

Supplementary Data for

A novel “turn-on” fluorescent probe for Fe³⁺ in aqueous media based on C=N isomerization

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Supporting information

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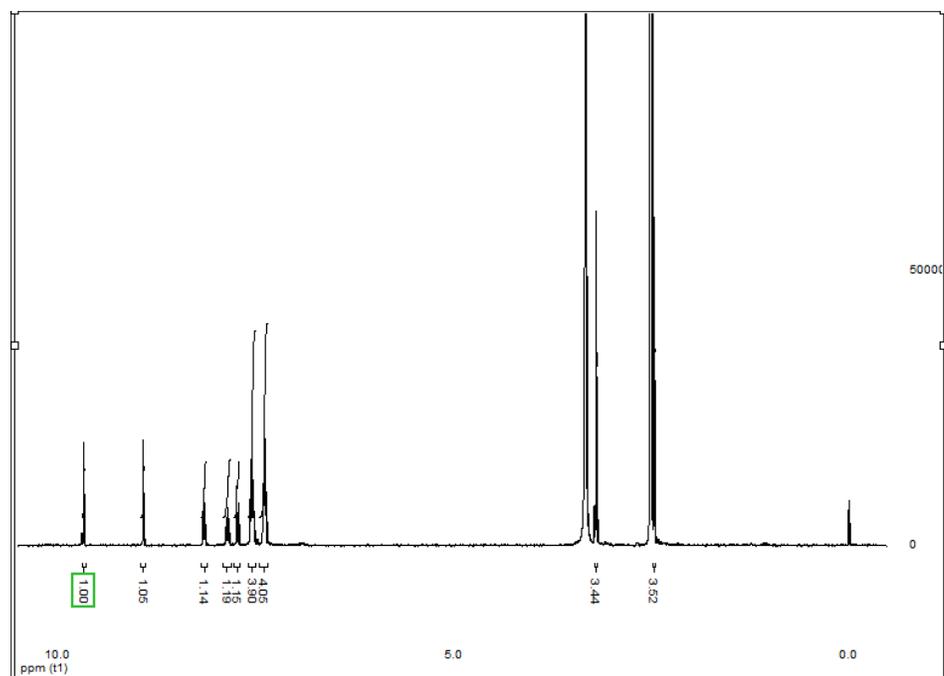
1. Materials and instruments

All the materials and solvents were purchased from commercial suppliers and used without further purification. The solution of metal ions were prepared from chloride salts of Ni²⁺, Fe³⁺, Cu²⁺, Mn²⁺, Hg²⁺, Na⁺, Ca²⁺, Zn²⁺, Mg²⁺, Pb²⁺, K⁺, Co²⁺, Li⁺, Cd²⁺, Cr³⁺, Al³⁺, Sr²⁺, Ba²⁺, and nitrate salts of Ag⁺. Stock solutions of metal ions (20 mM) were prepared in deionized water.

