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ORIGINAL PAPER

A Rhodamine-Based Off–On Fluorescent Chemosensor for Selectively Sensing Cu(II) in Aqueous Solution

Ruiren Tang · Kang Lei · Ke Chen · Hua Zhao · Jingwen Chen

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Abstract A novel chromogenic and fluorogenic chemosensor **RhB-pMOSal** comprising a rhodamine fluorophore and a salicylaldehyde receptor being connected by an iminohydrazine link was synthesized and fully characterized. Its sensing behavior toward various metal ions in neutral aqueous solution was investigated by absorption and fluorescence spectroscopy. **RhB-pMOSal** exhibited a reversible and sensitive "turn-on" response of absorption and fluorescence toward Cu^{2+} in aqueous acetonitrile solution. Approximate 65 and 6-fold enhancement in the absorbance at 556 nm and fluorescence intensity at 573 nm were estimated when equivalent Cu^{2+} was added to the **RhB-pMOSal** solution. Under the same conditions, **RhB-pMOSal** displayed more sensitive than a reported analogue **RhB-Sal** to Cu^{2+} ion. The competition experiments for Cu^{2+} mixed with common metal ions exhibited no obvious change in absorption and emission except Cr^{3+} ion that can induce the fluorescence quenching of **RhB-pMOSal** to some extent.

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R. Tang · K. Lei · K. Chen
School of Chemistry and Chemical Engineering,
Central South University,
Changsha 410083, People's Republic of China

H. Zhao
Product Quality Supervision and Inspection of Yancheng,
Yancheng 224005, People's Republic of China

J. Chen (✉)
School of Chemical and Biological Engineering,
Yancheng Institute of Technology,
Yancheng 224051, People's Republic of China
e-mail: jwchen@ycit.edu.cn

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Introduction

The design and construction of chemosensory reagents for probing specific analytes, especially the biologically and environmentally-important species, with high selectivity and sensitivity are still of a hot research subject in the communities of chemistry, biochemistry, biology, material science and others [1–9]. Fluorescent sensing, which translates molecular binding events into tangible fluorescence signals, has received much attention in this field [1–9]. Rhodamine-based derivatives are excellent candidates for construction of fluorescent chemosensors due to their well-known spectroscopic properties of large molar extinction coefficient, high fluorescence quantum yield, longer wavelength excitation, and good photostability [6, 10]. The rhodamine moiety in a free molecule takes a spirolactam ring-closed form, which usually shows little absorption and nonfluorescence. However, it transforms to ring-opened amide form upon binding with a specific species, the chelating or reaction of metal ions, which usually becomes highly absorbent and fluorescent [11–17]. Based on such structural character, many off–on-type chromogenic or fluorogenic rhodamine-based chemosensors and reagents for metal ions were fabricated in the past few years [11, 12, 14–16, 18–31]. Among them, considerable attention has been paid to the colorimetric/fluorescent sensing of Cu^{2+} ion [15, 19, 20, 23–25, 28, 29] due to its known important role in the biological, environmental, and chemical systems [32, 33]. Tong et al. [21] once reported a salicylaldehyde rhodamine B hydrazone (**RhB-Sal**) that can selectively recognize Cu^{2+} ion in neutral aqueous solution. In this

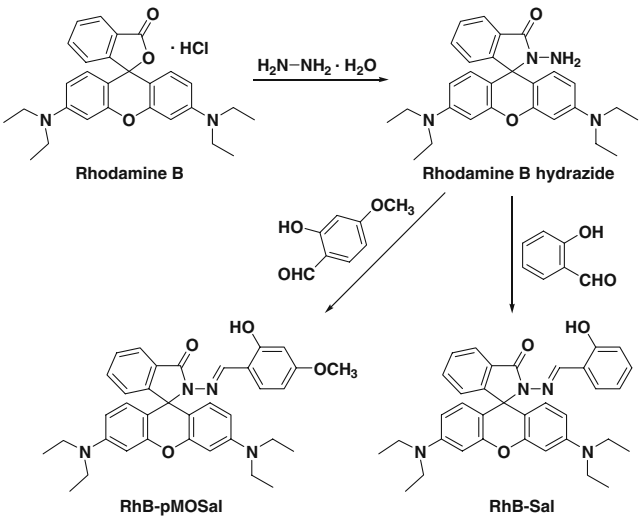
paper, an analogue of **RhB-Sal**, in which an electron-donating group $-OCH_3$ was introduced to the 4-position of 2-hydroxyphenyl moiety, was synthesized (**RhB-pMOSal**, Scheme 1). Its sensing behavior toward various metal ions in aqueous solution was investigated by means of absorption and fluorescence spectroscopy. The results exhibited that **RhB-pMOSal** displayed more sensitive and selective response than **RhB-Sal** to Cu^{2+} ion under the same conditions.

