Electronic Supplementary Information (ESI)

Xanthurenic acid: A natural ionophore with high selectivity and sensitivity for potassium ions in aqueous solution

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1. General procedure of fluorescence experiments

The fluorescence experiments were carried out in aqueous HEPES (50 mM) buffer at pH 7.2. 20 μM metal perchlorate stock solutions of 100 mL were prepared in H_2O. Final test solutions were prepared by taking 1 mL of the above 20 μM metal stock solution and 1 mL of 20 μM **H_3L** solution to further yield 10 μM each of **H_3L** and metal solutions. The resolution was set at 1 nm. The excitation was given at 360 nm and the emission spectrum was collected at 448 nm.

2. General procedure of fluorescence titrations

Stock solutions for fluorescence titrations were prepared in aqueous HEPES (50 mM) buffer at pH 7.2. The stock concentration of **H_3L** was kept constant at 20 μM and the stock solutions of potassium perchlorate were prepared by increasing its concentrations from 0.01 μM to 200 μM in water. The binding constant for **H_3L** was determined from the following equation and fitted in Origin Pro 8.1 software:

$$\mathbf{F = F_0 + \frac{F_{max} - F_0}{2}\left\{\left(1 + \frac{[M]}{C_L} + \frac{1}{C_L K}\right) - \sqrt{\left(1 + \frac{[M]}{C_L} + \frac{1}{C_L K}\right)^2 - 4 * \frac{[M]}{C_L}}\right\}},$$

where F_0 is the emission intensity of **H_3L** in absence of potassium salt, F is the emission intensity of **H_3L** in presence of different concentrations of potassium salts and F_{max} is the emission intensity of **H_3L** when the complete saturation is reached. All experiments were performed in triplicate. The data shown in **Fig. 3b** is the average of three values.

3. Determination of LOD from fluorescence titrations

The detection limit of **H_3L** for K^+ was determined from the following equation:

The LOD is (3σ/S) (R2 = 0.998, **Fig. S3**.). Here σ is the standard deviation and S is the slope of the calibration curve. Plotting fluorescence against [K^+] generates **Fig. S3**. From the **Fig. S3** we calculated slope = 1.3 x 10^8 and the standard deviation was found to be 2.296. Therefore, the LOD value was measured to be 0.53 nM of K^+.

$$LOD = \frac{3\sigma}{S} = 3\frac{\sqrt{\frac{\sum(F - Fi)^2}{n-1}}}{S}$$

In this case, n = 10, F is the fluorescence of **H_3L**.

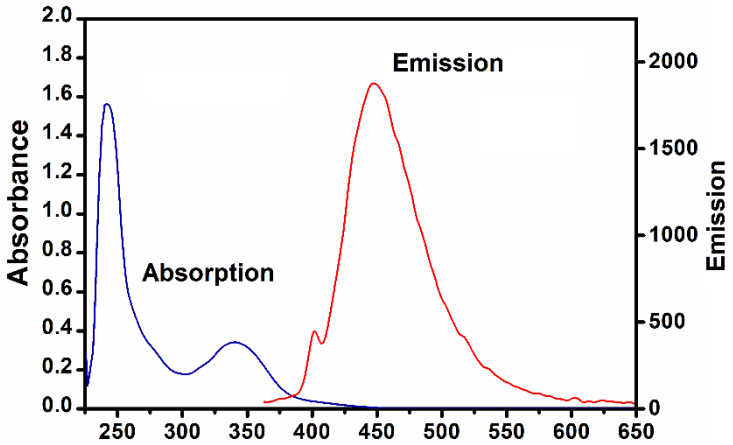


Fig. S1. Absorption and emission spectra of xanthurenic acid (10 μM) in aqueous HEPES buffer.

