

## **Electronic Supporting Information**

# **Chromone-based Multi-selective Sensor: Applications in paper strip and real sample**

Ashesh Das and Gopal Das\*

Department of Chemistry, Indian Institute of Technology Guwahati, Assam-781039, India.

E-mail: gdas@iitg.ac.in; Tel: +91-361-258 2313

## Experimental section

### General information and materials

All of the materials for synthesis were purchased from commercial suppliers and used without further purification. The absorption spectra were recorded on a Perkin-Elmer Lambda-25 UV–vis spectrophotometer using 10 mm path length quartz cuvettes in the range of 250–800 nm wavelength, while fluorescence measurements were performed on a Horiba Fluoromax-4 spectro- fluorometer using 10 mm path length quartz cuvettes with a slit width of 3 nm at 298 K. NMR spectra were recorded on a Varian FT-400/500 MHz instrument. The mass spectrum of **L** and their products were obtained using Waters Q-ToF Premier mass spectrometer. The chemical shifts were recorded in parts per million (ppm) on the scale. The following abbreviations are used to describe spin multiplicities in <sup>1</sup>H NMR spectra: s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet.

### Synthesis of the probe **L**

#### Synthesis of 5-(pyren-2-ylmethylene) pyrimidine-2, 4, 6(1H, 3H, 5H)-trione (Probe **L**)

3-Formyl-6-methylchromone (2 mmol) and Diethylenetriamine (1 mmol) were dissolved in ethanol (40 mL). The resulting mixture was refluxed for 12 hr. The solution cooled to room temperature. Evaporation of the brown-colored solution and work up with CHCl<sub>3</sub>/H<sub>2</sub>O yields the receptor **L**, (**Scheme S1**). The compound was finally dried in a vacuum over silica gel. The product **L** was obtained as a brown-colored solid which was later recrystallized with methanol before proceeding with further experiments.

<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, TMS, δ ppm): 10.53(s, 2H), 8.67(s, 2H), 8.23(s, 2H), 7.71-7.69(d, 2H, ArH), 7.59-7.57(d, 2H, ArH), 3.60(t, 4H), 2.64(s, 6H), 1.34(t, 4H); <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>, TMS, δ ppm): 188.80, 176.11, 160.58, 154.61, 136.95, 135.98, 129.04, 128.23, 125.55, 120.21, 118.36, 21.03; Mass spectrum of probe **L**, calculated [**L**+H]<sup>+</sup> = 443.1845, Found 444.1753. (Mass spectrum obtained in positive mode).

### UV–vis and fluorescence spectral studies

The stock solution of the probes **L** was prepared in DMSO at 5 × 10<sup>-3</sup> M concentration. Na or (NH)<sub>4</sub> or tetrabutyl ammonium (TBA) salts of various anions (0.05 M) were prepared in methanol/Millipore water for selectivity studies in a mixed-aqueous medium and accordingly diluted for further experiments. All UV-visible and fluorescence experiments were carried out in an aqueous and acetonitrile (1 mM HEPES buffer at pH = 7.4) medium. For the UV-visible and fluorescence titration experiments, a 50 μM solution of the probes **L** in a quartz optical cell of

1 cm optical path length was titrated with increasing concentration of the analyte solutions. For fluorescence measurements, excitation was provided at 370 nm for **L** in aqueous media whereas in acetonitrile media excitation wavelength of 440 nm was provided for **L** and emission was recorded from 390 nm to 650 nm (**L**) and 460 nm to 650 nm in aqueous and acetonitrile medium respectively for usual selectivity as well as titration experiments. Spectral data were recorded within 2 min after the addition of the external ions except for kinetic studies.

### Quantum yield calculation

Quinine Sulphate (QS) and Rhodamine 6G dye were used to determine quantum yield ( $\Phi$ ) values comprised with a quantum yield value of 54% and 95% respectively. At the time of the analysis, an aqueous solution of quinine sulphate (QS) (in 0.1 M H<sub>2</sub>SO<sub>4</sub> standard) and Rhodamine 6 G dye were prepared and its absorption and emission analysis were recorded accordingly<sup>1</sup>The given formula was used for the determination of quantum yield -

$$\Phi_X = \Phi_R (I_X/I_R) (\eta_X^2 / \eta_R^2) (A_R/A_X) \dots\dots\dots (1)$$

Where the terms  $\Phi$ ,  $F$ ,  $A$ , and  $n$  represent the quantum yield, the integrated area covered by the corrected emission spectra, the absorbance intensity at the excitation wavelength, and the refractive index of solvent, respectively. In addition,  $R$  refers to Quinine sulphate (QS) as the standard, and  $X$  refers to the target sample. Refractive Index: water = 1.33.

### Evaluation of the apparent binding constant

Probe **L** with an effective concentration of  $2 \times 10^{-6}$  M in an aqueous HEPES buffer (1 Mm; Ph 7.4) was used for the emission titration studies with an Al<sup>3+</sup> solution ( $1 \times 10^{-3}$  M). The effective Al<sup>3+</sup> concentration was varied between 0 and  $26 \times 10^{-6}$  M for this titration and the pH of the solution was adjusted to 7.4 using the buffered solution. Similarly, we have calculated the binding constants for the F<sup>-</sup> in pure acetonitrile medium from the emission and absorbance spectra.

### Calculations for the apparent binding constants using spectrophotometric titration data

The binding/association constants ( $K_a$ ) for Al<sup>3+</sup>, Zn<sup>2+</sup>, F<sup>-</sup>, PPI, and were determined from the fluorescence titration experiment using the following equation (1)

$$(F_i - F_{max}) = \Delta F = [X] (F_{sat} - F_o) / (K_d + [X]) \dots\dots\dots (1)$$

$F_i$  is the experimentally determined emission with different. equiv. of  $X$ ,  $F_{max}$  is the emission for the free **L**,  $F_{sat}$  is the saturation value of the emission intensity obtained after the addition of  $X$ . To obtain  $Y = AX + B$ , a linear equation, the reciprocal of  $\Delta F$  versus the reciprocal of the

concentration of X was plotted and the  $K_d$  was calculated from the ratio A/B and the reciprocal of  $K_d$  was determined to be the association constant ( $K_a$ ) in each case.