Experimental

Apparatus and chemicals

The absorption and the fluorescence spectra were measured on a Shimadzu UV-2450 spectrophotometer and a JASCO FP-6500 spectrofluorometer equipped with a thermostated cell compartment, respectively. A 1.0 cm quartz cuvette in a volume of 3.0 mL was used for all spectra collection. The pH measurements were carried out on a PHS-3C Exact Digital pH meter equipped with Phonix Ag-AgCl reference electrode (Cole-Paemer Instrument Co.), which was calibrated with standard pH buffer solutions. The mass spectra were obtained on an LCQ electron spray mass spectrometer (ESMS, Finnigan). The ^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer with tetramethylsilane (TMS) as an internal standard. All of the measurements were performed at about 298.0±0.2 K. Elementary analysis for C, H, N was performed on a Perkin-Elmer 240C analytic instrument.

Rhodamine B was purchased from TDI, and 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxybenzaldehyde and Tris (hydroxymethyl)aminomethane (Tris) were from Sigma-Aldrich. Silica gel (300–400 mesh) that used for thin layer and column chromatography were purchased from Qingdao Ocean Chemicals (Qingdao, China). All metal salts used in the spectroscopic experiments were obtained from Shanghai Chemical Reagent Corporation (Shanghai, China) and used without further purification. Acetonitrile in chromatographic grade and newly double-distilled water were used throughout the experiments as solvents. Aqueous Tris-HCl (50 mmol L^{-1})-NaCl (0.10 mol L^{-1}) solution was used as buffer to keep pH value (pH 7. 0), and to maintain the ionic strength of all solutions in experiments. The stock solution of Cu^{2+} and other metal cations (1.0×10^{-3} mol L^{-1}) were prepared from chloride salts using acetonitrile, respectively. The stock solution of **RhB-pMOSal** (1.0×10^{-4} mol L^{-1}) was prepared by dissolving the accurately weighed **RhB-pMOSal** in acetonitrile. The working solution of **RhB-pMOSal** (10 μmol L^{-1}) was prepared by diluting stepwise the stock solution with Tris buffer/acetonitrile (1/1, *v*/*v*).



Scheme 1 Synthesis of **RhB-pMOSal** and **RhB-Sal**

General methods

An aliquot of $CuCl_2$ stock solution was continuously syringed into 3 mL of **RhB-pMOSal** working solution in quartz cuvette. After full mixture and 5 min equilibration, the absorption spectra were collected by scanning the solution within 400–650 nm. The fluorescence spectra were recorded by the same procedures with excitation light of 520 nm. The slit width of the excitation and the emission were both set at 5 nm. The volume change for all spectroscopic experiments did not exceed 1%. All experiments were run in triplicate, and the average values were adopted. The stoichiometry of **RhB-pMOSal** and Cu^{2+} was determined by Job's method from the obtained absorption spectroscopic data, which was verified by ESI-MS results and Benesi-Hildebrand method [34]. In the determination, the sum of concentration of Cu^{2+} and **RhB-pMOSal** was kept at 40 μmol L^{-1} and the molar ratio of Cu^{2+} was changed from 0 to 1.0. Each solution of **RhB-pMOSal**/Cu (II) was prepared by adding appropriate volume of **RhB-pMOSal** and Cu^{2+} solution into a 10 mL volumetric flask, and diluting to the scale mark with the Tris buffer and then mixing fully.

Syntheses

Compound **RhB-pMOSal** was prepared by coupling rhodamine B hydrazide [35] with 2-hydroxy-4-methoxybenzaldehyde referring the reported procedures for **RhB-Sal** [21] with some modifications (Scheme 1). To 20 mL anhydrous ethanol containing rhodamine B hydrazide (0.23 g, 0.5 mmol), an excessive 2-hydroxy-4-methoxybenzaldehyde (0.6 mmol) was added and the mixture was stirred vigorously at room temperature for 24 h. The reaction progress was monitored by thin-layer chromatog-

raphy (TLC). After completion of the reaction, the formed precipitate was filtered, washed with cold ethanol (3× 10 mL) and then dried in vacuum, affording 0.17 g crude product, which was further purified by silica gel column chromatography using petroleum ether/ethyl acetate (2/1, *v*/*v*) containing 1% (*v*/*v*) triethylamine as eluent. 0.16 g of **RhB-pMOSal** as white powder solid was obtained, yield: 61.0%. ESI-MS for $C_{36}H_{38}N_4O_4$: *m*/*z*, calcd. ($M + H^+$) 591.29, found 591.42 (100%) (Supporting Information, Figure S1). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.18 (12H, t, $NCH_2\underline{CH_3}$), 3.34 (8H, q, $N\underline{CH_2}CH_3$), 3.76 (3H, s, $-OCH_3$), 6.27 (2H, d, Xanthene-H), 6.38 (2H, s, Xanthene-H), 6.48–6.51 (4H, t, Phen-H), 7.02 (1H, d, Phen-H), 7.18 (1H, d, Phen-H), 7.54 (2H, t, Ar-H), 7.99 (1H, d, Ar-H), 9.23 (1H, s, N=C-H), 11.084 (1H, s, Phen-OH) (Supporting Information, Figure S2). Elemental analysis. Found (calcd.) (%): C, 73.23 (73.20); H, 6.43 (6.48); N, 9.41 (9.48).