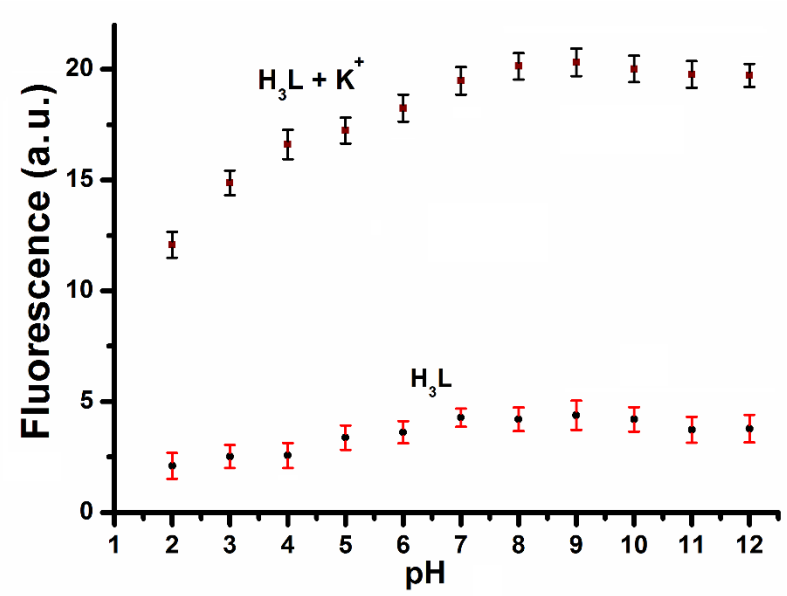


Fig. S2. pH titration profile of **H_3L** in absence and presence of K^+. The data points represent the average of three values and the error bars indicate the standard deviations.

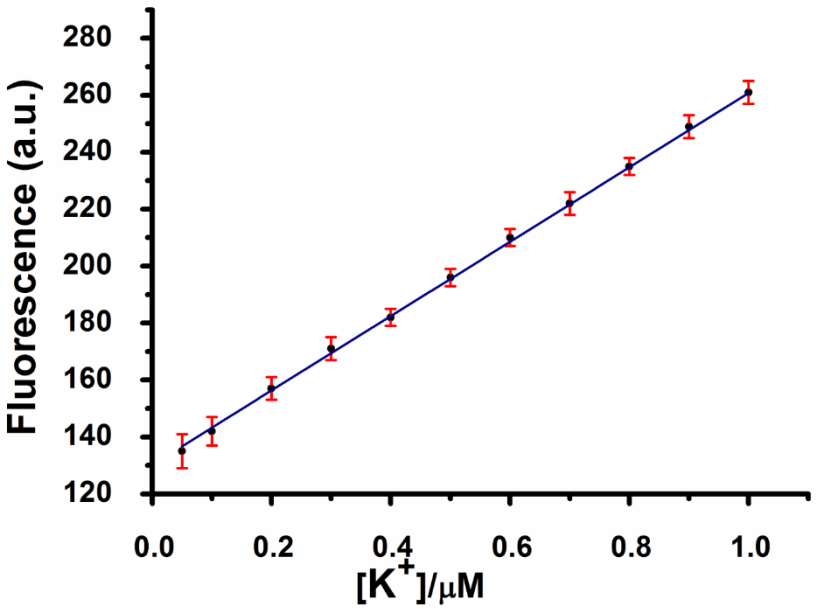


Fig. S3. Limit of detection (LOD) determination from fluorescence titration data of **H_3L** (10 μM) in presence of potassium salts. The data points represent the average of three values and the error bars indicate the standard deviations.

