Electronic Supplementary Information

Design specific mechanistic regulation of sensing phenomenon of two Schiff bases towards Al^{3+}†

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EXPERIMENTAL

1.1 Apparatus:

The IR Spectra for the receptors **R1** and **R2** were recorded on JASCO-FTIR Spectrophotometer while ^{1}H NMR and ^{13}C NMR spectra for the same were recorded on a JEOL AL 300 FT NMR Spectrometer. Mass spectrometric analysis was carried out on Bruker amaZon SL spectrometer in the ultrascan mode (Bruker Daltonics, Bremen, Germany). Electronic spectra were recorded at room temperature (298 K) on a UV-1700 pharmaspec spectrophotometer with quartz cuvette (path length = 1 cm). Emission spectra were recorded on JY HORIBA Fluorescence spectrophotometer.

1.2 Materials:

All reagents for synthesis were purchased from Sigma-Aldrich and were used without further purification.

1.3 General Methods:

All titration experiments were carried at room temperature. All the cations were used as their chloride salts. The ^{1}H NMR spectra were recorded by using tetramethylsilane (TMS) as an internal reference standard. For the ^{1}H NMR titration spectra of **R1** and **R2**, 5×10^{-3} M solutions was prepared in DMSO-d_6 while the stock solution of Al^{3+} was prepared in D_2O. For UV-visible / fluorescence titration experiments, the solutions of cations were prepared in aqueous medium. Chloride salt of metal ions was used for solution preparation. The stock solution of **R1** and **R2** both 1.0×10^{-3} M was prepared in DMSO which was used for fluorescence titration experiment in ethanol: water (4: 1, v/v).

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1.4. Determination of Detection limits:

The detection limit of **R1** and **R2** for Al^{3+} were calculated using fluorescence titration data according to the IUPAC definition. The detection limits of **R1** and **R2** as a fluorogenic sensor for the analysis of Al^{3+} were calculated from a plot of fluorescence intensity as a function of the concentration of the added Al^{3+} ion. To determine the S/N ratio, the fluorescence intensity of **R1** and **R2** without Al^{3+} was measured by 10 times and the standard deviation of blank measurements was determined. The detection was calculated as three times the standard deviation from the blank measurement (in the absence of Al^{3+}ion) divided by the slope of calibration plot between Al^{3+}ion concentration fluorescence intensity.

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Figure S1: ^{1}H NMR spectrum of **R1** (in DMSO-d_6):

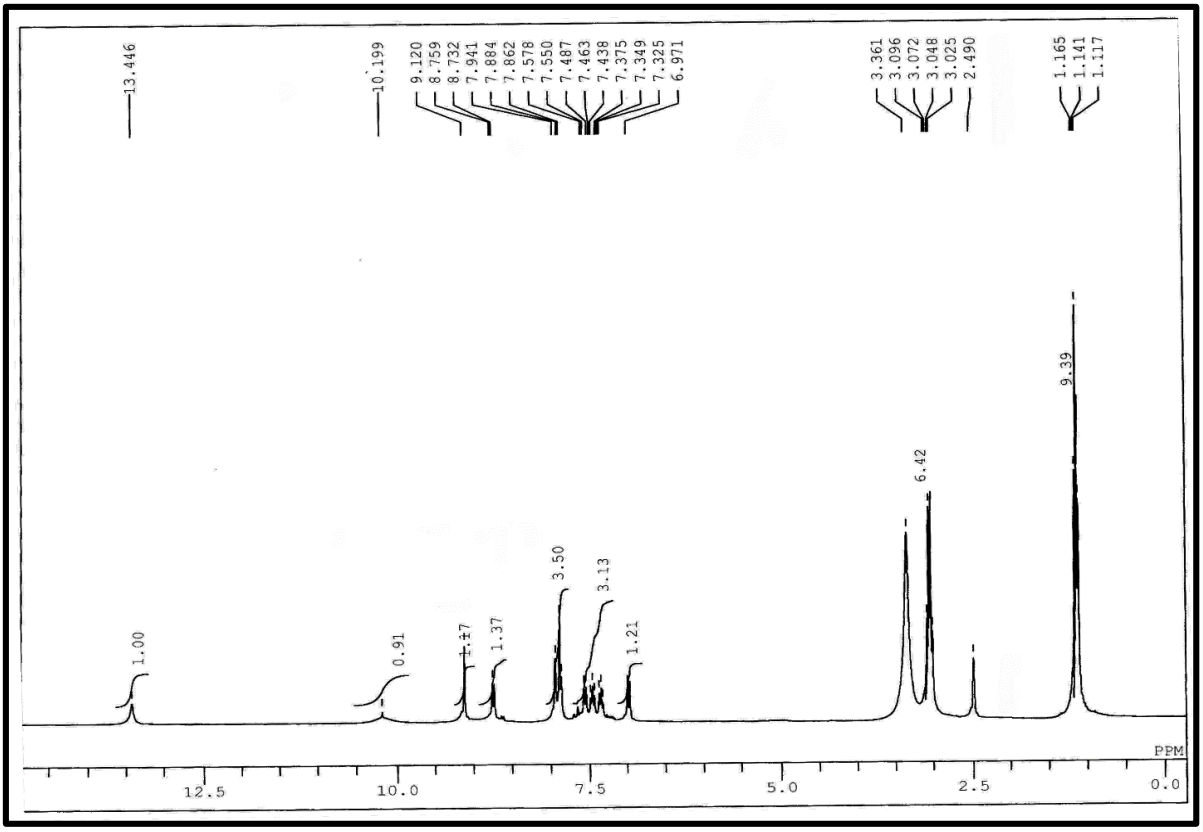

Figure S2: ^{13}C NMR spectrum of **R1** (in DMSO-d_6):

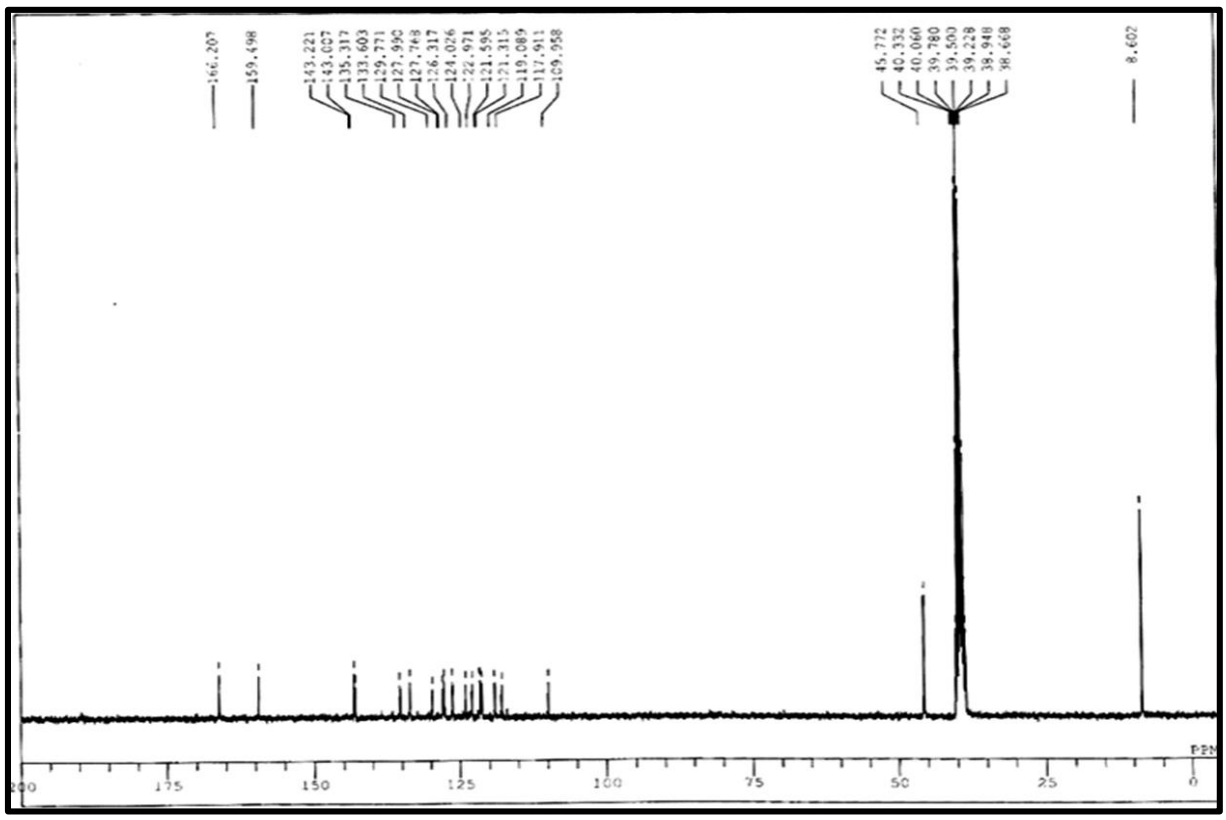

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Figure S3: IR spectrum of **R1:**

