



A rhodamine-based colorimetric and reversible fluorescent chemosensor for selectively detection of Cu^{2+} and Hg^{2+} ions

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ABSTRACT

A bifunctional colorimetric and fluorescent chemosensor RbCS has been successfully designed and synthesized by simple condensation of 3,5-dichlorosalicylaldehyde and rhodamine B hydrazide. In aqueous media, chemosensor RbCS exhibits remarkably enhanced absorbance intensity and color change from colorless to pink for Cu^{2+} , and shows significant “off-on” fluorescence accompanied with color changes from colorless to red upon binding to Hg^{2+} . The absorbance and fluorescence signals of RbCS can be restored with addition of EDTA disodium into solutions of RbCS– Cu^{2+} and RbCS– Hg^{2+} , showing that the binding of chemosensor RbCS and $\text{Cu}^{2+}/\text{Hg}^{2+}$ is chemically reversible.

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1. Introduction

The development of artificial chemosensors with high selectivity and sensitivity for biochemical agents and environmentally hazardous metal ions has been actively investigated in recent years [1–3]. Among these metal ions, Hg^{2+} is one of the most severe environmental contaminants because it is widely distributed in air, water and soil [4]. Hg^{2+} accumulation in the body can cause serious health problems, damaging central nervous and endocrine systems, leading to many cognitive and motion disorders [5]. On the other hand, Cu^{2+} is an essential trace element in biological systems, and plays as a catalytic cofactor for a variety of metalloenzymes in the lifecycle [6]. The Cu^{2+} disorder in its uptake, storage, and trafficking might stimulate the production of reactive oxygen species and thus exhibits toxicity associated with Alzheimer's and Wilson's diseases [7,8]. Moreover, free Cu^{2+} is a significant environmental pollutant and generally considered to be the most toxic form to organisms [9]. Therefore, a convenient and fast method to detect

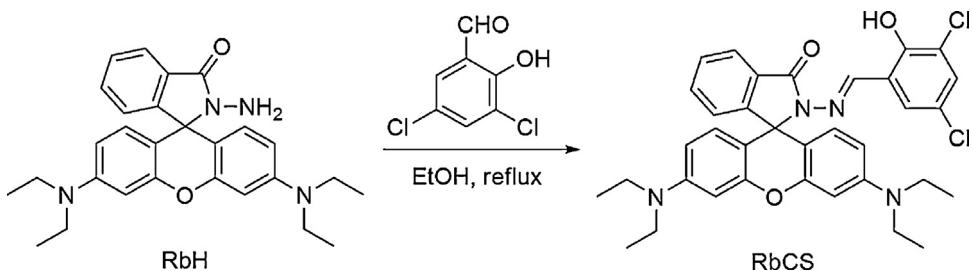
Cu^{2+} and Hg^{2+} existing in environmental and biological resources is of considerable importance [10,11].

To date, a great number of colorimetric and fluorescent sensors have been synthesized and applied to detect Cu^{2+} and Hg^{2+} ions owing to their simplicity, high sensitivity, and real-time detection [12–20]. Although there are various single-analyte sensors designed for Cu^{2+} and Hg^{2+} , few examples that could detect the two cations simultaneously have been reported [21–25]. More importantly, the greatest challenge for detecting Hg^{2+} comes from the interference of other transition-metal ions, in particular Cu^{2+} [26]. Recently, a suitable designed pyrene-substituted phenylthiourea fluorescent chemosensor was recently reported by Yen's group [27]. It shows selectively responses toward Hg^{2+} and Cu^{2+} ions by an orchid fluorescence in the presence of Hg^{2+} ions and a strong blue fluorescence in the presence of Cu^{2+} ions. Ghosh's group designed and synthesized a rhodamine-based bis sulfonamide which recognizes both Cu^{2+} and Hg^{2+} ions by exhibiting different emission characteristics in a semi-aqueous system [28].

In continuation of our research effort devoted to fluorescence sensors for ion recognition [29–32], we have successfully synthesized a new rhodamine B derivative RbCS, which was utilized as a bifunctional colorimetric and fluorescent chemosensor for Cu^{2+} and Hg^{2+} in aqueous media. Among the various metal ions, chemosensor RbCS exhibits remarkably enhanced absorbance intensity and color change from colorless to pink for Cu^{2+} , and shows significant

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Scheme 1. Synthesis and structure of Chemosensor RbCS.

"off-on" fluorescence accompanied with color changes from colorless to orange upon binding to Hg²⁺.