The binding constant was also calculated from the absorption titration experiment using the Benesi–Hildebrand (B–H) plot (equation (2))

$$1/(A-A_0) = 1/ \{K_a (A_{max}-A_0) [F^-]\} + 1/(A_{max}-A_0) \dots\dots\dots(2)$$

where  $A_0$  and A are the absorbances of L in the absence and presence of  $F^-$  ions respectively and  $A_{max}$  is the saturated absorbance of L in the presence of  $F^-$  ions and  $K_a$  ( $M^{-1}$ ) is the binding constant and was determined from the slope of the linear plot.<sup>2-4</sup>

### **Finding the detection limit**

The detection limits for the probes L with the corresponding ions were calculated on the basis of the fluorescence/absorbance titration experiments. The fluorescence/absorbance emission spectrum of L was measured 10 times, and the standard deviation of blank measurement was also attained from that experiment. To gain the slope, the fluorescence/absorbance intensity plot at various wavelength ranges was plotted as a concentration of corresponding ions. The detection limit was calculated using the following equation

$$\text{Detection limit} = 3\sigma/k \text{ (2)}$$

Where  $\sigma$  is the standard deviation of blank measurement, and k is the slope achieved from the plot of fluorescence emission intensity vs [different ions].

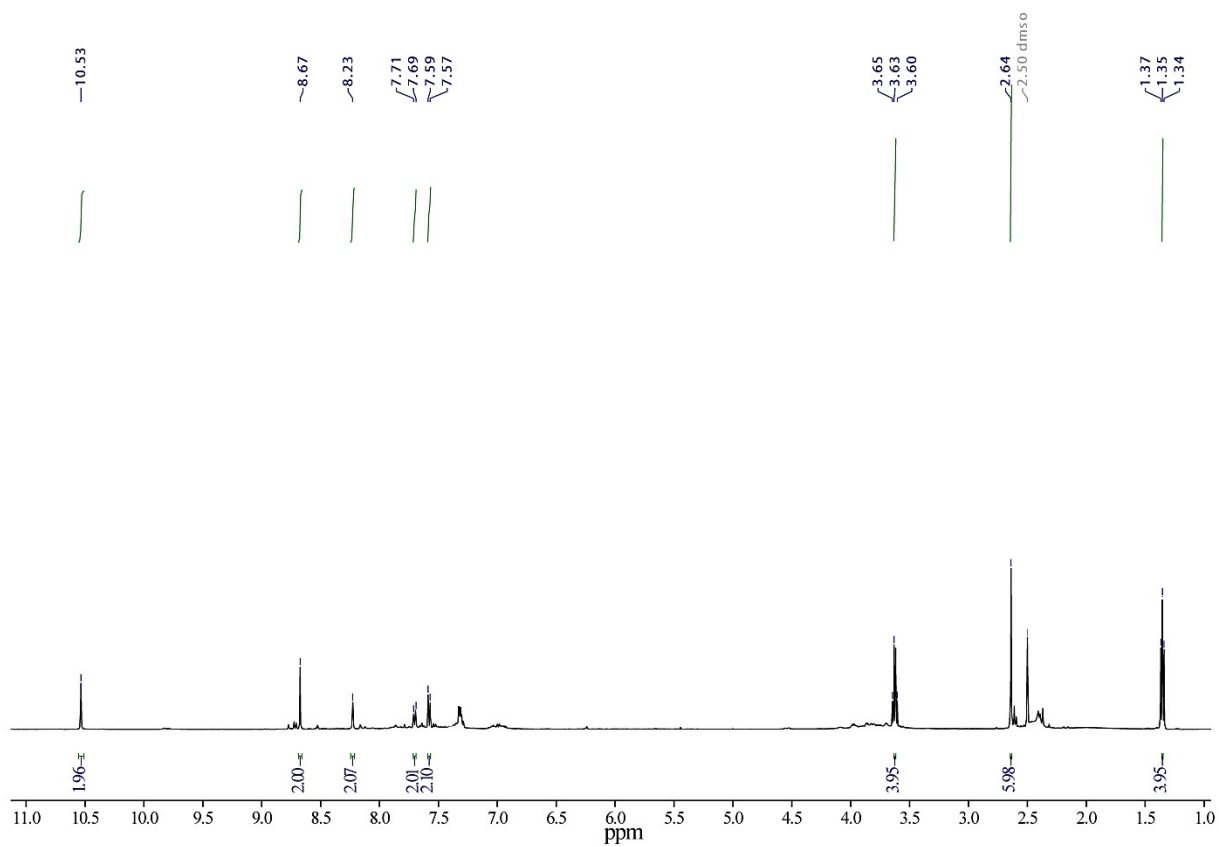


Figure S1  $^1\text{H}$  NMR spectra of L at 25 °C.