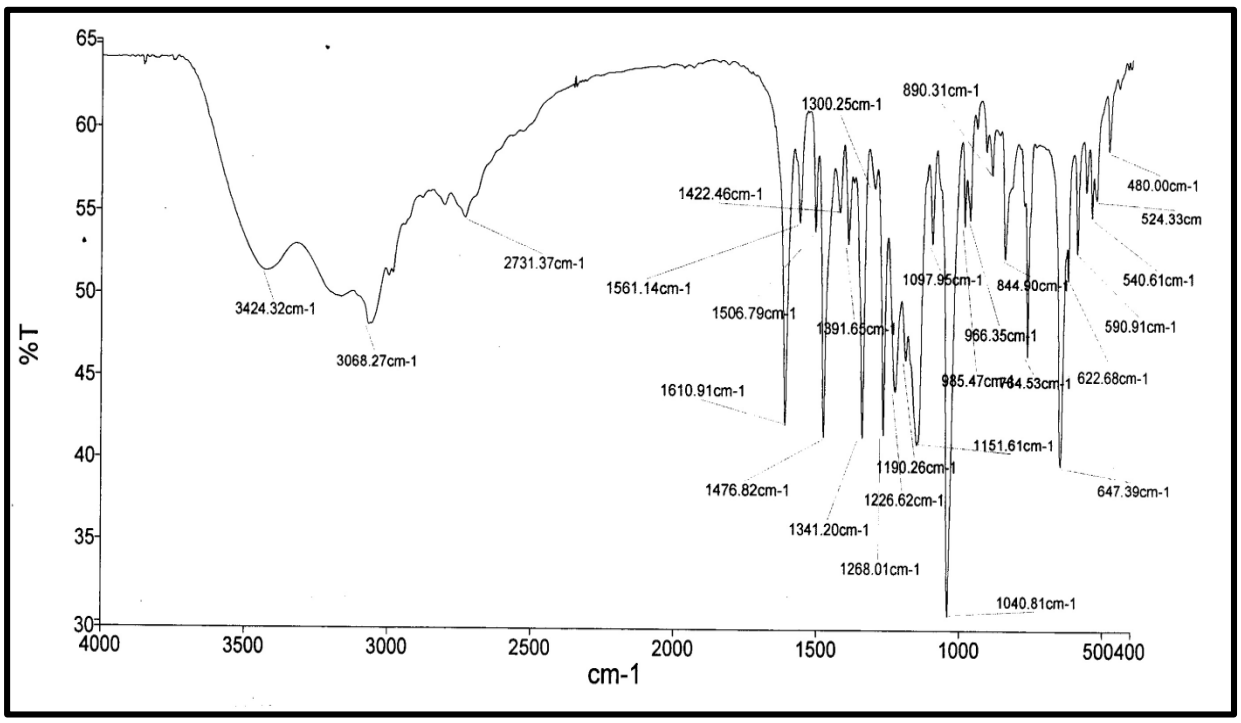

Figure S4: HRMS of **R1:**

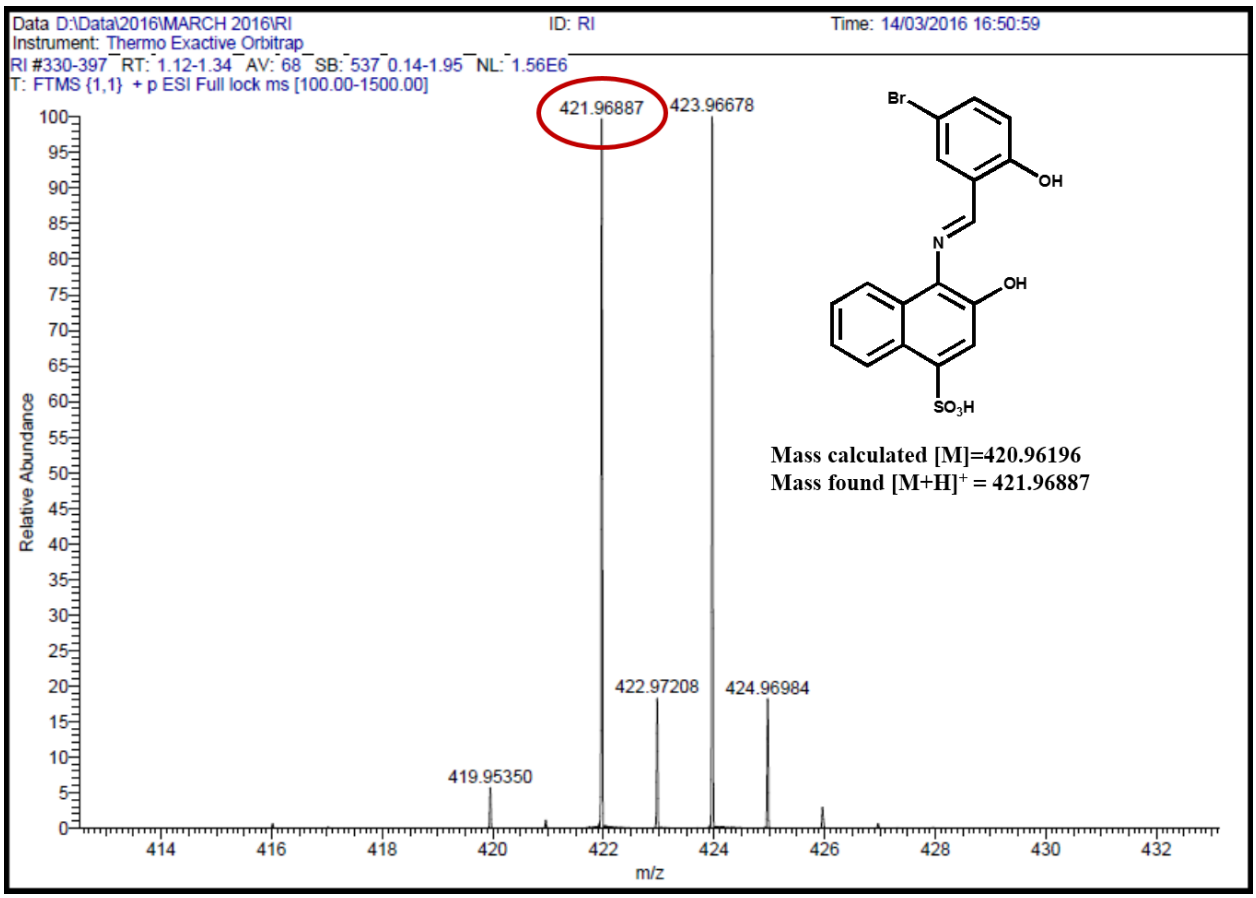

Figure S5: ^{1}H NMR spectrum of **R2** (in DMSO-d_6):

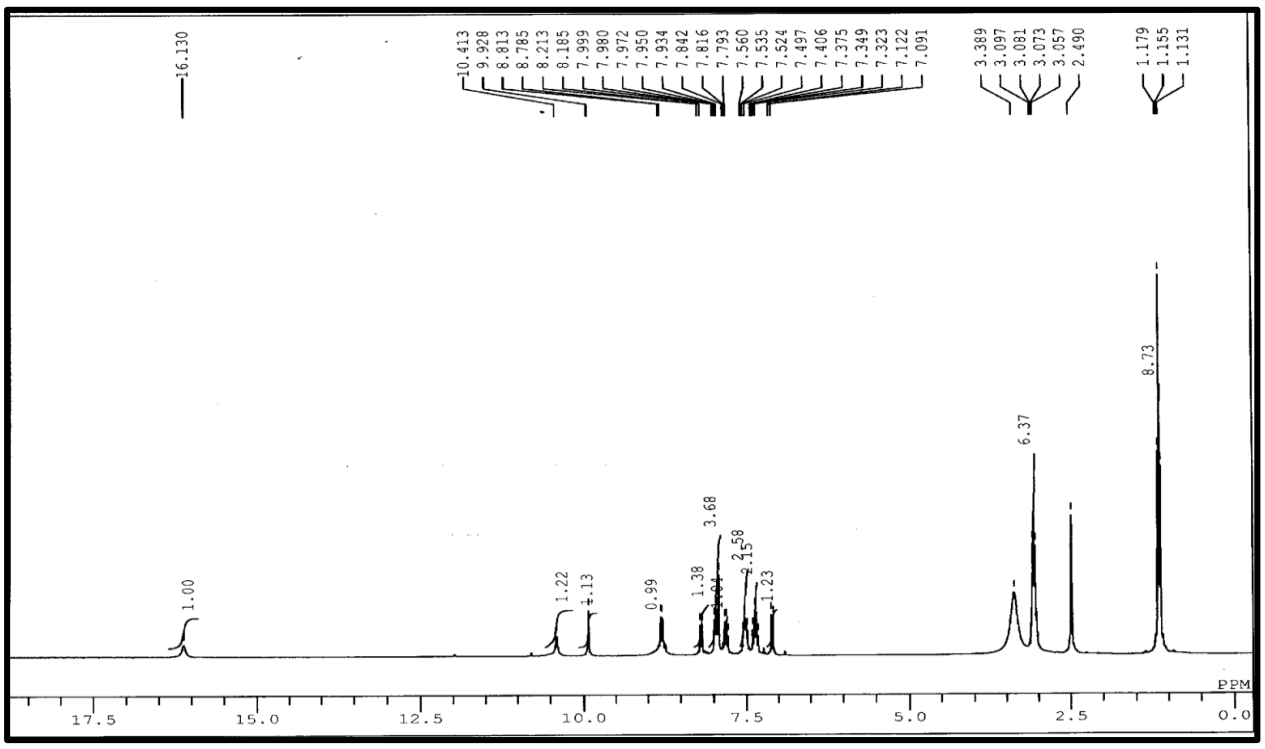

Figure S6: ^{13}C NMR spectrum of **R2** (in DMSO-d_6):

