

Two Highly Sensitive and Selective Colorimetric “Off-On” Rhodamine-Based Fluorescent Chemosensor for Hg(II) in Aqueous Media

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Abstract Two novel rhodamine derivatives were designed and synthesized. They were successfully characterized by HR-MS, ^1H NMR and ^{13}C NMR. They were found to exhibit a reversible colorimetric response and exhibit high selectivity and sensitivity for Hg(II) ion over other commonly coexistent metal ions. Their selectivity is excellent, and the detection of Hg(II) at ppb level is possible. The colorimetric and fluorescent response to Hg(II) can be conveniently detected even by the naked eye, which provides a facile method for visual detection of Hg(II).

Keywords Rhodamine · Hg^{2+} · Fluorescence · Off-on

Introduction

The design of artificial chemosensors for selective and sensitive quantification of biologically and environmentally

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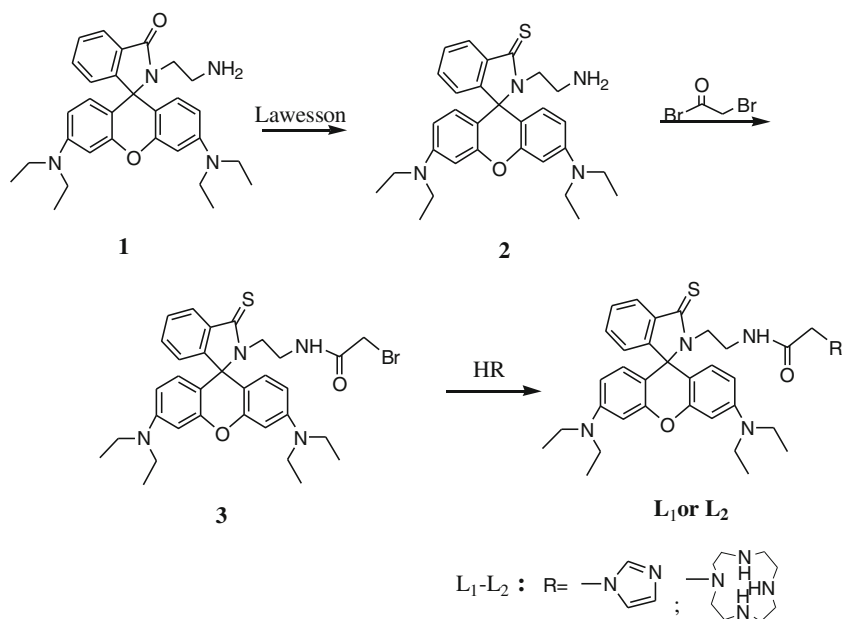
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heavy- and transition-metal ions in solution has attracted wide-spread interests of chemists, biologists, clinical biochemists and environmental scientists [1–3]. Mercury is a highly toxic and widespread global pollutant [4]. The mercuric ion, Hg [II], combines with both inorganic and organic ligands, which can readily penetrate through biological membranes even at very low concentrations, the US Environmental Protection Agency (EPA) standard for the maximum allowable level of inorganic Hg^{2+} in drinking water is 2 ppb [5]. There have been reported several traditional analytical techniques for Hg^{2+} include atomic absorption spectroscopy, cold vapor atomic fluorescence spectrometry and gas chromatography. These methods, however, require not only complicated instrumentation but also a long measuring time. Therefore, the design and development of fluorescent probes for Hg^{2+} has attracted a great deal of attention [6–8].

Several fluorescent chemosensors for Hg^{2+} have been reported, in which their signals are transduced either through a Hg^{2+} -complexation [9–12] or through a Hg^{2+} -induced desulfurization reaction [13–16]. The former mode has some shortcomings, such as emission quenching as signal output, cross-sensitivities with other metallic cations, poor biocompatibility and low water-solubility. Though the latter mode has high selectivity toward Hg^{2+} , these chemosensors are irreversible and can result in another contamination (HgS). In addition, these irreversible chemosensors cannot be used to monitor both the increase and the decrease of Hg^{2+} concentration in the environment or some biological metabolite. Therefore, development of reversibly fluorescent chemosensors for Hg^{2+} determination with light “off-on” and high selectivity is still highly desirable.

On the basis of the well-known spirolactam (nonfluorescent) to open-ring amide(fluorescent) equilibrium, rhodamine frameworks have been considered an

Scheme 1 Synthetic route of the title compounds



ideal mode for the construction of the off-on systems that have frequently been utilized to design fluorescence-enhanced probes for metal ions [17–24]. Recently, our group has developed a series of rhodamine-based chemosensors to sense metal ions [25–27]. We have even reported a rhodamine-based chemosensor for Hg^{2+} by a desulfurization reaction [28]. However, the irreversible reaction restricts its biological application. In this paper, two rhodamine-based chemosensors were designed for reversible and highly selective Hg^{2+} determination with a light “off-on” switch (Scheme 1).

