

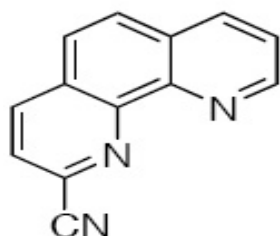
# Fluorescent Sensor Based on 2-Cyano-1,10-phenanthroline for Fe<sup>2+</sup> ion Analysis in Acetonitrile

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## Introduction

Fluorescent sensors for the detection and measurement of Fe<sup>2+</sup> will be actively investigated in this paper, as this metal ion is a significant environmental pollutant and essential element in biological systems. For most of the reported Fe<sup>2+</sup> fluorescent sensors, the binding of the metal ion causes a quenching of the fluorescent emission. Only a few sensors in which the binding of the metal ions causes an increase in the fluorescence have been reported (Zhaochao, Yi Xiao and Xuhong Qian, 2005). To increase the selectivity and sensitivity of a measurement, ratiometric measurements are utilized. Ratiometric measurements involve the observation of changes in the ratio of the intensities of the absorption or the emission at two wavelengths. However, ratiometric sensors for the detection of Fe<sup>2+</sup> are very rare. We designed and synthesized the fluorescent sensors (**1**), 2-Cyano-1,10-phenanthroline which contain fluorophore and ionophore and show the static quenching, fluorescent enhancement and dynamic quenching for a range of concentration. The fluorophore (**1**) shows high selectivity for Fe<sup>2+</sup> with detection limit 3.6×10<sup>-9</sup>M.



Compound (**1**)

## Experimental

### *Synthesis of (1)*

To a solution consisting of 5.0 g (0.026 mol) of 1,10-phenanthroline-1-oxide and 5.0 g of potassium cyanide dissolved in 40 ml of distilled water, 5.0 ml of benzoyl chloride was added dropwise, under magnetic stirring. The total addition required 1 hour, and the reaction mixture was stirred for an additional 2 hours. The resulting precipitate was collected by suction filtration, washed with distilled water, and dried as a brown solid in 87% yield. Crystallization from ethanol gives the pure compound melting point 237 °C. [Wen-Hua Sun, et al 2006, 237-238°C] IR  $\nu_{\max}$  (cm<sup>-1</sup>): 3058, 2228, 1502, 851.

## Results and Discussion

The cations binding properties of compound (**1**) were investigated by UV-vis absorption and fluorescence spectroscopy. All the experiments were carried out in acetonitrile medium by adding aliquots of different metal ions. The UV-vis absorption spectrum of compound (**1**)

exhibits one isobestic point at 274 nm on addition of metal ions, as shown in Figure 1. The addition of  $\text{Fe}^{2+}$  from 0-3.53  $\mu\text{M}$  resulted in an increase in absorption at 280nm to a limiting value. Absorption studies indicated that only one complex was formed.

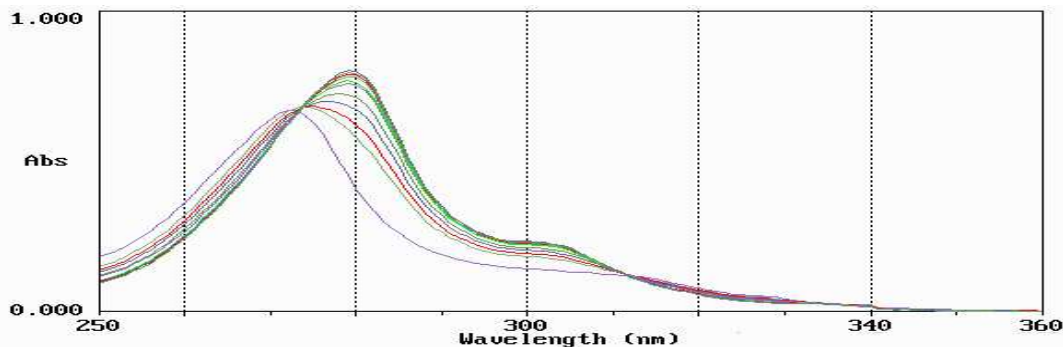


Fig.1.Uv spectra of compound (1) at  $1.95 \times 10^{-5}$  M in acetonitrile solution with added Fe(II) concentration of 0, 0.54, 0.72, 0.9, 1.08, 1.18, 1.35, 1.61, and 3.53  $\mu\text{mol dm}^{-3}$  from the smallest to the largest  $\lambda_{\text{max}}$ . Isobestic point is at 274 nm.