RhB-Sal that used as control was synthesized according to the above method using rhodamine B hydrazide and 2-hydroxybenzaldehyde as raw materials. After further purification of the crude product by silica gel chromatography using the same eluent, a white powder was obtained in 71.4% yield. ESI-MS for $C_{35}H_{36}N_4O_3$: *m*/*z*, calcd. ($M+H^+$) 561.28, found 561.40 (90%); ($2\ M+Na^+$) 1143.38, found 1143.25 (100%) (Supporting Information, Figure S3). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.18 (12H, t, $NCH_2\underline{CH_3}$, J=7.1 Hz), 3.33 (8H, q, $N\underline{CH_2}CH_3$, J=7.1 Hz), 6.28 (2H, dd, Xanthene-H, J_1=8.9 Hz, J_2=2.2 Hz), 6.48 (2H, d, Xanthene-H, J=2.2 Hz), 6.50 (2H, d, Xanthene-H, J=8.9 Hz), 6.78 (1H, dd, Phen-H), 6.85 (1H, d, Phen-H), 7.10 (1H, d, Phen-H), 7.17 (1H, s, Phen-H), 7.19 (1H, d, Ar-H), 7.51 (2H, m, Ar-H), 7.98 (1H, d, Ar-H), 9.26 (1H, d, N=C-H), 10.85 (1H, d, Phen-OH) (Supporting Information, Figure S4). Elemental analysis. found (calcd.) (%): C, 74.93 (74.98); H, 6.43 (6.47); N, 9.95 (9.99).

The intermediate rhodamine B hydrazide was prepared referring to the literature [34] with some modifications as follows. To a vigorously stirred solution of rhodamine B (1.20 g, 2.6 mmol) in 100 mL anhydrous ethanol at room temperature, 5.0 mL of hydrazine hydrate (80%) was added dropwise. After the addition, the mixture was heated to reflux in an oil bath. When the reaction finished, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. Dichloromethane (30 mL) and water (30 mL) were added to dissolve the resultant solid. The organic layer was collected, washed twice with water and dried over anhydrous Na_2SO_4. Filtration of sodium sulfate and evaporation of the solvent gave crude solid product, which was further purified by silica gel column chromatography using petroleum ether/ethyl acetate (1/1, *v*/*v*) containing 1% (*v*/*v*) triethylamine as eluent. White solid was obtained in 74.0% yield. ESI-MS for $C_{28}H_{32}N_4O_2$: *m*/*z*, calcd. ($M+H^+$) 457.25, found 457.58 (4 %); ($2\ M+Na^+$) 935.17, found 935.58 (100%) (Supporting Information, Figure S5). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.18 (12H, t, $NCH_2\underline{CH_3}$, J=7.0 Hz), 3.36 (8H, q, $N\underline{CH_2}CH_3$, J=7.0 Hz), 3.63 (2H, bs, NH_2), 6.30 (2H, dd, Xanthene-H, J_1=9.0 Hz, J_2=2.4 Hz), 6.44(2H, d, Xanthene-H, J=2.4 Hz), 6.48 (2H, d, Xanthene-H, J=9.0 Hz), 7.13 (1H, dd, Ar-H, J_1=5.4 Hz, J_2=3.3 Hz), 7.46 (1H, d, Ar-H, J=3.3 Hz), 7.47 (1H, d, Ar-H, J=3.3 Hz), 7.96 (1H, dd, Ar-H, J_1=5.4 Hz, J_2=3.3 Hz). (Supporting Information, Figure S6). Elemental analysis. found (calcd.) (%): C, 73.63 (73.66); H, 7.03 (7.06); N, 12.24 (12.27).