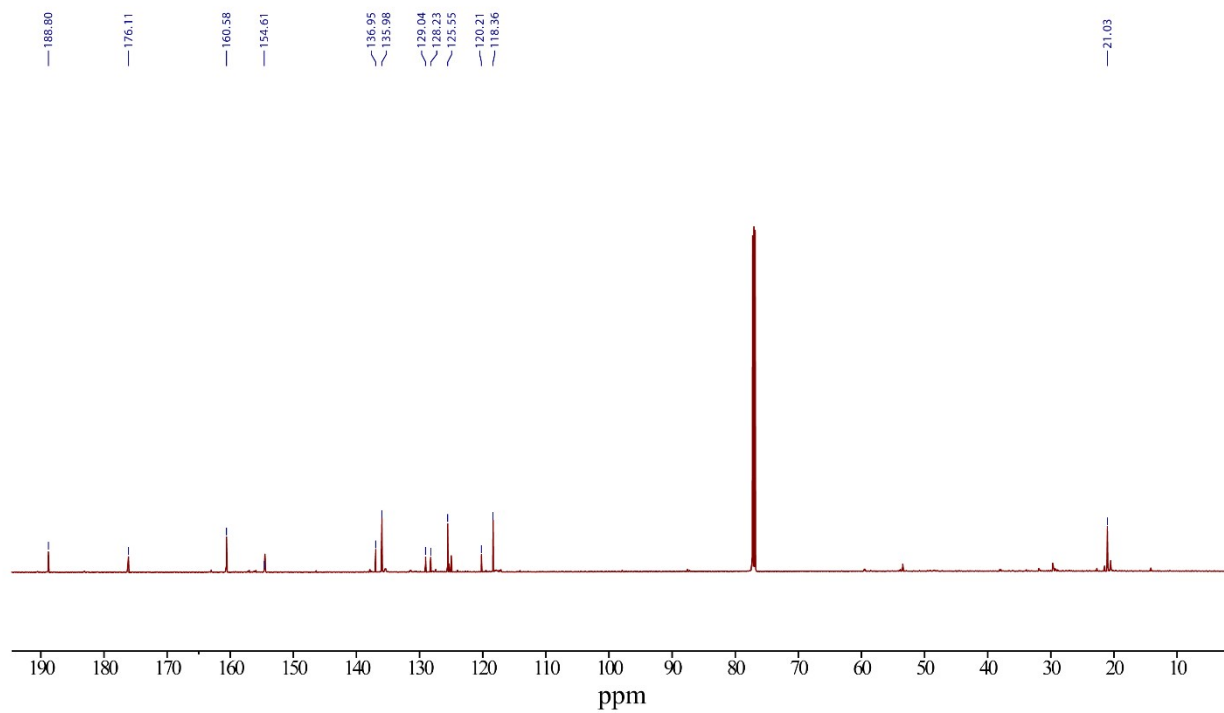
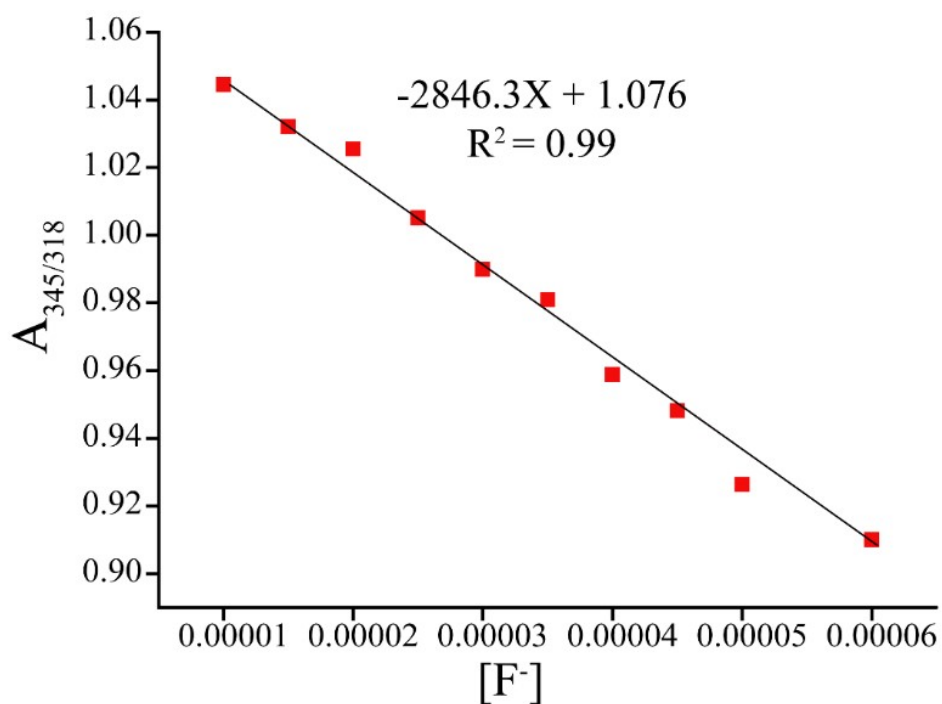
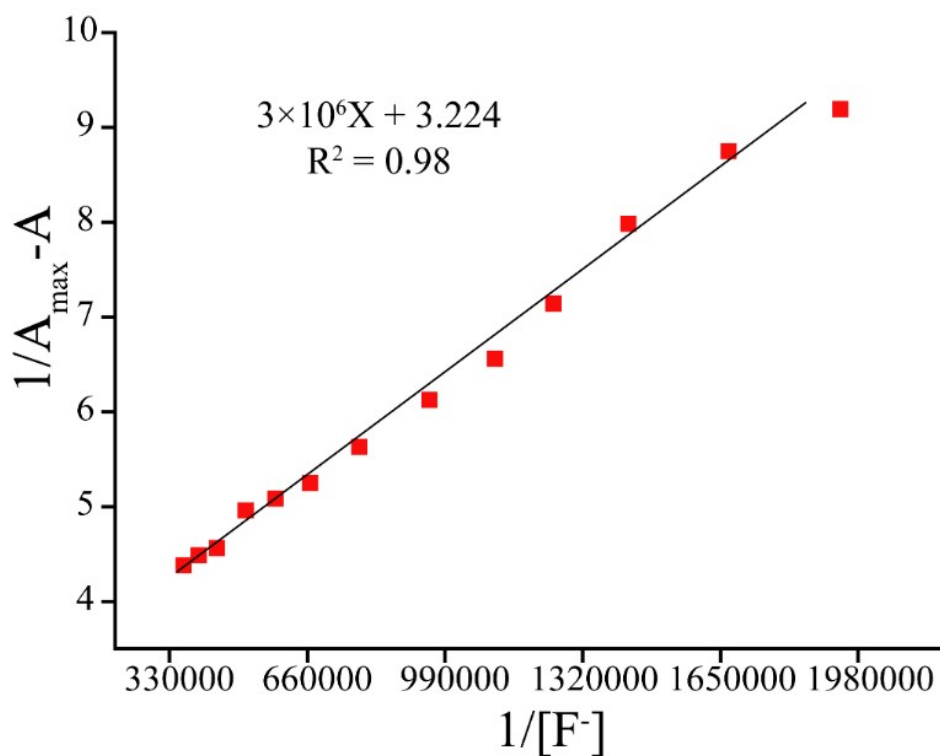