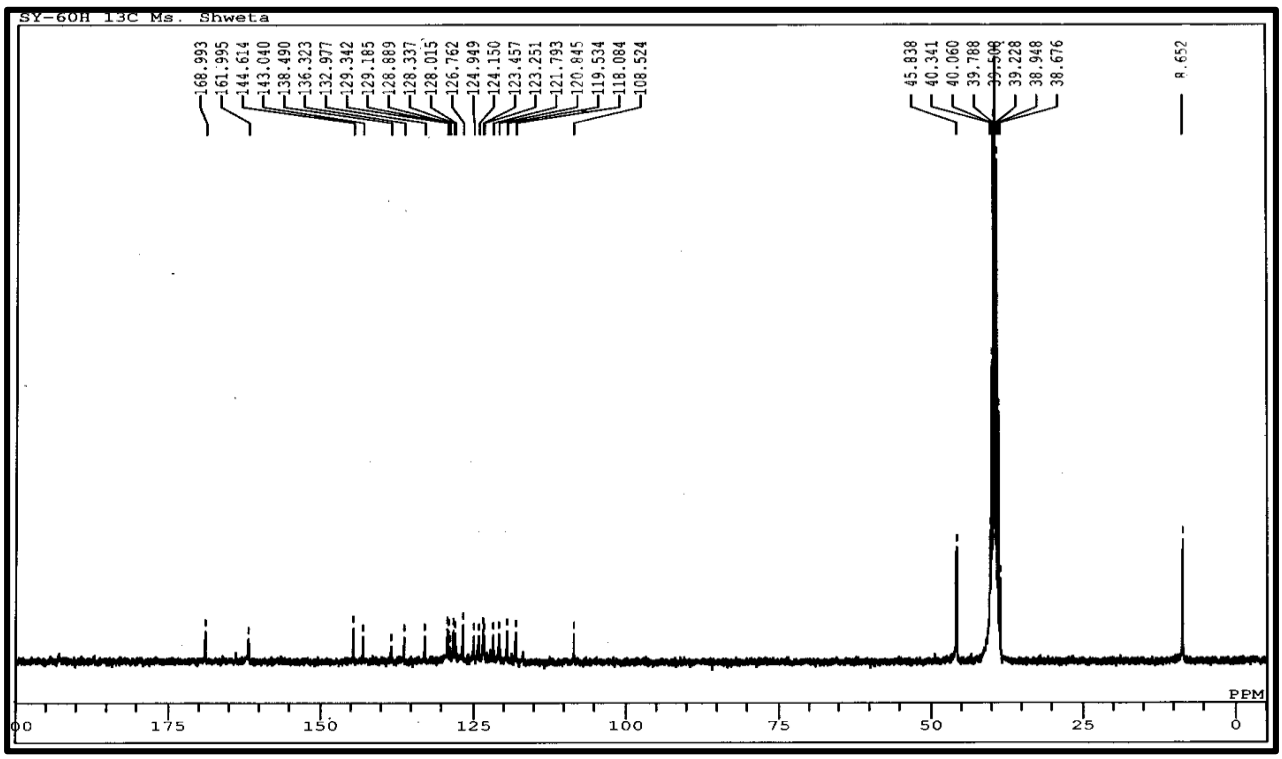

Figure S7: IR spectrum of **R2**:

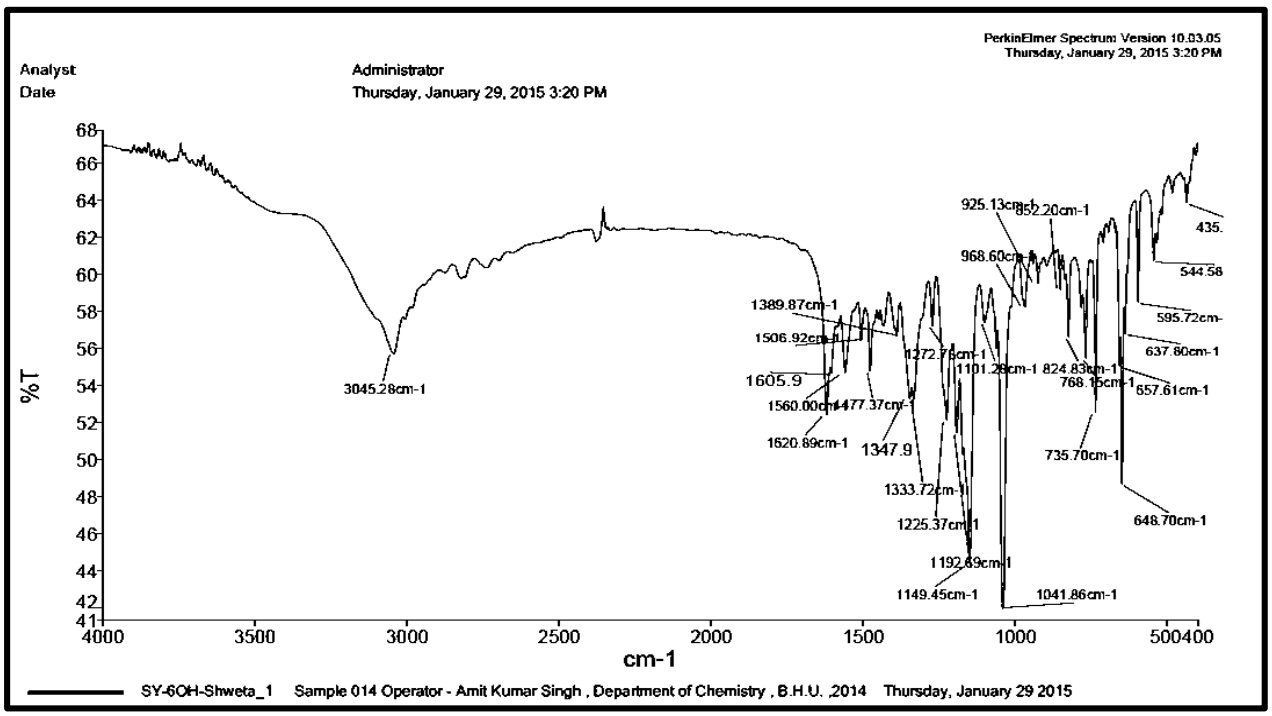

Fig S8: HRMS of **R2**:

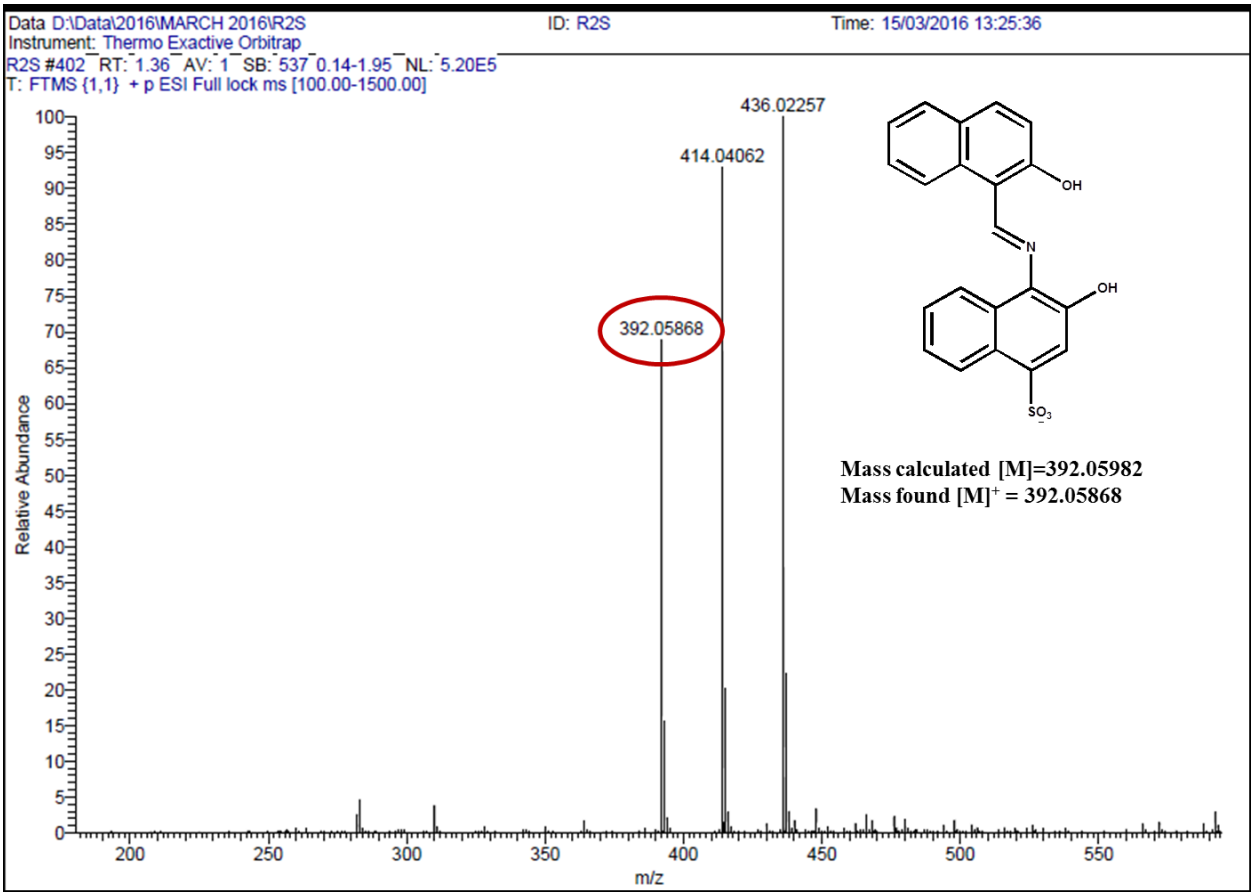

Fig S9: ^{1}H NMR spectrum of **R1**-Al^{3+} Complex (in DMSO-d_6):

