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New turn-on fluorescence sensors for Co^{2+} based on conjugated carbazole Schiff base

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Abstract Two novel conjugated Schiff bases were prepared and characterized by IR, ^{1}H NMR, and elementary analysis. Their fluorescence measurements indicated that both compounds have excellent performance on fluorescence emission, and the intensity of fluorescence emissions was enhanced sharply by adding Co^{2+}. These compounds can be used as highly sensitive fluorescence turn-on sensors for Co^{2+} with the detection limit below 10^{-14} M.

Keywords Carbazole · Fluorescence sensors · Schiff base · Co^{2+}

As an essential micronutrient, cobalt plays an important role in metabolic processes [1] of the human body. As a transition metal ion, cobalt supplementation benefits the formation of biological compounds such as Vitamin B12, which is widely responsible for the prevention of pernicious anemia [2]. The excess or lack of cobalt can cause a series of diseases [3]. Furthermore, in our daily life, cobalt is usually identified as the environmental pollutant. So, it is necessary to detect Co^{2+} for human health and environmental protection.

In recent years, many methods have been developed to trace the behaviors of Co^{2+} and to determine its concentration, which mainly refer to spectrophotometric [4, 5] and fluorophotometric [6] methods. Furthermore, chemists have made much progress in Co^{2+} detection [7–9]. Owing to the advantages in efficiency, sensitivity, and selectivity [10–12], the fluorophotometric method is widely used by many

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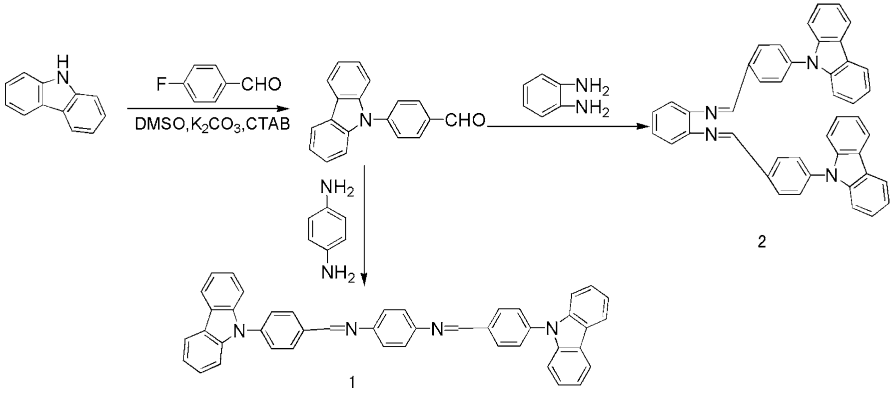
groups [13–15]. But the sensitivity [16] and selectivity [17] of the reported fluorescence sensors are not satisfactory. All these obstacles limit the development of Co^{2+} fluorescence probes. Therefore, it is important to search for new fluorophores of Co^{2+}, especially those that can overcome the disadvantages.

As reported in the literature [18], the fluorescent chemosensors for transition metal ions are numerous [10, 19]. The sensors based on Schiff base are widely used. A novel probe has been developed to behave as a highly selective fluorescent pH sensor [20]. A sensitive turn-on fluorescent Zn^{2+} chemosensor based on Schiff base has been reported as applying to the detection of intracellular Zn^{2+} and could be used as a potential recyclable component in sensing materials [21]. Owing to a special fragment consisting of the C=N group with a lone electron pair, Schiff base can cooperate with many metal ions [19]. However, according to the selectivity researches of many groups [22–24], rare Schiff base can detect Co^{2+}. Up to now, there have been few reports on fluorescence chemical sensors based on Schiff base for Co^{2+}. In this work, two new conjugated Schiff bases based on carbazole were synthesized and used as fluorescent chemosensors for Co^{2+}. Experiments revealed that both compounds have superior sensitivity and can be used as turn-on fluorescence sensors for detection of Co^{2+}.

Scheme 1 exhibits the synthesis routes of both compounds; the detailed experiments are shown in the supporting information. The 4-carbazol-9-ylbenzaldehyde was synthesized according to the previously reported method [25].

