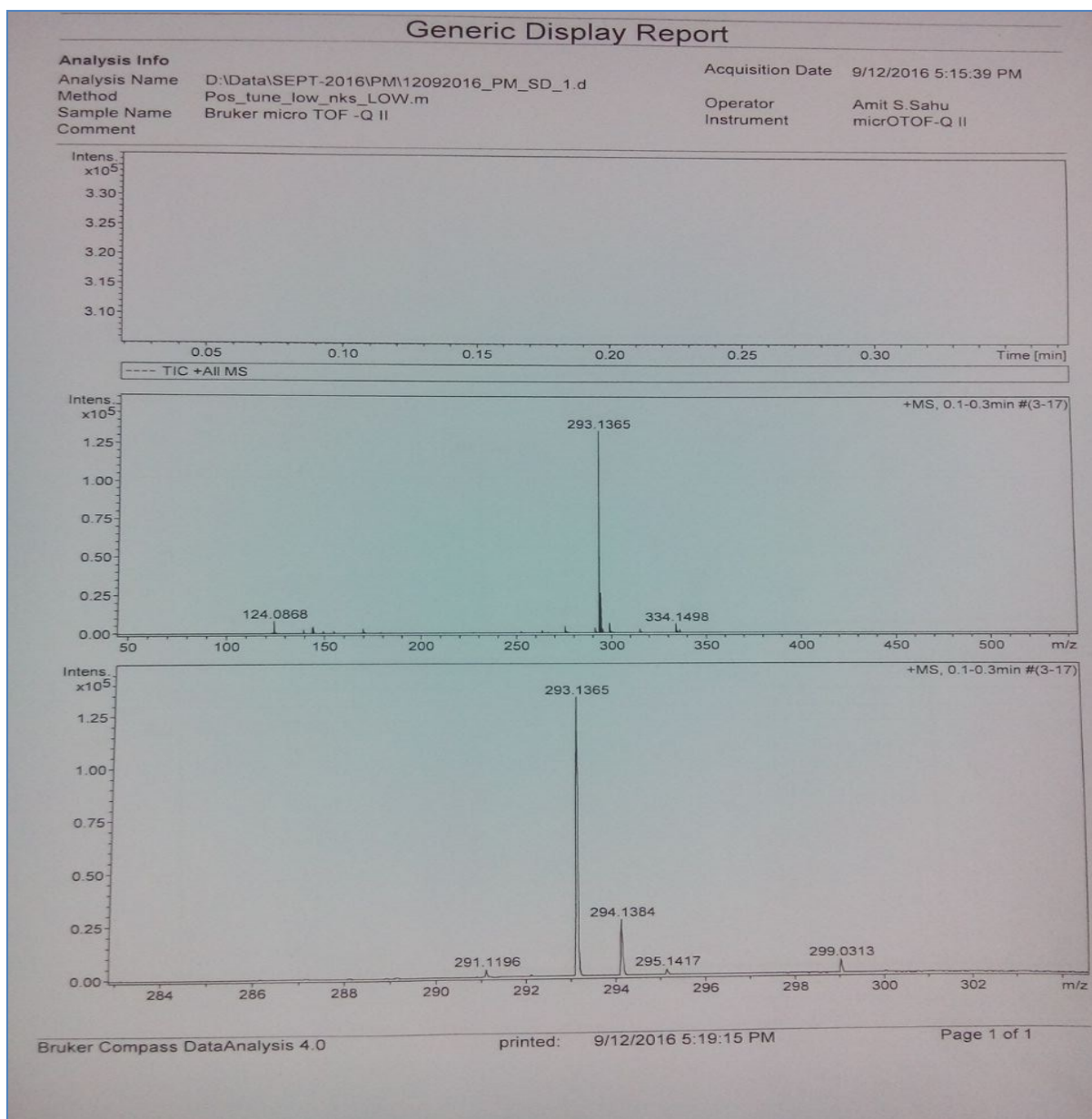