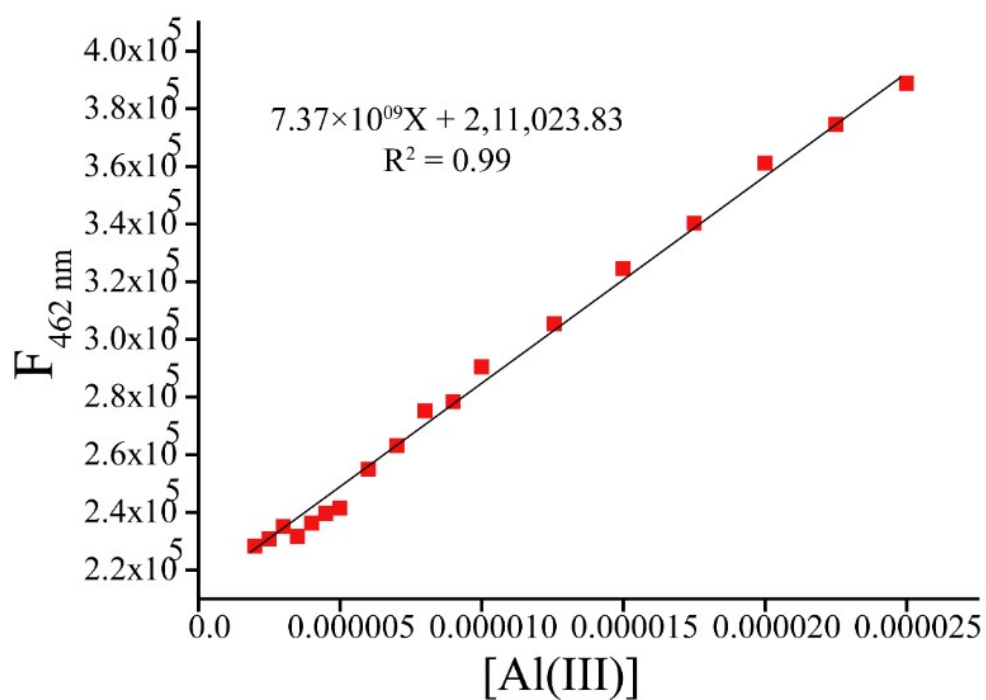
Figure S2  $^{13}\text{C}$  NMR spectra of L at 25 °C.



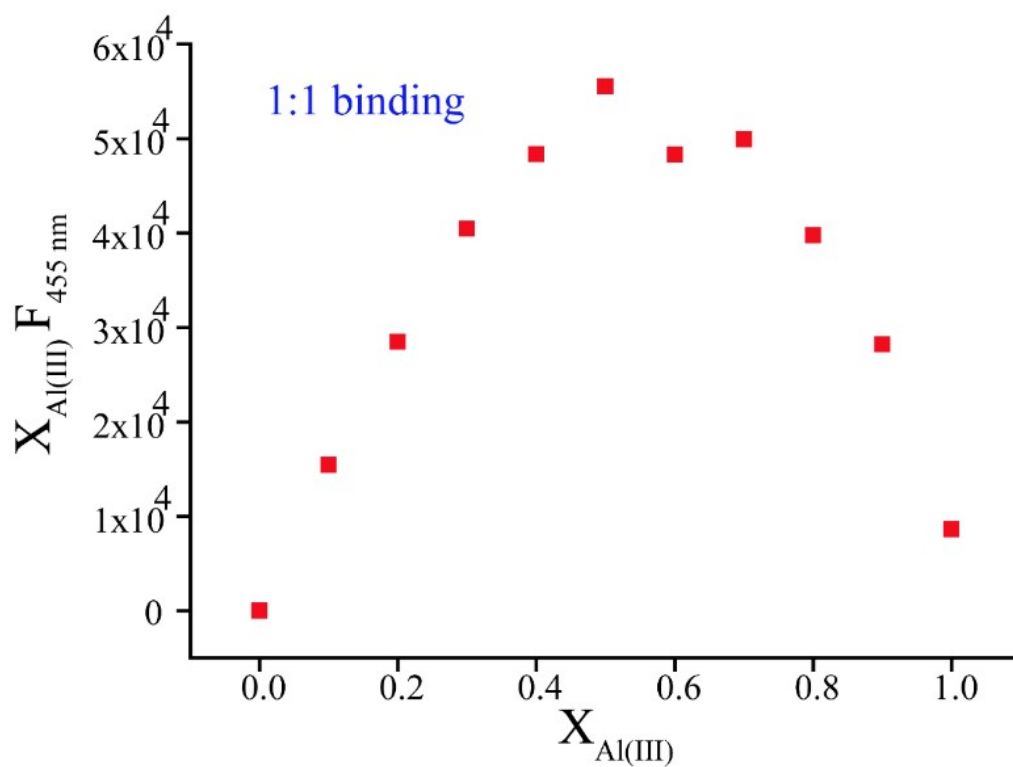
**Figure S3** Plot of absorbance ratio vs  $F^-$  [M] for the detection limit calculation (absorbance at  $A_{345/318}$ ).



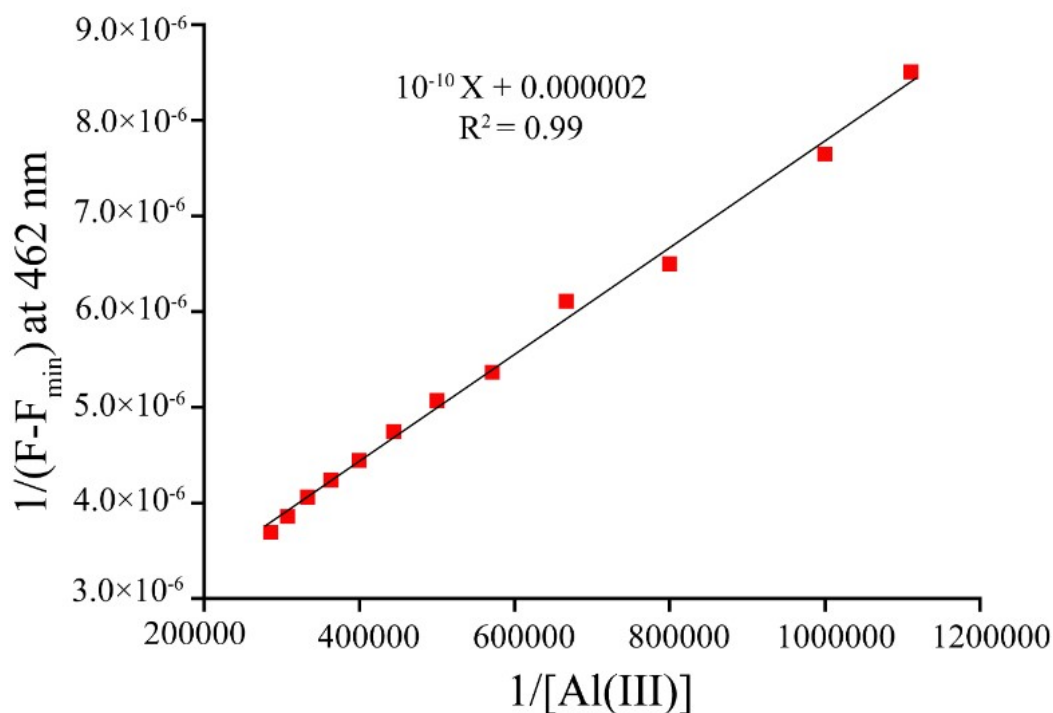
**Figure S4** Benesi-Hildebrand plot for calculation of association constant of  $F^-$  in acetonitrile medium from UV-visible experiment (absorbance at 318 nm).



