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A new selective phenanthroline-based fluorescent chemosensor for Co^{2+}

Xiuli Wang *, Wenyan Zheng, Hongyan Lin, Guocheng Liu, Yongqiang Chen, Jiani Fang

Faculty of Chemistry and Chemical Engineering, Liaoning Key Laboratory of Applied Chemistry, Bohai University, Jinzhou 121000, PR China

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ABSTRACT

An intramolecular charge transfer (ICT) chromophore 2-(2-pyridine)imidazo [4,5,*f*]-1,10-phenanthroline (**1**) has been synthesized and firstly used as a chemosensor with a reversible, 'on–off' sensing capability for biologically and environmentally significant Co^{2+} in DMF under buffered conditions. The experiment results also show that the response behavior of **1** to Co^{2+} is pH independent in range of pH 3.0–7.0 and show excellent selectivity for Co^{2+} over other cations.

It is well known that Co^{2+} as one of the most important transitional metal ions plays an important role in the metabolism of iron and synthesis of hemoglobin, and it is also a main composition of Vitamin B12 and other biological compounds.[1] Cobalt deficiency in human body may lead to pathological conditions and it is also a significant environmental pollutant.[2] Consequently, there has been a growing interest in the development of selective Co^{2+} sensors for biological and environmental applications. However, there are only a few sensors based on fluorescence reported for cobalt ions determination.[3] Most of the fluorophores respond to cobalt ions only in the presence of oxidizing agents such as hydrogen peroxide and in a basic medium.[4] Moreover, some of the fluorophores possess poor selectivity[5] and a relatively high background.[6] Therefore, searching for new fluorophores for the determination of cobalt ions with excellent analytical performance characteristics is still a challenge.

In our quest to exploit intramolecular charge transfer (ICT) as a promising design strategy to assess selective metal ion sensors,[7] we synthesized an intramolecular charge transfer (ICT) chromophore 2-(2-pyridine)imidazo [4,5,*f*]-1,10-phenanthroline (**1**)[8] that used the two nitrogen atoms of phenanthroline and the other two nitrogen atoms of imidazole ring and pyridyl ring to form two cation binding sites, and firstly studied the effects of various metal ions on its photophysical properties. 2-(2-Pyridine)imidazo [4,5,*f*]-1,10-phenanthroline (**1**) was synthesized by condensation of 1,10-phenanthroline-5,6-dione[9] and pyridine-2-carbaldehyde in refluxing glacial acetic acid and ammonium acetate for 2 h, then adjusting the pH value of the solution until yellow precipitate appears. The crude product was purified by chromatography on silica gel using CH_2Cl_2–EtOAc (10:1) as the eluent (Scheme 1).

We choose compound **1**, as a new chemosensor relies on the anticipation that metal ion coordination with compound **1** would provoke enhanced ICT assigned to intraligand $\pi\rightarrow\pi^*$ transitions. The ensuing photophysical perturbations of **1** could be used to harness its potential in metal sensing applications. Metal ions of biological and environmental interest, such as Na^+, K^+, Mg^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, and Hg^{2+}, were investigated for their photophysical effects on sensor **1**, which shows effective selectivity for Co^{2+} over other cations. Both spectrophotometric and fluorimetric experiments were carried out by adding metal nitrate to the DMF solutions that were buffered by 0.1 mM NaOAc–HOAc (pH adjusted to 6.8 by adding 0.1 M HCl). The UV–vis spectra of **1** displayed absorption bands in a range of 280–450 nm along with two main peaks at 318 and 327 nm in DMF buffered solution. Titrating above series of metal ions with 10 equiv ($c = 5 \times 10^{-5}$ M) to the solution of **1**, we can see remarkable changes in the UV–vis spectra of **1** + Co^{2+}, in which the absorption intensity of **1** at 318 and 327 nm decreased dramatically, accompanied with a red shift from 327 nm to 350 nm (Fig. 1). However, other metal cations only induced slightly decreasing in the band intensity by 7–27% (Fig. S1, Supplementary data).