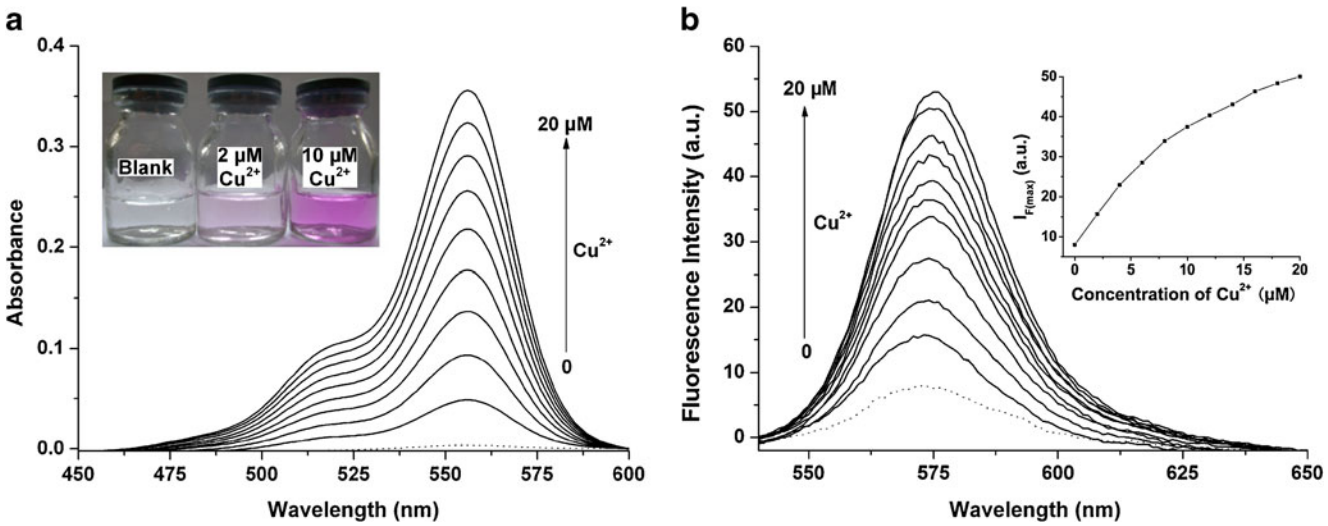


Fig. 1 Cu^{2+}-induced variations of the absorption (**a**) and the fluorescence spectra (**b**) of **RhB-pMOSal** in 50 mmol L^{-1} Tris-buffer/acetonitrile (1/1, *v*/*v*, pH 7.0) solution

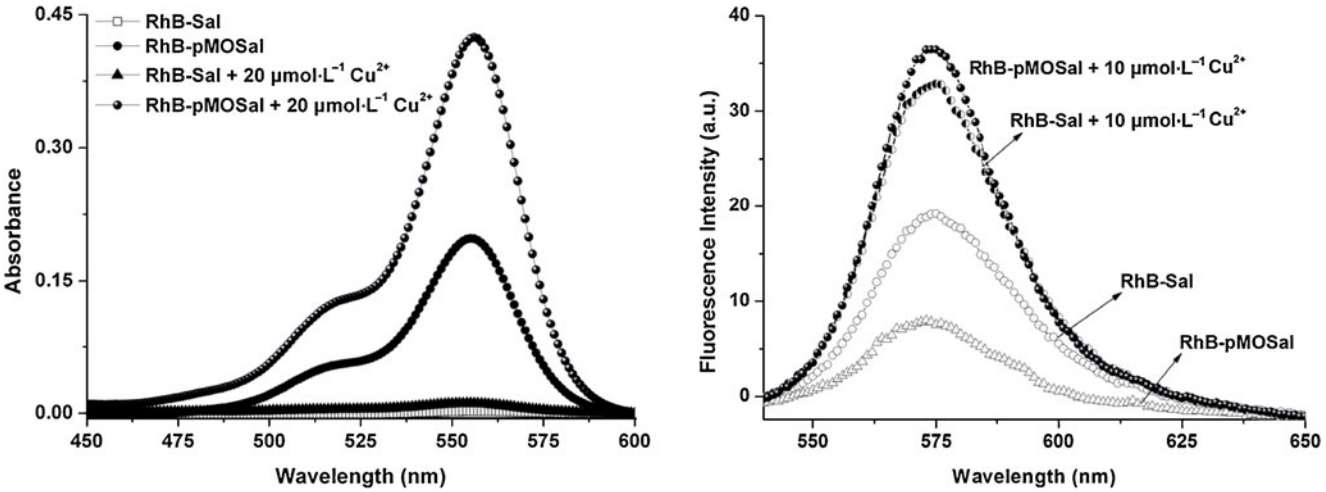


Fig. 2 Spectral response of **RhB-pMOSal** and **RhB-Sal** to Cu^{2+} in 50 mmol L^{-1} Tris-buffer/acetonitrile (1/1, *v*/*v*, pH 7.0) solution

