

# A New Fluorescent Chemosensor Detecting $\text{Co}^{2+}$ and $\text{K}^+$ in DMF Buffered Solution

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**Abstract** A new fluorescent chemosensor 2-(2-thiophene)imidazo [4,5,f]-1,10-phenanthroline (**L**) was prepared and characterized. By adding univalent or divalent metal ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  ions into the solution of **L** in DMF under buffered conditions with the working pH ranging from 7.0 to 8.0, we found that **L** could be used to detect  $\text{K}^+$  ratiometrically and it could also be applied to sense  $\text{Co}^{2+}$  with the phenomenon of fluorescence quenching of **L**. While the response behavior of **L** was not discernibly affected by other examined metal ions.

**Keywords** Fluorescence · Chemosensor · Phenanthroline-based · Ratiometric · Cation detection selectivity

## Introduction

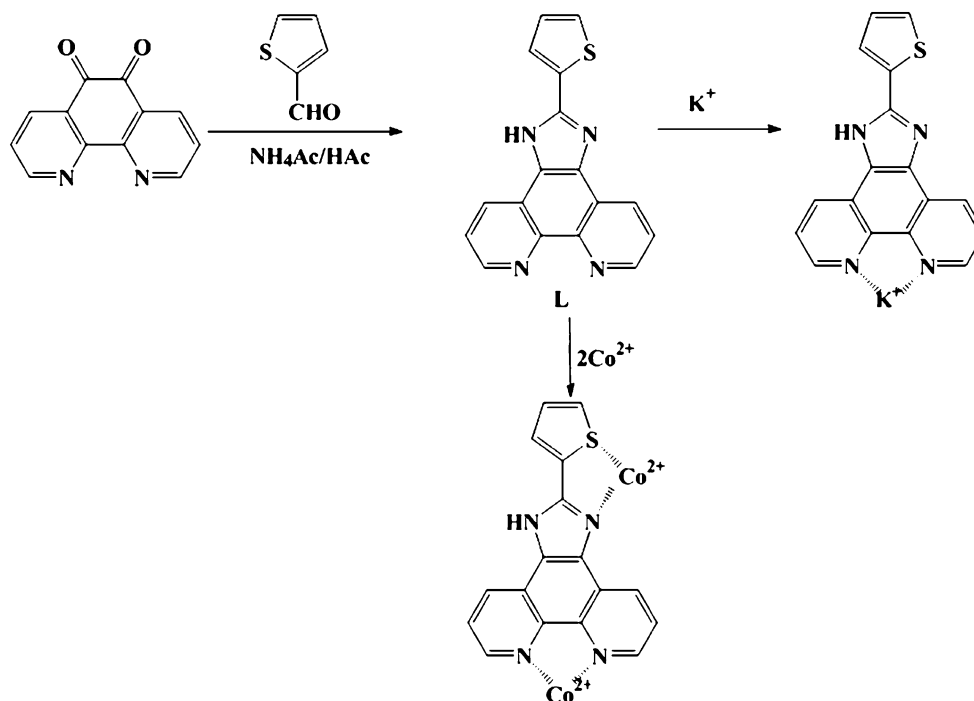
In recent years, the research of fluorescent chemosensors capable of effectively detecting transition- and alkali metal ions has caught much attention in scientific area, especially in analytical chemistry, clinical and medical science, biochemistry and environmental science [1–6]. Such sensors based on ion-induced changes in fluorescence appear to be particularly attractive due to their simplicity, high sensitivity, high selectivity, and instantaneous response and their capability to monitor in real-time and real-space the

concentration of the analytes [7–10]. Consequently, there has been a growing interest in the development of the design of efficient chemosensors and the analysis of transition- or alkaline earth–metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Mg}^{2+}$  [11–16]. Relatively few examples of fluorescent sensors for  $\text{Co}^{2+}$  and  $\text{K}^+$  have been reported, though more research has developed rapidly in recent years [17–22]. It is well-known that  $\text{Co}^{2+}$  as one of the most important transition 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, while its deficiency in human body may lead to pathological conditions and it is also a significant environmental pollutant [23–27]. Potassium is one of the most abundant univalent ions in the cell and plays a crucial role in cell proliferation and cell death, it also participates in the modulation of signal transduction, various transporters, and ion channels [28]. Therefore, there is a great need for the design and preparation of such chemosensors that have high sensitivity and selectivity for detecting and monitoring  $\text{Co}^{2+}$  and  $\text{K}^+$  by employing a simple response at physiological pH.