In the fluorescence spectrum, compound (1) exhibited emission band at 364 nm at the concentration  $4.875 \times 10^{-6}$  M, when increasing the concentration of  $\text{Fe}^{2+}$  from (0- $1.08 \times 10^{-7}$  M) resulted in decrease fluorescence at 364 nm due to the static quenching of fluorescence of 1 by  $\text{Fe}^{2+}$ . Further addition of  $\text{Fe}^{2+}$  ( $1.08 \times 10^{-7}$  -  $3.6 \times 10^{-7}$  M) to the solution of compound (1), a significant decrease in the 364 nm emission and a new band due to emission of complex appeared at 404 nm, which was attributed to 1-  $\text{Fe}^{2+}$  complex with an isoemissive point at 375 nm (Fig 2). The inset in Figure 2 shows the dependence of intensity ratios of emission at 404 nm to that at 364nm ( $I_{404}/I_{364}$ ) on Fe(II) which indicates the formation of complex between 1 and  $\text{Fe}^{2+}$ ; further increasing Fe(II) concentration from  $3.6 \times 10^{-7}$  M the emission from complex undergoes a dynamic quenching with  $\text{Fe}^{2+}$  (Fig 3).<sup>+</sup>

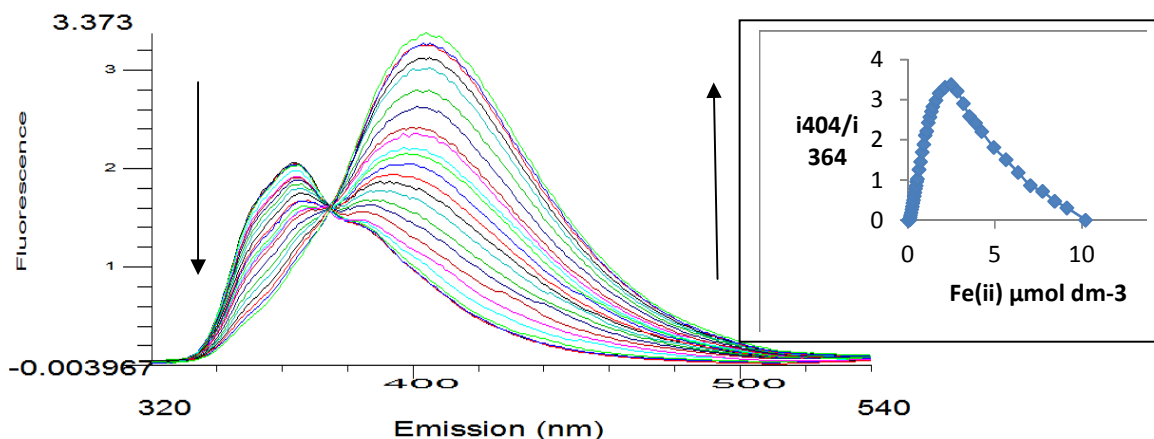


Figure 2. (a) Emission spectra of compound (1) at  $4.88 \times 10^{-6}$  M in acetonitrile solvent with increasing Fe(II) concentration from 0 to  $3.6 \times 10^{-7}$  M excitation wavelength =273 nm, isoemissive point at 375 nm inset: ratiometric calibration curve  $I_{404}/I_{364}$  as a function of Fe(II) concentration and dynamic quenching ratio.