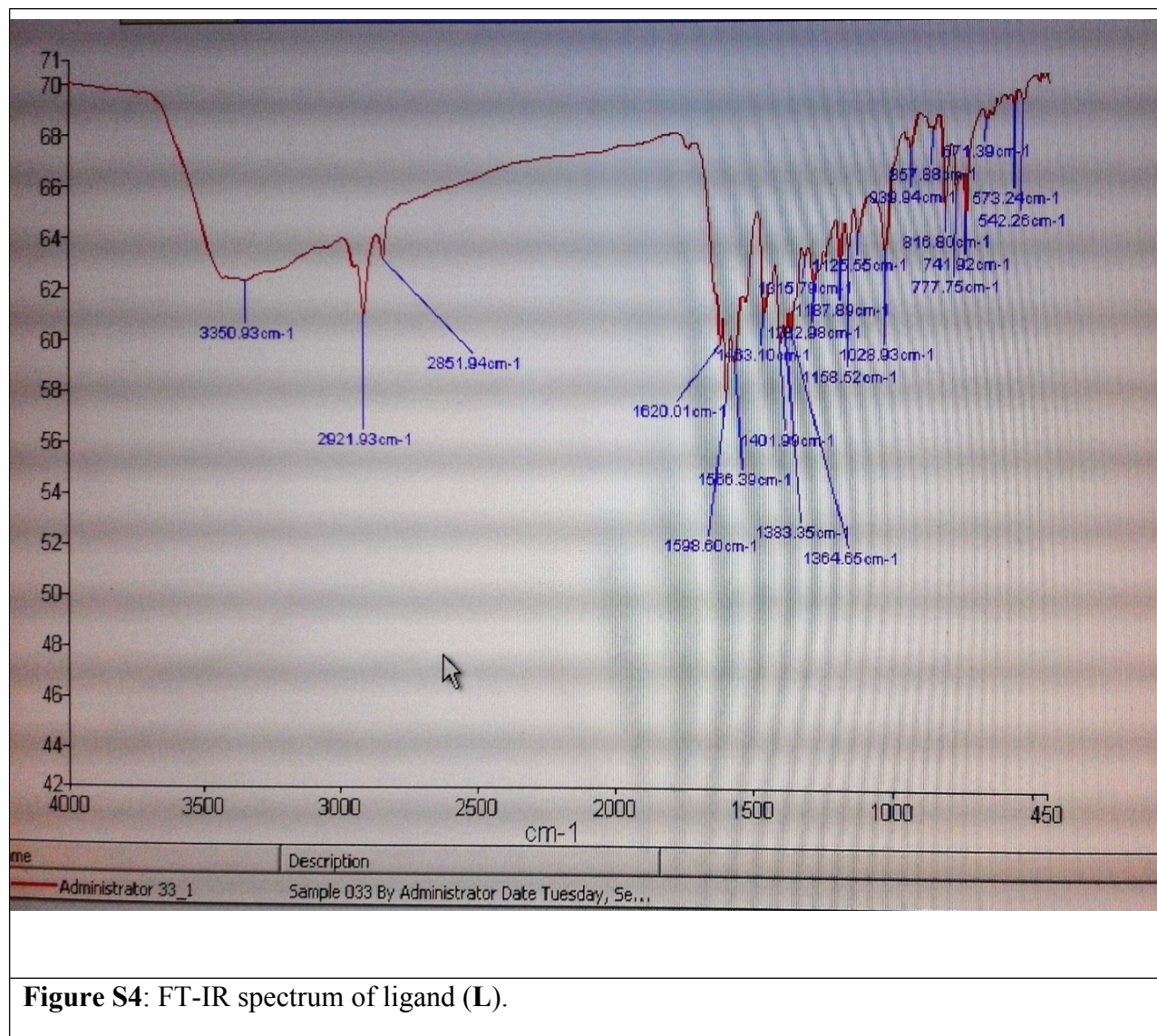