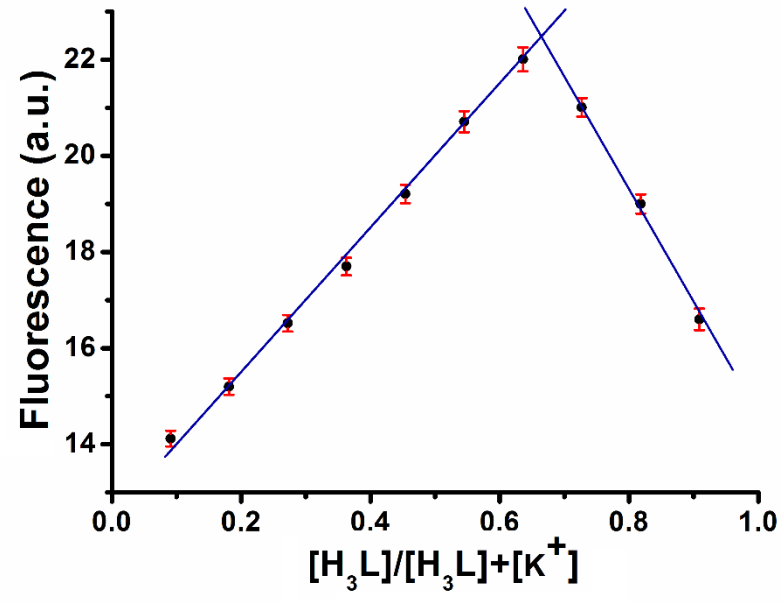


Fig. S4. Job's plot of **H_3L** with K-salt showing 2:1 stoichiometry monitored at 448 nm (emission) in presence of different concentrations of K^+. The data points represent the average of three values and the error bars indicate the standard deviations.

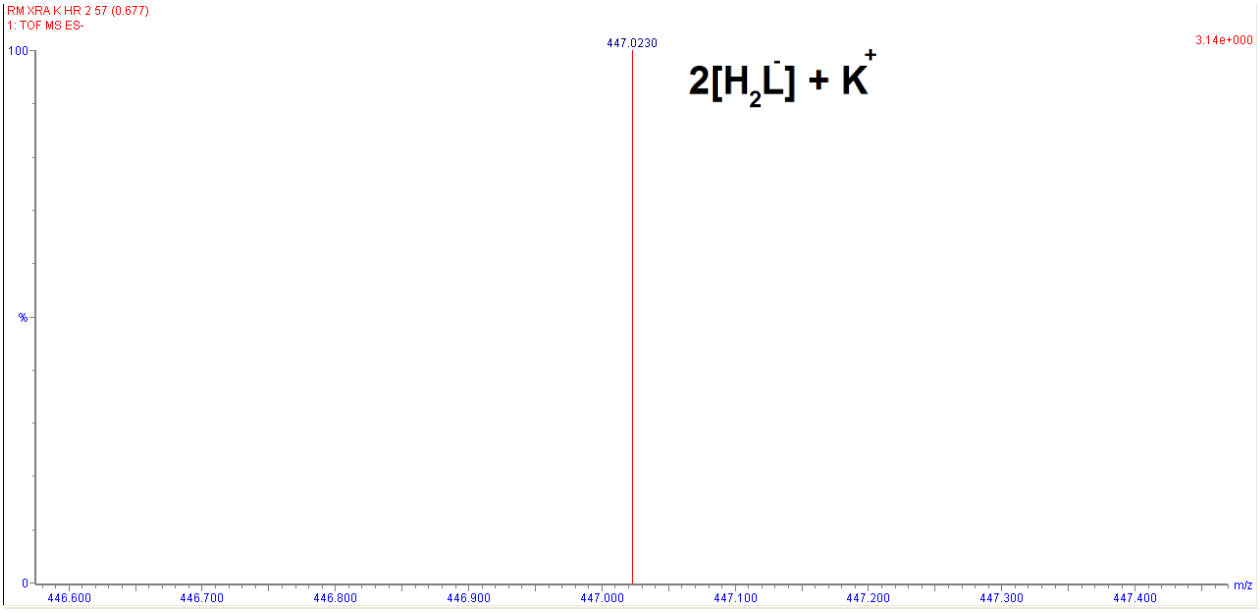


Fig. S5. HR-MS spectrum (in the negative ion mode) of **H_3L** in presence of K^+ showing 2:1 binding stoichiometry of the ionophore with K^+.