The absorption spectra of **1** in the presence of different concentrations of Co^{2+} were recorded in Figure 2. The incremental addition of Co^{2+} (1×10^{-6}–5×10^{-5} M) to the solution of **1** (5×10^{-6} M) resulted in gentle decline in absorbance at 318 and 327 nm, which were attributed to phenanthroline-pyridine rings intraligand $\pi\rightarrow\pi^*$ transition and imidazole-pyridine intraligand $\pi\rightarrow\pi^*$ transition,[10] respectively. With less than 1 equiv Co^{2+} was added, **1** may coordinate with Co^{2+} by two nitrogen atoms of phenanthroline–pyr-

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* Corresponding author. Tel./fax: +86 416 3400158.
E-mail address: wangxiuli@bhu.edu.cn (X. Wang).

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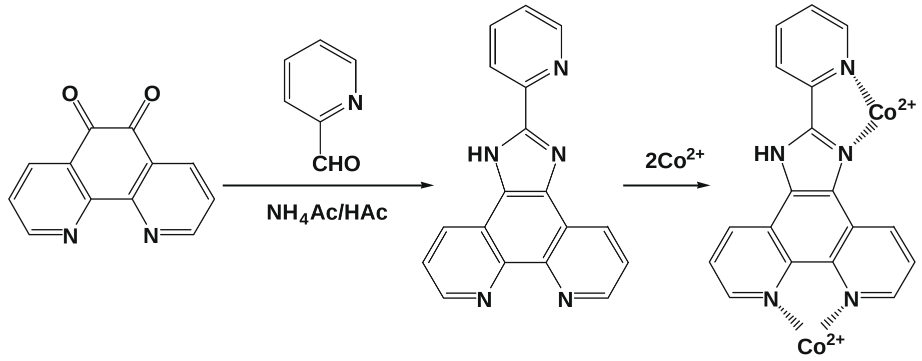

Scheme 1. Synthesis and proposed interaction of **1** with metal ions.

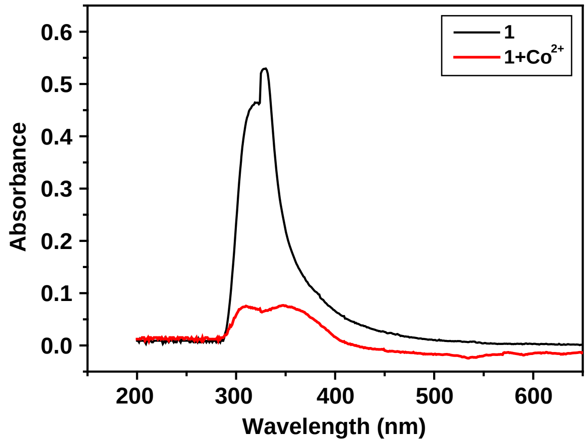

Figure 1. UV–vis spectra of **1** (5×10^{-6} M) in the absence of Co^{2+} (black line) and in the presence of Co^{2+} (5×10^{-5} M) (red line) in DMF with NaOAc–HOAc buffered solution at pH 6.8 ± 0.1.

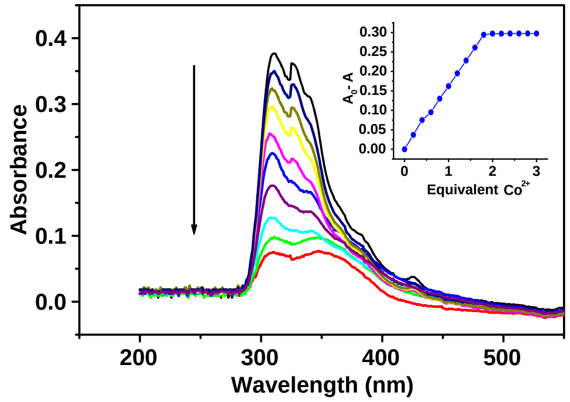

Figure 2. Response of **1** (5×10^{-6} M) with different concentrations of Co^{2+} (1×10^{-6}–5×10^{-5} M) at pH 6.8 ± 0.1 in DMF buffered solution. Inset: the stoichiometry formation of Co^{2+}–**1** in absorption experiment (pH 6.8 ± 0.1).

idine rings,[11] resulting in the absorption intensity gradually decreasing at 318 nm and 327 nm. It was noteworthy that the absorption intensity at 327 nm decreased dramatically, and after the addition of more than 1 equiv of Co^{2+}, the band at 327 nm gradually disappeared, while a new band appeared at 350 nm, which may be attributed to the coordination of Co^{2+} with **1** by two nitrogen atoms of imidazole-pyridine rings. Furthermore, no spectra change was observed after Co^{2+} was over 2.0 equiv (inset, Fig. 2), confirming the stoichiometry of 2:1 (Co^{2+}:**1**) complex formation. Amongst all the metal cations examined, we can see clearly that only Co^{2+} causes remarkable response in the UV–vis spectrum of **1**, while the response behavior of **1** is not discernibly affected by other metal cations.

