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SHORT COMMUNICATION

A Novel Chemosensor Based on Rhodamine Derivative for Colorimetric and Fluorometric Detection of Cu^{2+} in Aqueous Solution

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Abstract A new rhodamine-based reversible chemosensor (**2**) was synthesized, which exhibits high sensitivity and selectivity for Cu^{2+} but no significant response toward other competitive metal ions in aqueous solution. Upon the addition of Cu^{2+}, the spirolactam ring of **2** was opened and the solution color changed from colorless to red. Strangely, an unexpected fluorescence quenching was observed, which is contrary to the fluorescence turn-on of the most rhodamine-based chemosensors. The likely novel sensing mechanism has been proposed.

Keywords Rhodamine 6G · Chemosensor · Cu^{2+} · Fluorescence

Introduction

In recent years, the design and synthesis of selective and sensitive chemosensors for the detection of transition metal ions have attracted considerable attention [1, 2]. Among the various transition metal ions, Cu^{2+} plays a critical role as a catalytic cofactor for a variety of metalloenzymes, including superoxide dismutase, cytochrome *c* oxidase and tyrosinase. However, if unregulated, copper can cause oxidative stress and disorders associated with neurodegenerative diseases, such as Alzheimer's disease, Wilson's disease, and Menke's disease [3–5]. Besides, copper is a significant metal pollutant due to its widespread use. Considering the important roles of Cu^{2+} in biological and environmental systems [6–9], a considerable effort has been devoted to the development of Cu^{2+}-selective fluorescent chemosensors in the past few years [10]. However, in most cases fluorescence changes can only be observed in non-aqueous solvent [11–13], which greatly limits their analytical application in real samples. Therefore, the development of highly sensitive and selective fluorescent chemosensor for Cu^{2+} in aqueous solution is imperative.

Rhodamine-based dyes possess excellent spectroscopic properties such as a large molar extinction coefficient, high fluorescence quantum yield, and visible light excitation as well as long wavelength emission [14, 15]. Besides, rhodamine derivatives are well-known for their spirolactam (fluorescence "off") to ring-opened amide (fluorescence "on") equilibrium, during which significant fluorescence enhancement as well as color changes will take place, and based on this mechanism, a variety of rhodamine-based spirolactam derivatives have been designed as probes for the recognition of different metal ions such as Pb^{2+} [16, 17], Hg^{2+} [18–20], Cu^{2+} [21–24], Fe^{3+} [25–27], Cr^{3+} [28, 29].

Herein, we report a new rhodamine-based chemosensor **2**, which has been demonstrated to be a reversible, sensitive and selective chemosensor for Cu^{2+} in aqueous solution. Chemosensor **2** was readily synthesized in two steps (Scheme 1). Rhodamine 6G reacted with hydrazine hydrate to give the intermediate **1**, which was further treated with 4-(diethylamino) salicylaldehyde to afford chemosensor **2** in 66 % overall yield. All the compounds were confirmed by ^{1}H NMR, ^{13}C NMR spectra and MS data.

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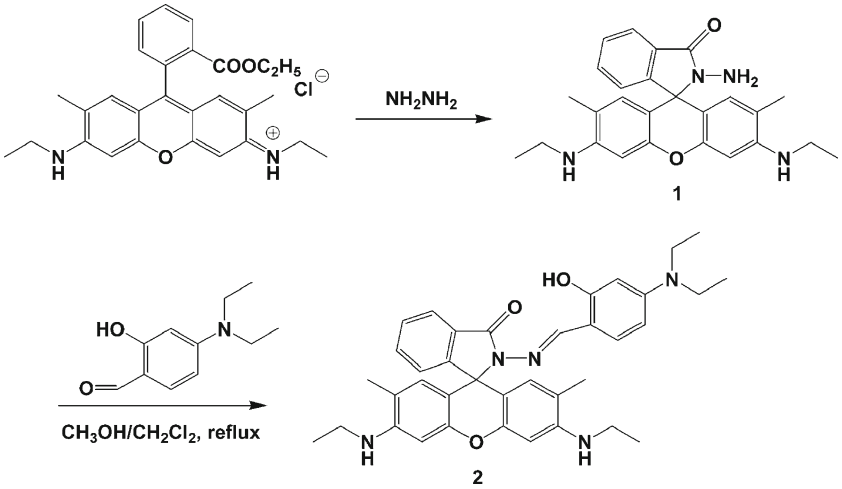
Scheme 1 Synthetic route of chemosensor **2**



Experimental Section

Reagents

Rhodamine 6G, Hydrazine hydrate, 4-(Diethylamino) salicylaldehyde and Tris(hydroxymethyl)aminomethane (Tris) were purchased from commercial suppliers and used as received. All the solvents were of analytic grade, and double distilled water was used throughout the experiment. The solutions of metal ions were prepared from their nitrate salts (Ag^{+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) in distilled water except for $CdCl_2$.

Apparatus

Absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer (Tokyo, Japan). Fluorescence spectra were performed on Perkin-Elmer LS 50B fluorescence spectrometer (both excitation and emission slit widths: 3 nm). ^{1}H NMR and ^{13}C NMR spectra were measured on a BrukerAV-300 spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. Mass spectra were obtained from a HP 1100 LC–MS spectrometer. All pH measurements were made with a Sartorius basic pH-MeterPB-10.

Procedures of Metal Ion Sensing

A stock solution of **2** (1.0 mM) was prepared in absolute CH_3CN. Tris–HCl buffer solution (10 mM, pH=7.0) was prepared under adjustment by a pH meter. To a 10-mL volumetric tube containing 2.9 mL of acetonitrile, 100 μL of 1.0 mM **2**, different concentration of Cu^{2+} (or other metal ions) was added and the reaction mixture was diluted to 10 mL with the buffer. The reaction solution was kept at room temperature for 2 min. Then, 3.0 mL of the solution was transferred to a 1 cm cell for the absorption or fluorescence measurement.

General experimental procedure for the synthesis of the chemosensor **2**

The synthetic route to chemosensor **2** is shown in Scheme 1.

*Synthesis of Rhodamine 6G Hydrazide (**1**)*

Rhodamine 6G hydrazide (**1**) was prepared according to a literature method [14]. To a 250 mL flask, rhodamine-6G (3.83 g, 8 mmol) was dissolved in 90 mL ethanol. 12.0 mL (excess) hydrazine hydrate (85 %) was then added dropwise with vigorous stirring at room temperature. After the addition, the stirred mixture was heated to reflux for 10 h, during which

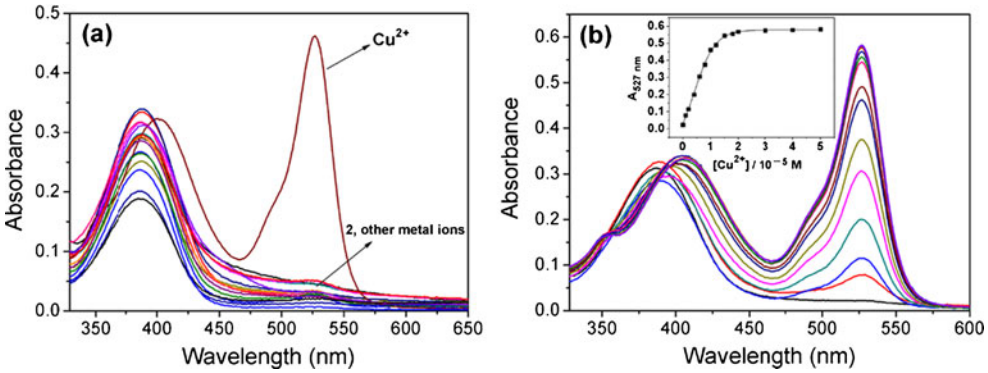


Fig. 1 UV–vis absorption spectra of **2** (10 μM) upon addition of (**a**) different metal ions (10 μM for all cations) and (**b**) Cu^{2+} (0~5 equiv.) in CH_3CN–water (3:7, *v*/*v*) at pH 7.0 aqueous solution. Inset (**b**) absorbance at 527 nm as a function of Cu^{2+} concentration

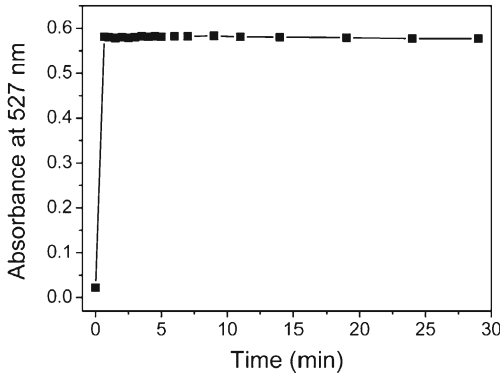


Fig. 2 Time course of the response of **2** (10 μM) to 5 equiv Cu^{2+} in CH_3CN–water (3:7, *v*/*v*) aqueous solution

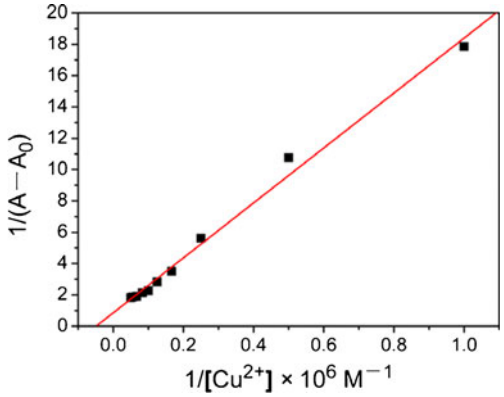


Fig. 4 The plot of absorption spectra of **2** at 527 nm: $[1/(A\text{-}A_0)]$ vs $1/[Cu^{2+}]$

the dark purple solution disappeared and pink precipitate appeared. The resulting precipitate was filtered, washed 4 times with 20 mL CH_3CH_2OH–H_2O (1:1, *v*/*v*) and dried in vacuo to afford rhodamine 6G hydrazide (2.75 g, yield 80 %) as light pink solid. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.98 (dd, 1H, Ar–H), 7.48 (dd, 2H, Ar–H), 7.08 (dd, 1H, Ar–H), 6.41 (s, 2H, xanthene–H), 6.28 (s, 2H, xanthene–H), 3.49–3.68 (b, 4H, N–*NH*$_2$, *NH*CH_2CH_3), 3.24 (q, 4H, NH*CH*$_2$CH$_3$), 1.94 (s, 6H, xanthene–*CH*$_3$), 1.35 (t, 6H, NHCH$_2$*CH*$_3$). ^{13}C NMR ($CDCl_3$) δ (ppm): 166.2, 152.2, 151.8, 147.5, 132.6, 129.9, 128.1, 127.7, 123.8, 123.0, 118.0, 104.9, 96.8, 66.1, 38.4, 16.7, 14.8. ESI-MS: *m*/*z* 429.1 for $[\mathbf{1}+H]^+$, cal. For $C_{26}H_{28}N_4O_2$, **1**, 428.53.

Synthesis of Target Compound **2**

Rhodamine 6G hydrazide (**1**) (2.0 mmol, 0.857 g) and 4-(diethylamino) salicylaldehyde (4.0 mmol, 0.774 g) were mixed in 2:1 (*v*/*v*) methanol/dichloromethane (90 mL) with 0.10 mL of acetic acid and refluxed for 20 h (if precipitation appeared, then added 5 ~ 10 mL dichloromethane). Then the solvent was removed in vacuo. The residue was washed by ethanol (5 × 15 mL) and dried in vacuo to afford **2** (1.0 g, yield 83 %) as yellow solid. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 11.01 (s, 1H), 9.10 (s, 1H), 7.99 (dd, 1H), 7.51 (dd, 2H), 7.13 (dd, 1H), 6.92 (d, 1H), 6.44 (s, 2H), 6.32 (s, 2H), 6.13 (b, 2H), 3.49 (s, 2H), 3.32 (q, 4H), 3.23 (q, 4H), 1.90 (s, 6H), 1.33 (t, 6H), 1.13 (t, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 163.7, 160.6, 154.1, 151.9, 151.0, 150.4, 147.5, 133.0, 132.7, 130.5, 128.4, 127.9, 124.0, 123.0, 117.9, 107.5, 106.1, 103.3, 98.3, 96.8, 66.5, 44.5, 38.3, 16.8, 14.8, 12.6. ESI-MS: *m*/*z* 604.1 for $[\mathbf{2}+H]^+$, cal. For $C_{37}H_{41}N_5O_3$, **2**, 603.76.

Results and Discussion

UV Absorption Studies

Figure 1a shows the representative chromogenic behavior of the dye towards various competitive metal ions in CH_3CN–water (3:7, *v*/*v*) at pH 7.0. Absorption spectra of free **2** (10 μM) in CH_3CN–water (3:7, *v*/*v*) at pH 7.0 showed an absorbance at 388 nm and no absorption band above 500 nm, indicating that spirolactam form exists predominantly. The

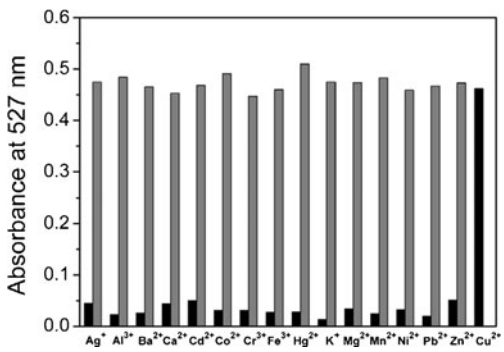


Fig. 3 The UV–vis absorbance response of **2** (10 μM) upon the addition of various metal ions in CH_3CN–water (3:7, *v*/*v*) aqueous solution. *Black bars* represent the absorbance of **2** to the metal ions of interest (10 μM for Cu^{2+}; 20 μM for all other metal ions). *Gray bars* represent the changes that occur upon subsequent addition of Cu^{2+} (10 μM) to the solution. The absorbance was measured at 527 nm

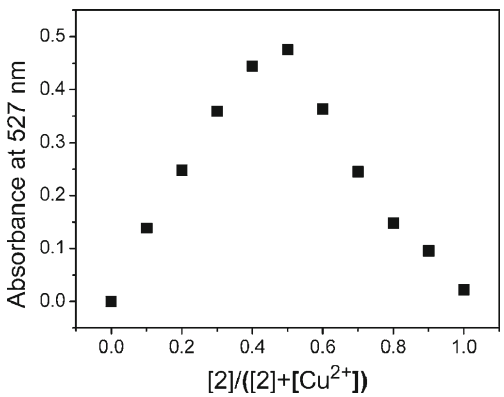


Fig. 5 Job's plot of the complexation between **2** and Cu^{2+}. The total concentration of **2** and Cu^{2+} was kept at a fixed 20 μM. The absorbance was measured at 527 nm

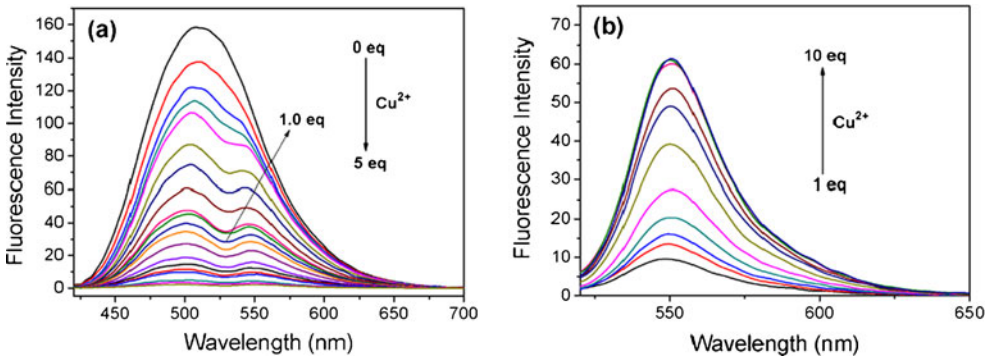


Fig. 6 Fluorescence titration of **2** (10 μM) by excitation at (**a**) λ_{ex}=386 nm; **b** λ_{ex}=512 nm in CH_3CN–water (3:7, *v*/*v*) at pH 7.0 aqueous solution

characteristic peak at 66.5 ppm (spiro carbon) in the ^{13}C NMR spectrum of **2** also supports this consideration [30]. The addition of various metal ions such as Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} have little change to the UV–vis spectrum of chemosensor **2** and the color of the solutions containing these ions remained relatively unchanged. In contrast, Cu^{2+} resulted in a prominent change. Upon the addition of Cu^{2+}, the absorption was significantly enhanced with a new absorption band centered at 527 nm, clearly suggesting spirolactam bond cleavage followed by the formation of a delocalized xanthenes moiety of the rhodamine group as a result of Cu^{2+} binding. Accordingly, the solution exhibited an obvious and characteristic color change from colorless to pink, which was clearly visible to the naked eye. Moreover, the change in the solution color was very fast and observed within 1 min upon addition of 5 equiv. Cu^{2+} to the solution of **2** (10 μM) (Fig. 2). These results indicated that compound **2** exhibited a high selectivity for Cu^{2+} over various other metal ions and thus, could serve as a good selective naked-eye chemosensor for Cu^{2+} in CH_3CN aqueous media. The excellent selectivity was further demonstrated by the competition experiment, which revealed that the Cu^{2+} induced absorbance enhancement was not significantly interfered in the presence of various coexistent ions (2 equiv.) (Fig. 3).

Stoichiometry of Metal Complexation

To understand the coordination behavior between **2** and Cu^{2+}, the UV–vis absorption spectral titration experiment of **2** (10 μM) with Cu^{2+} (0 to 50 μM) in aqueous solution (pH=7.0) was carried out. As shown in Fig. 1b, the intensity of the new 527 nm absorption band increased with increasing Cu^{2+} concentration. According to the linear Benesi-Hildebrand expression [31, 32], the association constant of **2** with Cu^{2+} ion was found to be 4.877×10^4 M^{-1}, and the measured absorbance $[1/(A-A_0)]$ at 527 nm varied as a function of $1/[Cu^{2+}]$ in a linear relationship (R=0.99603), indicating the 1:1 stoichiometry between the Cu^{2+} ion and **2** (Fig. 4). This binding mode was further supported by a Job's plot evaluated from the absorption spectra of **2** and Cu^{2+} with a total concentration of 20 μM. As shown in Fig. 5, the Job's plot shows that a maximum absorption was observed when the molar fraction reached 0.5, which is indicative of a 1:1 stoichiometric complexation between **2** and Cu^{2+}.

Fluorescence Properties

The fluorescence responses of chemosensor **2** towards Cu^{2+} and other metal ions were also investigated. As shown in Fig. 6, fluorescence spectra (λ_{ex}=386 nm) of free **2** (10 μM) in CH_3CN–water (3:7, *v*/*v*) at pH 7.0 displayed an emission band centered at 512 nm and a strong green fluorescence was observed, which is quite different from most of the reported rhodamine-based chemosensors with no obvious fluorescence signal before the complexation of ions due to the predominant spirocyclic form. The green fluorescence of **2** is possibly due to contribution from Schiff base of salicylaldehyde. More interestingly, upon the addition of Cu^{2+}, the original emission band at 512 nm decreased significantly accompanied by a blue-shift to 500 nm, and concomitantly a

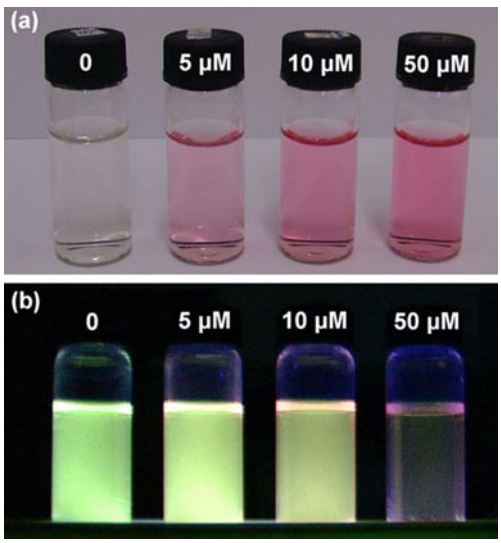
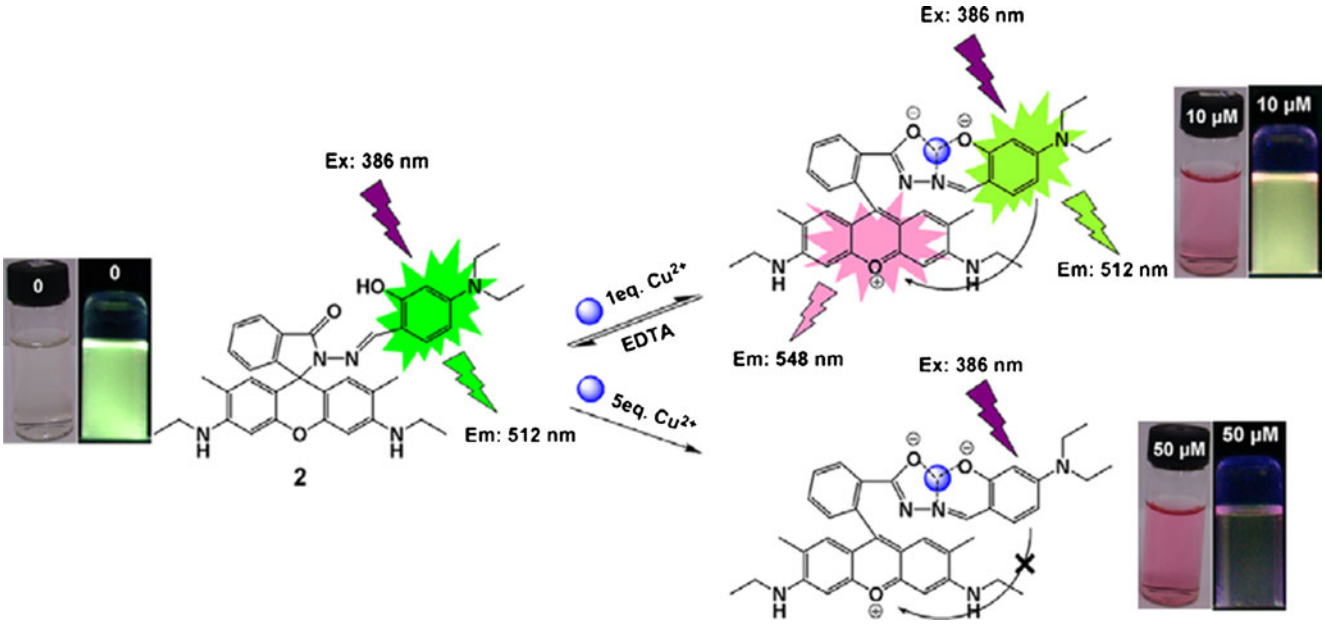


Fig. 7 **a** Visible and **b** fluorescence (excitation at 365 nm) color change of **2** (10 μM) in the presence of different concentrations of Cu^{2+} in CH_3CN–water (3:7, *v*/*v*) aqueous solution



Scheme 2 Proposed mechanism and binging mode between **2** and Cu^{2+}. (The colored starlike patterns represent for fluorescence of fluorophores at different conditions by excited **2** at 386 nm)

new emission band centered at 548 nm appeared which also decreased with increasing Cu^{2+} concentration. And when the Cu^{2+} concentration increased up to 5 equiv. of chemosensor **2**, its fluorescence was completely quenched (Fig. 6a). The visible and fluorescence color change of **2** in the presence of different concentrations of Cu^{2+} are shown in Fig. 7. It is well known that rhodamine-based chemosensors always show a fluorescence enhancement response (turn on) upon the addition of analytes. As far as we know, there is only one reported example showing the similar phenomenon that has been described above [33].

Interestingly, when **2** was excited by 512 nm, the intensity of the fluorescent peak at 548 nm gradually increased with increasing amount of Cu^{2+} as usual rhodamine-based chemosensors act (Fig. 6b), which suggests that the new emission band at 548 nm should be attributed to the ring-opening of the spirocycle and the formation of a delocalized xanthenes moiety of the rhodamine group. Based on the finding from the afore-mentioned experiments and the chemistry regarding the Cu^{2+}-mediated decylization of rhodamine [34], we proposed the likely mechanism of the Cu^{2+}-induced fluorescence turn-off response as shown in Scheme 2. Chemosensor **2** is most likely to chelate with Cu^{2+} via its carbonyl O, imino N, and phenol O atoms to induce the ring opening of rhodamine spirocycle [35]. As a consequence, a new absorption band at 527 nm characteristic of the opened rhodamine group appeared. We conjecture that, when excited by 386 nm, the salicylaldehyde Schiff base part of **2** was excited and gave green fluorescence at 512 nm which overlap with the absorption band of the newly formed opened rhodamine fluorophore. As a result, the rhodamine fluorophore was excited to give a corresponding new emission band at 548 nm when Cu^{2+} was added. However, Cu^{2+} might act as a quencher toward green fluorescence of Shiff base of salicylaldehyde, thus, both of the two emission band (512 nm and 548 nm) decreased with gradual addition of Cu^{2+}.

As shown in Fig. 8, the addition of other metal ions such as Ag^{+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} did not induce obvious change in the fluorescence spectra (λ_{ex}=386 nm) except for a small decrease in the emission intensity, indicating the good selectivity for Cu^{2+}. This result also suggests that the new emission band at 548 nm should be attributed to the Cu^{2+}-induced opening of the rhodamine spirocycle.

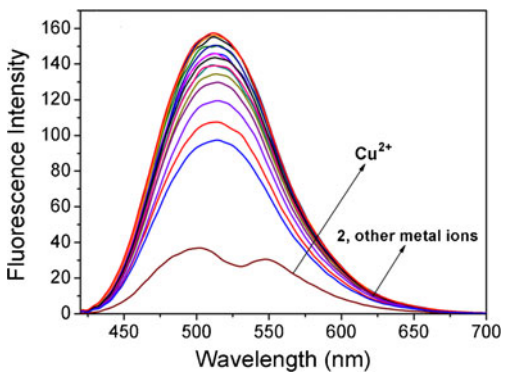


Fig. 8 Fluorescence emission (λ_{ex}=386 nm) changes of **2** (10 μM) upon addition of different metal ions (10 μM for all cations) in CH_3CN–water (3:7, *v*/*v*) at pH 7.0 aqueous solution

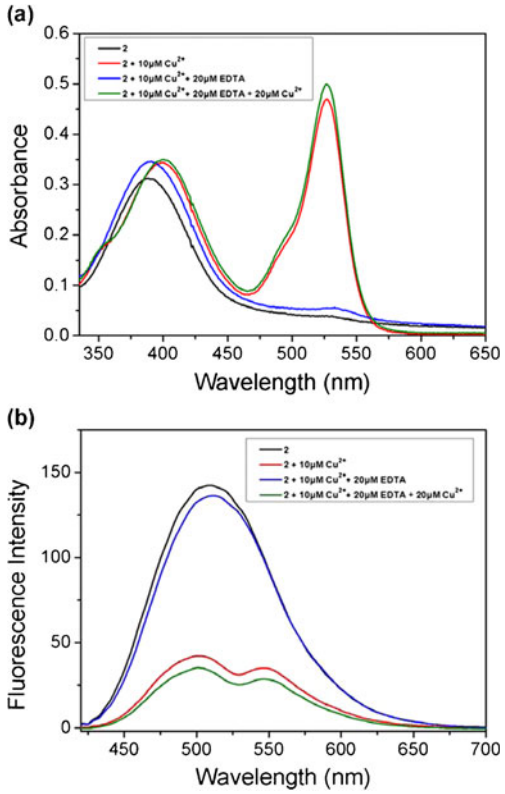


Fig. 9 **a** UV–vis and **b** fluorescence spectra of **2** (10 μM) in the presence of 10 μM of Cu^{2+}. Excess of EDTA (Na salt) was added to **2**+Cu^{2+} in CH_3CN–water (3:7, *v*/*v*) mixture, and then 20 μM Cu^{2+} was added to show the reversible binding nature of Cu^{2+} with **2**. Excitation was performed at 386 nm

Reversibility Study

Reversible binding of **2** with Cu^{2+} was also examined. Upon addition of 2 equivalents of EDTA to a mixture of **2** (10 μM) and Cu^{2+} (10 μM) in CH_3CN–water (3:7, *v*/*v*) solution, the color changed from red to colorless and fluorescent emission intensity at 512 nm increased to almost initial value, indicating that the EDTA replaced the receptor **2** to coordinate with Cu^{2+}. Further addition of Cu^{2+} (20 μM) still resulted in almost the same absorption and fluorescence changes (Fig. 9). Thus, **2** can be classified as a reversible chemosensor for Cu^{2+}.

Conclusions

In conclusion, we have synthesized a new rhodamine derivative **2**, which displayed a reversible absorption enhancement and fluorescence quenching response to Cu^{2+} via a 1:1 binding mode. Meanwhile, the chemosensor exhibits a highly selectivity for Cu^{2+} over other metal ions in CH_3CN–water (3:7, *v*/*v*) aqueous media. We anticipate that this probe will be used in the direct detection of Cu^{2+} in the presence of the other species in biological systems and contribute to the development of fluorescent sensors for transition-metal ions based on the rhodamine platform.

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