Recently, we have reported a phenanthroline-based chemosensor 2-(2-pyridine)imidazo [4,5,f]-1,10-phenanthroline with two pairs of chelating nitrogen coordination sites, which undergoes a reversible, ‘on-off’ sensing capability for biologically and environmentally significant  $\text{Co}^{2+}$  in DMF under buffered conditions [20]. In continuation of our research on phenanthroline-based derivatives, we designed and synthesized another phenanthroline-based compound (**L**) with two pairs of coordination sites of chelating N–N and N–S as fluorescent sensor for  $\text{Co}^{2+}$  and  $\text{K}^+$  (Scheme 1), which shows distinctly different optical properties upon the addition of  $\text{Co}^{2+}$  and  $\text{K}^+$  to the solution of **L** in DMF under buffered conditions.

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**Scheme 1** Synthesis and proposed interaction of **L** with  $\text{K}^+$  and  $\text{Co}^{2+}$

## Experimental

### General method

Solvents and reagents were obtained from commercial sources and used as received. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. The elemental analyses (C, H, N and S) were carried out with a Perkin-Elmer 240Q elemental analyzer. UV-visible absorption spectra were recorded on a UV-2550 spectrophotometer. Emission spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

### Synthesis

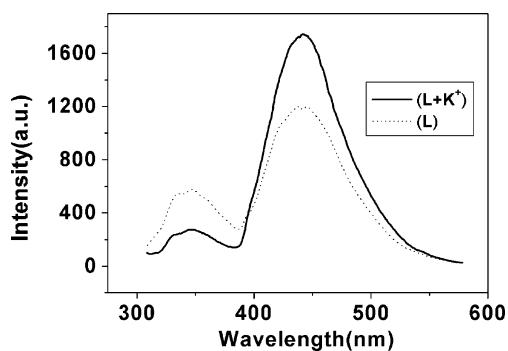
A mixture of 2 mmol 1,10-phenanthroline-5,6-dione [29, 30], 2.2 mmol thiophene-2-carbaldehyde, 15 mL of glacial acetic acid, and 3.2 g ammonium acetate in a 100 mL flask was refluxed for 2 h, resulting in a yellow precipitate. After cooling, the mixture was diluted with 25 mL distilled water and the pH value of the solution was adjusted with concentrated aqueous ammonia to 5.5. The yellow product was filtered from the mixture and was purified by chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$ -EtOAc (10:1) as the eluent [31]. Yield: 87% based on 1,10-phenanthroline-5,6-dione. Anal. Calcd. for  $\text{C}_{17}\text{H}_{10}\text{N}_4\text{S}$ : C, 67.53; H, 3.33; N, 18.53; S, 10.61. Found: C, 67.41; H, 3.38; N, 18.51; S, 10.58. IR (KBr pellet,  $\text{cm}^{-1}$ ), 3402s, 2372w,

1734m, 1684m, 1653s, 1636s, 1647m, 1560s, 1542m, 1508m, 1474w, 1458w.  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  7.27–7.29 (m, 1H, 4'-H) 7.74 (dd, 1H,  $J=4.8$  and 1.2 Hz, 3'-H). 7.83 (br s, 2H, 5-H and 10-H), 7.90 (dd, 1H,  $J=4.0$  and 1.2 Hz, 5'-H), 8.82 (br s, 2H, 4-H and 11-H), 9.01 (dd, 2H,  $J=4.4$  and 1.2 Hz, 6-H and 9-H), 13.86(s, 1H, NH).  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  119.03, 123.25, 126.07, 126.29, 128.28, 129.55, 133.42, 135.51, 143.58, 146.27, 147.83.