Results and discussion

Fluorescence response of **RhB-pMOSal** to solution pH

Rhodamine-based compounds are usually sensitive to solvent character and solution pH, etc. [17]. A suitable pH scope in which **RhB-pMOSal** is capable of acting as a chemosensor for metal ions was firstly investigated. As shown in Figure S7, with the solution acidity increasing, the fluorescence of **RhB-pMOSal** (excited at 520 nm) in 50% aqueous Tris-buffered acetonitrile gradually enhanced along with a clear color changes from colorless to pink. Within the pH values of 10.0 to 7.0, the fluorescence and the solution color could hardly be observed, which suggests that the rhodamine moiety of **RhB-pMOSal** adopted a spirocyclic form and this tautomer was insensitive to such pH span. When pH was lower than 7.0, a remarkable fluorescence enhancement accompanied by appearance of pink was observed, which implies that the spirolactam ring of **RhB-pMOSal** was opened due to protonation [36] (Supporting Information, Figure S7). Considering the higher pH range could lead to hydrolysis for transition metal ions, the proper pH span for **RhB-pMOSal** to sense metal ions in aqueous solution was selected to be *ca* 7.0. An aqueous Tris buffer with pH value of 7.0 was used throughout the experiments. The ESI-MS result for **RhB-pMOSal** stayed in neutral Tris-buffered acetonitrile solution for 6 days indicates this compound is highly stable (Supporting Information, Figure S8).

Absorption and fluorescence variation of **RhB-pMOSal** in the presence of Cu^{2+}

The electronic absorption and fluorescence spectra of **RhB-pMOSal** in Tris-buffer/acetonitrile (1/1, *v*/*v*, pH 7.0) solution are presented in Fig. 1. As shown in the figure, **RhB-pMOSal** (10 μmol L^{-1}) shows only a very weak absorption and emission (excitation at 520 nm), which is ascribed to its spirolactam form dominating in the solution [6]. The characteristic absorption band appears in the range of 450–600 nm with a λ_{max} of 556 nm ($\varepsilon = 3.37 \times 10^2$ L mol^{-1} cm^{-1}). Upon addition of Cu^{2+} to the **RhB-pMOSal** solution, the absorption enhanced dramatically accompanied by an appearance of a new shoulder peak at *ca* 521 nm. The absorbance increased gradually with increasing Cu^{2+} concentration and the solution color turned instantaneously from colorless to clear pink (Fig. 1a, inset).

Similar to the absorption response, a significant enhancement of fluorescence corresponding to the delocalization in the xanthenes moiety of rhodamine [37] occurred (Fig. 1b). Meanwhile, the maximum emission wavelength underwent a slight red shift from 573 to 576 nm. When the

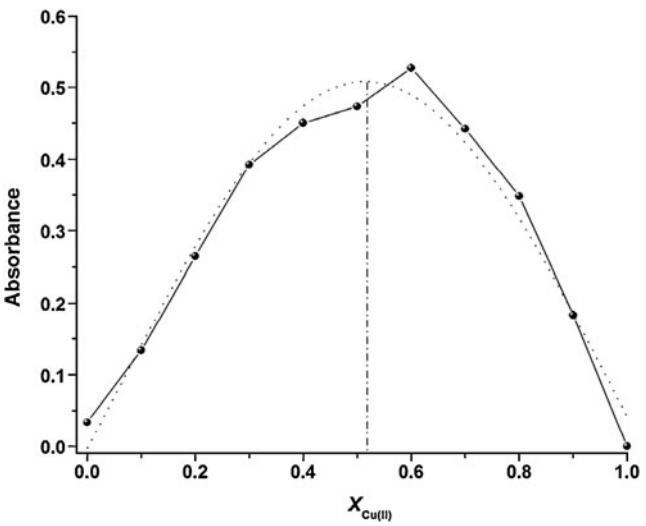


Fig. 3 Job's plot evaluated from the absorption spectra of **RhB-pMOSal** and Cu^{2+} at 556 nm in 50 mmol L^{-1} Tris-buffer/acetonitrile (1/1, *v*/*v*, pH 7.0) solution