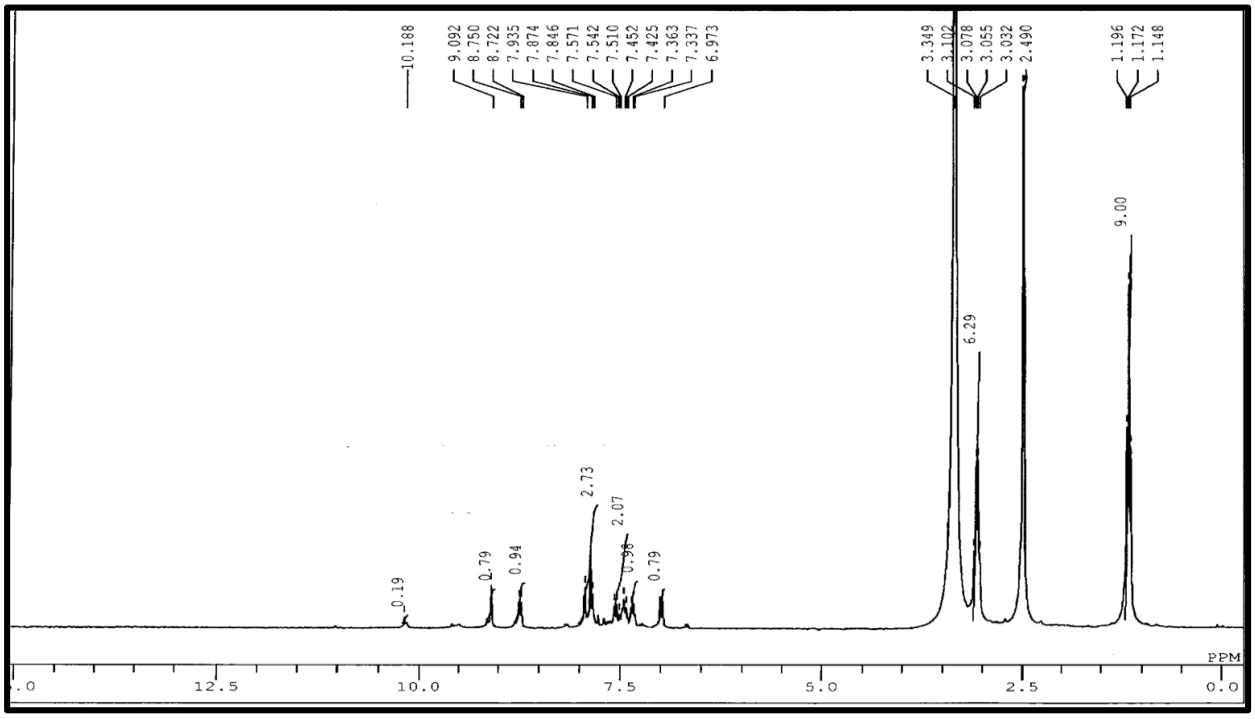

Fig S10: ^{13}C NMR spectrum of **R1**-Al^{3+} Complex (in DMSO-d_6):

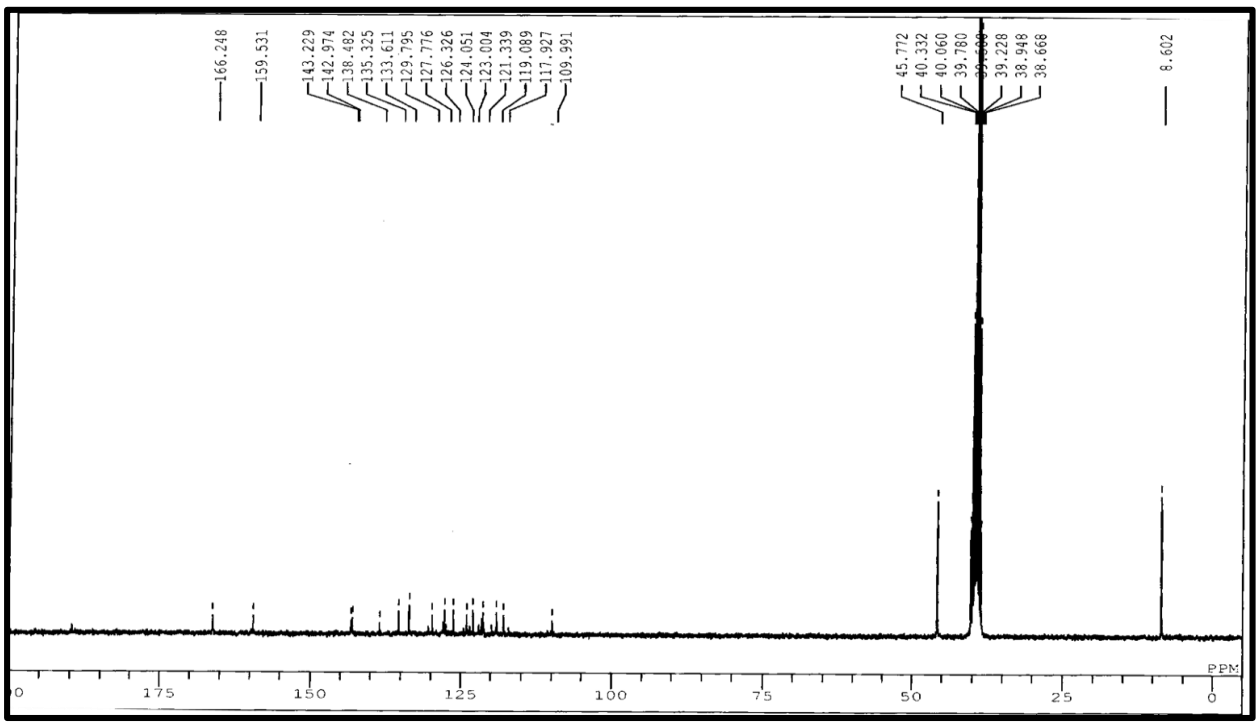

Figure S11: IR spectrum of R1-Al^{3+}:

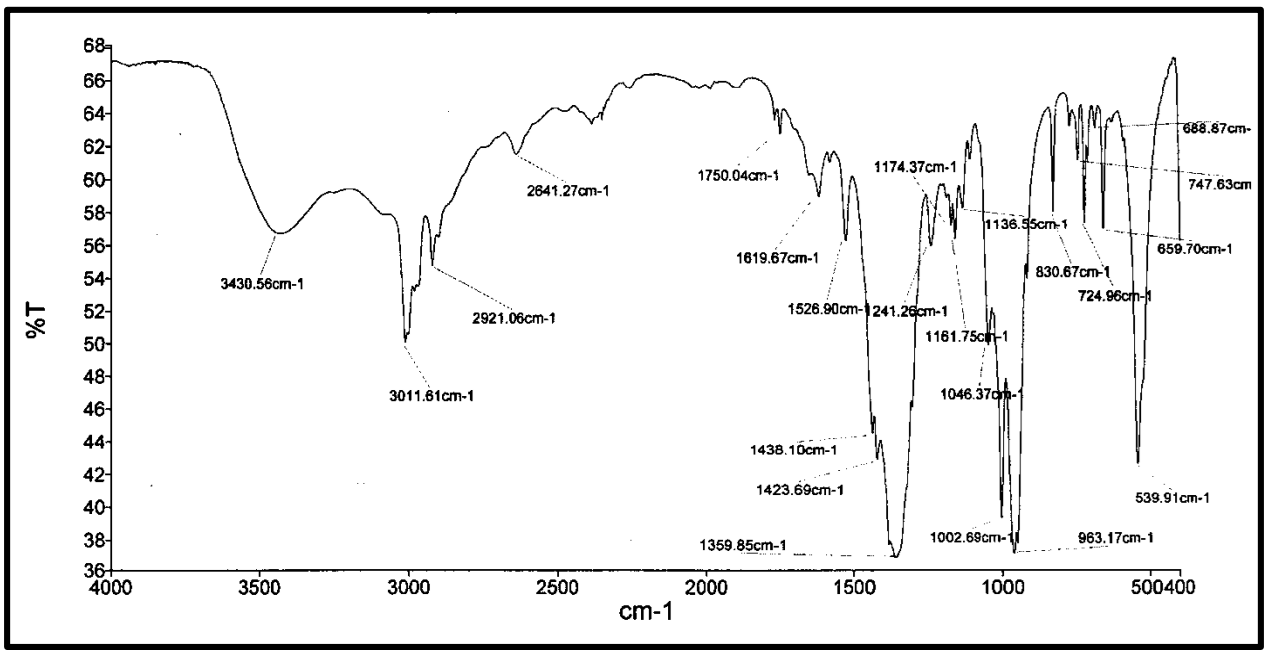

Fig S12: HRMS of **R1**-Al^{3+}:

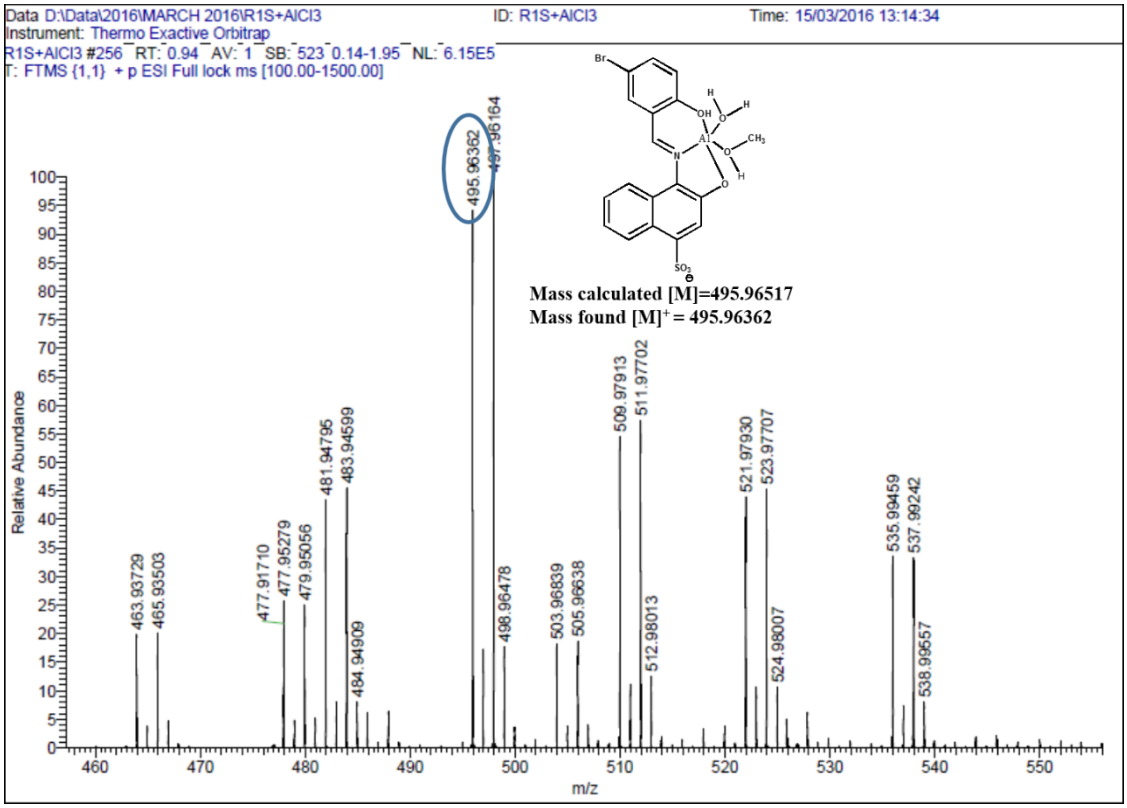

Fig S13: ^{1}H NMR spectrum of **R2**-Al^{3+} Complex (in DMSO-d_6):