The optical properties of compounds **1** and **2** have been investigated by UV–Vis absorption and F-4500 fluorescence spectrometer. The spectra are shown in Fig. 1 and the optical data are listed in Table 1. Both compounds exhibited long-wavelength absorption bands centered at 376 and 333 nm, respectively, which could be assigned to the n-π* transition associated with imine chromophore [26, 27]. The maximum emission wavelengths (λ_{em}) of both compounds were 495 and 397 nm, respectively, when excited at their maximum absorption wavelength (λ_{abs}). The fluorescent intensity of compound **1** was 222 a.u. when the excitation voltage was 900 V. However, the compound **2** was 246 a.u. with a lower excitation voltage



Scheme 1 Synthesis routes of compound **1** and compound **2**

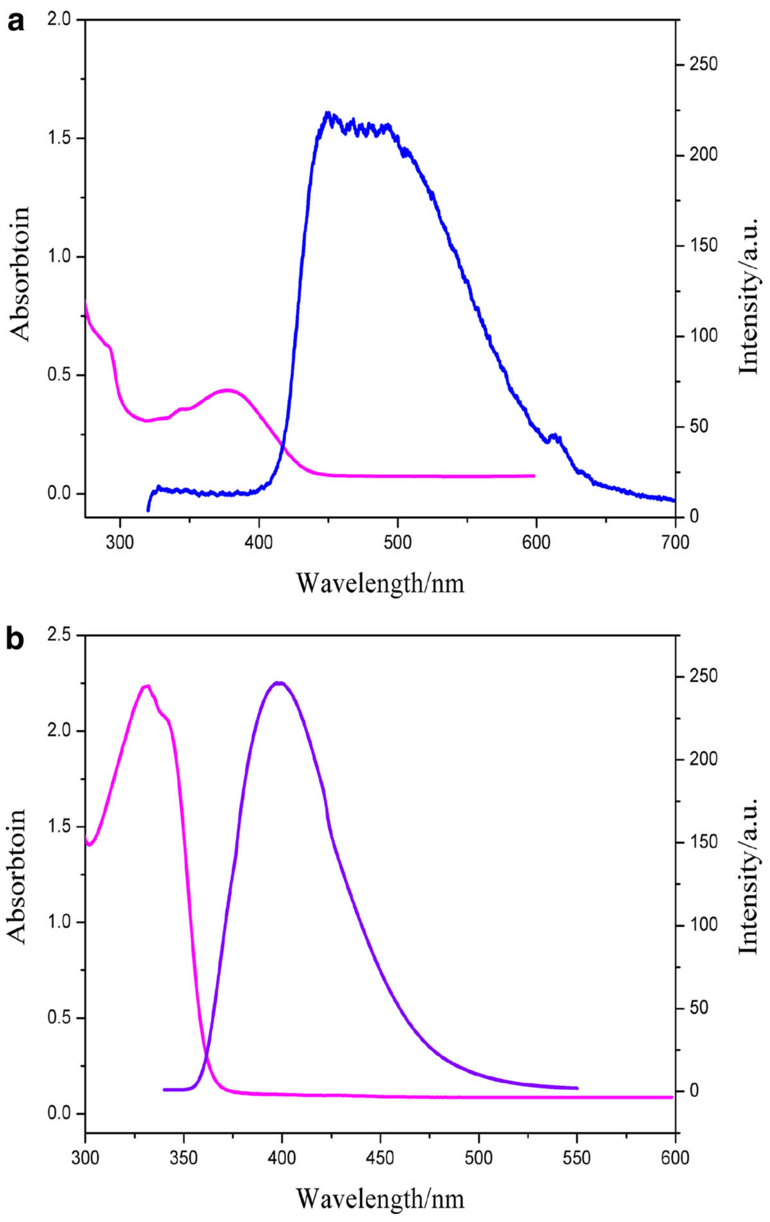


Fig. 1 Liner absorption and fluorescence spectra of compound **1** (**a**) and compound **2** (**b**) in DMSO (1.0×10^{-4} mol/L)

(400 V). The compound **1** was poorly fluorescent, which can be explained by the isomerization of the C=N double bonds in the excited state [28]. The isomerization could break a molecular coplanar structure and, consequently, have a great effect on the conjugation of compound **1**. However, the special structure of compound **2**

Table 1 Photophysical data of compounds

Compound	λ_{abs}/nm	λ_{em}/nm	I/a.u.[a]
1	376	495	222
2	333	397	246

[a] *I* Fluorescence intensity at λ_{em}

Table 2 Photophysical data of compounds in different solvents

Solvent	Polarity	Compound **1**		Compound **2**	
		λ_{em}/nm	I/a.u.	λ_{em}/nm	I/a.u.
DMSO	7.2	495	28.58	398	242.20
Chloroform	4.4	458	166.00	394	243.20
THF	4.2	451	131.70	381	260.01

provided a steric hindrance effect, which restricted the isomerization of the C=N double bonds. In addition, from Fig. 1, we also found that the emission spectrum of compound **1** was broad. This was attributed to the structure of compound **1**, and several allowed transitions occurred when excited due to the poor conjugacy.