The complex formation constant was calculated using Benesi and Hildebrand method that was  $\log(K) = 5.73$ . An interference study was carried out with same conditions for different metal ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ . No significant fluorescence was observed in the presence of these metal ions. To test the practical applicability of 2-Cyano-1,10-phenanthroline as  $\text{Fe}^{2+}$  selective fluorescence sensors competitive experiments were carried

out in the presence of Fe(II) at  $3 \times 10^{-7}$  M mixed with  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{Ni}^{2+}$  at  $3 \times 10^{-7}$  M. There was no significant variation found in the intensity ratio ( $I_{404}/I_{364}$ ). This confirms that compound (**1**) has higher selectivity for  $\text{Fe}^{2+}$ .

In order to determine the stoichiometry of the **1**-  $\text{Fe}^{2+}$  complex, the method of continuous variation (Jobs plot) was also used. The total concentration of the compound (**1**) was constant ( $1.2 \times 10^{-6}$  M), with a continuous variable molar fraction of guest ( $[\text{Fe}^{2+}]/([\text{1}]+[\text{Fe}^{2+}])$ ). Figure 4 shows the jobs plot of compound **1** with  $\text{Fe}^{2+}$  at 404 nm. The **1**-  $\text{Fe}^{2+}$  complex concentration approaches a maximum when the molar fraction of  $\text{Fe}^{2+}$  is 0.25, indicating a formation of 1:3 complex.

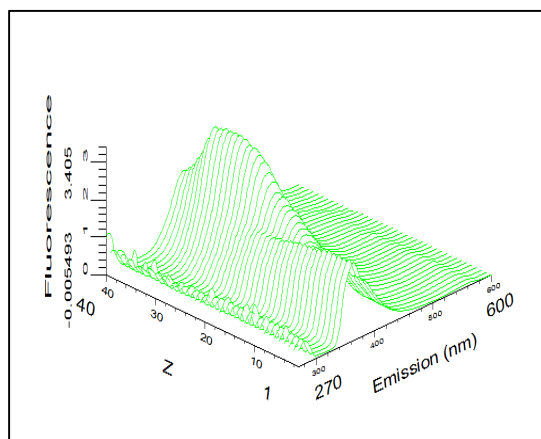


Fig 3. Fluorescence spectra of **1** in the presence of different concentration of Fe(II) (0-1.8  $\mu\text{M}$ ) in 3D

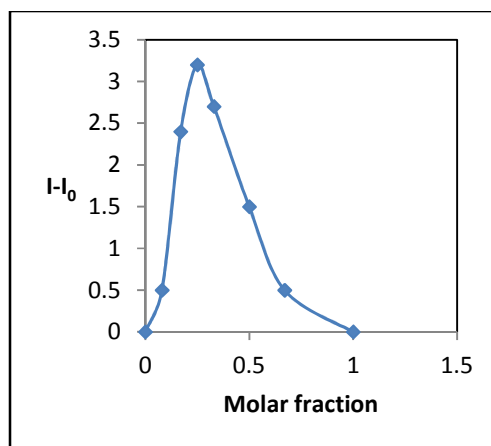


Fig 4. Jobs plot for **1** and Fe(II)  $1.2 \times 10^{-6}$  M in acetonitrile.

## Conclusion

We developed highly selective fluorescence sensor for  $\text{Fe}^{2+}$  based on 2-cyano-1,10-phenanthroline. The recognition of  $\text{Fe}^{2+}$  gave rise to ratiometric change at the ratio of the fluorescent intensity of 364 and 404 nm for the complexation. For the very low concentration of  $\text{Fe}^{2+}$ , 2-cyano-1,10-phenanthroline undergoes static quenching and in higher concentration of Fe(II) it undergoes the dynamic quenching. The detection limit for  $\text{Fe}^{2+}$  was found to be  $3.6 \times 10^{-9}$  M. Thus 2-cyano-1,10-phenanthroline may be considered as a potential fluorescent chemosensor for Fe(II).

## References

- Wen-Hua Sun, Suyun Jie, Shu Zhang, Wen Zhang, and Yingxia Song. *organometallics* **2006**, 25, 666-677.
- Zhaochao, Yi Xiao, Xuhong Qian. Ratiometric and selective fluorescent sensors for Cu(II) based on internal charge transfer, *Organic letters* **2005**:7 889-892