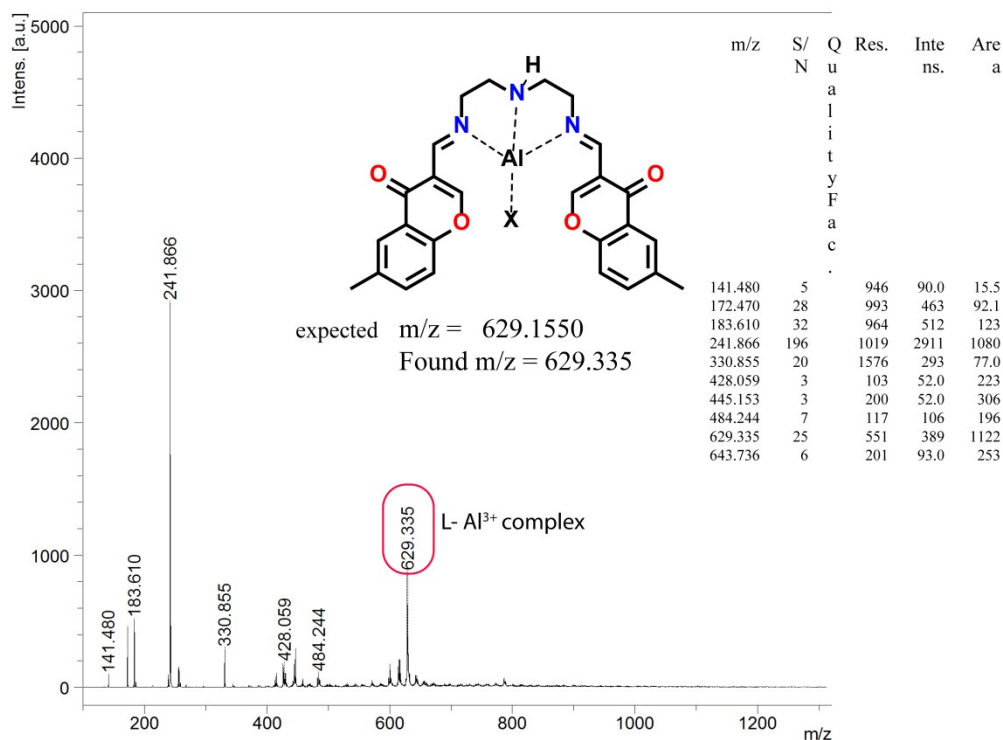
**Figure S5** Plot of emission intensity vs  $[\text{Al}^{3+}]$  for the detection limit calculation (emission intensity at 462 nm).



**Figure S6** Job's Plot for **L** with  $\text{Al}^{3+}$  from fluorescence emission spectrum at 455 nm.  $X_{\text{Al(III)}}$  = mole fraction of  $\text{Al}^{3+}$  in the presence of the guest.

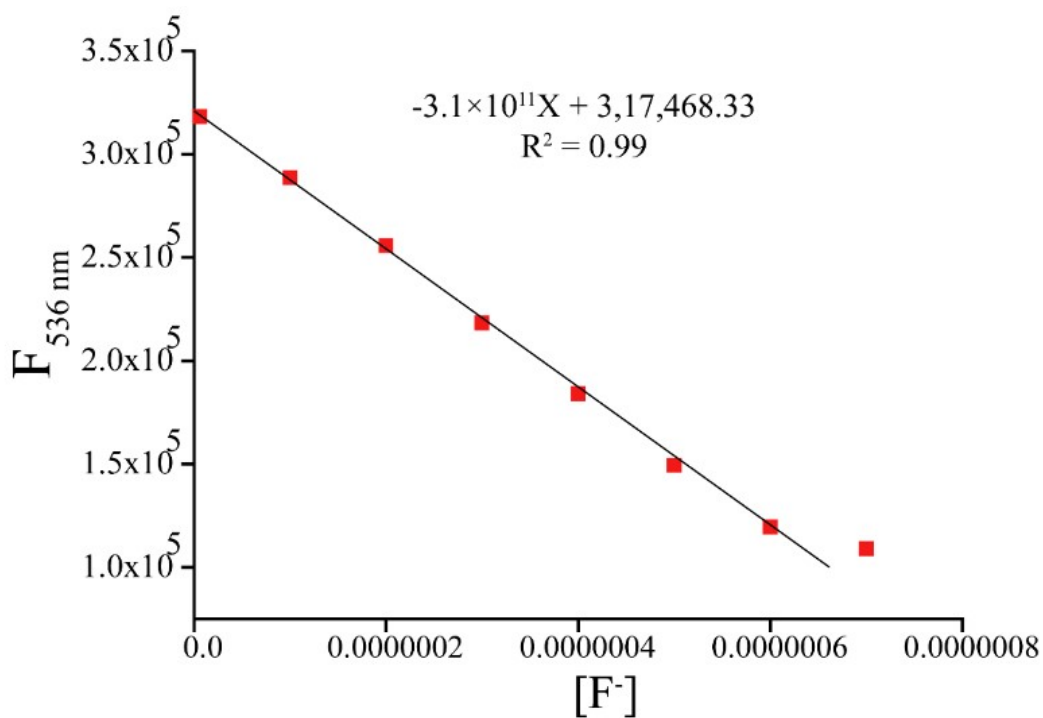


**Figure S7** Benesi-Hildebrand plot for calculation of association constant of  $Al^{3+}$  in aqueous medium from fluorescence experiment (emission intensity at 462 nm).