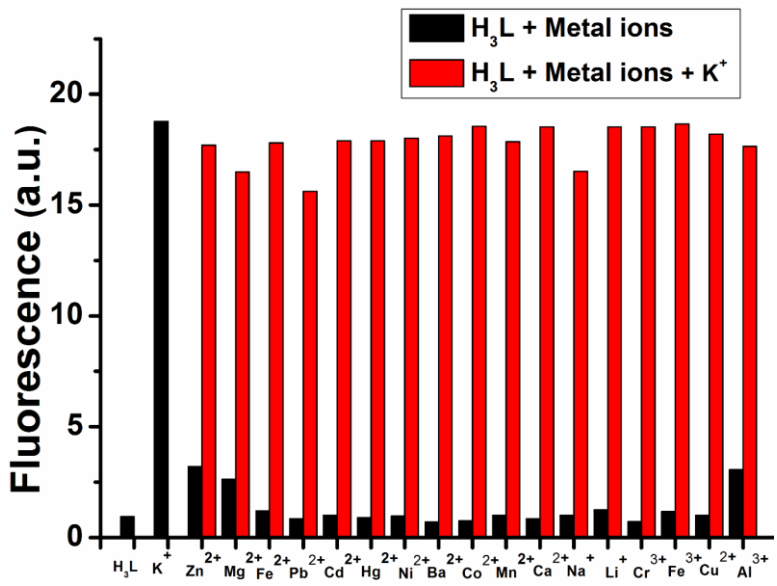
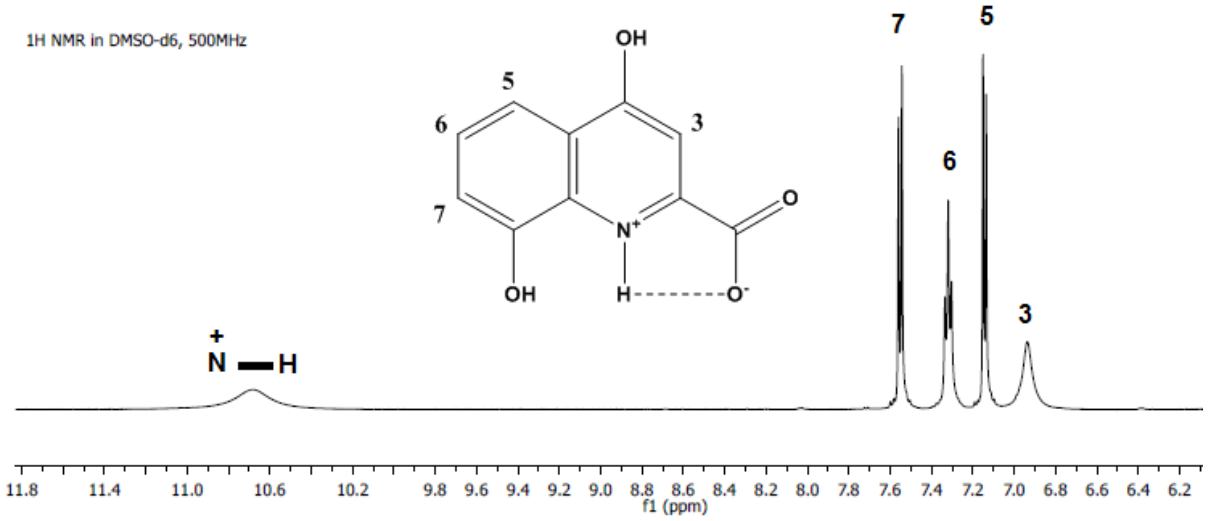


Fig. S6. Fluorescence responses of equimolar (10 μM) **H_3L** and K^+ in the presence of 5-fold (50 equiv in case of Na^+) of other metal ions in water HEPES buffer.

Table S1. ^{1}H NMR spectral data for **H_3L** in DMSO-d_6 with the successive addition of K^+. Chemical shifts are against internal TMS.

Sample	δ_{N^+-H}, ppm	δ_{H7}, ppm	δ_{H6}, ppm	δ_{H5}, ppm	δ_{H3}, ppm
2 mmol H_3L	**10.68**	**7.55**	**7.31**	**7.15**	**6.94**
2 mmol H_3L : 0.5 mmol K^+	**10.71**	**7.55**	**7.31**	**7.15**	**6.96**
2 mmol H_3L : 0.75 mmol K^+	**10.75**	**7.55**	**7.31**	**7.15**	**6.97**
2 mmol H_3L : 1 mmol K^+	**10.77**	**7.55**	**7.31**	**7.15**	**6.97**
2 mmol H_3L : 1.5 mmol K^+	**10.77**	**7.55**	**7.31**	**7.15**	**6.97**
2 mmol H_3L : 2 mmol K^+	**10.77**	**7.55**	**7.31**	**7.15**	**6.97**



^{1}H NMR spectrum and assignments of different protons of **H_3L** in DMSO-d_6.