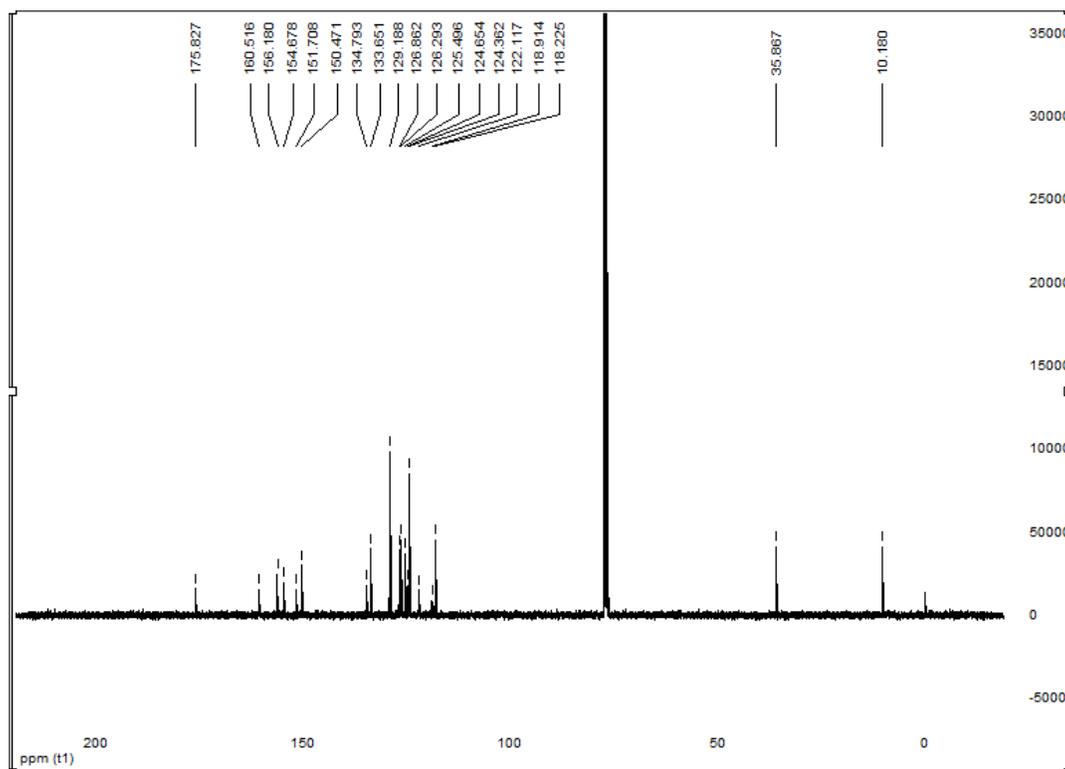
A stock solution of **L** (200 μM) was prepared in CH₃CN. In selectivity experiments, the test samples were prepared by appropriate amount of metal ion stock into 3 mL solution of **L** (20 μM). Absorbance spectra measurements were measured on a Purkinje general UV-1901 spectrophotometer. Fluorescence spectra measurements were performed on a Cary Eclipse fluorescence spectrophotometer. ¹H-NMR, ¹³C-NMR spectra were obtained on a Bruker Avance 400 MHz NMR spectrometer with tetramethylsilane (TMS) as internal standard. X-ray data were collected on Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation.