2. Experimental

2.1. Apparatus

¹H and ¹³C NMR (DMSO-*d*₆) was recorded using a Bruker Avance 300 spectrometer with tetramethylsilane (TMS) as internal standard. IR spectra were recorded in diffuse reflection with a Thermo Nicolet 5700 FT-IR spectrophotometer. Mass spectra were performed on a Bruker micro TOF-Q mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. The UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. All photoluminescence (PL) spectra were measured on a Jasco FP-6500 fluorescence spectrophotometer, with the excitation and emission wavelengths set at 10 and 5 nm, respectively.

2.2. Reagents

All reagents were purchased from commercial suppliers and used without further purification. Rhodamine B hydrazide (RbH) was synthesized according to literature [33]. Solvents for chemical synthesis and analysis were purified according to standard procedures. Double distilled water was used throughout the experiment. Stock solution (1.0×10^{-3} mol/L) of RbCS was prepared by dissolving the requisite amount of it in CH₃CN solvent. Nitrate salts of metal ions (K⁺, Na⁺, Ca²⁺, Mg²⁺, Zn²⁺, Fe³⁺, Pb²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Ag⁺, Hg²⁺) and the chloride salts of Fe²⁺ and Co²⁺ ions were used to evaluate the metal ion binding properties by synthesized compounds.

2.3. Synthesis

The chemosensor RbCS is readily prepared by one-step condensation of rhodamine B hydrazide and 3,5-dichlorosalicylaldehyde

in absolute ethanol as shown in Scheme 1. To a stirring solution of corresponding rhodamine B hydrazide (0.46 g, 1.0 mmol) in absolute ethanol (20 mL), 3,5-dichlorosalicylaldehyde (0.21 g, 1.1 mmol) was added and the reaction mixture was refluxed for 10 h under N₂ atmosphere. After cooling to room temperature, a yellow precipitated formed, which was filtered and washed with ethanol for three times. The product was purified by column chromatography with petroleum ether/CH₂Cl₂ (5:1, v/v), gave a yellow solid in 75% yield. ¹H NMR (300 MHz, DMSO-*d*₆): δ 11.24 (s, 1H), 9.11 (s, 1H), 7.95 (d, *J* = 7.0 Hz, 1H), 7.71–7.56 (m, 2H), 7.54 (d, *J* = 2.5 Hz, 1H), 7.46 (d, *J* = 2.6 Hz, 1H), 7.14 (d, *J* = 7.1 Hz, 1H), 6.50–6.30 (m, 6H), 3.32 (q, *J* = 7.0 Hz, 8H), 1.08 (t, *J* = 6.9 Hz, 12H); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 163.79, 152.73, 150.92, 148.59, 134.38, 130.49, 129.05, 128.13, 127.58, 123.96, 123.24, 121.60, 121.13, 108.34, 104.39, 97.51, 65.80, 43.65, 12.36; IR (KBr, cm⁻¹): ν = 3436, 2970, 2928, 1721, 1697, 1633, 1613, 1515, 1449, 1307, 1266, 1219, 1118, 1078, 821, 786; ESI-MS: *m/z* = 628.3; Elemental analysis (calcd. %) for C₃₅H₃₄Cl₂N₄O₃: C, 66.77; H, 5.44; N, 8.90; Found: C, 66.50; H, 5.70; N, 8.06.

3. Results and discussion

Fluorescence and UV-vis studies were performed using a 10 μM CH₃CN solution of RbCS in water with appropriate amounts of metal ions. Solutions were shaken for 20 min before measuring the absorption and fluorescence in order to make the metal ions chelate with the sensors sufficiently. The absorption spectra of compounds RbCS in CH₃CN-H₂O (4:1, v/v) solutions did not show any peaks above 450 nm indicating the ring-closed spirolactam is predominant. In addition, a very weak fluorescence signal was observed at 582 nm upon excitation at 552 nm, confirming the presence of ring-closed spirolactam.