Table 2 depicts the emission data of compound **1** and compound **2** in solvents with various polarities. It is easily seen that the fluorescence intensity of two compounds decreased with increasing solvent polarity, which can be explained by the "twisted intra-molecular charge transfer" (TICT) mode [29]. According to the TICT model and Table 2, the larger the solvent polarity, the more obvious the solvation for the non-emissive TICT state, so the compounds gave low fluorescence intensity in higher polar solvent. On the other hand, with the increase of solvent polarity, fluorescence spectra of two compounds showed a remarkable red-shift. For example, λ_{em} of compound **1** was located at 451 nm in THF and red-shifted to 458 and 495 nm in Chloroform and DMSO, respectively. This was because the fluorophore has a larger dipole moment in the excited state than in the ground state, as the enhanced dipole–dipolar interactions caused by the increasing polarity of solvent will lead to a more significant energy level decrease for the exited state.

As shown in Fig. 2, the emission spectra for compounds were observed with Co^{2+} concentrations increasing from 1.0×10^{-14} to 1.0×10^{-8} M. The fluorescence emissions of compounds **1** and **2** could be enhanced 17-fold and 3.4-fold, respectively, when 1.0×10^{-8} M Co^{2+} was added to the solution. The improvement of the fluorescence originates from the strong chelation-enhanced fluorescence effect (CHEF) [30] between Schiff base and Co^{2+}. Therefore, a large fluorescence enhancement was observed. This indicated that both compounds exhibited a high sensitivity to Co^{2+} in the solvent. The enhancement processes can be analyzed by the Stern–Volmer relationship,

$$I_0/I = 1 + K_{sv}[Q]$$

where I_0 and I are the maximum fluorescence intensities in the absence and presence of Co^{2+}, $[Q]$ is the concentration of Co^{2+}. By fitting the linear curve (Fig. 2), the

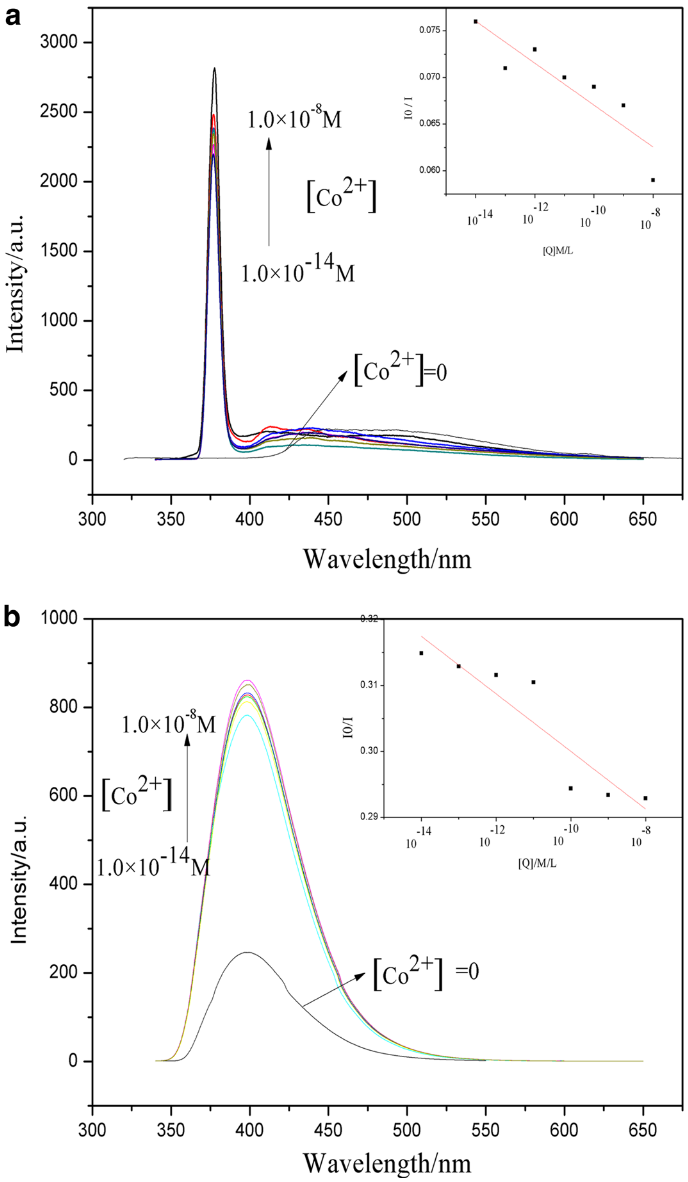


Fig. 2 Fluorescence spectra change of compound **1** (**a**) and compound **2** (**b**) as a function of Co^{2+} concentration in DMSO. [compound **1**] = [compound **2**] = 1.0×10^{-4} mol/L; $[Co^{2+}] = 1.0 \times 10^{-8}$ to 1.0×10^{-14} M (from *top* to *bottom*). The *inset* shows the corresponding Stern–Volmer plot

Stern–Volmer fluorescence enhancement constant K_{sv} of compound **1** and compound **2** were −0.00225 and −0.00436 L/mol, respectively. The results suggested that both exhibited a certain extent of sensitivity toward Co^{2+}.