2. Synthesis and characterization of **L**

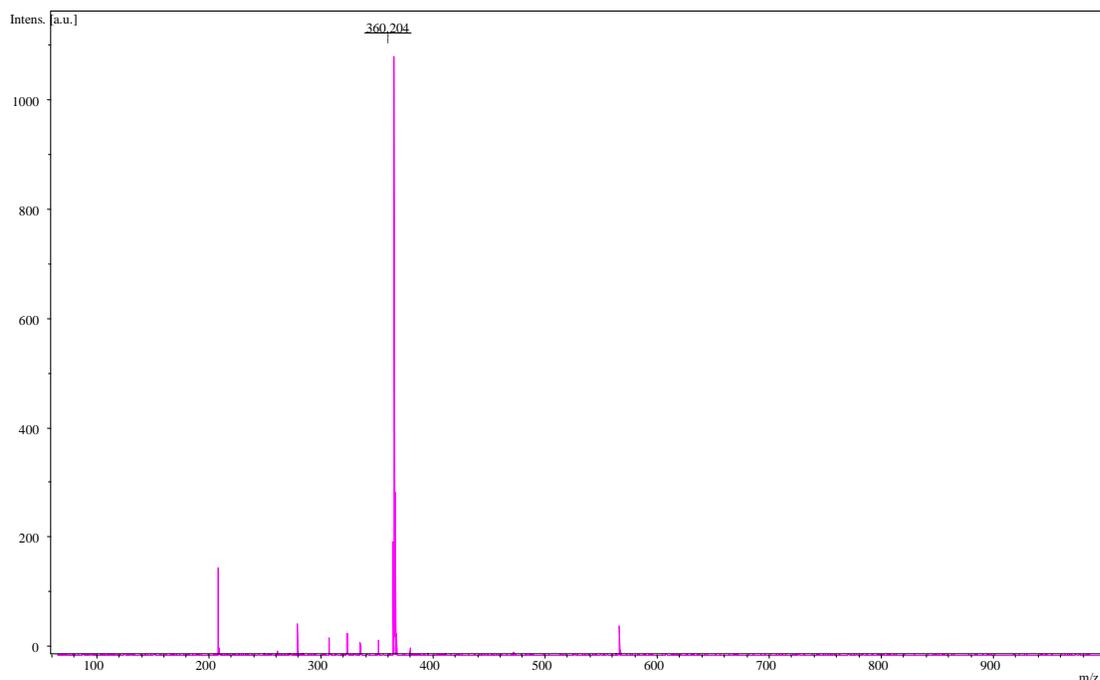
A solution of chromone-3-carboxaldehyde (0.34 g, 2 mmol) and 4-Aminoantipyrine (0.40 g, 2 mmol) in 30 mL ethanol was stirred at 50 °C for 2 h. After completion of the reaction, the obtained yellow precipitate was filtered and washed several times with cold ethanol. After drying under reduced pressure, the reaction afforded 0.58 g (79%) as a yellow solid. ¹H NMR (400 MHz, *d*₆-DMSO) δ: 9.67 (s, 1H), 8.92 (s, 1H), 8.14(d, *J* = 8 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.52-7.56 (m, 4H), 7.39 (t, *J* = 6 Hz, 4H), 3.19 (s, 3H), 2.46 (s, 3H). ¹³C NMR (100 MHz, *d*-CDCl₃) : δ (ppm) 175.83, 160.52, 156.18, 154.68, 151.71, 150.47, 134.79, 133.65, 129.19, 126.29, 125.49, 124.65, 124.36, 122.18, 118.91, 118.22, 35.87, 10.18. MALDI-TOF MS: ([M + H]⁺), 360.204.



^1H NMR spectrum of L in d_6 -DMSO



^{13}C NMR spectrum of L in d - CDCl_3



MALDI-TOF MS spectrum of **L**

3. Crystal structure determination of **L**

A crystal ($0.2 \times 0.2 \times 0.1$ mm) was mounted on Bruker Smart APEX II CCD equipped with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The $T_{\max} = 0.991$ and $T_{\min} = 0.982$. The relevant crystal data and structural parameters are: fw 359.38; space group R-3 is trigonal; $a = b = 34.465(13)$ (Å), $c = 7.825(3)$ (Å), $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; $V = 8050(5)$ (Å³); $Z = 18$; $\rho = 1.334$ g/cm³; μ (MoK α) = 0.091 cm⁻¹, the intensities were collected at 296(2) K. 13438 reflections were measured and after merging (Rint 0.0215), some 3152 reflections (of which 2409 were labelled as observed) were used in the refinement. The final R_1 ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$) value was 0.0415, wR_2 ($[\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) value was 0.1007.

4 Calculation of binding constant

We estimated the binding constants by using the fluorometric titration data. The equations below was used to calculate the binding constants with stoichiometry of 1:1.

$$\frac{F - F_0}{F_{Lim} - F_0} = \frac{1}{2C_L} \left[\left(C_L + C_M + \frac{1}{K_s} \right) - \sqrt{\left(C_L + C_M + \frac{1}{K_s} \right)^2 - 4C_L C_M} \right]$$

where F is the recorded fluorescent intensity, F_0 is the start value without addition of Fe³⁺, F_{lim} is

the limiting value, C_M is the Fe^{3+} concentration, and C_L is the sensor L concentration.