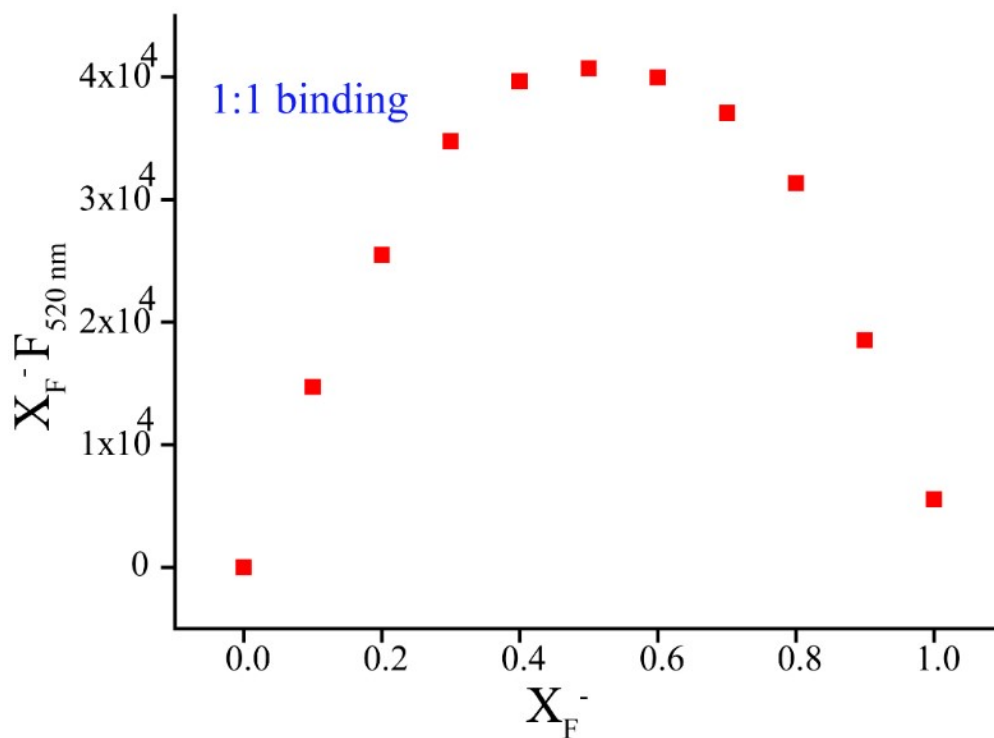


**Figure S8** Mass analysis of the solution of **L** with  $Al(NO_3)_3 \cdot 9H_2O$  (positive mode). The peak corresponds to  $[L+Al^{3+} + 2NO_3^- + OH^- + H_2O]$ , where X= counter anion /solvent.

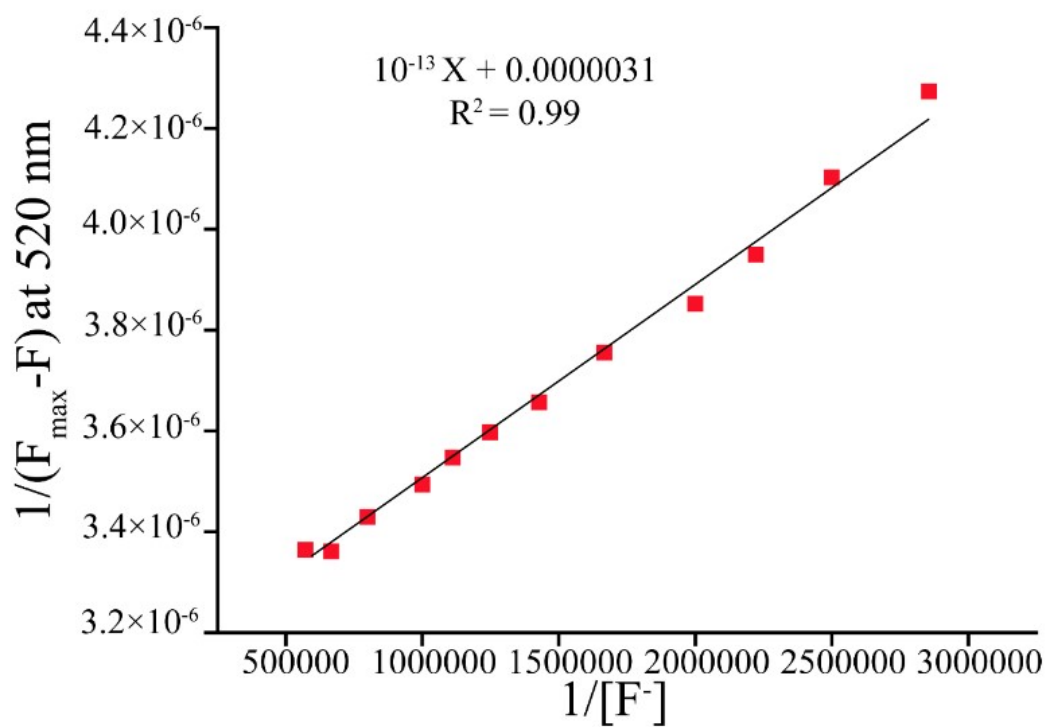




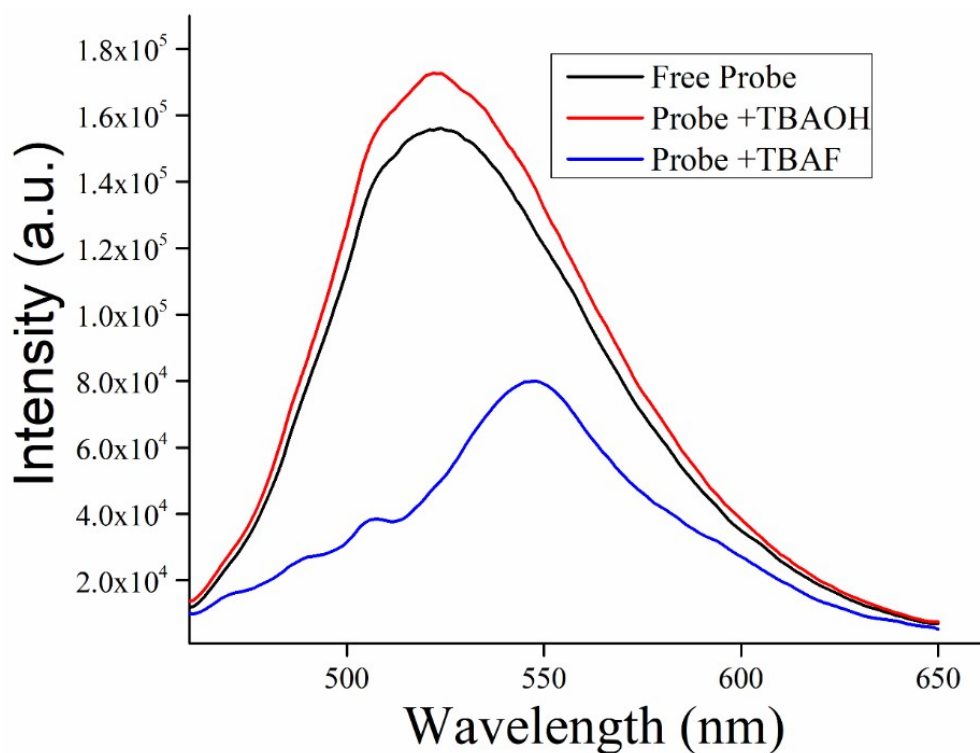
**Figure S9** Plot of emission intensity vs  $F^-$  [M] for the detection limit calculation. (emission intensity at 536 nm).



