A New Rhodamine B-coumarin Fluorochrome for Colorimetric Recognition of Cu²⁺ and Fluorescent Recognition of Fe³⁺ in Aqueous Media

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A new rhodamine B-coumarin conjugate (**1**) capable of recognizing both Cu^{2+} and Fe^{3+} using two different detection modes have been designed and synthesized. The metal ion induced optical changes of **1** were investigated in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0) solution. Sensor **1** exhibits selective colorimetric recognition of Cu^{2+} and fluorescent recognition of Fe^{3+} with UV-vis and fluorescence spectroscopy, respectively. Moreover, both of the Cu^{2+} and Fe^{3+} recognition processes are observed to be barely interfered by other coexisting metal ions.

Key Words : Chemosensor, Colorimetric, Fluorescent, Rhodamine B, Recognition

Introduction

The development of optical molecular or polymeric systems capable of sensing various biologically and/or environmentally important cations, as chemosensors, has generated significant interest in recent years. At the present time, UV-vis and fluorescence spectroscopy are the most frequently used modes of detection of these sensors, due to their high sensitivity and easy operability. The emerging new concept of "single sensor for multiple analytes' for chemosensor design is the analysis of two or more analytes by one receptor utilizing a single detection method or an array of detection method.[1] This can be realized by two different sensor design strategies. The first one, is by combination of multichromogenic units into a single receptor,[2] and the second, is by using a variety of detection methods such as UV-vis and fluorescence.[3,1f] Since the former usually needs tedious receptor design and synthesis, the later has now become increasingly popular. In addition, the ability of screening samples for multiple targets with a single sensor also leads to faster analytical processing and potential cost reductions.

As a fluorophore and chromophore probe, the rhodamine fluorochrome based derivatives are excellent candidates for construction of colorimetric and fluorescent chemosensors for specific heavy and transition metal ions.[4] Both the Cu^{2+} and Fe^{3+} can produce diverse effects on human health and environment. Under overloading conditions, Cu^{2+} exhibits toxicity associated with neurodegenerative diseases like Alzheimer's disease, prion diseases,[5] and also has been suspected to cause infant liver damage in recent years.[6] On the other hand, Fe^{3+} plays a vital role in many biological processes, as it provides the oxygen-carrying capacity of heme and acts as a cofactor in many enzymatic reactions involved in the mitochondrial respiratory chain. The defici-

ency or excess of Fe^{3+} are toxic or can lead to a variety of diseases.[7] Therefore, detection of Cu^{2+} and Fe^{3+} by simple and cost-effective methods are important in biological and environmental concerns. Herein, we report the design, synthesis and metal ion recognition properties of a new fluorochrome, rhodamine B-coumarin conjugate **1**. Sensor **1** exhibits highly selective and sensitive recognition of Cu^{2+} and Fe^{3+} by colorimetric and fluorescent detection modes, respectively.

Experimental Section

General Methods and Materials. All the solvents were of analytic grade from commercial sources and used without further purification. Column chromatography was performed on silica gel (200-300 mesh). NMR spetra were recorded on a Varian 400 MHz NMR spectrometer. HRMS was carried out on a UPLC/Q Tof mass spectrometer. UV spectra were measured on a SP-1900 spectrophotometer. Fluorescence measurements were performed on a 970 CRT spectrofluorometer (Shanghai Sanco, China). The pH measurements were made with a Model phs-25B meter.

Synthesis of Sensor 1. A mixture of rhodamine B hydrazide (**2**)[8] (0.460 g, 1.0 mmol), coumarin 3-carboxylic chloride (**3**)[9] (0.228 g, 1.1 mmol) and triethylamine (0.150 g) in 50 mL of dry THF was stirred at room temperature for 2 hours. After the solvent was removed under reduced pressure, the residue was dissolved in ethyl acetate and washed with brine. The organic layer was dried and evaporated in vacuo and the product was obtained by recrystallization from ethanol in 85% yield. Pale yellow solid; mp 262.1-263.4 °C. IR (KBr, neat): ν 2970, 1734, 1707, 1636, 1611, 1568, 1547, 1514 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 9.95 (s, 1H), 8.78 (s, 1H), 7.99 (d, *J* = 6.9 Hz, 1H), 7.64-7.59 (m, 2H), 7.52-7.45 (m, 2H), 7.34-7.31 (m, 2H), 7.13 (d, *J* = 4.0
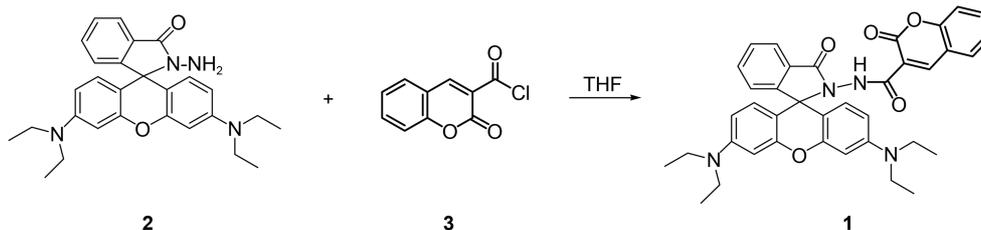
Scheme 1. Synthesis of sensor **1**.