## Results and discussion

### Optical observation

The selectivity test was conducted in DMF under buffered conditions, the concentrations of **L** and measured metal ions were kept at 10  $\mu\text{M}$  and 20  $\mu\text{M}$ , respectively. The following metal ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  ions were added to **L**. Fluorescence spectrum of **L** showed main emission band at 336 and 442 nm (Fig. 1). A slight decrease at 336 nm and a significant increase at 442 nm were observed with the addition of  $\text{K}^+$  (10  $\mu\text{M}$ ) to the solution of **L**. There were no obvious changes in the fluorescence intensity of **L** to other examined metal ions (Fig. 2).  $\text{Co}^{2+}$  was not included in Fig. 2, because **L** showed gentle fluorescence quenching at 336 nm and nearly complete fluorescence quenching at 442 nm with the addition of  $\text{Co}^{2+}$  (20  $\mu\text{M}$ ) (Fig. 3). Clearly, the results

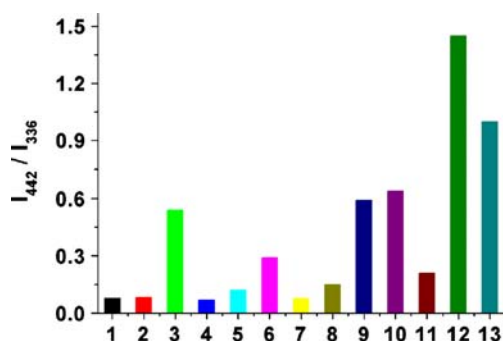


**Fig. 1** Fluorescence spectrum of **L** (10  $\mu\text{M}$ ) in the absence of  $\text{K}^+$  (dot line) and in the presence of  $\text{K}^+$  (10  $\mu\text{M}$ ) (solid line) in DMF with NaOAc–HOAc buffered solution at  $\text{pH}=7.2\pm 0.1$

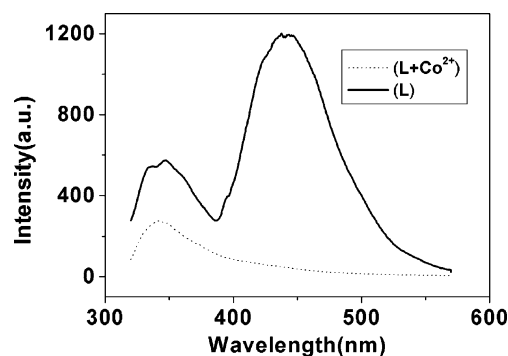
indicated that **L** could distinguish  $\text{K}^+$  and  $\text{Co}^{2+}$  from other tested metal ions and act as a sensor for  $\text{K}^+$  and  $\text{Co}^{2+}$ .

The UV–vis absorption spectra of **L** and its titration with  $\text{K}^+$  and  $\text{Co}^{2+}$  were measured in DMF solution that buffered by 0.1 mM NaOAc–HOAc ( $\text{pH}$  was adjusted to 7.2 by adding 0.1 M HCl). **L** showed its low energy absorption at 308 and 336 nm, which increased linearly in intensity and the peak at 336 nm shifted to short wavelength with the sequential addition  $\text{K}^+$  ion at first (Fig. 4a), then reached its maximum and absorption intensity did not change after  $\text{K}^+$  was more than 1.0 equiv, indicating the binding of **L** and  $\text{K}^+$  was most probably a 1:1 stoichiometry (Fig. S1, see supporting information). Moreover,  $\text{Co}^{2+}$  could also induce absorption spectra change. Figure 5a exhibited the absorption intensity increased at 308 and 336 nm, while the peak at 336 nm shifted to long wavelength 348 nm upon the addition of  $\text{Co}^{2+}$  with different concentrations. Furthermore, no spectra change was observed after  $\text{Co}^{2+}$  was over 2.0equiv (Fig. S2, see supporting information), confirming the stoichiometry of 2:1 ( $\text{Co}^{2+}$  : **L**) complex formation.

In order to understand better the variation of absorption spectrum, the fluorescence titration experiments were