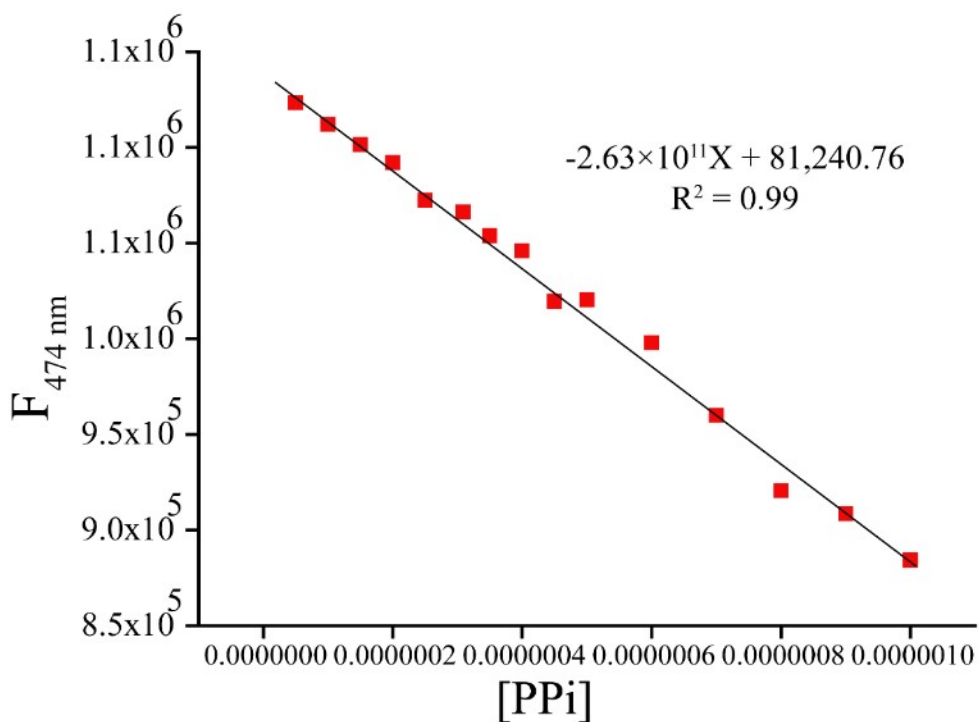
**Figure S10** Job's Plot for L with  $F^-$  from fluorescence emission spectrum at 520 nm.  $X_{F^-}$  = mole fraction of  $F^-$  in the presence of the guest.



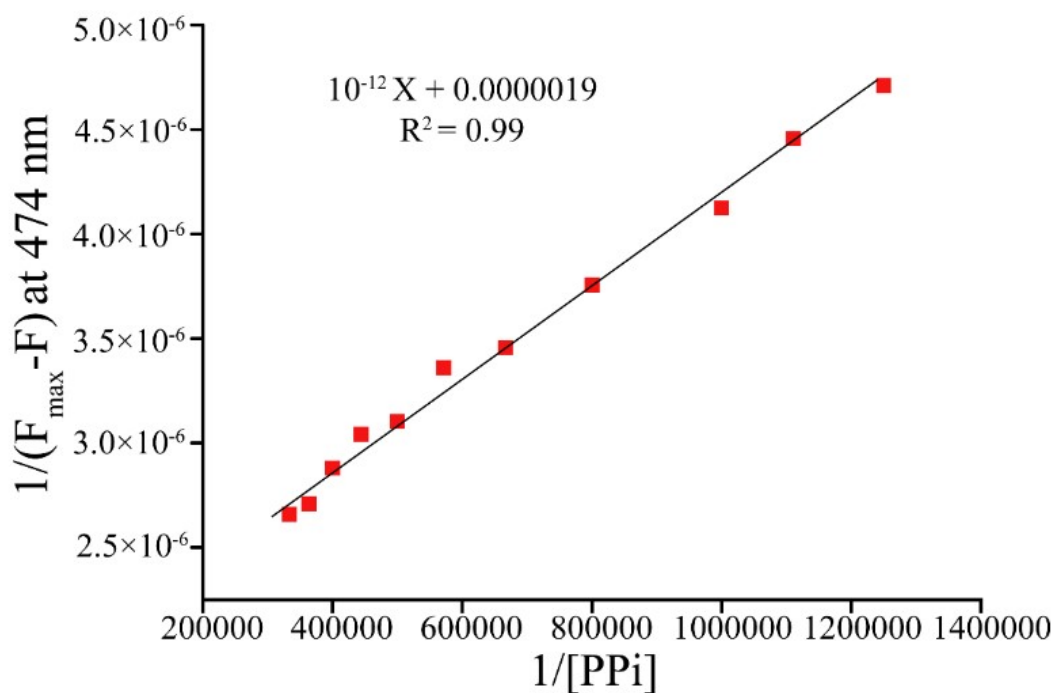
**Figure S11** Benesi–Hildebrand plot for calculation of association constant of  $F^-$  in acetonitrile medium from fluorescence experiment (emission intensity at 520 nm).