Hz, 1H), 6.78 (d, J = 9.2 Hz, 2H), 6.38-6.34 (m, 4H), 3.38-3.27 (m, 8H), 1.15 (t, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 164.8, 160.8, 159.9, 154.5, 153.6, 153.5, 152.1, 149.3, 149.0, 134.3, 133.1, 129.8, 129.0, 128.7, 128.2, 125.3, 123.9, 123.6, 118.4, 117.7, 116.6, 108.2, 104.3, 97.9, 66.3, 44.4, 12.6. HRMS (ESI+): calcd for C$_{38}$H$_{37}$N$_4$O$_5$ [**1**+H]$^+$ 629.2764, found 629.2762.

Results and Discussion

Chemosensor **1** is readily prepared by a one-step amidation of rhodamine B hydrazide (**2**) and coumarin 3-carboxylic chloride (**3**) in dry THF as shown in Scheme 1. The structure of **1** was characterized by NMR spectroscopy and HRMS. The receptor moiety in the chemosensor **1** was selected based on the fact that the C=O usually behaves high affinity toward transition metal ions.[10]

The optical properties of **1** (1.0 × 10^{-5} M) were investigated in a CH$_3$CN-H$_2$O (1:1, v/v, HEPES 50 mM, pH = 7.0) co-solvent solution and Figure 1 shows the absorption response of **1** toward various metal ions. Free sensor **1** remained colorless and exhibited no apparent absorption above 450 nm in the aforementioned buffered solution. Upon addition of 8.0 equiv. of Cu^{2+} to **1** solution, a new strong absorption band centered at 563 nm appeared with an immediate color change from colorless to pink. Whereas, other metal ions such as Hg^{2+}, Ag$^+$, Pb^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Ce^{3+}, Mg^{2+}, K$^+$ and Na$^+$ (8.0 equiv. of each) did not induce noticeable absorption changes under the above identical conditions. These results demonstrate that sensor **1**
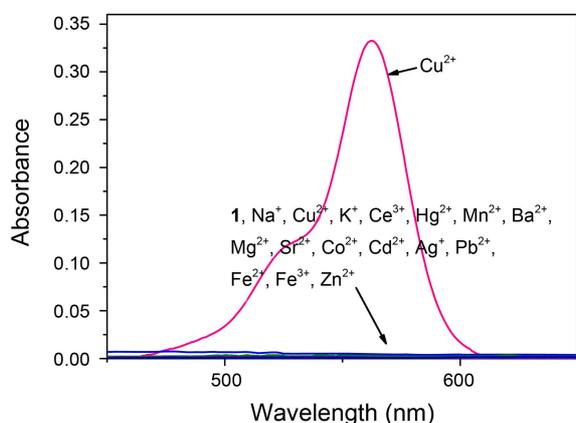
has a remarkable colorimetric selectivity to Cu^{2+}.

Subsequently, titration of **1** solution using different amounts of Cu^{2+} was carefully carried out. Upon incremental addition of Cu^{2+} to **1** solution (1.0 × 10^{-5} M), the absorption band centered at 563 nm gradually increased and reached the saturation point, when 8.0 equiv. of Cu^{2+} was added (Fig. 2). Linear fitting of the titration profiles using Benesi-Hildebrand plot based on a 1:1 binding mode[11] resulted in a good linearity (correlation coefficient is over 0.99) (Fig. S1), which strongly supports the 1:1 binding stoichiometry of **1** and Cu^{2+}. The association constant (K_a) of **1** with Cu^{2+} was estimated to be 2.44 × 10^5 M^{-1}. The 1:1 binding stoichiometry of Cu^{2+} and **1** was further proved by the continuous variation method (Job's plot) with a total concentration of [Cu^{2+}]+[**1**] as 5.0 × 10^{-5} M. (Fig. S2). The absorbance exhibited a maximum when the molar fraction of Cu^{2+} was 0.5, which also demonstrates the 1:1 binding stoichiometry is adopted between **1** and Cu^{2+}.

As a chemosensor, achieving highly selective response to the target analyte over a complex background of potentially competitive species is an important requirement. Thus, the competition experiments in the presence of potentially competitive metal ions were conducted and the results are shown in Figure 3. Except Cu^{2+}, all other metal ions (8.0 equiv. to **1**) did not induce distinct absorption changes. Nevertheless, upon addition of Cu^{2+} (8.0 equiv.) to the solution containing **1** and other metal ion, a significant increase in absorption at 563 nm is observed. These results indicate that the recognition of Cu^{2+} by **1** is not significantly interfered by other coexisting metal ions and therefore **1** exhibits

Figure 1. Absorbance changes of **1** (1.0 × 10^{-5} M) solution (CH$_3$CN-H$_2$O, 11, v/v, HEPES 50 mM, pH = 7.0) upon addition of various metal ions.
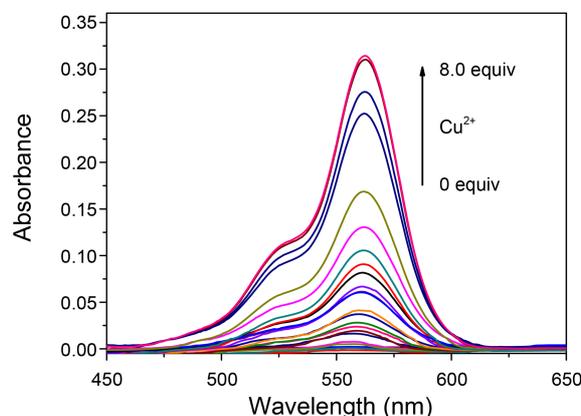
Figure 2. Changes in absorption of **1** (1.0 × 10^{-5} M) in CH$_3$CN-H$_2$O (1:1, v/v, HEPES 50 mM, pH = 7.0) upon addition of Cu^{2+} (0 to 8.0 equiv.).
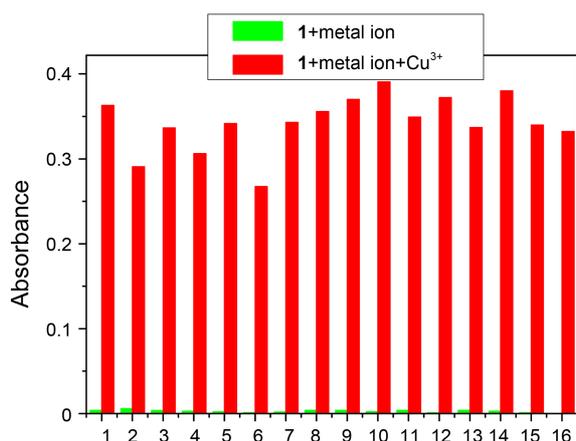
Figure 3. Absorption of **1** (1.0×10^{-5} M) solution (563 nm) to various metal ions in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0). The green bars represent the absorption of **1** in the presence of 8.0 equiv. of the metal ions; the red bars represent the absorption of the above solution upon the addition of 8.0 equiv. of Cu^{2+}. 1. Ni^{2+}; 2. Hg^{2+}; 3. Ba^{2+}; 4. Mg^{2+}; 5. Ag^+; 6. Fe^{2+}; 7. K^+; 8. Mn^{2+}; 9. Pb^{2+}; 10. Na^+; 11. Sr^{2+}; 12. Co^{2+}; 13. Zn^{2+}; 14. Cd^{2+}; 15. Fe^{3+}; 16. Cu^{2+}.
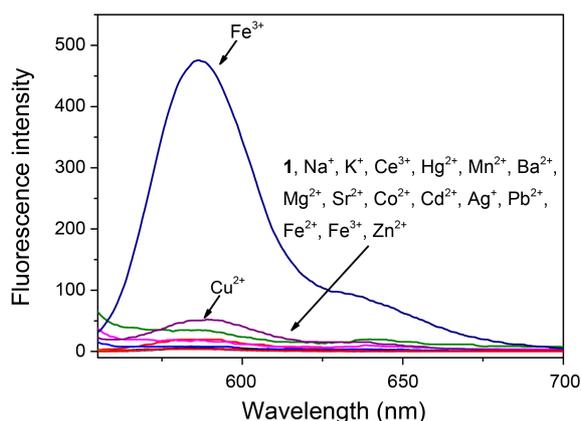
Figure 4. Fluorescence changes of **1** (1.0×10^{-5} M) solution (CH_3CN-H_2O, 11, v/v, HEPES 50 mM, pH = 7.0) in the presence of various metal ions (60 equiv. of each, excited at 530 nm).

a high selectivity toward Cu^{2+}.

On the other hand, when the colored solution containing **1** and Cu^{2+} was subjected to fluorescence, the solution exhibited a very weak emission, indicating that the fluorescence of the rhodamine spirolactam ring-opened form was quenched by Cu^{2+} due to its paramagnetic nature.[11] At the same time, it is worth noting that the solution consisted of **1** (1.0×10^{-5} M) and 60 equiv. of Fe^{3+} showed relatively strong fluorescence intensity. Similar to some reported rhodamine type Fe^{3+} selective fluorescent sensors,[12] the fluorescence enhancement of solution **1** in the presence of Fe^{3+} is also attributed to the formation of rhodamine spirolactam ring-opened form induced by Fe^{3+}. Whereas, other tested metal ions did not induce any distinct fluorescence enhancement (Fig. 4). Thus, sensor **1** is capable of fluorescent recognition of Fe^{3+} in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0).

Titration of **1** solution (1.0×10^{-5} M) in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0) by using 0-180 equiv. of Fe^{3+}
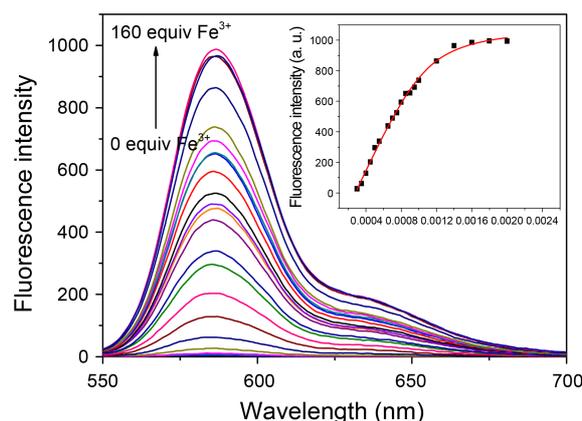
Figure 5. Changes of fluorescence intensity of **1** (1.0×10^{-5} M) solution (CH_3CN-H_2O, 11, v/v, HEPES 50 mM, pH = 7.0) upon addition of different amounts of Fe^{3+} (0-180 equiv, excited at 530 nm).

was subsequently carried out. Upon incremental addition of Fe^{3+}, the fluorescence intensity at 586 nm of **1** solution increased gradually and reached the saturation when 160 equiv. of Fe^{3+} was added (Fig. 5). Nonlinear least-squares fitting of the titration profiles (Fig. 5, inset) employing the 1:1 binding mode equation strongly support the formation of a 1:1 complex of **1** and Fe^{3+} and the association constant K_a was calculated to be 1.7×10^4 M^{-1}.[12a] It should be pointed out that when a small amount (0-25 equiv.) of Fe^{3+} was added to **1** solution, it shows detectable fluorescence responses to Fe^{3+} but not a significant color change due to the high sensitivity of fluorescence (Fig. S3). When much more amount of Fe^{3+} was used, it also leads to dramatic color changes, as it is well known that the fluorescence induced by Fe^{3+} is come from the pink colored rhodamine spirolactam ring-opened form. These results indicate that the colorimetric recognition of Cu^{2+} by dual sensor **1** is restricted when a high concentration of Fe^{3+} coexist.

The 1:1 binding stoichiometry of Fe^{3+} and **1** was also proved by Job's plot according to the continuous variation method with a total concentration of $[Fe^{3+}]+[\mathbf{1}]$ as 5.0×10^{-4} M (Fig. S4). The fluorescence intensity reached a maximum when the molar fraction of Fe^{3+} was 0.5, which further confirms the 1:1 binding stoichiometry between **1** and Fe^{3+}.

Furthermore, competition experiments in the presence of potentially competitive metal ions were also carried out and the results are shown in Figure 6. Except Fe^{3+}, other metal ions (60 equiv. to **1** of each) do not produce significant fluorescence changes. However, upon addition of Fe^{3+} (60 equiv.) to the solution containing **1** and other metal ion, a significant increase in fluorescence intensity at 586 nm is observed. These results demonstrate that the fluorescent recognition of Fe^{3+} by **1** is hardly influenced by other coexisting metal ions.

In addition, the effect of pH on the fluorescence of **1** in the absence of Fe^{3+} was explored. As shown in Figure 7, sensor **1** alone has no effective fluorescence between pH 5.5 and 13, but its fluorescence increased distinctly when the pH value is smaller than 5.5. In the presence of Fe^{3+}, the
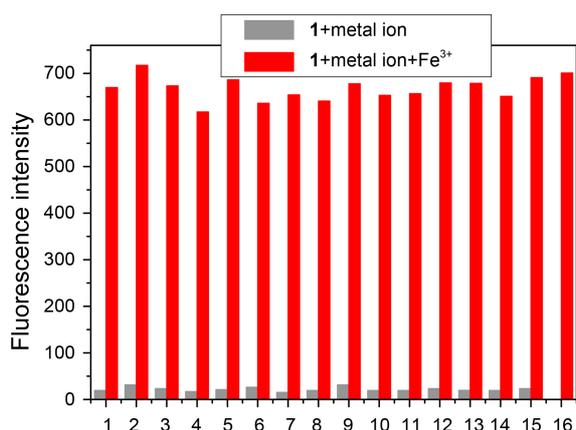
Figure 6. Fluorescence of **1** (1.0×10^{-5} M) solution to various metal ions in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0). The grey bars represent the fluorescence of **1** in the presence of 60 equiv. of different metal ions; the red bars represent the fluorescence of the above solution upon the addition of 60 equiv. of Fe^{3+}. 1. Ni^{2+}; 2. Hg^{2+}; 3. Ba^{2+}; 4. Mg^{2+}; 5. Ag^+; 6. Fe^{2+}; 7. K^+; 8. Mn^{2+}; 9. Pb^{2+}; 10. Na^+; 11. Sr^{2+}; 12. Cu^{2+}; 13. Co^{2+}; 14. Zn^{2+}; 15. Cd^{2+}; 16. Fe^{3+}.

fluorescence intensity of **1** solution increased remarkably between pH 6 and 8. These results strongly advocate that **1** is suitable for detection of Fe^{3+} at near neutral pH conditions. Nevertheless, under a strong acidic condition which can be caused in an aqueous solution of Fe^{3+}, the rhodamine molecule can undergoes H^+-catalyzed ring opening to give fluorescence emission. Hence, the pH changes of **1** solution in the presence of different amounts of Fe^{3+} were examined (Fig. 7, inset). In a typical experiment, we found that when 160 equiv. of Fe^{3+} was added to the above **1** solution, the solution pH is 5.5. From the pH titration experiment, it is evident that in the absence of Fe^{3+} at the same pH (5.5), the fluorescence intensity of **1** solution is as weak as that of **1** under neutral conditions. These results clearly indicate that the fluorescence changes of **1** upon addition of Fe^{3+} in the
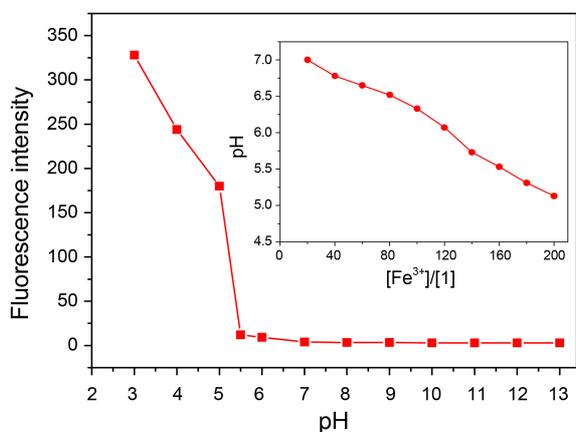
Figure 7. Effect of pH on fluorescence intensity of **1** (1.0×10^{-5} M) solution (CH_3CN-H_2O, 1:1, v/v, HEPES 50 mM, pH = 7.0). Inset: The pH of **1** (1.0×10^{-5} M) solution in the presence of different amounts of Fe^{3+}.
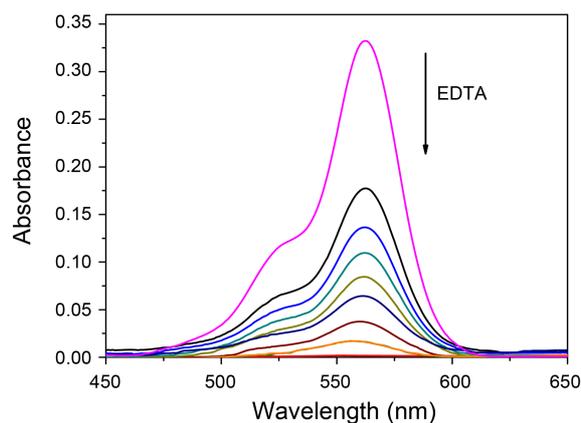
Figure 8. Changes in absorption spectra of solution composed of **1** (1.0×10^{-5} M) and Cu^{2+} (8.0×10^{-5} M) upon addition of $EDTANa_2$ in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0) solution.
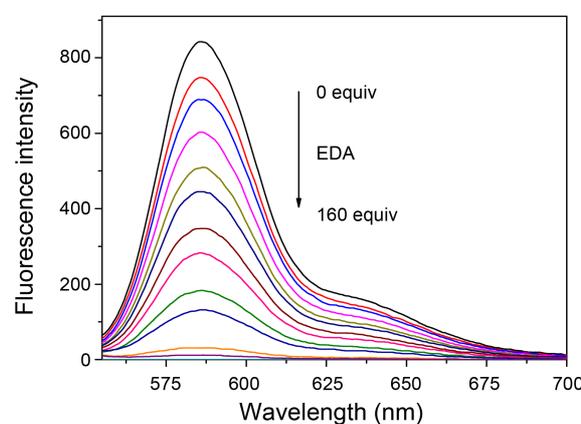
Figure 9. Changes in fluorescence spectra of solution containing **1** (1.0×10^{-5} M) and Fe^{3+} (1.6×10^{-3} M) upon addition of EDA in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0) solution.

buffered solution are mainly attributed to Fe^{3+} induced rhodamine spirolactam ring-opening effect.

For a chemosensor, the reversibility is an important requirement. We examined the reversibility of the binding between **1** and Cu^{2+} in the CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0) solution. Ethylenediamine tetraacetic acid disodium salt ($EDTANa2$) was selected as the titration reagent due to its high affinity to Cu^{2+}. Upon incremental addition of $EDTANa_2$ to a buffered solution composed of **1** (1.0×10^{-5} M) and Cu^{2+} (8.0×10^{-5} M) led to a significant absorption decrease at 563 nm, and the solution turned into its original colorless state when excess $EDTANa_2$ was added (Fig. 8). We also examined the reversibility of the **1**-Fe^{3+} binding by titration with ethylenediamine (EDA). Accordingly, titration of a buffered solution (CH_3CN-H_2O, 1:1, v/v, HEPES 50 mM, pH = 7.0) containing **1** (1.0×10^{-5} M) and Fe^{3+} (1.6×10^{-3} M) with EDA gave rise to significant decrease of fluorescence intensity and reached completely quenching when excess EDA was used (Fig. 9). These results demonstrate the colorimetric response of **1** to Cu^{2+} and the fluorescent recognition of Fe^{3+} are all reversible rather than a cation catalyzed reaction.

Conclusion

In summary, we have developed a new rhodamine B-coumarin conjugate sensor **1** as a dual sensor for Cu^{2+} and Fe^{3+} ions. Sensor **1** exhibits selective colorimetric recognition of Cu^{2+} and fluorescent recognition of Fe^{3+} in CH_3CN-H_2O (1:1, v/v, HEPES 50 mM, pH = 7.0) solution. The interactions of **1** with Cu^{2+} and Fe^{3+} are proven through a 1:1 bind stoichiometry and the Cu^{2+} and Fe^{3+} recognition processes of **1** are barely interfered by other coexisting metal ions.

Supporting Information. Synthesis and characterization of sensor **1**, Benesi-Hildebrand plot of **1** with Cu^{2+} (Figure S1), Job's plot of **1** with Cu^{2+} (Figure S2), fluorescence and absorbance changes of **1** solution at low Fe^{3+} concentration range (Figure S3), Job's plot of **1** with Fe^{3+} and fluorescence intensity of solution **1** *versus* the concentration of Fe^{3+} (Figure S4) are available.

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