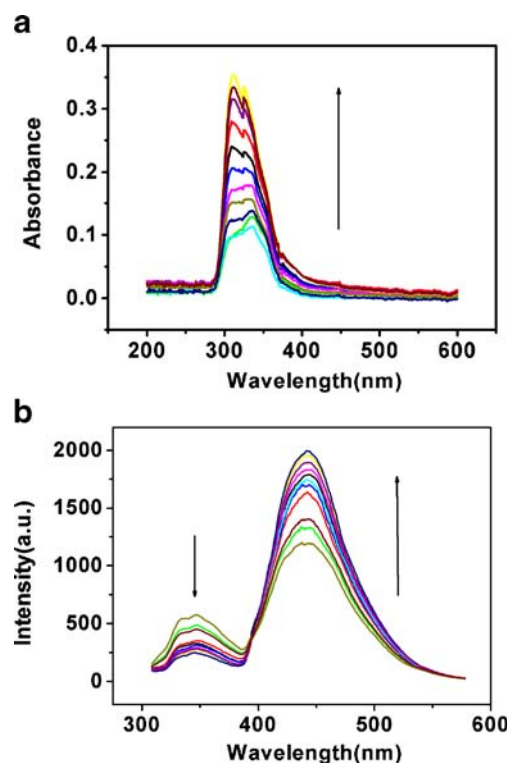


**Fig. 2** Selectivity sensing of **L** (10  $\mu\text{M}$ ): the concentration of each cation added is 5 equivalent to that of **L** in DMF with NaOAc–HOAc buffered solution at  $\text{pH} 7.2\pm 0.1$ . 1–13 represent (1) **L** +  $\text{Ni}^{2+}$ ; (2) **L** +  $\text{Hg}^{2+}$ ; (3) **L** +  $\text{Fe}^{3+}$ ; (4) **L** +  $\text{Zn}^{2+}$ ; (5) **L** +  $\text{Cd}^{2+}$ ; (6) **L** +  $\text{Mn}^{2+}$ ; (7) **L** +  $\text{Cu}^{2+}$ ; (8) **L** +  $\text{Ag}^+$ ; (9) **L** +  $\text{Mg}^{2+}$ ; (10) **L** +  $\text{Ba}^{2+}$ ; (11) **L** +  $\text{Na}^+$ ; (12) **L** +  $\text{K}^+$ ; (13) **L**. Excitation was at 298 nm

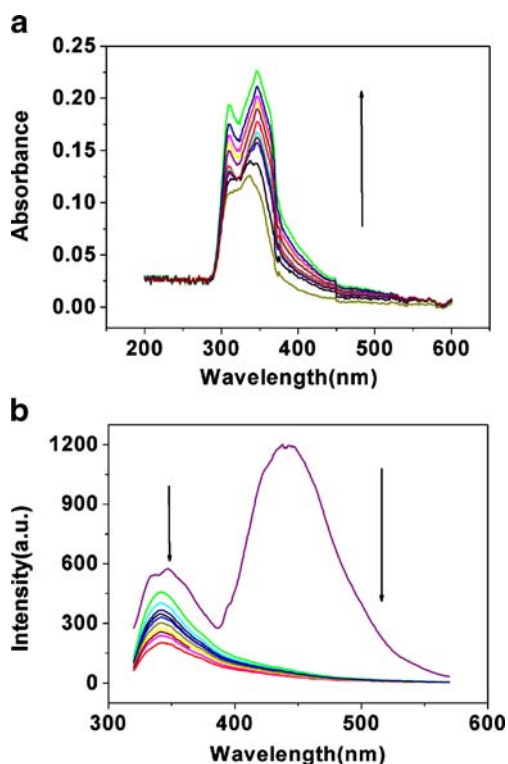


**Fig. 3** Fluorescence spectrum of **L** (10  $\mu\text{M}$ ) in the absence of  $\text{Co}^{2+}$  (dot line) and in the presence of  $\text{Co}^{2+}$  (10  $\mu\text{M}$ ) (solid line) in DMF with NaOAc–HOAc buffered solution at  $\text{pH}=7.2\pm 0.1$

performed simultaneously in DMF buffered solution with the excitation wavelength of 298 nm and emission wavelength of 310–520 nm. As depicted in Fig. 4b, when  $\text{K}^+$  was gradually added to the buffered solution of **L**, a significant increase in the 442 nm emission and a decrease in the intensity of the 336 nm emission, which was attributed to the formation of **L**/ $\text{K}^+$  complex by the coordination of  $\text{K}^+$  with **L** by two nitrogen atoms of