In addition, it is interesting that a blue shift occurs for compound **1** from 448 nm to 375 nm with the presence of Co^{2+}; however, no shift occurs for compound **2**.

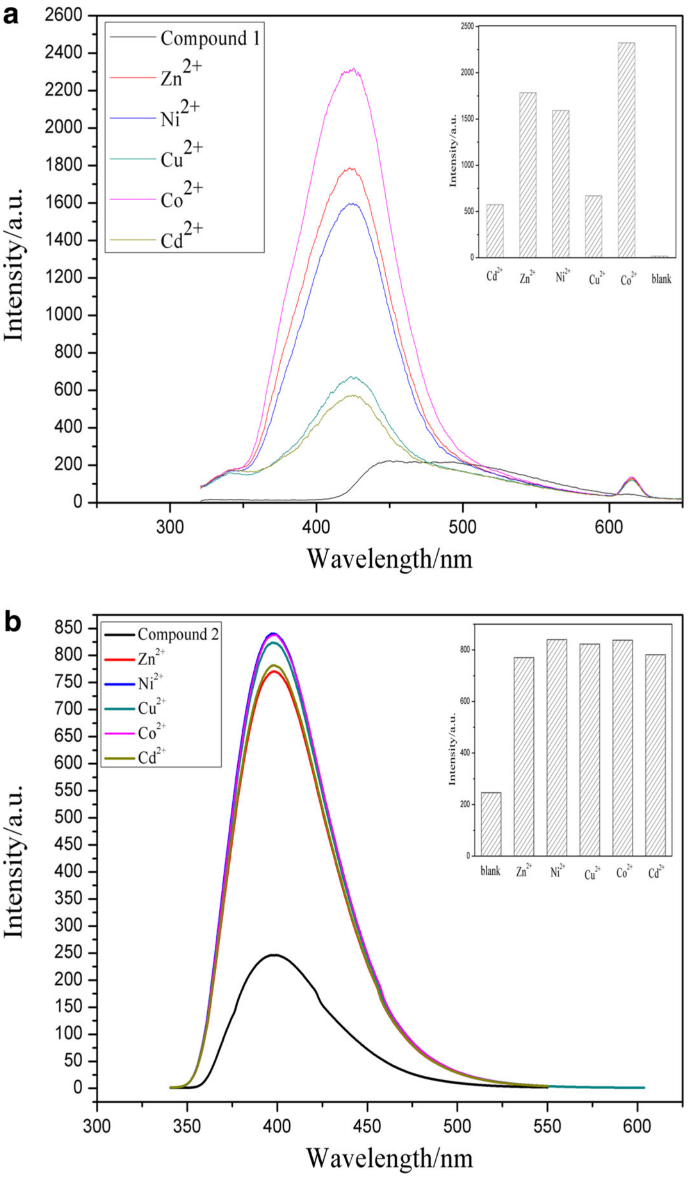


Fig. 3 Selectivity of L for Co^{2+} over other cations. The *bars* indicate the fluorescence change that occurs immediately following the addition of interfering ions (1.0 equiv.) to the solution of compound **1** (**a**) and compound **2** (**b**) with Co^{2+} in DMSO

This indicated the Co^{2+} can significantly affect the excited state of compound **1**, but have no effect on compound **2**.

As a probe, the highly selective response to target ions is an essential requirement. The spectral changes were examined upon addition of various other metal ions. The experiments were carried out in DMSO with emission wavelengths at 495 nm for compound **1** and 397 nm for compound **2**, respectively. As shown in Fig. 3, fluorescence emissions of the two compounds were significantly enhanced with Co^{2+}. However, when the interfering ions, such as Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+}, were added individually to the solution of compounds, the fluorescence intensity of compound **1** has a relatively slight change, but the emission intensity of compound **2** was also dramatically enhanced. This indicated that the recognition to Co^{2+} for compound **1** was not significantly perturbed by other coexisting metal ions, and that compound **1** has a high selectivity toward Co^{2+}. In contrast, compound **2** has a poor selectivity for Co^{2+}.

In summary, two new conjugated Schiff base have been prepared. These compounds were easily obtained in high yield using low-cost commercially available materials. Significant emission enhancements in the wavelengths of the compounds were detected in the presence of Co^{2+}. While compound **1** exhibited high selectivity for Co^{2+} over other metal ions with 17-fold fluorescence enhancement, when 1.0×10^{-8} M Co^{2+} ions were added, the selectivity of compound **2** was poor. Furthermore, the detection limit of the two compounds could reach below 10^{-14} M in solvents. This suggests that both compounds could serve as fluorescence probes for Co^{2+}.

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