3.1. Spectral recognition of Cu²⁺ and Hg²⁺

As shown in Fig. 1a, upon addition of a constant amount (10 Eq) of Cu²⁺ ions to the chemosensor RbCS, a significant enhancement

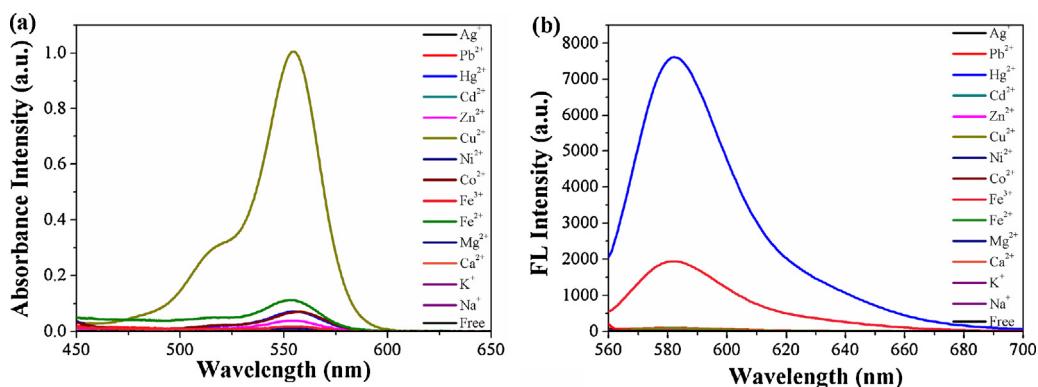


Fig. 1. (a) Absorption spectra of RbCS (10 μM) in CH₃CN-H₂O (4:1, v/v) in the presence of various metal ions (10 Eq). (b) Fluorescence spectra of RbCS (10 μM) in CH₃CN-H₂O solution in the presence of various metal ions (10 Eq).

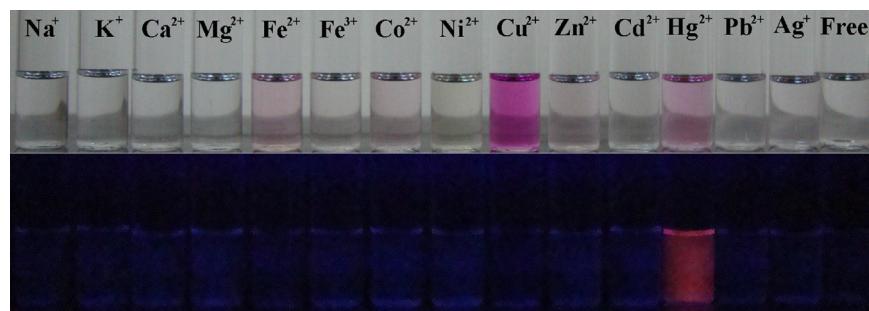


Fig. 2. Photograph of RbCS ($10 \mu\text{M}$) showing the color (top) and the fluorescent (bottom) changes in the presence of various cations (20 Eq).

in absorbance at 554 nm was observed, which induced a clear color change from colorless to pink. This phenomenon clearly indicates the formation of the ring opened form of RbCS as a result of Cu²⁺ binding. Excepting Fe²⁺, Hg²⁺ and Co²⁺ ions, addition of other competitive metal ions, such as K⁺, Na⁺, Ca²⁺, Mg²⁺, Ni²⁺, Cd²⁺, Fe³⁺, and Zn²⁺ did not cause any significant color or spectral change under identical conditions. The results demonstrated that RbCS was characteristic of high selectivity toward Cu²⁺ over other competitive metal ions.

To further investigate the selectivity of RbCS to Cu²⁺, we also studied the fluorescence response of chemosensor RbCS in CH₃CN–H₂O solution (Fig. 1b). To our surprise, no marked changes in the emission were observed upon addition of 10 Eq excess of Cu²⁺ ions. Since Cu²⁺ is paramagnetic in nature, the binding of the metal ion causes a quenching of the fluorescence emission that leads to a “turn-off” signal [34]. However, under the same conditions, the chemosensor RbCS developed an intense fluorescence emission at 582 nm upon addition of 10 Eq Hg²⁺ ions; it gave a slight fluorescence response to the addition of Fe³⁺ ions, and remained unchanged in the presence of other competing metal ions. These results indicate that chemosensor RbCS has remarkable “turn-on” fluorescence selectivity with Hg²⁺.

Fig. 2 exhibits the naked-eye colorimetric changes (top) and the fluorescent (bottom) changes of RbCS with different cations. A clear and selective color change from colorless to pink was observed for Cu²⁺ and striking “turn-on” fluorescence were observed by introducing of Hg²⁺.