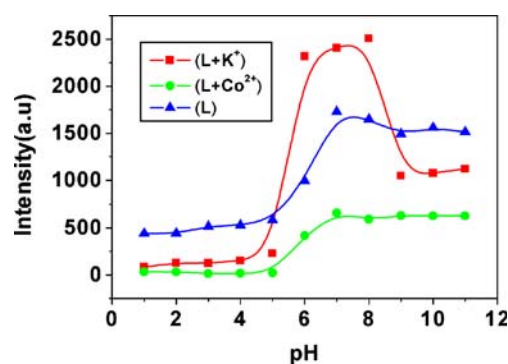
**Fig. 4** a UV–vis responses of **L** (10  $\mu\text{M}$ ) upon the additions of  $\text{K}^+$  (0, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30  $\mu\text{M}$ ) in DMF with NaOAc–HOAc buffered solution at  $\text{pH} 7.2\pm 0.1$ ). b The fluorescence response of **L** (10  $\mu\text{M}$ ) to increasing concentrations of  $\text{K}^+$  (0, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30  $\mu\text{M}$ ) in DMF with NaOAc–HOAc buffered solution at  $\text{pH} 7.2\pm 0.1$ . Excitation was at 298 nm. Isoemission point was found at about 394 nm



**Fig. 5** **a** UV-vis responses of **L** (10  $\mu\text{M}$ ) upon the additions of  $\text{Co}^{2+}$  (0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50  $\mu\text{M}$  in DMF with NaOAc-HOAc buffered solution at pH  $7.2 \pm 0.1$ ). **b** The fluorescence response of **L** (10  $\mu\text{M}$ ) to increasing concentrations of  $\text{Co}^{2+}$  (0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50  $\mu\text{M}$  in DMF with NaOAc-HOAc buffered solution at pH  $7.2 \pm 0.1$ ). Excitation was at 298 nm

phenanthroline-pyridine rings [32], was observed with a clear isoemission point at 394 nm. Figure S3 (see supporting information) exhibits the dependence of the intensity ratio of emission at 442 nm to that at 336 nm ( $I_{442}/I_{336}$ ) on  $\text{K}^+$ , which also indicates the formation of a **L**/ $\text{K}^+$  adduct of 1:1 stoichiometry.

Although we could not clearly identify  $\text{K}^+$  and  $\text{Co}^{2+}$  through UV-vis absorption titration because either one of the two related metal ions would induce slight absorption spectra changes as mentioned above, it turned out to be useful to carry out the fluorescence titration of  $\text{Co}^{2+}$ . With the addition of  $\text{Co}^{2+}$  to the buffered solution of **L**, a remarkable quenching of fluorescence signal at 442 nm while a gentle one at 336 nm was observed (Fig. 5b). At the limiting concentration of 100 equiv ( $c = 1 \times 10^{-4}$  M), the emission of **L** was reached to ca. 68% at 336 nm and fully quenched at 442 nm, which may be attributed to the formation of **L**- $\text{Co}^{2+}$  complex that **L** coordinated to  $\text{Co}^{2+}$  with phenanthroline-pyridine rings and imidazole-thiophene rings [20]. Moreover, emission intensity did not change after the addition of  $\text{Co}^{2+}$  higher than 2.0 equiv, also indicating the formation of a new 2:1 ( $\text{Co}^{2+} : \text{L}$ ) complex (Fig. S4, see supporting information).



**Fig. 6** Effect of pH on the fluorescence intensity of **L** (10  $\mu\text{M}$ ) in the absence (blue line) and in the presence of  $\text{K}^+$  (red line, 10  $\mu\text{M}$ ) and  $\text{Co}^{2+}$  (green line, 20  $\mu\text{M}$ ) in the DMF buffered solution

### pH effects

The effects of pH on the fluorescence intensity of **L** in the absence and presence of  $\text{K}^+$  and  $\text{Co}^{2+}$  were carried out by adjusting the pH value of the solution with hydrochloric acid and sodium hydroxide. The concentrations of  $\text{K}^+$  and  $\text{Co}^{2+}$  are fixed at  $2 \times 10^{-5}$  mol  $\text{L}^{-1}$ , and the results are shown in Fig. 6. **L** is strongly fluorescent in the range of pH 7.0–8.0, and its complex with  $\text{Co}^{2+}$  is largely quenched while its complex with  $\text{K}^+$  is largely increased. When pH is lower than 7.0, the fluorescence of **L** is largely quenched, which may correspond to the association of **L** with proton [33, 34]. From the view of sensitivity and response behavior of sensor, pH 7.2 was chosen as optimum experimental condition.

### Conclusion

In this contribution, a new fluorescent chemosensor **L** is synthesized that shows a strong ratiometric response as well as highly selective of  $\text{K}^+$ . It is also an “on-off” fluorescent chemosensor for  $\text{Co}^{2+}$ . The remarkable photophysical properties of sensor **L** will help to extend the development of fluorescent sensors for metal ions.

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