Figure S3: ESI-MS⁺ (M/Z) of ligand (**L**).



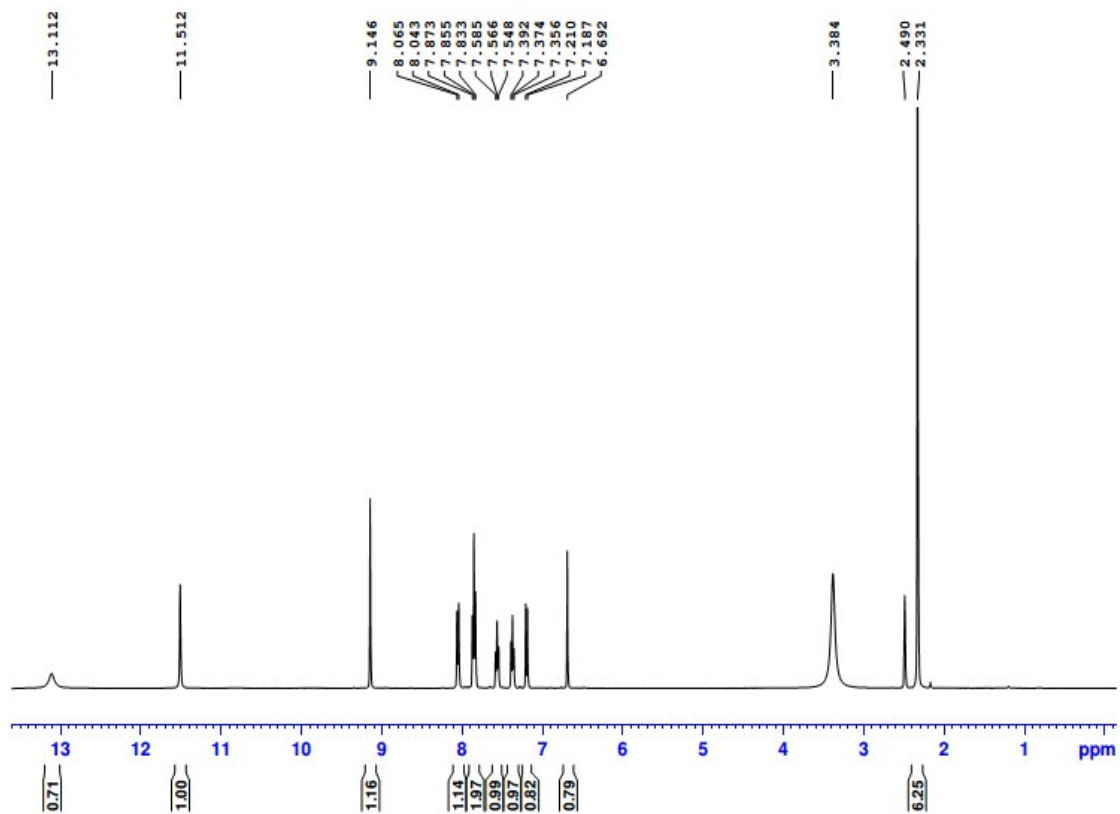