3.2. Spectral titration experiment

In order to obtain a better insight into the response mechanism of RbCS toward Cu²⁺ and Hg²⁺, the UV-vis and fluorescence titration experiment was carried out. Fig. 3a shows the absorbance

changes of RbCS in CH₃CN–H₂O (4:1, v/v) upon addition of different Cu²⁺ concentrations. The absorbance band centered at 554 nm showed an exponential enhancement, which can be ascribed to the formation of the ring-opened amide form of RbCS upon Cu²⁺ ions binding. With the concentration of Cu²⁺ up to 10.0 Eq, a 170-fold enhancement was observed (Fig. 3a). The fluorescence titration of the Hg²⁺ ion was carried out under the same working conditions. As shown in Fig. 3b, when excited at 552 nm, the fluorescence intensity at 582 nm increased more than 80-fold on increasing the concentration of Hg²⁺ from 0 to 20 Eq. A satisfactory linear relationship between fluorescence intensity and Hg²⁺ concentration was observed with the correlation coefficient as high as 0.995 at high concentration from 0.5 to 15 Eq. (Fig. S5).

3.3. Selectivity and tolerance of RbCS to Cu²⁺ and Hg²⁺

Achieving excellent selectivity for specific analyte over complex competing species has been a challenge in the development of sensors. To evaluate the selectivity of chemosensor RbCS in practice, competition experiments were also carried out in which RbCS was added to a solution of Cu²⁺/Hg²⁺ in the presence of other individual cations, including Na⁺, K⁺, Mg²⁺, Ca²⁺, Ag⁺, Cd²⁺, Fe²⁺, Co²⁺, Ni²⁺, Fe³⁺, Zn²⁺ and Pb²⁺. As shown in Fig. 4a, these ions did not exhibit obvious interference for Cu²⁺ detection, and the relative error of other metal ions is less than $\pm 5\%$, which demonstrates that the absorbance of RbCS is enhanced effectively by Cu²⁺ with these metal ions as backgrounds. Moreover, the competitive experiments also confirmed that the background metal ions showed very low interference with the detection of Hg²⁺ in aqueous media, only Cu²⁺ has posed a significant decrease in fluorescence intensity effect at 582 nm (Fig. 4b). This observation further confirms that the selective detection of Cu²⁺ is not influenced by the presence of common metal ions including major highly competing Hg²⁺ ions.

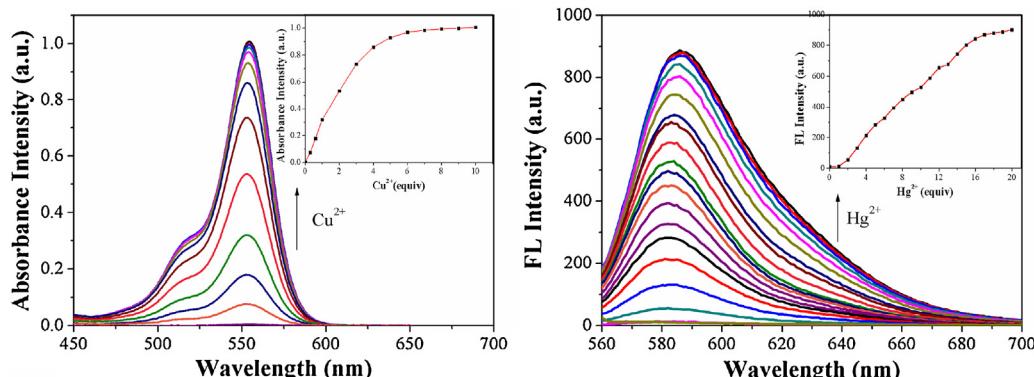


Fig. 3. (a) Changes in the absorption spectra of RbCS ($10 \mu\text{M}$) with increasing concentrations of Cu²⁺ (0–10 Eq) in CH₃CN–H₂O solution. The inset shows the relative absorption value at 554 nm as a function of the Cu²⁺ concentration. (b) Changes in the fluorescence intensity of RbCS ($10 \mu\text{M}$) with increasing concentrations of Hg²⁺ (0–20 Eq) in CH₃CN–H₂O solution ($\lambda_{\text{ex/em}} = 552/582 \text{ nm}$; slit: 2.5 nm/2.5 nm).

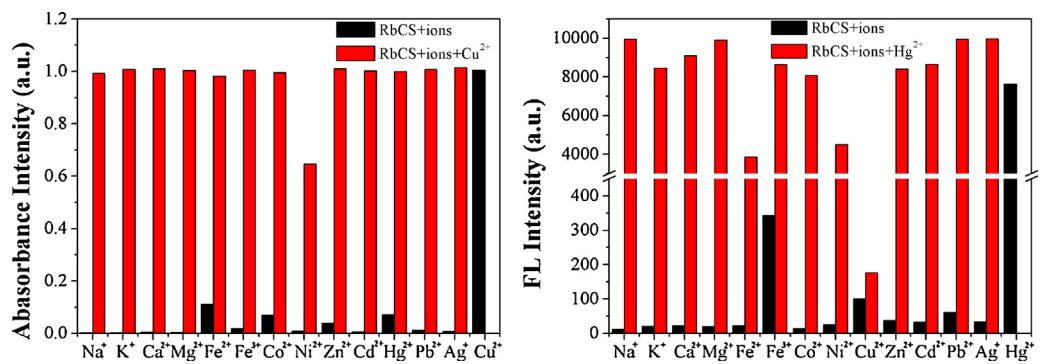


Fig. 4. Absorption (a) and fluorescence (b) spectra of RbCS in the presence of various cations (10 Eq) and Cu²⁺/Hg²⁺ (10 Eq) in CH₃CN–H₂O (4:1, v/v). The black bars represent the emission intensity of RbCS in the presence of other metal ions (10 Eq); the red bars represent the emission intensity of RbCS in the presence of the indicated metal ions, followed by 10 Eq of Cu²⁺/Hg²⁺ ion.

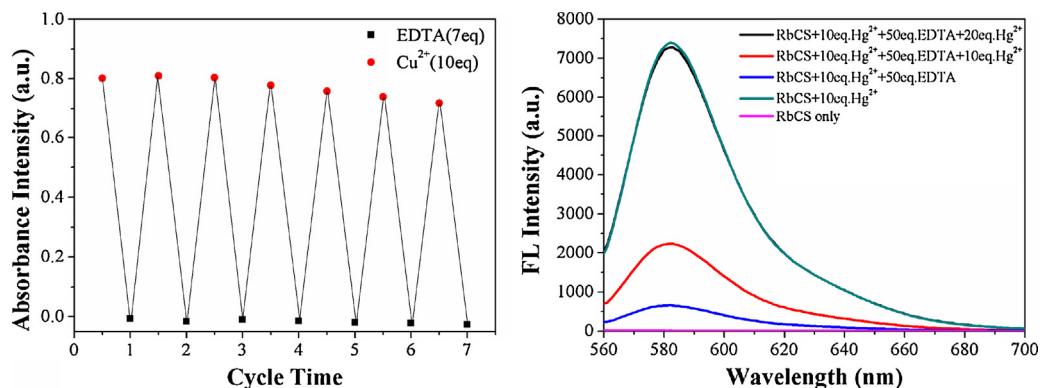


Fig. 5. (a) Absorbance responses of RbCS (10 μ M) by alternated adding Cu²⁺ and EDTA (sodium salt) in CH₃CN–H₂O (4:1, v/v). The cyclic time is the number of alternating Cu²⁺/EDTA cycles. (b) Fluorescence responses of RbCS (10 μ M) by alternated adding Hg²⁺ and EDTA (sodium salt) in CH₃CN–H₂O (4:1, v/v). (λ_{ex} = 552 nm).

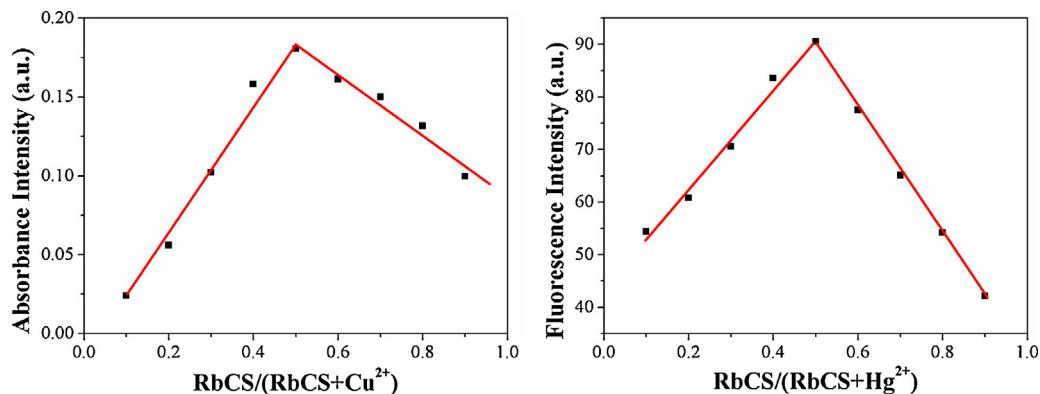
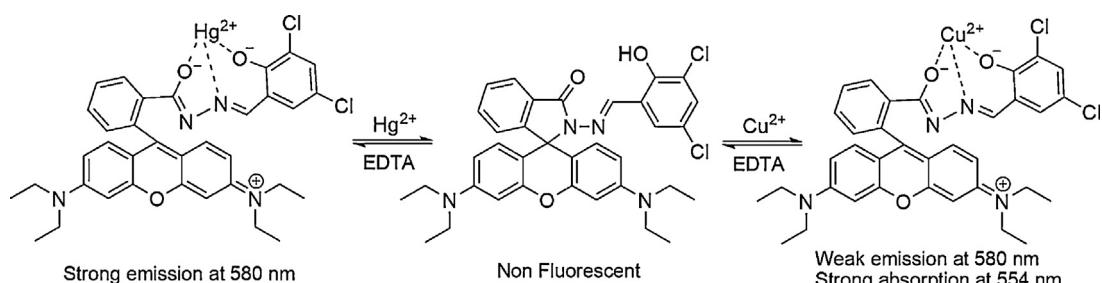


Fig. 6. Job's plots of the complexation between (a) RbCS–Cu²⁺ and (b) RbCS–Hg²⁺ in CH₃CN–H₂O (4:1, v/v) solution. The absorbance intensity was measured at 554 nm. The fluorescence intensity was measured at 582 nm. The total concentration of RbCS and Cu²⁺/Hg²⁺ is 100 μ M.



Scheme 2. Proposed mechanism for the fluorescent and colorimetric changes of RbCS upon the addition of Cu²⁺/Hg²⁺.

3.4. Repeatability of RbCS for sensing Cu²⁺ and Hg²⁺

To understand the stability and reversibility of the proposed RbCS–Cu²⁺ and RbCS–Hg²⁺ species, EDTA-addition experiments were conducted in the CH₃CN–H₂O solution (Fig. 5). It can be clearly observed that chemosensor RbCS exhibits a fully reversible response under periodically alternating addition of Cu²⁺ and EDTA. From the absorbance intensity measured at 554 nm, the response and the recovery times can be calculated (Fig. 5a). This regeneration ability indicates that RbCS could be reused with proper treatment. The response of RbCS to Hg²⁺ was confirmed to be reversible by EDTA titration. After adding specific concentration of EDTA (20 Eq), the color changed from pink to almost colorless, and more than 90% fluorescence intensity of the system was quenched (Fig. 5b). When Hg²⁺ was added again, the signals were almost completely recovered, and the colorless solution turned back to pink. These results confirmed that both of the Cu²⁺ and Hg²⁺ recognition processes are reversible.

3.5. Proposed sensing mechanism

According to the titration and reversibility experiment, we assumed that the sensor is most likely to chelate Cu²⁺/Hg²⁺ ions via the carbonyl O, imide N and phenol O atoms like other reported [35–37]. This could be further confirmed by the Job's plot (Fig. 6). Total concentration of RbCS and Cu²⁺ was maintained constant at 1.0×10^{-5} M and the mole fraction of Cu²⁺ changed from 0 to 1. The absorbance intensity at 554 nm went through a maximum when the mole fraction of Cu²⁺ was 0.5, which indicated that a 1:1 stoichiometry was the most possible binding mode of RbCS and Cu²⁺. From Fig. 6b, the fluorescence intensity went through a maximum at a molar fraction of about 0.5, indicating that a 1:1 stoichiometry for Hg²⁺ and RbCS. Thus, in accordance with the 1:1 stoichiometry, the possible binding mode between RbCS toward Cu²⁺/Hg²⁺ was proposed in Scheme 2.

4. Conclusions

In conclusion, we have developed a new bifunctional colorimetric and fluorescent chemosensor RbCS, which exhibited prominent absorption enhancements upon Cu²⁺ addition with particular selectivity and sensitivity, and it shows significant “off-on” fluorescence accompanied with color changes from colorless to red upon binding to Hg²⁺. The spectral response of RbCS toward Cu²⁺/Hg²⁺ was demonstrated to be reversible and robust against interference from coexisting metal ions. Further work aimed at RbCS's biological utilization as well as the development of materials for Hg²⁺-contamination treatment is currently under way.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2014.03.064>.

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