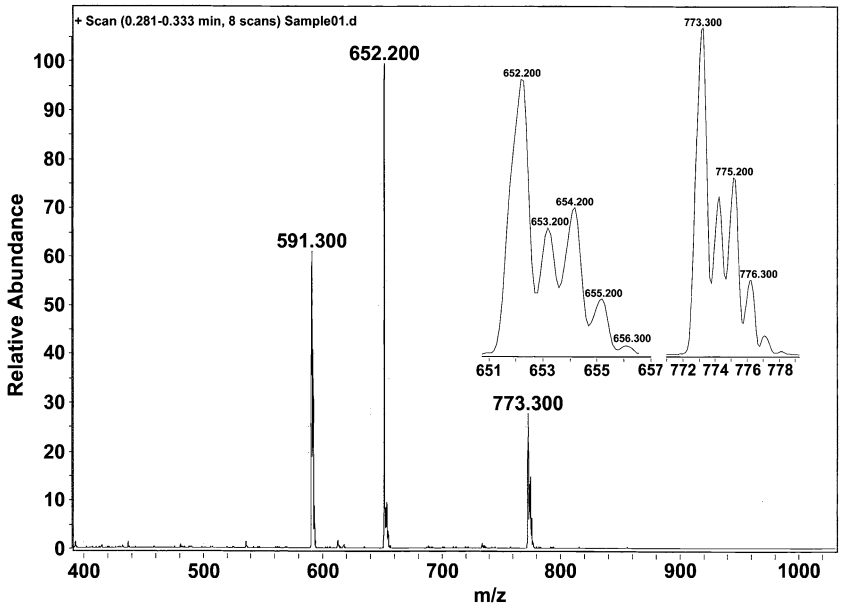


Fig. 4 ESI-MS spectrum of **RhB-pMOSal** (10 μmol L^{-1}) and Cu^{2+} (10 μmol L^{-1}) in 50 mmol L^{-1} Tris-buffer/acetonitrile (1/1, *v*/*v*, pH=7.0) solution

concentration of Cu^{2+} reached to 10 μmol L^{-1}, approximate 65 and 6-fold enhancements in the absorption (at 556 nm) and fluorescence (at 576 nm) were observed, respectively, which were much more sensitive than the known compound **RhB-Sal** for Cu^{2+} (*ca* 30 and 2-fold, respectively) under the same conditions (Fig. 2). The spectroscopic variations suggest that Cu^{2+} ion coordinated to **RhB-pMOSal**, resulting in the spirolactam ring open and concomitant formation of **RhB-pMOSal**-Cu(II) complex. Similar to the previously reported [21], copper(II) could chelate with the carbonyl oxygen, imino nitrogen, and phenol oxygen of **RhB-pMOSal**. The sensitivity difference between **RhB-pMOSal** and its analogue **RhB-Sal** for Cu (II) may be ascribed to the additional methoxy group at *para*-position of benzene ring of **RhB-pMOSal**, which could enhance the conjugation effect, and thus enhance the binding capacity of **RhB-pMOSal** to Cu(II). Fitting of the Job's plot evaluated from the absorption spectra of **RhB-pMOSal** and Cu^{2+} at 556 nm gave rise to a 1:1 stoichiometry for the complex (Fig. 3), which was confirmed by the ESI-MS result (Fig. 4) and the Benesi-Hildebrand method [34].

When assuming a stoichiometry of 1:1 for **RhB-pMOSal**-Cu(II), the association constant (K_a) of **RhB-pMOSal** with Cu^{2+} was determined using the Benesi-Hildebrand equation as follow.

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

A and A_0 is the absorbance of **RhB-pMOSal** solution in the presence and absence of Cu^{2+}, respectively; $A_{\max}$ is the saturated absorbance of **RhB-pMOSal** in the presence of excess amount of Cu^{2+}; $[Cu^{2+}]$ is the concentration of Cu^{2+} ion added (mol L^{-1}).

Plotting of $1/(A–A_0)$ versus $1/[Cu^{2+}]$ showed a liner relationship (Fig. 5), which suggests that **RhB-pMOSal** bound with Cu^{2+} in a 1:1 stoichiometry. The association constant (K_a) was determined from the slope to be 3.09×10^4 L mol^{-1}.

Moreover, when an appropriate amount of EDTA was added to the **RhB-pMOSal**-Cu(II) solution, an instant color change from pink to almost colorless and a simultaneous fluorescence quenching were observed. The ESI-MS results provided a direct evidence that **RhB-pMOSal** molecule was liberated from the **RhB-pMOSal**-Cu(II) complex (Supporting Information, Figure S9). In Fig. 4, there are

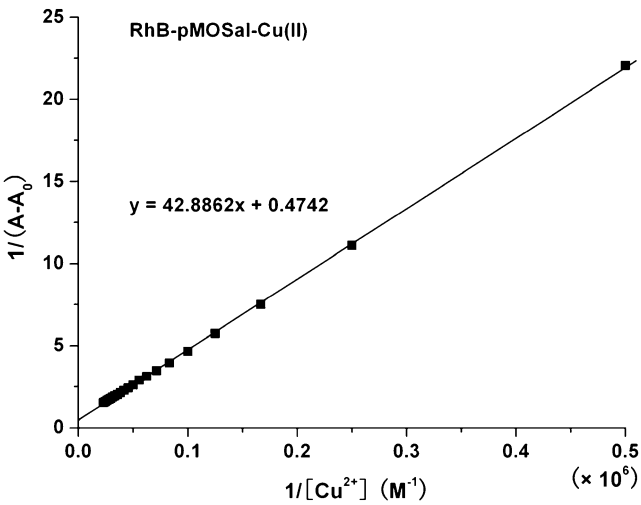


Fig. 5 Benesi-Hildebrand plot (absorbance at 556 nm) of **RhB-pMOSal** using eq. 1, assuming 1:1 stoichiometry for association between **RhB-pMOSal** and Cu^{2+}

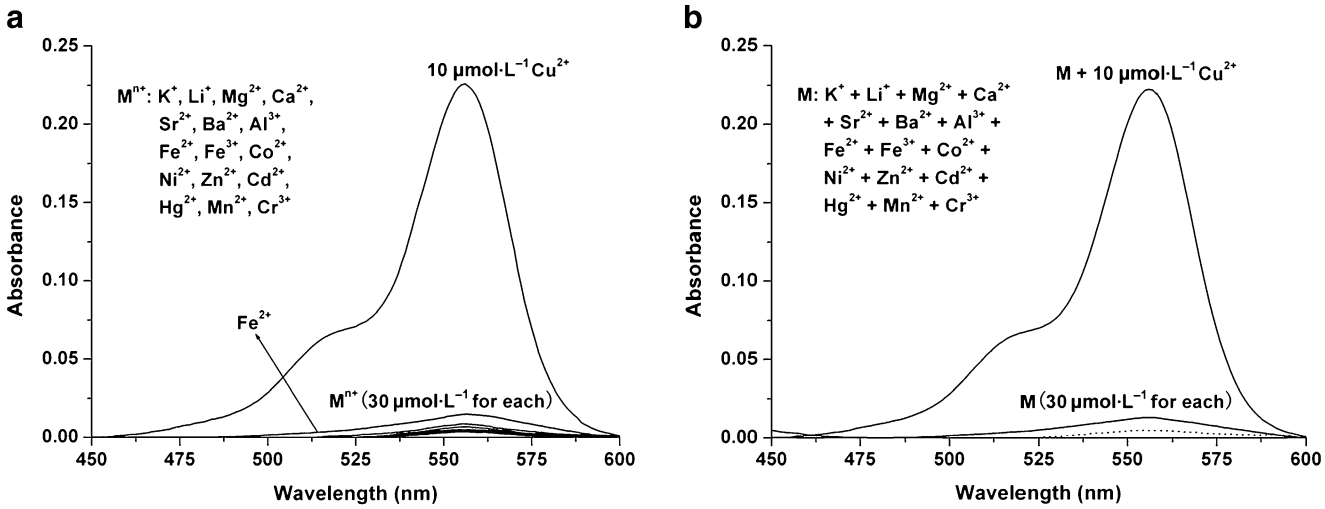


Fig. 6 Absorption spectra of **RhB-pMOSal** in the presence of different metal ions (**a**) and the effect of the mixed metal ions on the Cu^{2+}-induced absorption of **RhB-pMOSal** (**b**)

three peaks at *m*/*z* of 591.30, 652.20 and 773.30 corresponding to $[M + H^+]^+$ (calcd. 591.29), $[M - H^+ + Cu^{2+}]^+$ (calcd. 652.21), and $[M - H^+ + Cu^{2+} + Tris]^+$ (calcd. 773.28), respectively. While in Figure S9, the intensity of peaks at *m*/*z*=652.20 and 773.30 decreased dramatically whereas the peak at *m*/*z*=591.30 increased. These results indicated clearly that the binding of **RhB-pMOSal** with Cu^{2+} and the subsequent spirolactam ring opening are a reversible process, and furthermore, compound **RhB-pMOSal** may act as a turn-on chemosensor for Cu^{2+} in aqueous solution.

Selective sensing of Cu^{2+} ion in aqueous solution

The selectivity is one of the essential requirements for a chemosensor to signal a specific species in a complex system. To validate the selectivity of **RhB-pMOSal** for sensing Cu^{2+}, common metal ions including alkali, alkaline earth, and transition-metal ions were investigated under the same conditions (50 mmol L^{-1} Tris-buffer/acetonitrile solution, 1/1, *v*/*v*, pH 7.0). When each of the tested metal ions such as Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, Cd^{2+}, Cr^{3+}, etc (30 μmol L^{-1} for each) was added to the **RhB-pMOSal** solution, respectively, its absorbance and color hardly changed. Only ferrous ion (Fe^{2+}) led to a faint pink and a weak absorption enhancement. However, a strong absorption around 556 nm together with a shoulder peak around 521 nm was observed when 10 μmol L^{-1} Cu^{2+} was syringed into the **RhB-pMOSal** solution containing above mixed metal ions (Fig. 6a). When each of the above metal ions was mixed and reversely added to the **RhB-pMOSal** solution containing 10 μmol L^{-1} Cu^{2+}, only slight enhancement in absorption but no further color changes was observed

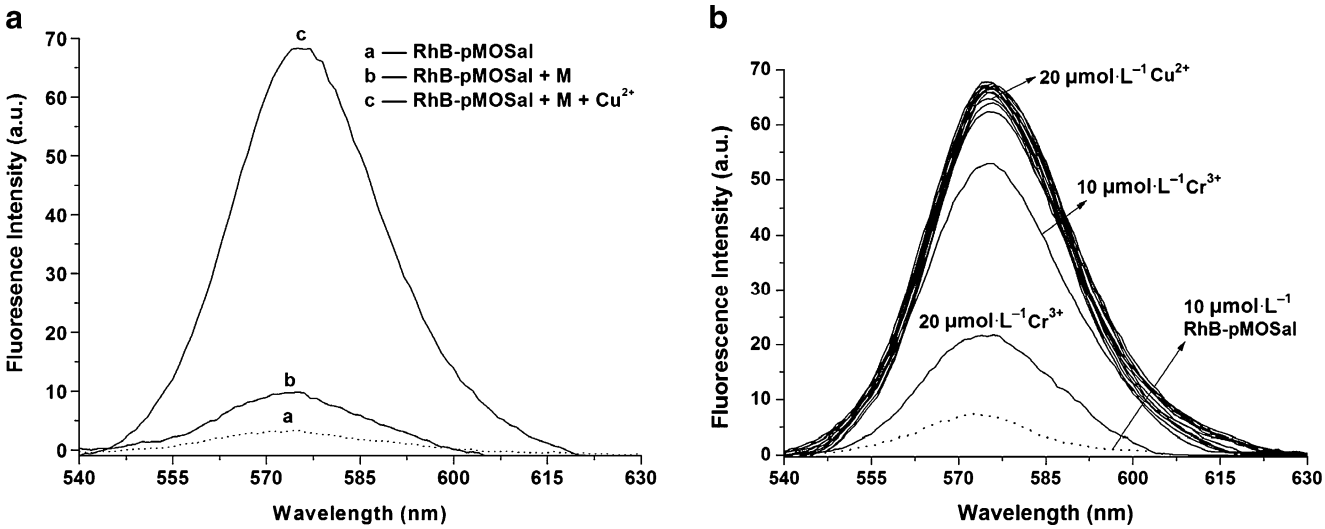


Fig. 7 Effect of various metal ions on the fluorescence of **RhB-pMOSal** in Tris-buffered acetonitrile (1/1, *v*/*v*, pH=7.0) solution

(Fig. 6b), which indicates a good selectivity of **RhB-pMOSal** for Cu^{2+} ion in aqueous solution. Such distinct effect was so substantial that it could act as a naked-eye chemosensor for Cu^{2+}.

The results obtained from the fluorimetric response of **RhB-pMOSal** to all above metal ions corroborated its selectivity for Cu^{2+}. Figure 7 presents the fluorescence spectral changes of **RhB-pMOSal** (10 μmol L^{-1}) in Tris-buffered acetonitrile solution upon addition of various metal ions (30 μmol L^{-1} for each). The alkali and alkaline-earth metal cations hardly caused interference, and transition-metal and heavy-metal ions except Cr^{3+} ion resulted in a weak response of **RhB-pMOSal**. In contrast, upon addition of Cu^{2+} (20 μmol L^{-1}) into **RhB-pMOSal** (10 μmol L^{-1}) solution containing mixed interfering metal ions (30 μmol L^{-1} for each), a remarkable emission centered at 576 nm in addition to an obvious absorption enhancement was observed (Fig. 7a). Furthermore, the results obtained from an independent experiment indicated that the Cu^{2+}-induced fluorescence enhancement of **RhB-pMOSal** was not greatly influenced by subsequent addition of other metal ions except for Cr^{3+} ion (Fig. 7b). Chromium (III) can greatly quench the Cu^{2+}-induced fluorescence of **RhB-pMOSal** under the same conditions, which could be avoided by previously removing Cr^{3+} through elevation of solution pH. All of these results reveals that **RhB-pMOSal** is highly selective for Cu^{2+} over the competing cations tested in aqueous solution.

Conclusion

The rhodamine-based derivative **RhB-pMOSal** in Tris-buffered acetonitrile aqueous solution displayed almost no absorption and week fluorescence. Upon addition of Cu^{2+} ion at micromolar level, significant enhancement of its fluorescence centered at 573 nm accompanied by obvious absorption around 556 nm corresponding to an instantaneous and reversible "turn-on" pink was observed. Approximate 65 and 6-fold enhancement in the absorbance at 556 nm and fluorescence intensity at 573 nm were estimated when 10 μmol L^{-1} Cu^{2+} was added to the **RhB-pMOSal** solution. The results obtained from the disturbance experiments indicated that both changes in the fluorescence and absorption of **RhB-pMOSal** were remarkably selective for Cu^{2+} over various competing metal ions, which meets the basic requirements for a chemosensory reagent. Chromium (III) was able to quench the fluorescence to some extent; however, its disturbance could be eliminated by hydrolysis at higher pH before sensing Cu^{2+} in practice. In comparison with the known **RhB-Sal**, **RhB-pMOSal** exhibited higher sensitivity toward Cu^{2+} in neutral aqueous solution.

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