Figure S5: ^1H NMR of complex

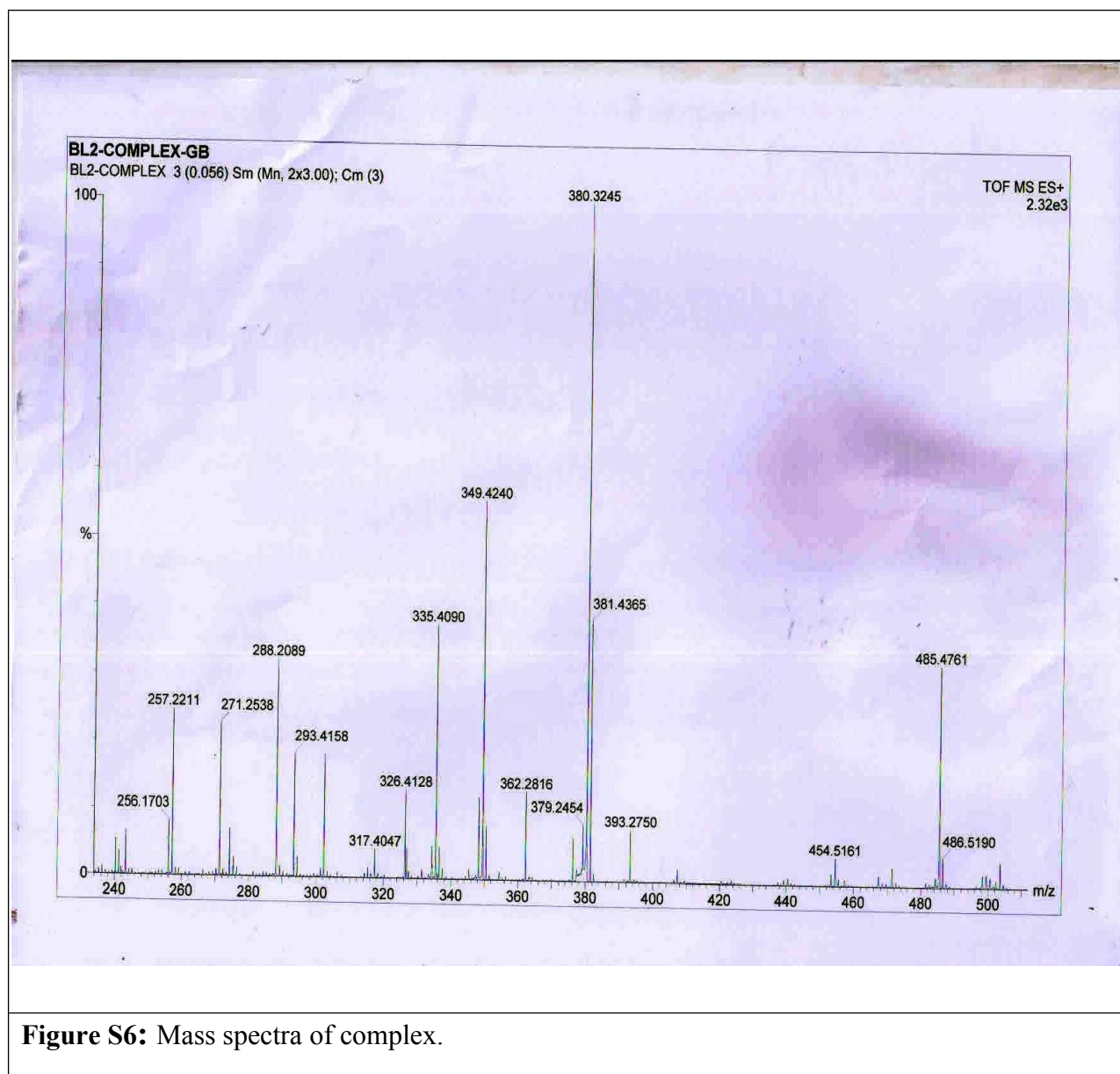


Figure S6: Mass spectra of complex.