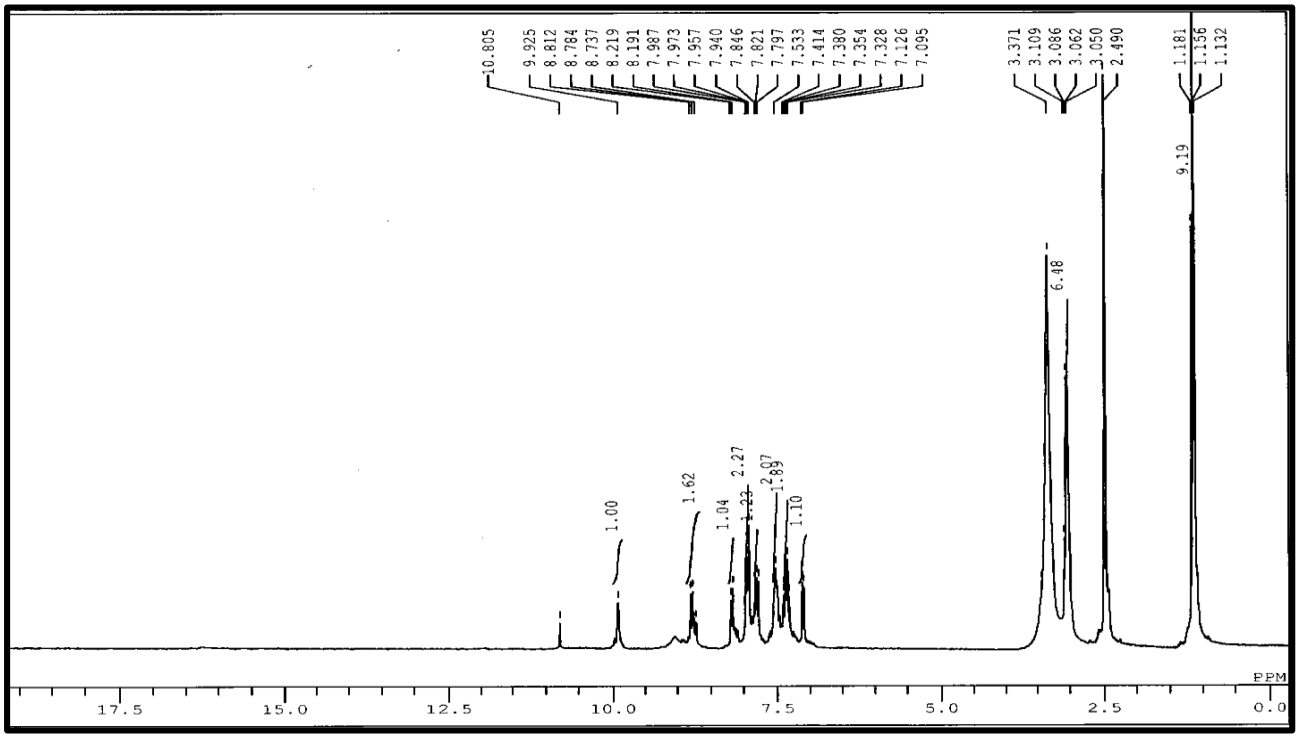

Figure S14: ^{13}C NMR spectrum of **R2** -Al^{3+} Complex (in DMSO-d_6):

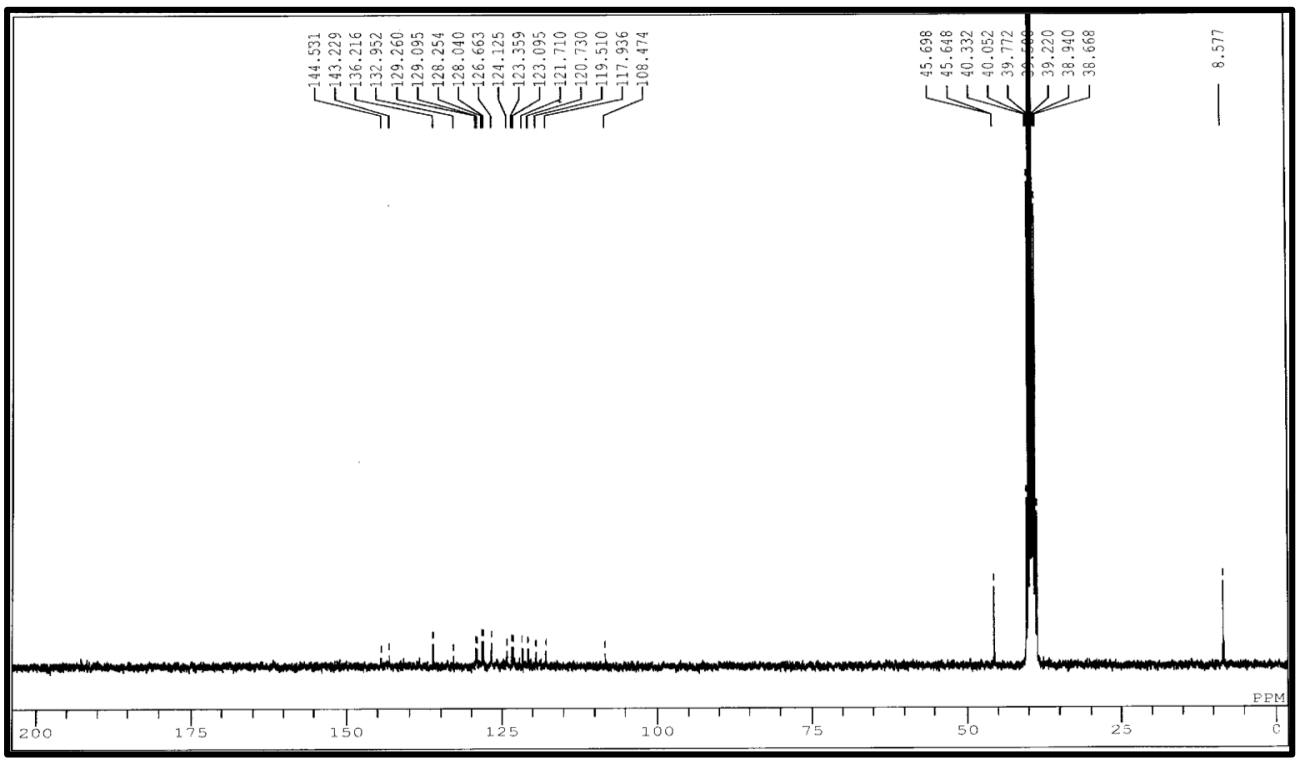

Figure S15: IR spectrum of **R2**-Al^{3+}:

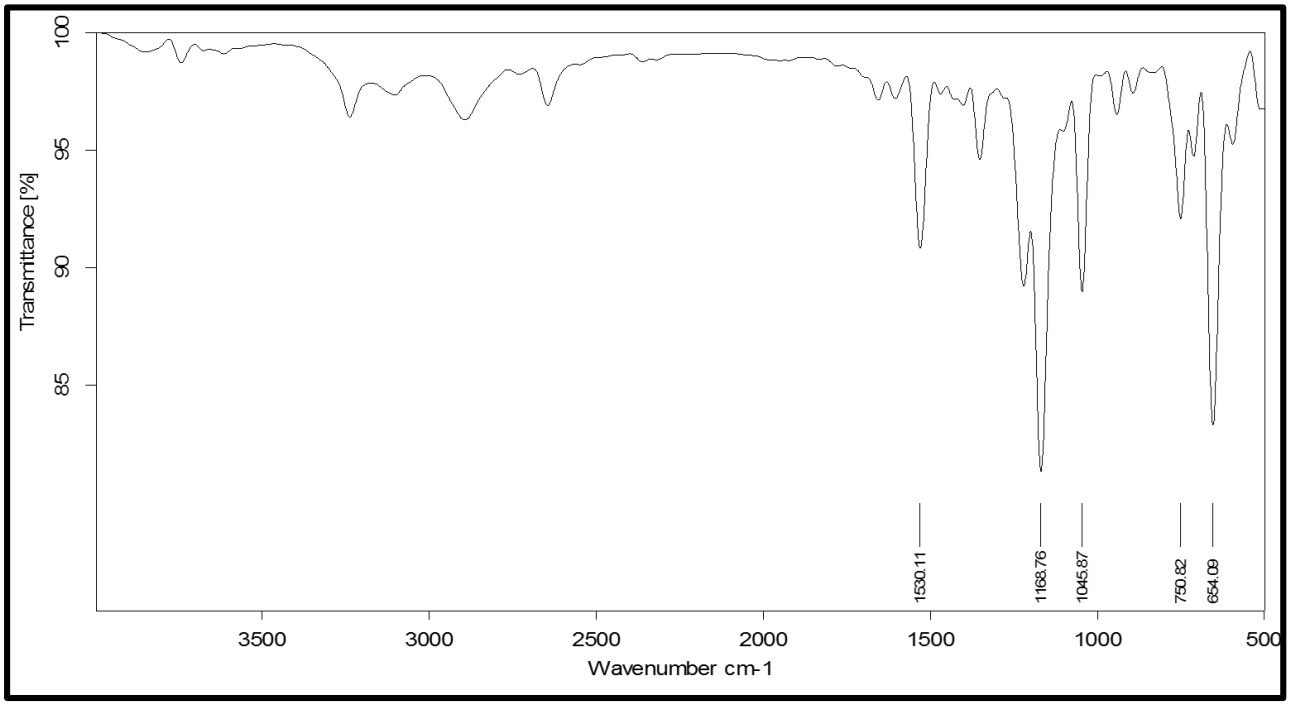

Figure S16: HRMS of **R2**-Al^{3+} complex:

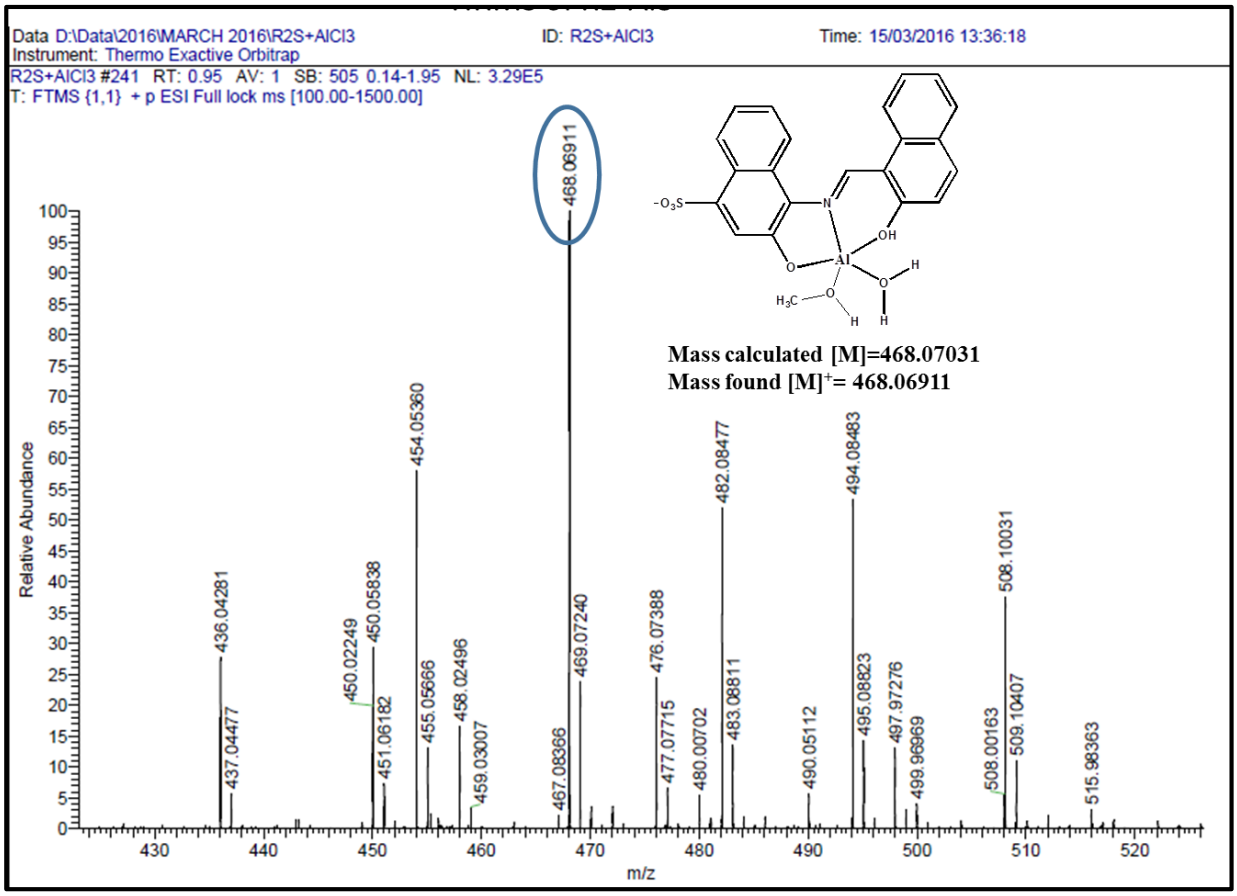

Figure S17: Visible color responses of **R2** in the presence of various metal ions in ethanol-water (4: 1, v/v) solution:

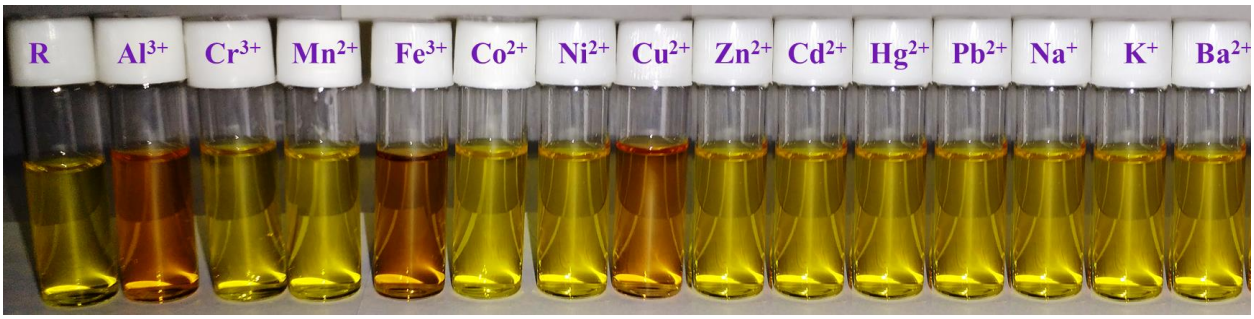

Figure S18: UV-visible spectrum of **R2** (10 μM) with different metal ions at in ethanol-water (4: 1, v/v) solution:

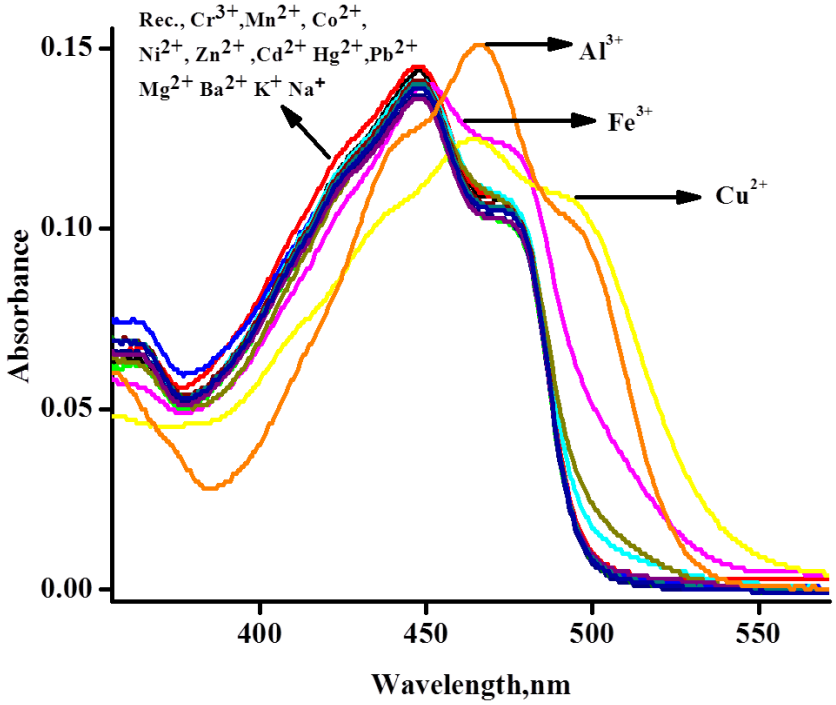

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Figure S19: Visible color responses of **R1** in the presence of various metal ions in ethanol-water (4: 1, v/v) solution:

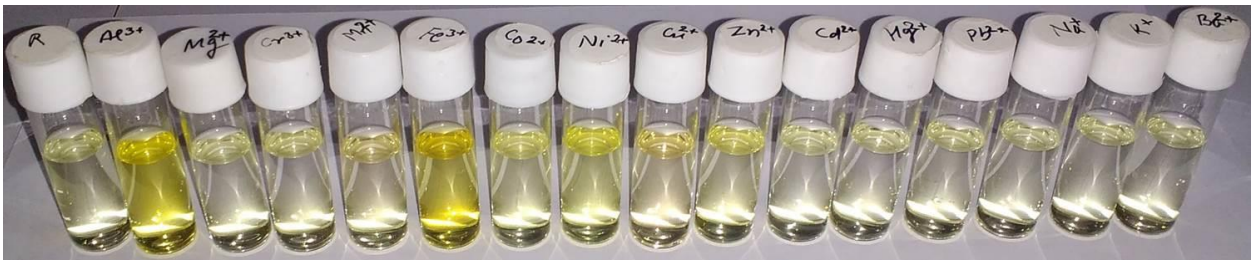

Figure S20: UV–visible spectrum of **R1** (10 μM) with different metal ions at in ethanol-water (8: 2, v/v) solution:

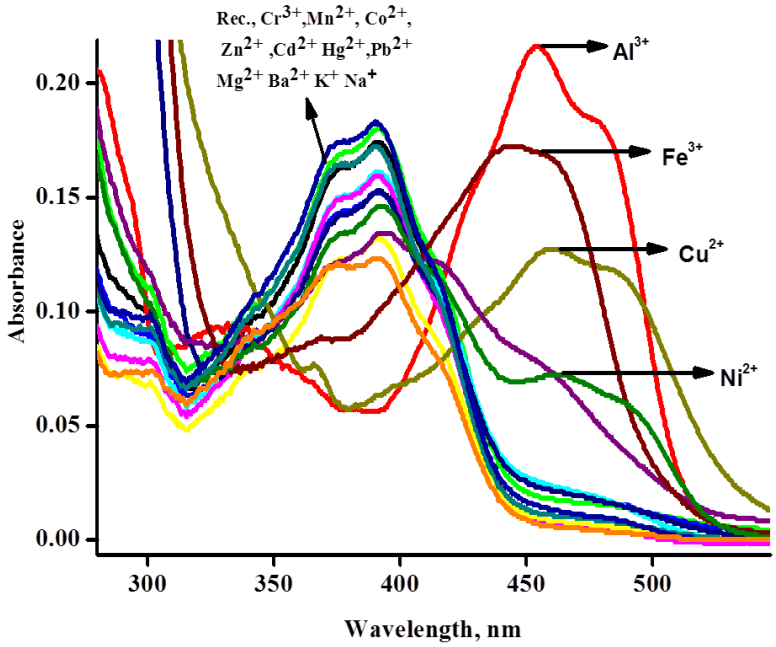

Figure S21: Bar graph of emission spectrum showing competition experiment of **R1.**Al^{3+} ensemble with various metal ions:

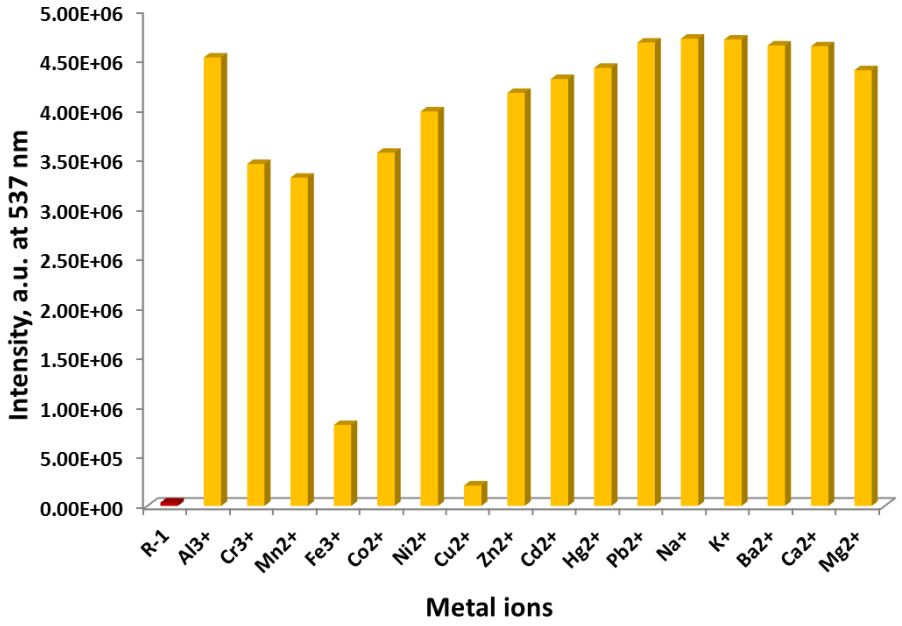

Figure S22: Bar graph of emission spectrum showing competition experiment of **R2.**Al^{3+} ensemble with various metal ions:

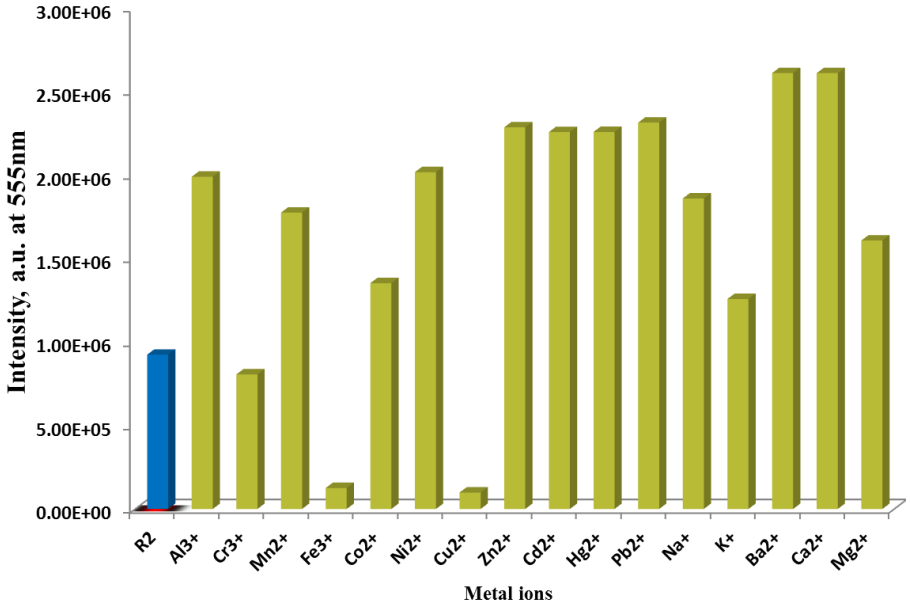

Figure S23: The variation in fluorescence intensity in **R1** with the change in pH in the presence of Al^{3+}:

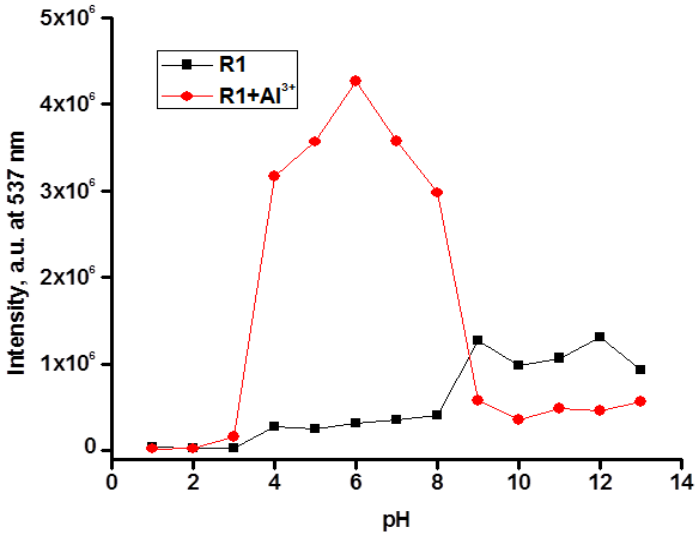

Figure S24: The variation in fluorescence intensity in **R2** with the change in pH in the presence of Al^{3+}:

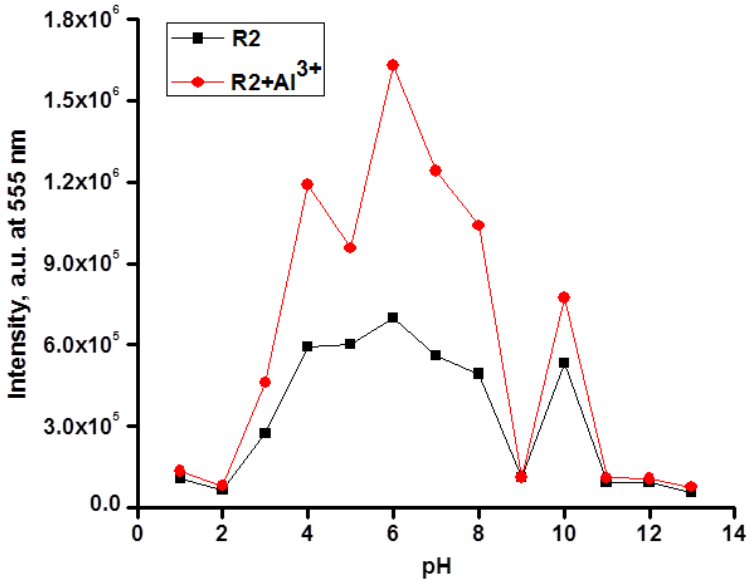

Figure S25: Job's plot of **R1** with Al^{3+} showing 1: 1 binding stoichiometry:

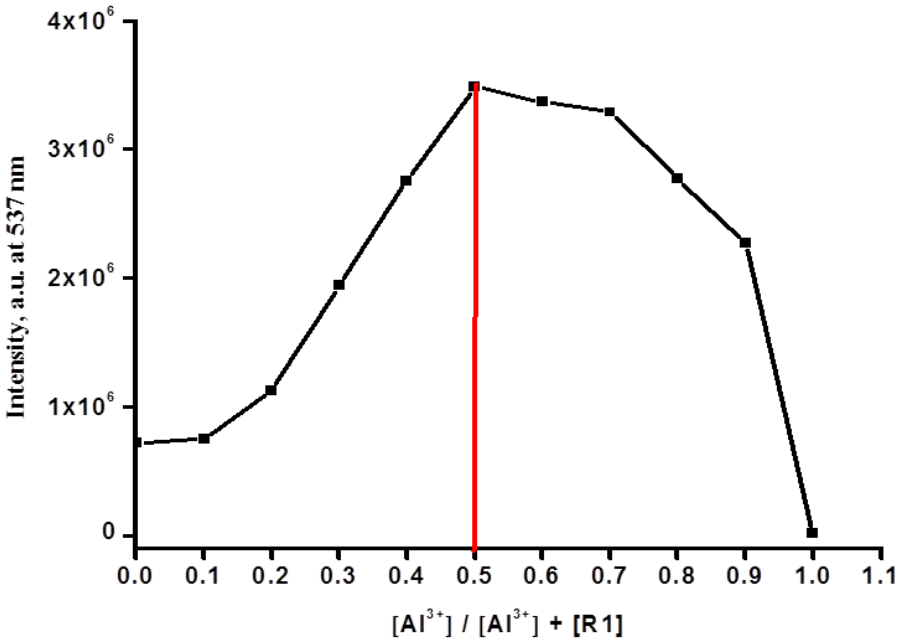

Figure S26: Job's plot of **R2** with Al^{3+}showing 1:1 binding stoichiometry:

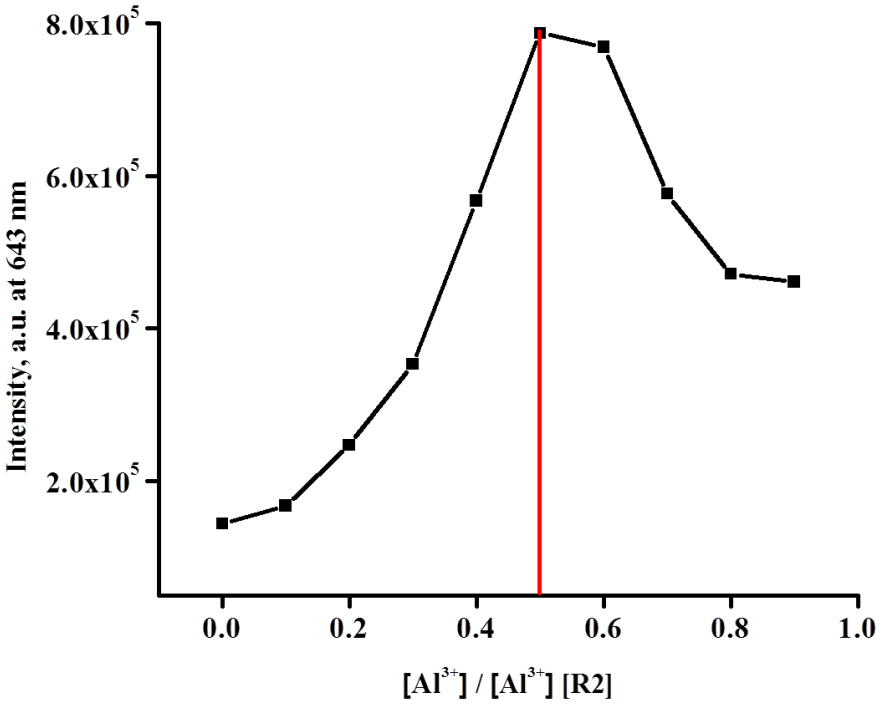

Figure S27: Non-linear fit plot of **R1** from fluorescence titration data:

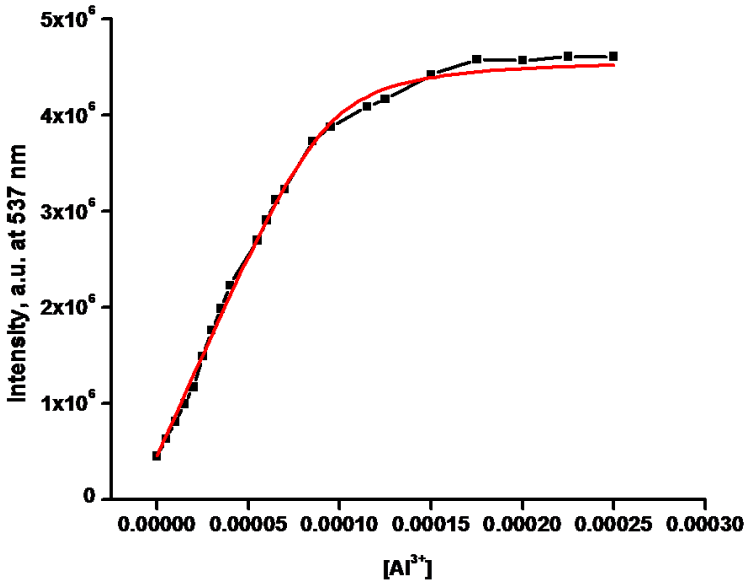

Figure S28: Non-linear fit plot of **R2** from fluorescence titration data:

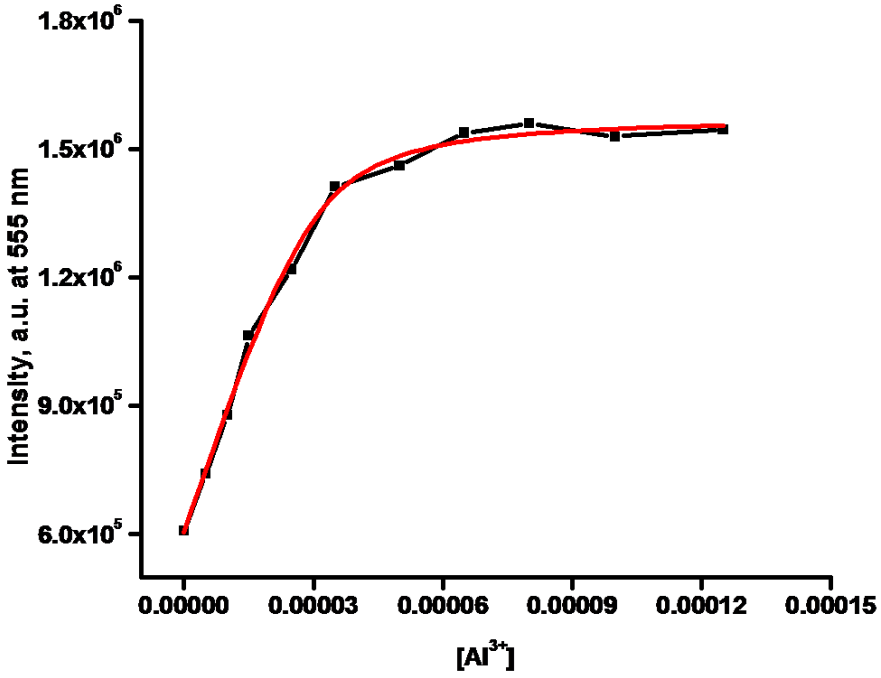

Figure S29: Calibration curve for determination of detection limit of **R1** for Al^{3+}:

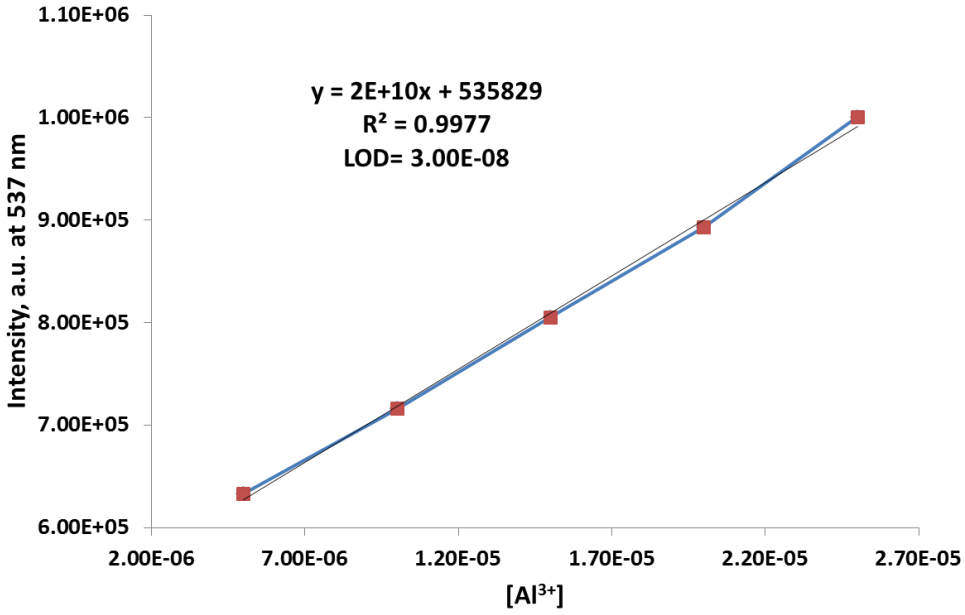

Figure S30: Calibration curve for determination of detection limit of **R2** for Al^{3+}:

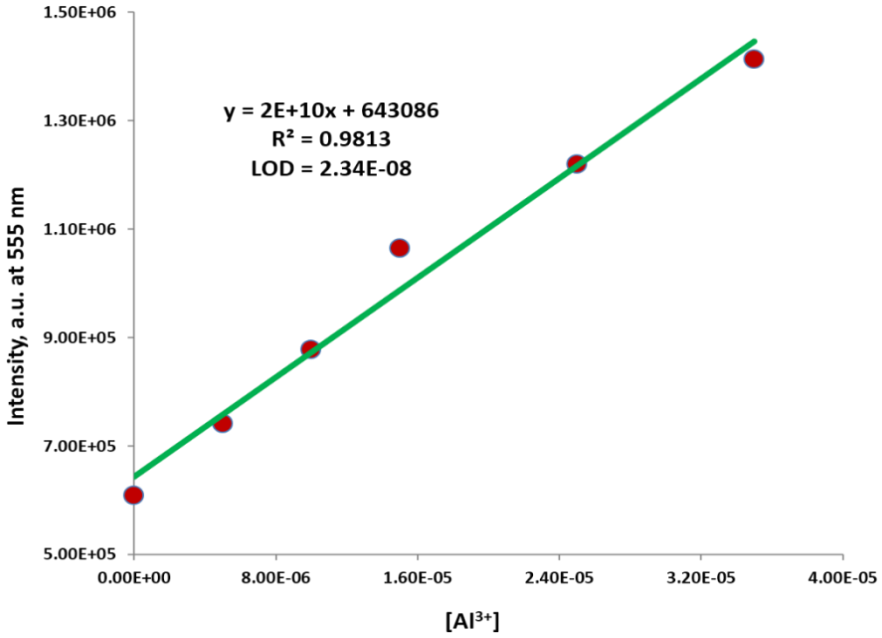

Figure S31: Theoretically optimised structure of **R1** and **R1**-Al^{3+} ensemble:

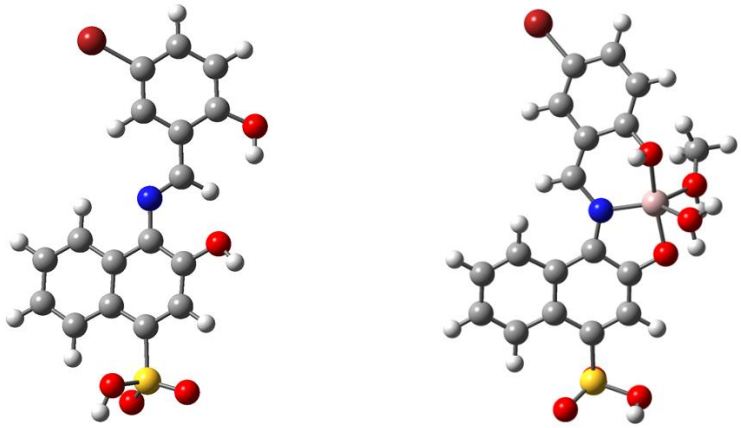

Figure S32: Theoretically optimised structure of **R2** and **R2**-Al^{3+} ensemble: