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Rhodamine-derived Schiff base for the selective determination of mercuric ions in water media

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ABSTRACT

A new rhodamine-derived Schiff base (**RS**) was synthesized and its sensing property to metal ions was investigated by UV/vis and fluorescence spectroscopies. Addition of Hg^{2+} ions to the aqueous solution of **RS** gave a visual color change as well as significantly fluorescent enhancement, while other ions including Pb^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} ions did not induce any distinct color/spectral changes, which constituted a Hg^{2+}-selective fluorescent *OFF–ON* chemosensor. The Hg^{2+}-induced ring-opening of spirolactam of rhodamine in **RS** resulted in the dual chromo- and fluorogenic observation.

1. Introduction

Mercury, one of the most prevalent toxic metal elements in the environment, can easily pass through biological membranes such as skin, respiratory, and gastrointestinal tissues [1]. When absorbed in the human body, mercury causes damage to the central nervous and endocrine system. A variety of symptoms are observed upon mercuric exposure including digestive, kidney, and especially neurological diseases [2]. Concerns over toxic exposures to mercury provide motivation to explore new methods for monitoring Hg^{2+} ions from biological and environment samples. Several methods, including atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry, electrochemical sensoring, and the use of piezoelectric quartz crystals, make it possible to detect low limits of Hg^{2+} ions [3–6]. However, these methods require expensive equipment and involve time-consuming and laborious procedures that can be carried out only by trained professionals. Alternatively, analytical techniques based on fluorescence detection are very popular because fluorescence measurements are usually very sensitive (parts per billion/trillion), easy to perform, and inexpensive [7–11]. Furthermore, the photophysical properties of a fluorophore can be easily tuned using a range of routes: charge-, electron-, energy-transfer, the influence of the heavy metal ions as well as the destabilization of non-emissive n–π^* excited states [7]. Consequently, a large number of papers involving fluorescent chemosensors have been published [7–9,12–15]. However, many of these systems displayed shortcomings in practical use, such as the lack of aqueous solubility, cross-sensitivities toward other metal ions, short emission wavelength, narrow pH span, and delayed response, etc. Accordingly, developing new and practical sensing systems for Hg^{2+} ions is still a challenge.

Rhodamine-based fluorescent chemosensors have been received considerable attention for the sensing of heavy metal ions in recent years because of their particular structural properties [16,17]. As well known, the rhodamine with spirolactam structure is non-fluorescent, whereas ring-opening of the spirolactam gives rise to a strong fluorescence emission. This property provides an ideal mode to construct *OFF–ON* fluorescent switch sensors. Moreover, they have a longer emission wavelength (about 550 nm), which is often preferred to serve as reporting groups for analyte to avoid the influence of the background fluorescence (below 500 nm) [18,19]. Actually, to date, many spirolactam-based fluorescent chemosensors have been developed for Hg^{2+} ions, in which rhodamine–hydrazine structure is widely applied for the ring-opening of spirolactam [8,10,20–23], while rhodamine–ethylenediamine structure was still relatively scarce [24,25].

Herein, we reported a rhodamine–ethylenediamine derived Schiff base (**RS**) for the selective determination of Hg^{2+} ions in aqueous solution (Scheme 1). Rhodamine–ethylenediamine was selected as a good binding framework for Hg^{2+} ions, and

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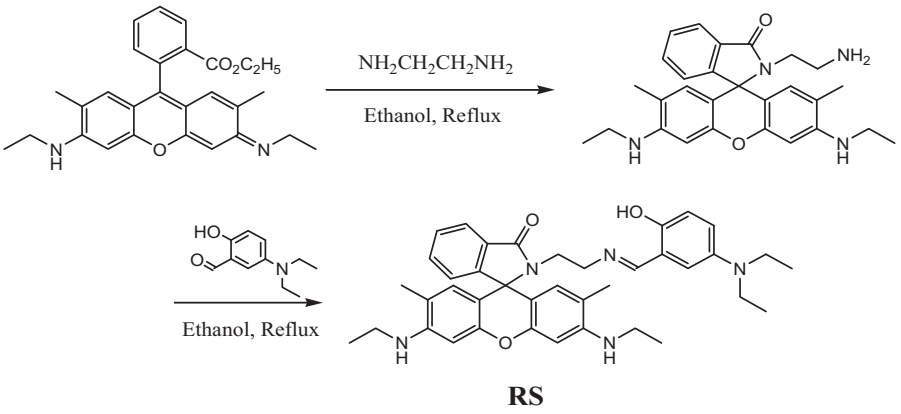


Scheme 1. Synthetic route of chemosensor **RS**.

the attached 4-diethylaminosalicylaldehyde provided additional binding groups to induce the ring-opening of spirolactam upon complexation with Hg^{2+} ions. As expected, upon addition of Hg^{2+} ions, the aqueous solution of **RS** gave rise to an obviously enhanced fluorescence as well as visual change from colorless to pink, indicating that Hg^{2+} did induce the ring-opening of spirolactam in **RS**.

2. Experimental

2.1. Instruments and reagents

All UV–vis spectra and fluorescence spectra were recorded in S-3100 spectrophotometer and Hitachi F-4500 fluorescence spectrometer, respectively. ^{1}H NMR spectra were recorded at 400 MHz, Bruker-400 instrument. Mass spectra were recorded at Finnigan 4021C MS-spectrometer.

Rhodamine 6G, ethylenediamine, and 4-diethylaminosalicylaldehyde were purchased from Aldrich and used without further purification. All cationic compounds of Pb^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ ions (perchlorate or chloride), were purchased from Aldrich and used as received. Ethanol for spectral detection was HPLC reagent without fluorescent impurity and H_2O was deionized water. All solvents were analytical reagents.

2.2. Synthesis

2.2.1. Synthesis of N-(rhodamine-6G)lactam–ethylenediamine

The preparation of *N*-(rhodamine-6G)lactam–ethylenediamine was based on the reported procedure [10]. Rhodamine 6G (958 mg, 2 mmol) was dissolved in 20 mL of hot ethanol, followed by addition of ethylenediamine (1 mL, 15 mmol). The reaction mixture was refluxed for 4 h till the fluorescence of the solution was disappeared. The reaction was cooled to room temperature, and the precipitate was collected and washed with absolute ethanol for three times. Crude product was purified by recrystallization from acetonitrile to give 824 mg of *N*-(rhodamine-6G)lactam–ethylenediamine (white solid) in 90.3% yield. ^{1}H NMR ($CDCl_3$): δ 7.95 (d, 1H), 7.47 (t, 2H), 7.05 (d, 1H), 6.34 (s, 2H), 6.23 (s, 2H), 3.50 (t, 2H), 3.24 (t, 4H), 2.39 (t, 2H), 1.90 (s, 6H), 1.36 (t, 6H). FAB-MS (M+H$^+$): m/z = 457.

2.2.2. Synthesis of chemosensor *RS*

A portion of *N*-(rhodamine-6G)lactam–ethylenediamine (456 mg, 1.0 mmol) and 4-diethylaminosalicylaldehyde (212 mg, 1.1 mmol) were combined in absolute ethanol (30 mL). The reaction solution was refluxed for 6 h under N_2 atmosphere and stirred for another 2 h at room temperature to form precipitate. The solid was filtrated, washed with ethanol for three times. Crude product was purified by recrystallization from absolute ethanol to give 514 mg of **RS** (white crystal) in 81.2% yield. ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 1H), 7.66 (s, 1H), 7.46 (s, 2H), 7.06 (m, 1H), 6.93 (m, 1H), 6.36 (s, 2H), 6.17 (m, 3H), 3.56–3.48 (m, 4H), 3.38–3.36 (m, 4H), 3.22 (m, 4H), 1.88 (s, 6H), 1.34–1.31 (t, 6H), 1.19 (t, 6H). FAB-MS (M+H$^+$): m/z = 632.

2.3. General procedures of spectral detection

A 1.0×10^{-3} M stock solution of **RS** was prepared in C_2H_5OH and diluted to 1.0×10^{-5} M in 1:4 EtOH/H_2O solution (v/v). The metal ion stock solutions are dissolved in deionized water with a concentration of 1.0×10^{-3} M for the spectral analysis. Each time a 2 mL solution of **RS** was filled in a quartz cell of 1 cm optical path length, and different stock solutions of metal ions were added into the quartz cell gradually by using a micro-pipette. The volume of anionic stock solution added was less than 100 μL with the purpose of keeping the total volume of testing solution without obvious change. Excitation wavelength was 500 nm and the temperature is 20 °C.

3. Results and discussion

Fig. 1 shows spectral changes of **RS** in C_2H_5OH/H_2O solution (1/4, v/v) upon addition of various competitive metal ions, such as Hg^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ ions. From UV/vis spectra of **RS** (5 μM) (Fig. 1A), we can clearly observe a new absorption band centered at 530 nm in the presence of 5 equiv. of Hg^{2+} ions. In contrast, other metal ions do not lead to any distinct spectral changes. On the other hand, fluorescence spectra (Fig. 1B) also show a similar result, which is well consistent with that of UV/vis spectra. Addition of only 5 equiv. Hg^{2+} ion results in an obviously enhanced fluorescence peaked at 556 nm (*OFF–ON*), while other metal ions including Pb^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ ions do not give rise to any fluorescence increases. Further experiments for Hg^{2+}-selective sensing were performed using 5 μM of **RS** in aqueous solution in the presence of multifarious ions including Pb^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ ions (1 equiv., respectively). Upon addition of Hg^{2+} ions, the solution above still displays a distinctly enhanced fluorescence. Both UV/vis and fluorescence results indicate that **RS** shows a good selectivity and sensitivity toward Hg^{2+} ions over other competitive ions.

Fig. 2 shows a spectral variation of **RS** upon the gradual addition of $Hg(ClO_4)_2$. The UV–vis titration spectra of Hg^{2+} ions was conducted using 5 μM of **RS** in ethanol aqueous solution at pH ~7. Upon the addition of increasing concentrations of the Hg^{2+} ion

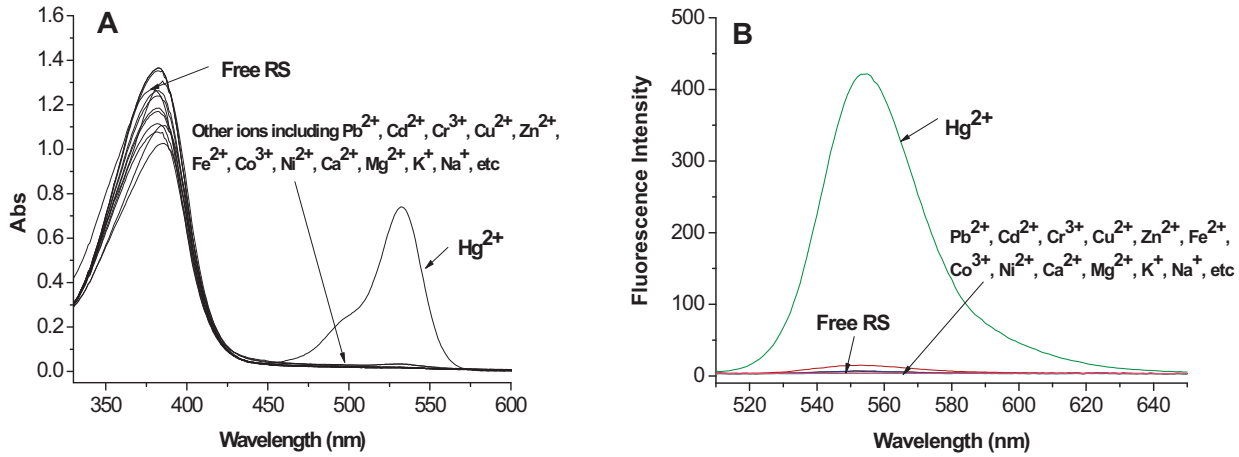


Fig. 1. (A) UV–vis spectra and (B) fluorescence spectra of **RS** (5 μM) in 1:4 C_2H_5OH/H_2O (v/v) at pH ~7 upon addition of different metal ions including Hg^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{3+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ ions (25 μM, respectively) with an excitation wavelength at 500 nm.

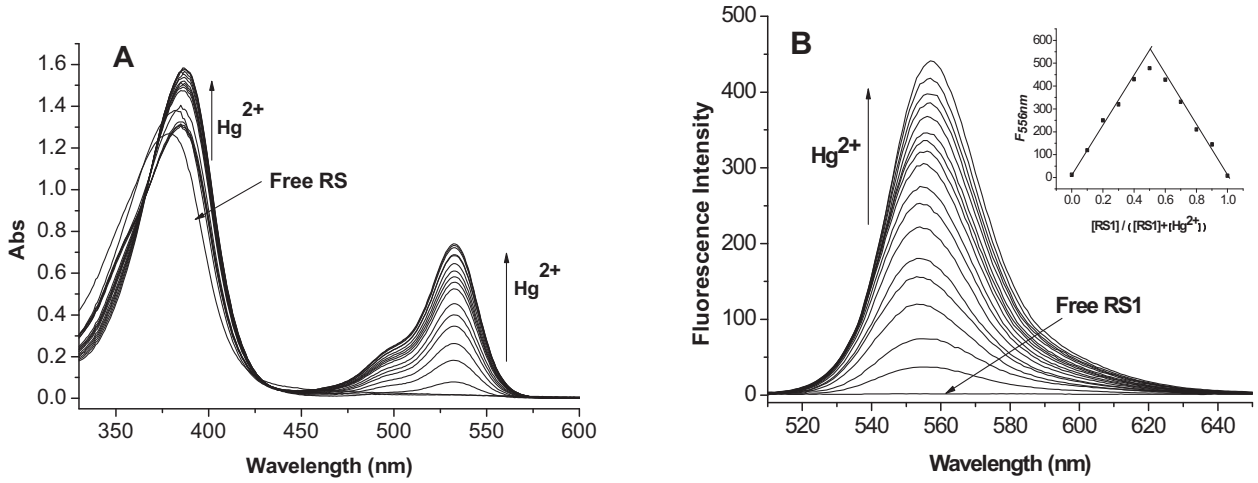
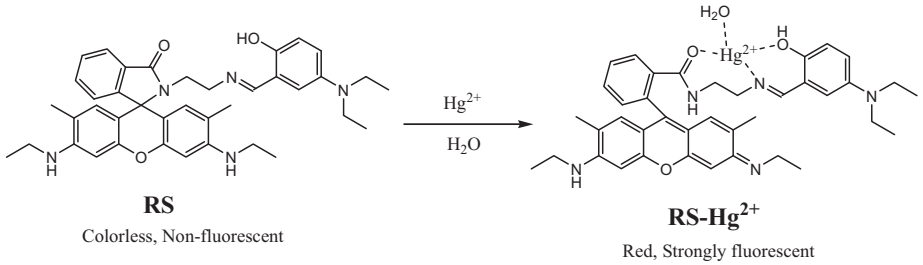


Fig. 2. (A) UV–vis titration spectra and (B) fluorescence titration spectra of **RS** (5 μM) in C_2H_5OH/H_2O solution (1/4, v/v) at pH ~7 upon gradual addition of $Hg(ClO_4)_2$ with an excitation wavelength at 500 nm (Hg^{2+} concentrations: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, and 25 μM).

(0–25 μM), a new absorption band centered at 530 nm appeared with increasing intensity, which induced a clear color change from colorless to pink (Fig. 2A). On the other hand, for the fluorescence titration spectra of **RS**, in the presence of Hg^{2+} ions there was also a new emissive peak at 556 nm (Fig. 2B), which was in good consistency with the results of UV–vis spectra. Both UV–vis and fluorescence data lead to a significant fluorescence *OFF–ON* signal. From the molecular structure and spectral results of **RS**, it is probably concluded that the addition of Hg^{2+} ions induced its complexation with carbonyl group in spirolactam, N atom in Schiff base, and hydroxyl in salicylaldehyde. As a result, a ring-opening of the spirolactam in rhodamine framework took place, observed by the distinct color change and fluorescence *OFF–ON*, as depicted in Scheme 2.

Job's plot analysis (inset of Fig. 2B) indicates probe **RS** and Hg^{2+} form a 1:1 complex in aqueous solution. On the basis of 1:1 stoichiometry, we can calculate the stability constant of the complex through a nonlinear curve fitness as following expression [6]:

$$Y = Y_0 + \frac{Y_{\lim} - Y_0}{2}\left\{1 + \frac{C_M}{C_L} + \frac{1}{K_s C_L} - \left[\left(1 + \frac{C_M}{C_L} + \frac{1}{K_s C_L}\right)^2 - 4\frac{C_M}{C_L}\right]^{1/2}\right\}$$



Scheme 2. The proposed mechanism for Hg^{2+}-induced ring-opening of spirolactam in **RS** with fluorescence *OFF–ON*.

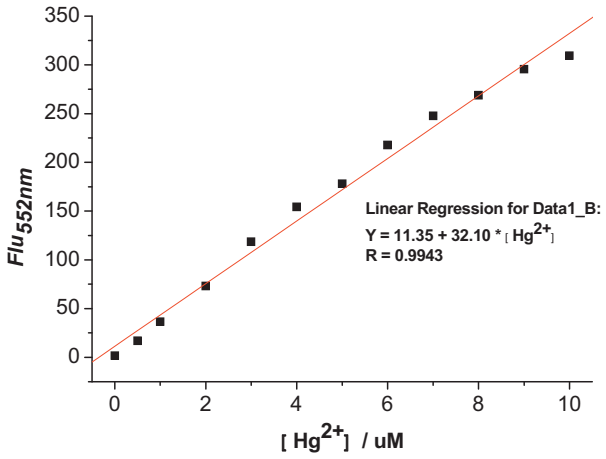


Fig. 3. Variation of the fluorescence intensity at 552 nm of **RS** (5 μM) in C_2H_5OH/H_2O solution (1/4, v/v) at pH ~7 *vs* the concentration of Hg^{2+} ions.

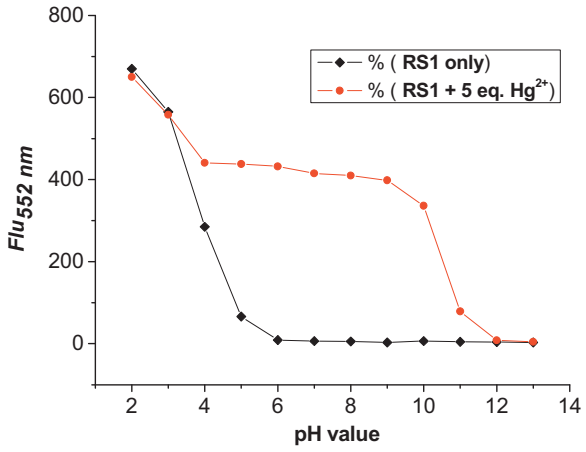


Fig. 4. Fluorescence intensity (552 nm) of **RS** (5 μM) in the absence and presence of 5 equiv Hg^{2+} ions in C_2H_5OH/H_2O solution (1/4, v/v) with different pH conditions.

where Y and Y_0 are the fluorescence intensity at 552 nm of the aqueous solution of **RS** in the presence and absence of Hg^{2+} ions; C_M and C_L are the concentrations of Hg^{2+} ions and **RS**; K_s is the stability constant of the complex **RS**/**Hg^{2+}**. According to fluorescence titration data, the stability constant between **RS** and **Hg^{2+}** was determined to be 3.5×10^6 with a good relationship ($R = 0.995$).

The high sensitivity of **RS** for Hg^{2+} ions might be used to generate a calibration curve for quantitative measurement of Hg^{2+} ions in aqueous solution. By adding Hg^{2+} ions with different concentrations ranged from 0 to 10 μM, the fluorescence intensity of **RS** (5 μM) at 552 nm was recorded to generate a calibration curve. As shown in Fig. 3, when Hg^{2+} concentration added was from 0.5 to 10 μM, an almost perfect linearity ($I_{552} = 11.35 + 32.10 \times [Hg^{2+}]$, $R = 0.9943$) was found between fluorescence intensity of **RS** and Hg^{2+} concentration, indicating a linear detection range for Hg^{2+} determination.

For practical application, the proper pH environment of this new chemosensor is also evaluated. Fig. 4 shows that for free **RS**, at acidic conditions (pH < 6), the ring-opening of rhodamine framework took place due to the strong protonation. When pH > 6, no significant ring-opening was observed. However, in the presence of Hg^{2+} ions, there was an obvious fluorescence *OFF–ON* change between pH 6 and 10. Thus, chemosensor **RS** can detect Hg^{2+} ions with a wide pH span (6–10) because in this region **RS** with Hg^{2+} induces a remarkable fluorescence *OFF–ON*, whereas **RS** without Hg^{2+} does not lead to such change.

4. Conclusions

In conclusion, we report a new rhodamine-derived Schiff base (**RS**) serving as a sensitive chemosensor, which can show a good selectivity toward Hg^{2+} over other competitive ions in aqueous solution. Hg^{2+} ions can cause the solution of **RS** to be subject to an obvious color change and fluorescence *OFF–ON*, which is arisen from the ring-opening of spirolactam. **RS** can determine Hg^{2+} ions with a good linear relationship between the concentration range from 0.5 to 10 μM. Two good features of this system, a remarkably high selectivity toward Hg^{2+} ions over miscellaneous competitive ions and a wide pH span (6–10), make it promising to determine Hg^{2+} ions for the practical analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.12.010.

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