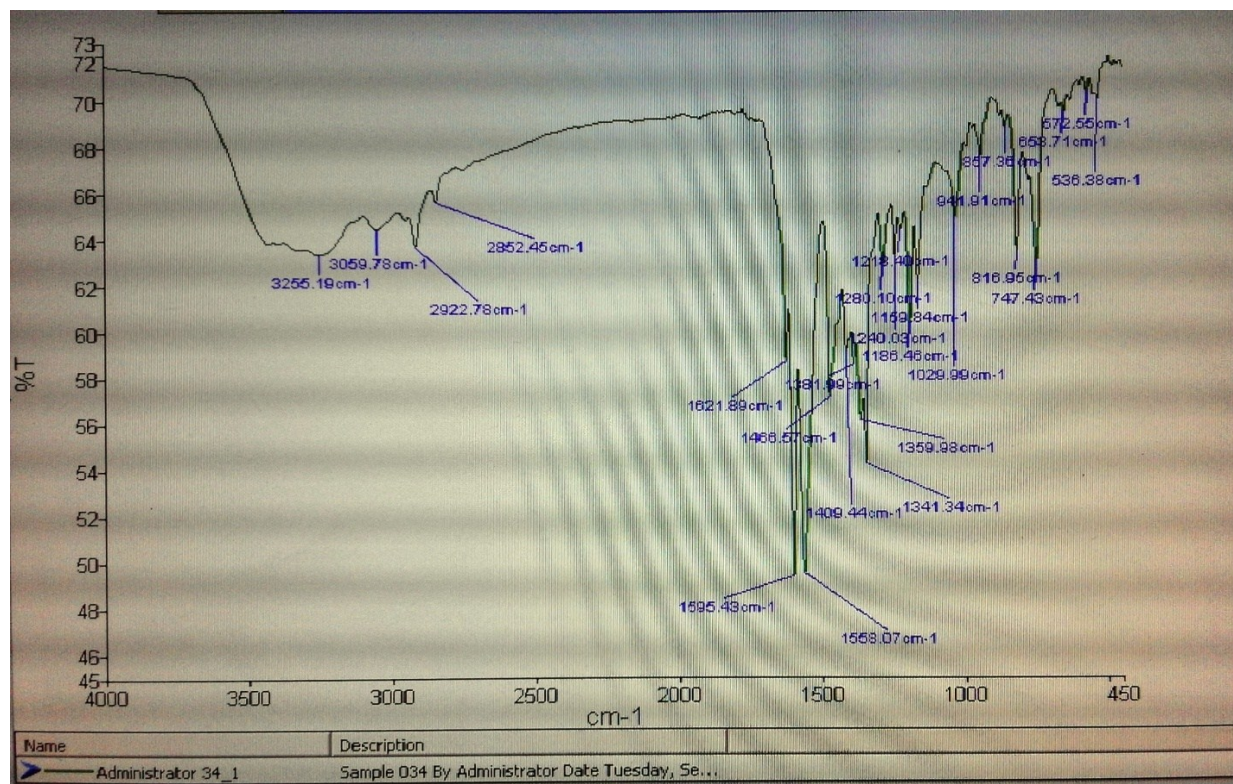


Figure S7: FT-IR spectrum of complex

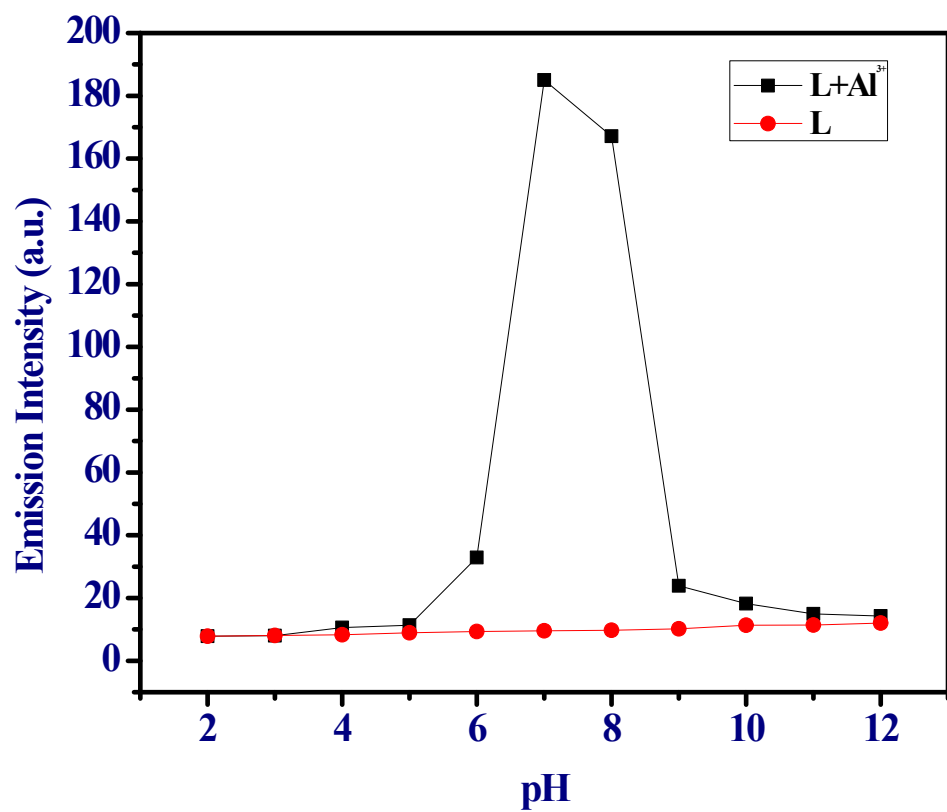


Figure S8: pH effect on