5 Fig S1-S5

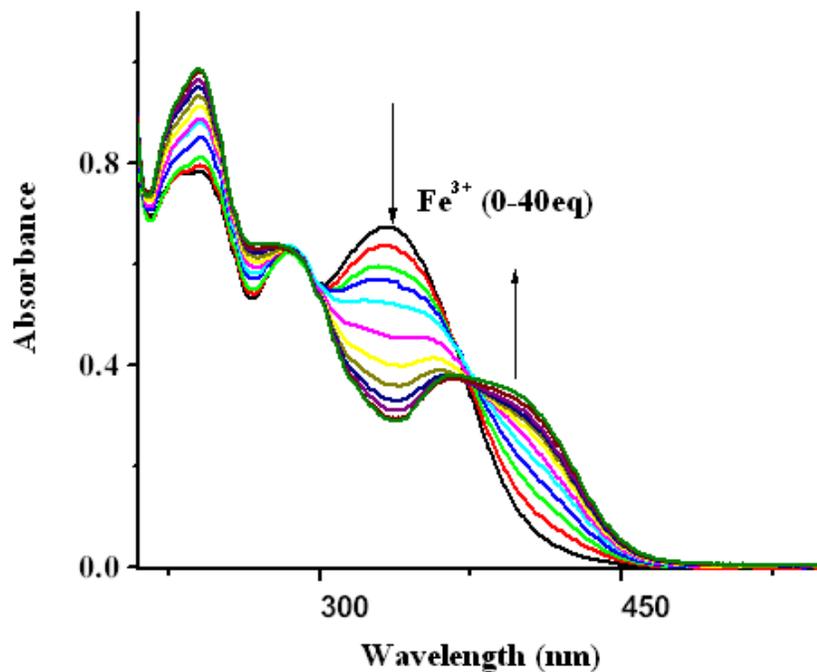


Fig. S1 Uv-Vis spectral changes of L (20 μM) upon addition of Fe^{3+} (40 equiv.) in CH_3CN -water (1/9, v/v).

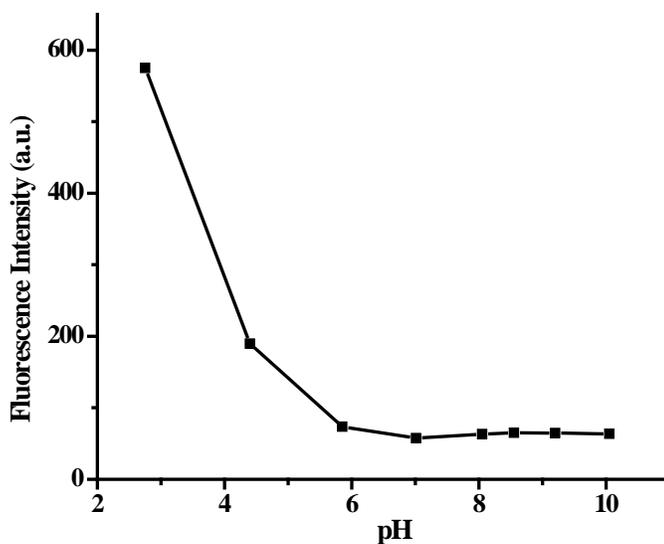


Fig. S2 Fluorescence intensity of L (20 μM) at 420 nm in CH_3CN -water (1/9, v/v). ($\lambda_{\text{ex}} = 372$ nm)

