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A novel coumarin Schiff-base as a Ni(II) ion colorimetric sensor

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ABSTRACT

A novel coumarin Schiff base compound (**L**) prepared from 7-diethylaminocoumarin-3-aldehyde and 3-amino-7-hydroxycoumarin was synthesized and evaluated as a chemoselective Ni^{2+} sensor. Addition of Ni^{2+} to CH_3CN solution of **L** resulted in a rapid color change from yellow to red together with a large red shift from 465 to 516 nm. Moreover, other common alkali-, alkaline earth-, transition- and rare earth metal ions induced no or minimal spectral changes. Experimental results indicated that **L** could be used as a potential Ni^{2+} colorimetric and naked-eye chemosensor in CH_3CN solution.

1. Introduction

The design and synthesis of chemosensors for detection of metal ions in aqueous and nonaqueous media are active and fascinating areas. Along with other transition metal ions, Ni^{2+} is an essential trace element in biological systems such as respiration, biosynthesis, and metabolism. For example, an undersupply of Ni^{2+} leads to deficiency and an oversupply results in toxic effects. However, as an industrial pollutant in a wide variety of metallurgical processes such as electroplating and alloy production as well as nickel–cadmium batteries, nickel is a toxic element that can cause lung injury, allergy and carcinogenesis. Selective monitoring of Ni^{2+} in environmental evaluation and clinic analysis is, therefore, needed [1–4]. Up to date, most of Ni^{2+}-selective sensors are based on potentiometric methods [5,6]. Although the fluorescence quenching nature of paramagnetic Ni^{2+}, several Ni^{2+}-sensitive fluorescent sensors with serious interferences from other transition metal ions have been reported [7–11,3]. Recently, selective luminescent probes based on benzothiadiazoyl-triazoyl cyclodextrin and zinc compound containing symmetrical Schiff base ligand for Ni^{2+} were also investigated [12,13]. On the other hand, colorimetric sensors are promising due to their simplicity, real-time and on-line analysis, especially a significantly lower capital cost than closely related methods, such as fluorescent sensors, for which both spectrophotometric equipment and a UV light source are required. Accordingly, development of a novel colorimetric chemosensor for the rapid and convenient detection of Ni^{2+} is attractive.

Because coumarins possess desirable photophysical properties such as a large Stokes shift and visible excitation and emission wavelengths, they are ideal platforms for development of colorimetric chemosensors for specific heavy and transition metal ions [14,15]. On the other hand, it is well known that C=N isomerization is responsible for the predominant decay of the excited states of compounds containing an unbridged C=N structure, which usually results in weak fluorescence emission of the attached chromophore. If this isomerization is stopped by bonding to metal ions, high-intensity emission can be achieved. Therefore, there are already many coumarin Schiff base compounds developed for selective detection of different metal ion species (Hg^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, etc.) so far due to their high selectivity, sensitivity and simplicity [16–20]. However, colorimetric chemosensors based on coumarin Schiff base for selective detection of Ni^{2+}, are rather rare [21].

Herein, we develop a simple, facile and reliable Ni^{2+} colorimetric chemosensor based on a new coumarin Schiff base compound (**L**) with two different coumarin groups connected via an imine linkage. Addition of Ni^{2+} to CH_3CN solution of **L** results in a rapid color change from yellow to red together with a large red shift from 465 to 516 nm, which allows it to selectively detect Ni^{2+} ion by the naked eye over a great number of environmental ions including common alkali-, alkaline earth-, transition- and rare earth metal ions.

2. Experimental

2.1. Chemicals and instruments

All reactants were commercially available and used without further purification. All melting points were uncorrected. The IR

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spectra were measured on a Nicolet/Nexus-870 FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1}. Nuclear magnetic resonance spectra were recorded on Bruker Avance III 400 MHz and chemical shifts are expressed in ppm using TMS as an internal standard. The UV–vis absorption spectra were recorded using a Helios Alpha UV-Vis scanning spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 FL spectrophotometer with quartz cuvette (path length = 1 cm).

The recognition between coumarin Schiff base compound (**L**) and different metal cations was investigated by UV–Vis and fluorescence spectroscopy in CH_3CN solution. The stock solution of **L** and metal ions was at a concentration of 10.0 mM. All absorption and emission spectral studies were carried out in freshly purified CH_3CN at room temperature.

2.2. Synthesis of coumarin Schiff base compound (L)

3-Amino-7-hydroxycoumarin and 7-diethylaminocoumarin-3-aldehyde were synthesized according to previous methods [18,22], respectively.

A portion of 7-diethylaminocoumarin-3-aldehyde (247 mg, 1 mmol) and 3-amino-7-hydroxycoumarin (195 mg, 1.1 mmol) were combined in hot absolute ethanol (20 mL) to yield a scarlet precipitate for a moment. The solution was stirred under reflux conditions for 6 h, and the precipitate was filtrated, washed with hot absolute ethanol three times, then recrystallized with DMF/H_2O (v/v, 1/3) to get scarlet crystal **L** (347 mg, 0.86 mmol) in 86% yield. IR (KBr, cm^{-1}): 2966, 2927, 1718, 1620, 1349, 1506, 1456, 1420, 845, 811, 770, 729, 693. ^1H NMR (DMSO-d_6, 400 MHz, δ): 10.54(s, 1H, —*OH*), 9.04(s, 1H, —N═*CH*), 8.56(s, 1H, *Ar—H*), 7.81(s, 1H, *Ar—H*), 7.70(d, 1H, *J* = 12 Hz, *Ar—H*), 7.58(d, 1H, *J* = 8 Hz, *Ar—H*), 6.81 (t, 1H, *J* = 8 Hz, *Ar—H*), 6.77 (s, 1H, *Ar—H*), 6.61(s, 1H, *Ar—H*), 3.49(q, 4H, *J* = 8 Hz, $-CH_2CH_3$), 1.16(t, 6H, *J* = 8 Hz, $-CH_2CH_3$). Anal. Calcd for $C_{23}H_{20}N_2O_5$: C 68.31%, H 4.98%, N 6.93%, Found: C 68.55%, H 5.04%, N 6.66%.

3. Results and discussion

3.1. The design and synthesis of compound L

Diethylamino coumarin and hydroxyl coumarin derivatives with intramolecular charge transfer (ICT) character are selected as chromophores, and are linked by C═N bond to form a potential chromogenic-sensing molecule for metal cations. It is known that chelating groups C═N, C═O exhibit a high affinity to transition and post-transition metal cations, but less binding affinity toward alkali metal and alkaline earth metal cations due to the difference of electronic structures [23]. In this design, therefore, we constructed compound **L** as chromogenic chemosensor. Firstly, by reacting 2,4-dihydroxy benzaldehyde with N-acetylglycine in acetic anhydride, and subsequently converted into 3-amino-7-hydroxycoumarin through hydrolysis in HCl/ethanol solution. When 4-diethylaminosalicylaldehyde was allowed to react with diethylmalonate, the corresponding intermediate was then treated by $POCl_3$/DMF to give 7-diethylaminocoumarin-3-aldehyde. **L** was readily synthesized by one-step condensation of 7-diethylaminocoumarin-3-aldehyde and 3-amino-7-hydroxycoumarin in absolute ethanol as shown in Scheme 1 and characterized by FT-IR, ^1H NMR and elemental analysis.

3.2. Selective recognition of Ni^{2+} with L

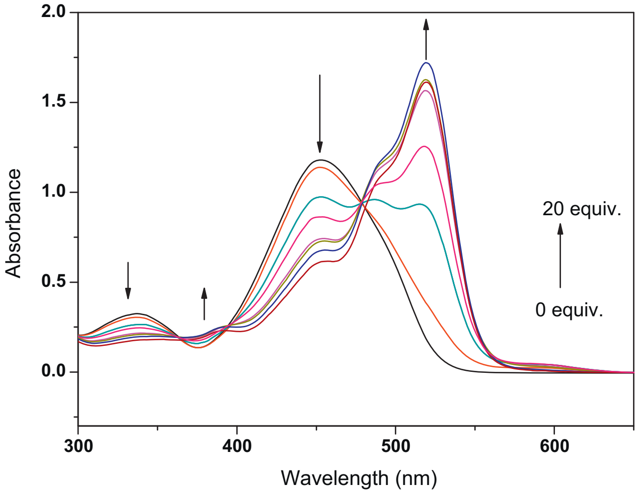


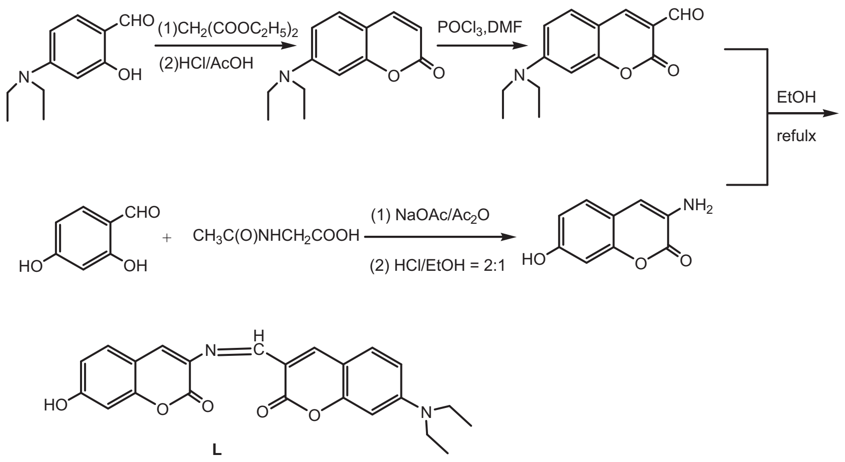
Fig. 1. UV–vis absorption spectra of **L** (10.0 μM) with gradual addition of Ni^{2+} [0, 4, 12, 20, 32, 40, 80 and 200 μM, respectively].

Firstly, the metal ion binding and sensing ability of **L** was investigated in CH_3CN. Fig. 1 demonstrates the changes in the absorption spectrum of **L** (10 μM) in CH_3CN in the absence and presence of Ni^{2+}. The free **L** exhibited main absorption at 465 nm in CH_3CN solution, which could be assigned to the charge transfer (CT) absorbance, as observed in other compounds with similar results [16]. As soon as Ni^{2+} was added at room temperature, the absorption intensity at λ_{max} of 465 nm decreased and two new bands at 486 and 516 nm due to ICT appeared. Notably, when the concentration of Ni^{2+} increased stepwise, absorption intensity at λ_{max} of 486 and 516 nm gradually increased and finally exceeded that of 465 nm. Correspondingly, the color changes of **L** were also observed by eye simultaneously from yellow to red in presence of Ni^{2+} (Fig. 2). This result indicated that the color changes were most probably owing to the formation of a new complex species with different electronic properties from that of **L**, and therefore a new color (red) was observed. The significant color change also suggested that **L** was a sensitive naked-eye indicator for Ni^{2+}, which was different from structurally similar *bis*-coumarin derivative acting as a fluorescence signaling system selectively for Mg(II) [17]. Moreover, well-defined isosbestic points at 363, 394 and 478 nm further demonstrated that a stable complex was present having a certain stoichiometric ratio between the **L** and Ni^{2+} formed in CH_3CN solution.

3.3. Job's plot analyses

For determination of stoichiometry between **L** and Ni^{2+}, Job's plot analyses were used. The method is that keeping total concentration of **L** and Ni^{2+} at 10.0 mM, and changing the molar ratio of Ni^{2+} (X_M; $X_M = [Ni^{2+}]/\{[\mathbf{L}] + [Ni^{2+}]\}$) from 0.1 to 0.9. From Fig. 3, when molar fraction of Ni^{2+} was 0.5, the absorbance at 516 nm got to maximum, indicating that forming a 1:1 complex between **L** and Ni^{2+}.

Fig. 2. Photographs of **L** color changes (10.0 μM) with gradual addition of Ni^{2+} from left to right: 0, 4, 10, 20 and 50 μM, respectively in CH_3CN solution.



Scheme 1. Synthesis of compound **L**.

The association constant (K_a) of **L** with Ni^{2+} was determined using the Benesi–Hildebrand equation as follows:

$$\frac{1}{A-A_0}=\frac{1}{K_a(A_{max}-A_0)[Ni^{2+}]}+\frac{1}{A_{max}-A_0}$$

where A and A_0 represent the absorbance of **L** in the presence and absence of Ni^{2+}, respectively, A_{max} is the saturated absorbance of **L** in the presence of excess amount of Ni^{2+}; $[Ni^{2+}]$ is the concentration of Ni^{2+} ion added. The measured absorbance $[1/(A-A_0)]$ varied as a function of $1/[Ni^{2+}]$ in a linear relationship ($R=0.991$), indicating formation of 1:1 stoichiometry between Ni^{2+} and **L**. This further corroborated 1:1 complex formation based on Job's plot analyses. The association constant of **L** with Ni^{2+} in CH_3CN solution was calculated to be $2.9\times10^4\ M^{-1}$.

3.4. Interference from other metal ions

Selectivity is an important characteristic of an ion-selective chemosensor. To examine the selectivity of **L**, the affinity of **L** for other surveyed metal ions, such as Na^+, K^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Sb^{3+} and Fe^{3+} was investigated. As shown in Fig. 4, addition 1 equiv. of these alkali-, alkaline earth-, transition and rare earth metal ions did not cause significant UV–vis absorption spectral changes of **L**. However, under the same conditions, addition of Ni^{2+} resulted in an obvious change, indicating **L** had higher binding affinity toward Ni^{2+} than other surveyed metal ions.

Furthermore, competition experiment was carried out by adding 20.0 μM Ni^{2+} to solution of **L** (10.0 μM) in the presence of miscellaneous cations including Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Sb^{3+} and Fe^{3+} (20.0 μM, respectively). These miscellaneous competitive cations did not induce significant absorption changes of **L** in the absence of Ni^{2+}. However, upon addition of 2 equiv. of Ni^{2+} to the solution, the unique spectral and color changes were still displayed under the above conditions. These results revealed that **L** had a remarkable selectivity toward Ni^{2+} over other competitive cations, and more, the detection of Ni^{2+} by **L** was hardly affected by these common coexistent metal ions.

3.5. Influence of metal ions on the fluorescence intensity of *L*

The fluorescence properties of **L** (1.0 μM) with 0.2–10 equiv. of Ni^{2+} were studied in CH_3CN solution, where excitation wavelength was 465 nm and fluorescence emission intensity was recorded at 498 nm. In CH_3CN solution, the fluorescence intensity of **L** was weak, which was probably due to the fact that C=N isomerization was the predominant decay process of the excited states for **L** with an unbridged C=N structure.

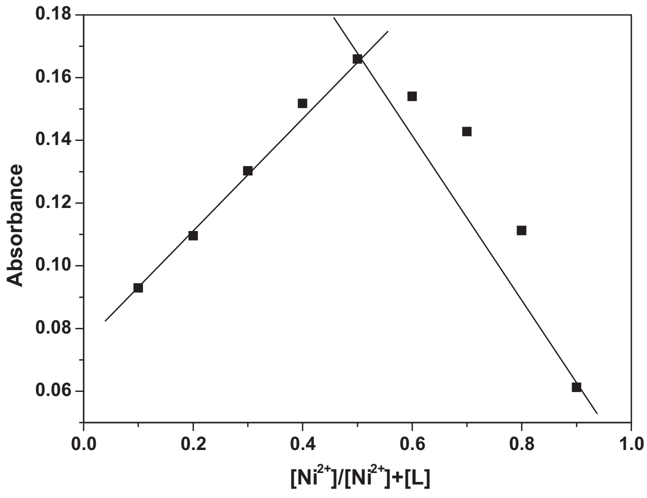


Fig. 3. Job's plot of **L** with Ni^{2+} in CH_3CN solution. Total concentration of $[L]+[Ni^{2+}]$ was kept constant at 10.0 mM. The absorbance at 516 nm was used.

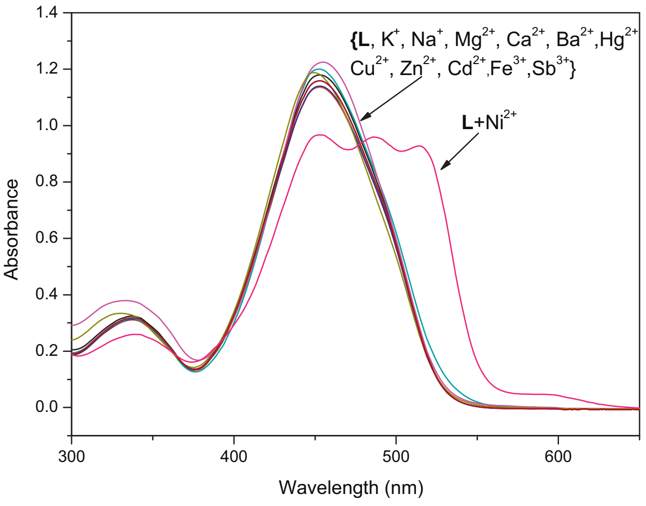
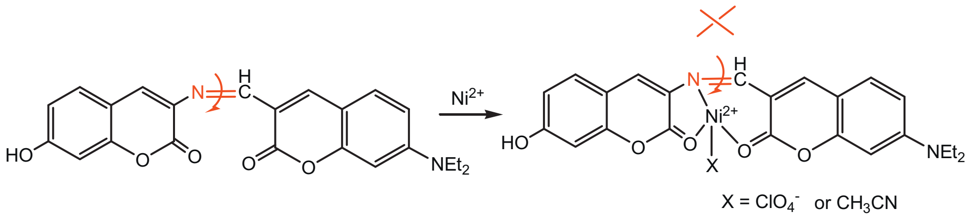


Fig. 4. UV–vis absorption spectra of **L** (10.0 μM) upon addition of various metal ions (10.0 μM) in CH_3CN solution.



Scheme 2. Schematic representation of possible binding mode between Ni^{2+} and **L**.

When Ni^{2+} concentration was low or equal to that of **L**, a fluorescence emission increase of **L** was observed with slightly changes in the spectral shapes, as shown in Fig. 5. The maximum increase of fluorescence emission at 498 nm was found to be 48.3% with 1 equiv. of Ni^{2+}, which was agreement with the data of 1:1 complex between **L** and Ni^{2+} from Job's plot. The enhancement of fluorescence was attributed to the introduction of Ni^{2+} and consequently occurrence of the strong complexation with **L**, resulting in decreased non-radiative decay of the excited-state and increased radiative decay. The remarkable increase of the fluorescence intensity is due to the inhibition of the $C{=}N$ isomerization process upon Ni^{2+} binding at the NO_2 site. The fourth or higher coordination site of Ni^{2+} may be occupied by the counteranion ClO_4^- or acetonitrile molecule. The proposed interaction mode between **L** and Ni^{2+} was shown in Scheme 2.

When Ni^{2+} concentration was higher than that of **L**, emission intensity of **L** began to gradually decrease as compared with maximum emission intensity in presence of 1 equiv. Ni^{2+} (Fig. 6). For instance, emission intensity of **L** decreased 8.7% in presence of 2 equiv. of Ni^{2+} than that of observed in presence of 1 equiv. Ni^{2+}. Upon addition of 10 equiv. of Ni^{2+}, the fluorescence emission of **L** was strongly quenched and decrease of fluorescence intensity at 498 nm was found to be 74.2% as compared with that of free **L**. Because the maxima and shapes of the fluorescence spectra did not change and no new peaks appeared, possible mechanism for the remarkable fluorescence quenching induced by the paramagnetic Ni^{2+} was attributed to an electron or energy transfer between excess Ni^{2+} and **L** known as the fluorescence quenching mechanism [24,25]. Similar phenomena were also observed in other experiments [26].

Addition of 1 equiv. of other surveyed metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Sb^{3+} and Fe^{3+}, respectively) produced different changes in the fluorescence spectra of **L**, in terms of maximum emission intensity. As shown in Fig. 7, the fluorescence emission was not affected by Na^+, K^+, Ca^{2+}, Ba^{2+} and Mg^{2+}, and fluorescence intensity ratios of **L** in the presence and absence of these surveyed metal ions at 498 nm are almost equal to one. The fluorescence emission was slightly quenched (no more than 10%) by $Zn^{2+}$and Sb^{3+}. However, the fluorescence emission increased in range of 15–48% with the addition of Hg^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+}.

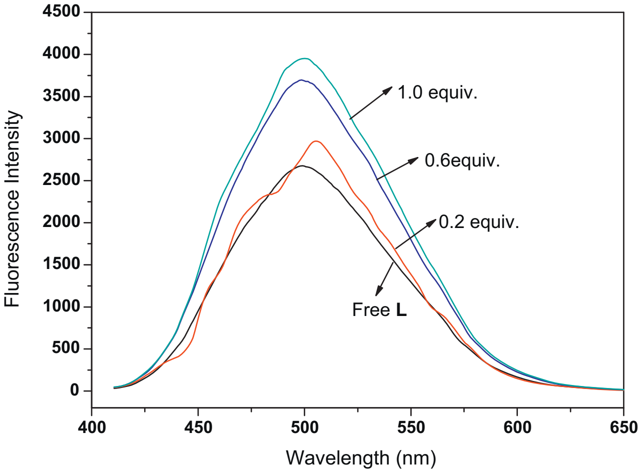


Fig. 5. Fluorescence emission spectra of **L** (1.0 μM) with gradual addition of Ni^{2+} [0,0.2, 0.6 and 1.0 μM, respectively].

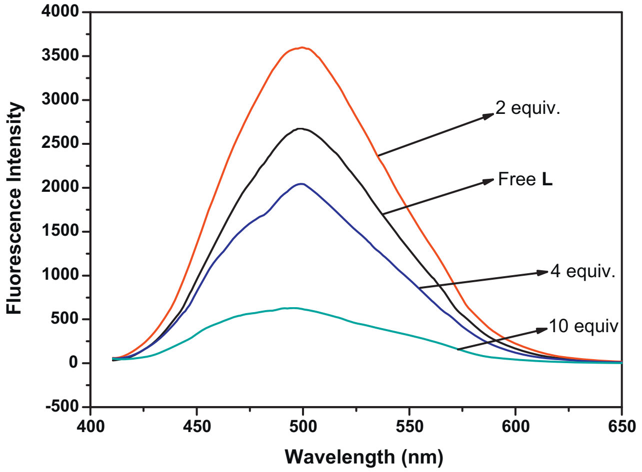


Fig. 6. Fluorescence emission spectra of **L** (1.0 μM) with gradual addition of Ni^{2+} [2,4 and 10.0 μM, respectively].

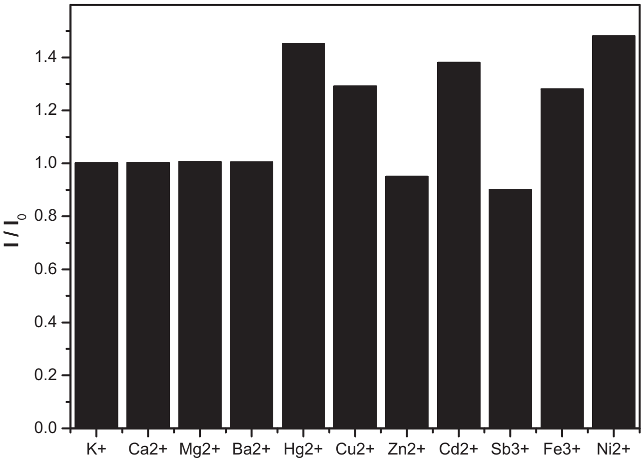


Fig. 7. Changes in fluorescence emission intensity ratio (I/I_0) at 498 nm of **L** (1.0 μM) in the presence of 1 equiv. of various metal ions in CH_3CN solution. I_0 is the intensity of free **L**, and I is the intensity of **L** after addition of metal ion.

4. Conclusions

A colorimetric Ni^{2+} sensor based on novel coumarin Schiff base compound (**L**) was designed and synthesized. Addition of Ni^{2+} to CH_3CN solution of **L** resulted in an obvious color change (from yellow to red) in a very short time. This made the real-time, simple-to-use and naked-eye detection of Ni^{2+} possible. Moreover, **L** possessed a good selectivity toward Ni^{2+}over other competitive cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Sb^{3+} and Fe^{3+}). These features indicated that **L** was a good candidate, for rapid, selective and sensitive detecting Ni^{2+} in CH_3CN media.

Acknowledgement

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