fluorescence behavior towards ligand **L** and $L-Al^{3+}$ complex

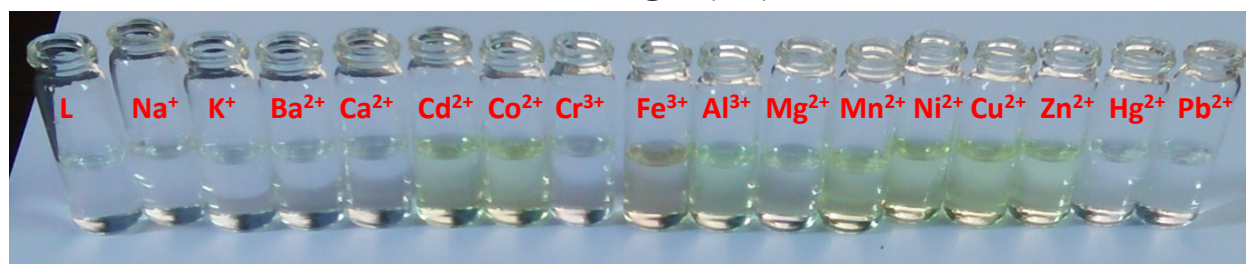
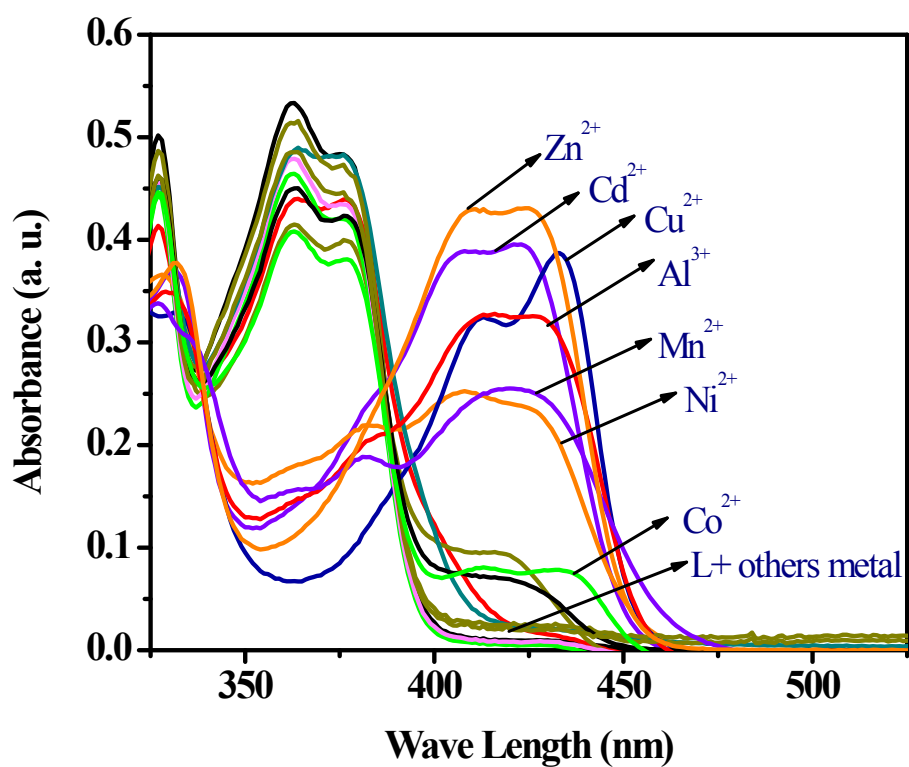