In order to further understand the variation of absorption spectrum, the fluorescence titration experiments were performed in DMF buffered solution with an emission wavelength at 441 nm, upon excitation wavelength at 350 nm. As depicted in Figure 3, the addition of the metal ions induced various degrees of emission quenching depending on the identity of the metal ions. Among all the cations examined, **1** gave a specific response to Co^{2+}. The addition of 10 equiv (5×10^{-5} M) of Co^{2+} resulted in a strong fluorescence quenching of 81%. However, other examined cations at 10 equiv with respect to sensor **1** led to only about 6–31% and no further quenching of **1** was detected on the addition of up to 100 equiv of these cations, which indicates that **1** presents excellent selectivity for Co^{2+} over other cations.

With the addition of Co^{2+} to the solution of **1,** a remarkable quenching of fluorescence signal was observed (Fig. 4). At the limiting concentration of 10 equiv ($c = 5 \times 10^{-5}$ M), the emission of **1** was reached to ca. 81% quenching due to the formation of **1**–Co^{2+} complex. Moreover, emission intensity did not change after the addition of Co^{2+} higher than 2.0 equiv, also indicating the formation of a new 2:1 (Co^{2+}:**1**) complex (inset, Fig. 4). The binding constant for Co^{2+} was measured ($K_1 = 5.7 \times 10^4\ M^{-1}$, $K_2 = 1.2 \times 10^4\ M^{-1}$) by a nonlinear least-square (Supplementary data).

In addition, the spectrophotometric responses were reversible since the addition of EDTA (1×10^{-4} M) fully revived the original absorption of **1** (Fig. S2, Supplementary data). This phenomenon proves that **1** could serve as a reversible molecular sensor for Co^{2+}, which is conformed to the requirement of relatively high

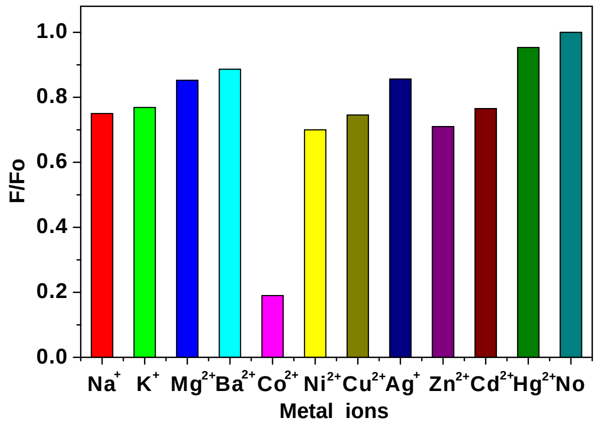

Figure 3. Response of various metal ions (5×10^{-5} M) on the fluorescence intensity of **1** (5×10^{-6} M).

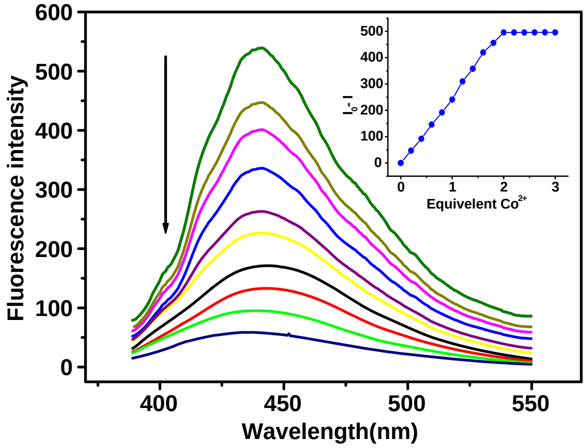

Figure 4. Fluorometric titration of **1** with different concentrations of Co^{2+} (1×10^{-6}–5×10^{-5} M) at pH 6.8 ± 0.1 in DMF buffered solution. Inset: the stoichiometry formation of Co^{2+}–**1** in fluorescence titration experiment, λ_{ex} = 350 nm.

detection for Co^{2+} and potential reutilization. It could be seen that the original fluorescence of **1** was recovered after the addition of EDTA (1×10^{-4} M), demonstrating that **1** has a potential ability as a selective 'on–off' sensor for Co^{2+}, as shown in Figure 5.

The effects of pH on the fluorescence intensity of **1** in the absence and presence of Co^{2+} were carried out by adjusting the pH value of the solution with hydrochloric acid and sodium hydroxide, results are shown in Figure 6. At 3.0 < pH < 7.0, **1** is strongly fluorescent while the fluorescence of its complex with Co^{2+} is largely quenched. When pH is lower than 3.0, the fluorescence of **1** is largely quenched, which corresponds to the association of **1** with proton. At pH higher than 7.0, the fluorescence of **1**–Co^{2+} complex begins to revive. This is because too higher pH would lead to formation of the precipitation of $Co(OH)_2$, which in turn would reduce its complexation with **1**.[12] These results show that the response behavior of **1**–Co^{2+} complex is pH independent in the pH range of 3.0–7.0. From the view of sensitivity and response behavior of sensor, pH 6.8 was chosen as optimum experimental condition.

In conclusion, we have developed a novel fluorescent sensor **1**, which undergoes reversible changes and fluorescence 'on–off' signalling for the detection of Co^{2+}, and firstly studied the effects of various metal ions on its properties. The remarkable photophysical properties of sensor **1** will help to extend the development of fluorescent sensors for metal ions.

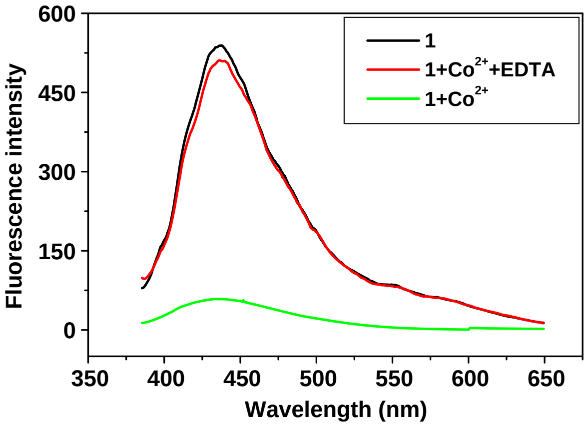

Figure 5. Fluorescence spectra of **1**, **1** + Co^{2+} and **1** + Co^{2+} + EDTA in DMF buffered solution (pH 6.8 ± 0.1).

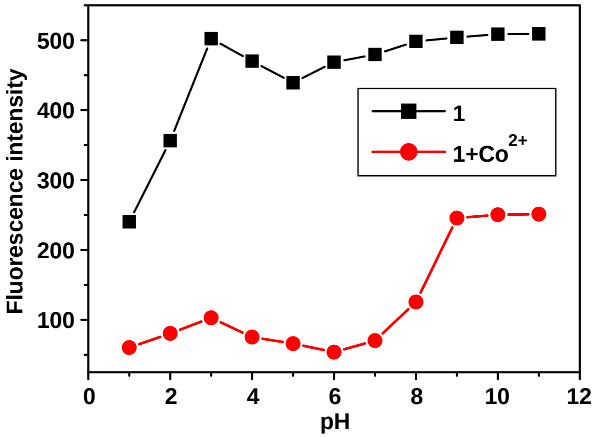

Figure 6. Effect of pH on the fluorescence intensity of **1** (5×10^{-6} M) in the absence (black line) and in the presence (red line) of Co^{2+} (5×10^{-5} M) in the DMF buffered solution.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.12.109.

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8. a *Preparation of* **1**: A mixture of 2 mmol 1,10-phenanthroline-5,6-dione, 2.2 mmol pyridine-2-carbaldehyde, 15 mL of glacial acetic acid, and 3.2 g ammonium acetate in a 100 mL flask with a condenser was refluxed for 2 h, resulting in a yellow precipitate. After cooling, the mixture was diluted with 25 mL of water and the pH value of the solution was adjusted with concentrated aqueous ammonia to 5.5. The yellow product was filtered from the mixture and washed with water and acetone, oven-dried at 60 °C (yield: 85% based on 1,10-phenanthroline-5,6-dione). IR (KBr pellet, cm^{-1}): 3143s, 2341s, 2338m, 1709m, 1585s, 1497s, 1423m, 1393s, 1308w, 1250m, 1011w, 783w, 741m, 686w.; b Wang, S.; Wang, R. Pub. No.: US 2004/0265628 A1.
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