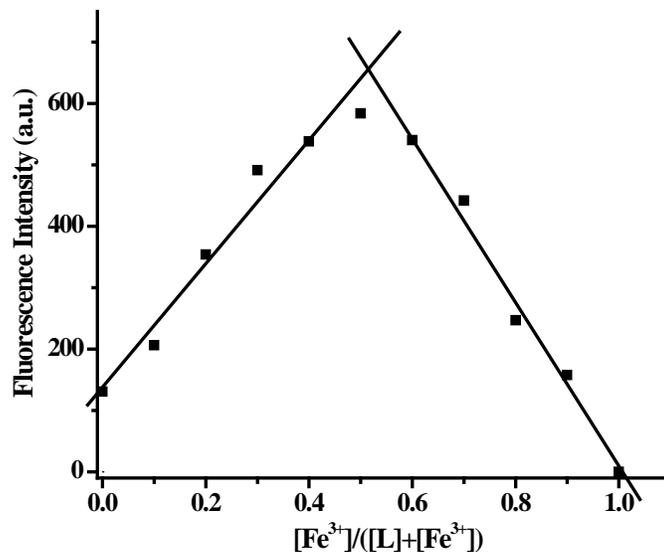


Fig. S3 Job's plots for determination of the stoichiometry of L-Fe³⁺ in CH₃CN-water (1/9, v/v, pH=7.0) solution, indicating the 1:1 stoichiometry for L-Fe³⁺ (the total concentration of L and Fe³⁺ is 100 μM).

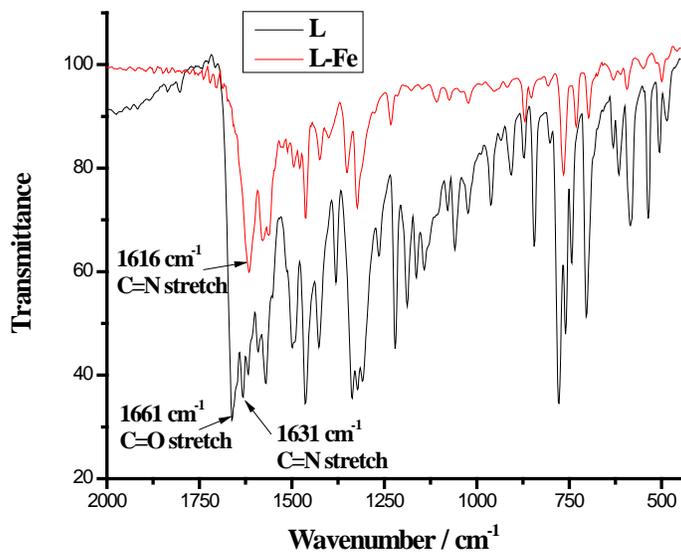


Fig. S4 IR spectra of L and L-Fe³⁺.

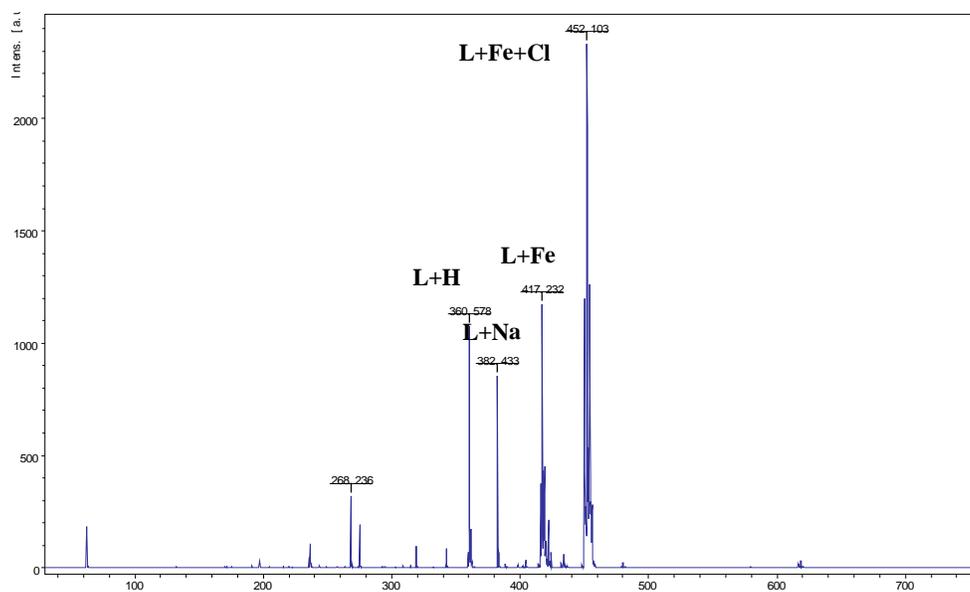


Fig. S5. The MALDI-TOF MS spectra of L in CH₃CN