Figure S9: Absorption spectral change of **L** (20 μM) towards various metals (50 equivalent) in ethanol (20 μM HEPES buffer, pH 7.2) and corresponding photographic image under ambient light.

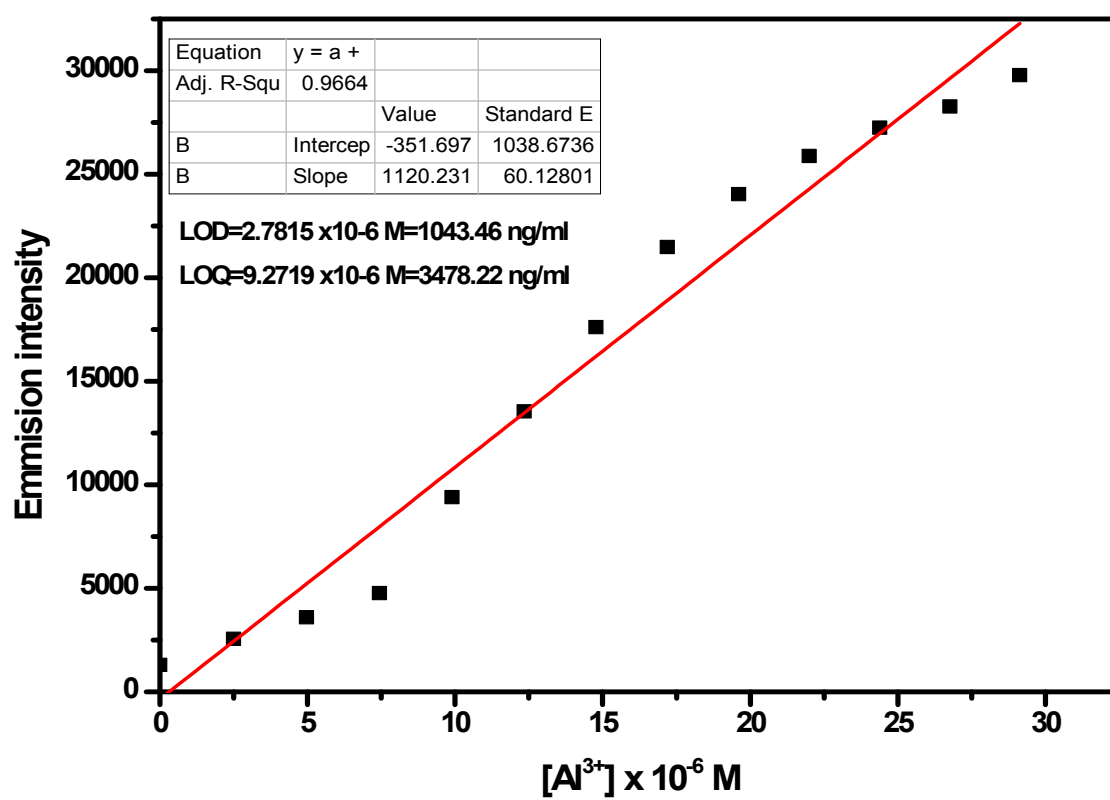


Figure S10: LOD and LOQ calibration curve.