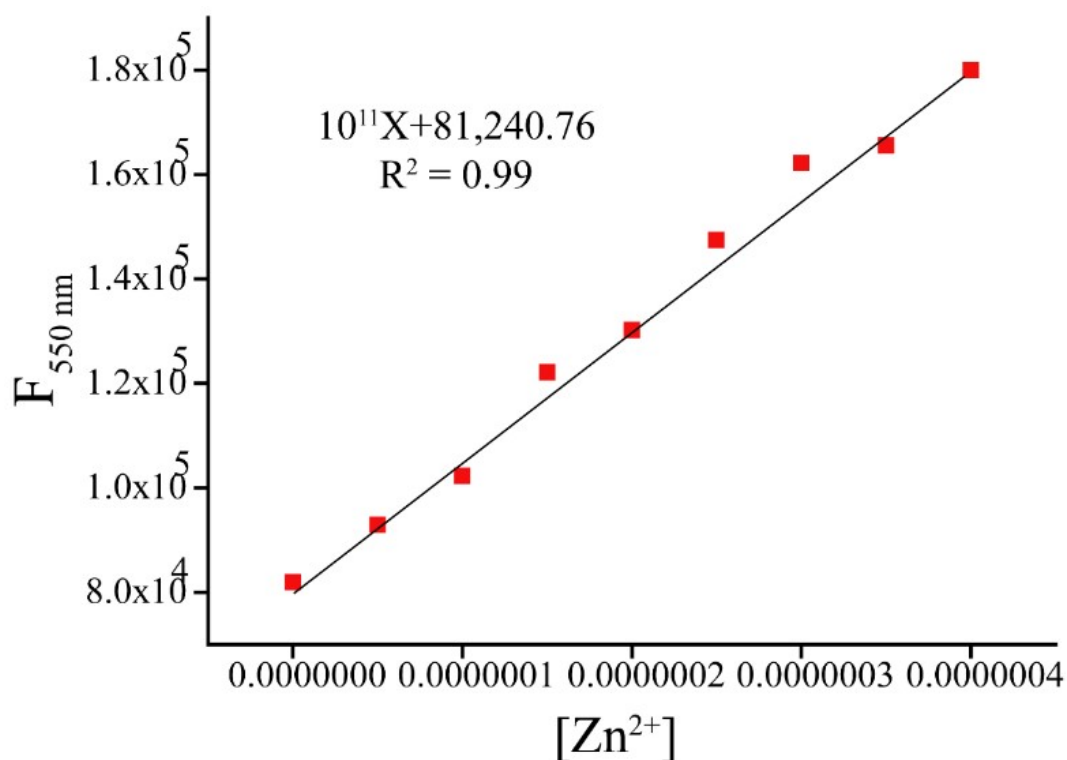
**Figure S12** Emission spectra of **L** with TBAOH and TBAF solution in acetonitrile medium.



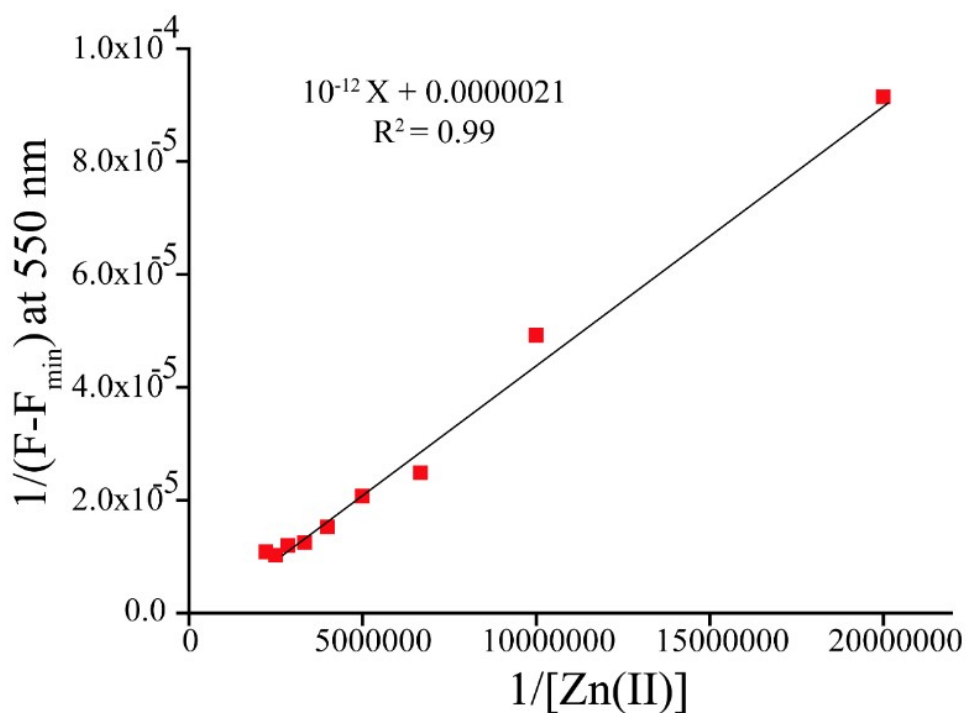
**Figure S13** Graph for the calculation of detection limit of PPI towards [L-Al<sup>3+</sup>] ensemble (emission intensity at 474 nm).



**Figure S14** Benesi-Hildebrand plot for calculation of association constant of PPI towards [L-Al<sup>3+</sup>] in aqueous medium from fluorescence experiment (emission intensity at 474 nm).



**Figure S15** Graph for the calculation of detection limit of  $\text{Zn}^{2+}$  towards  $[\text{L-F}^-]$  ensemble (emission intensity at 550 nm).



**Figure S16** Benesi-Hildebrand plot for calculation of association constant of  $\text{Zn}^{2+}$  towards  $[\text{L-F}^-]$  in acetonitrile medium from fluorescence experiment (emission intensity at 550 nm).

## References

1. S. Johnson, B. T. Couch, A. Meyer and B. Heller, *Bull. Am. Phys. Soc.*, 2020, **65**.
2. J. Rosenthal and S. J. Lippard, *J. Am. Chem. Soc.* 2010, **132**, 5536-5537.
3. S. Mizukami, S. Okada, S. Kimura and K. Kikuchi, *Inorg. Chem.*, 2009, **48**, 7630-7638.
4. Z. Xu, K. H. Baek, H. N. Kim, J. Cui, X. Qian, D. R. Spring, I. Shin, J. Yoon, *J. Am. Chem. Soc.*, 2009, **132**, 601-610.