Experimental Section

Apparatus

Fluorescence spectra measurements were performed on a HITACHI F-4500 fluorescence spectrophotometer, and the excitation and emission wavelength band passes were both set at 4.0 nm. Absorption spectra were measured on a Lambda 35. UV/VIS spectrometer, Perkin Elmer precisely. The melting points were determined by an X-4 microscopic melting point apparatus with a digital thermometer (Shanghai, China). The pH was measured with a Model pHs-3C

Fig. 1 Absorbance spectra of $10 \mu M$ L2 in the presence of 50 eq. different metal ions in $CH_3OH/H_2O(9:1, v/v)$. Insert shows the photos of sensor L2 with different metal ions

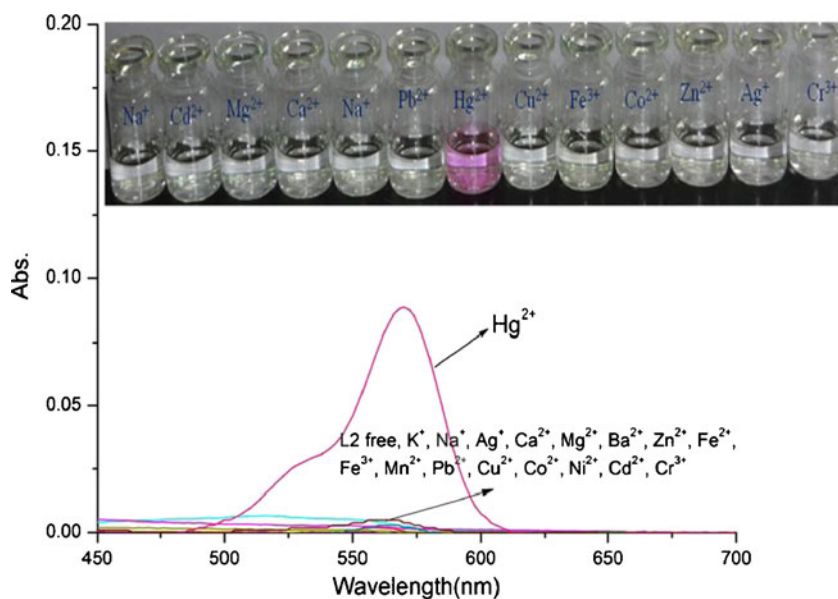
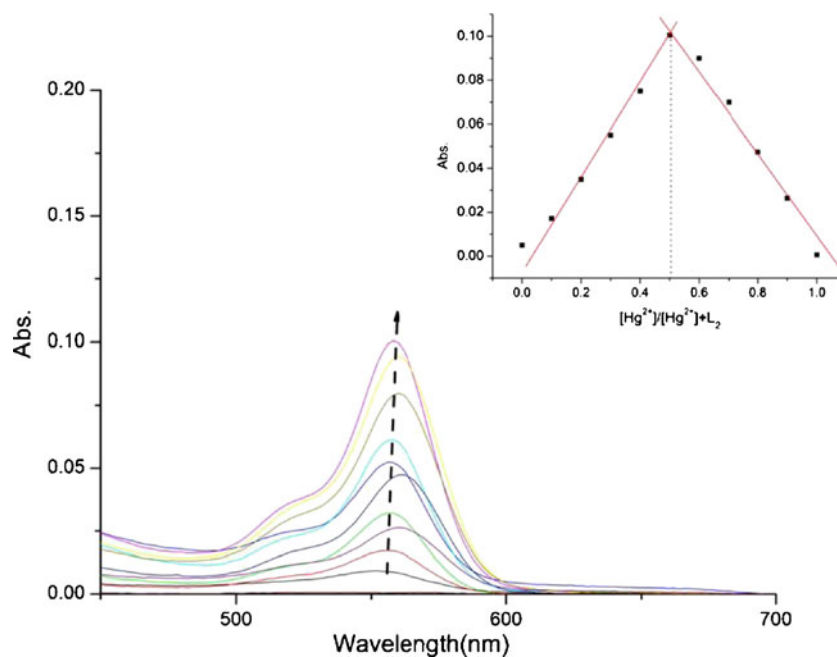


Fig. 2 Job's plot evaluated from the absorption spectra of **L2** and Hg^{2+} in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9/1, v/v) solution. Inset: Job's plot of changes of absorbance at 558 nm, the total concentration of $[\text{Hg}^{2+}] + [\text{L2}]$ was 100 μM



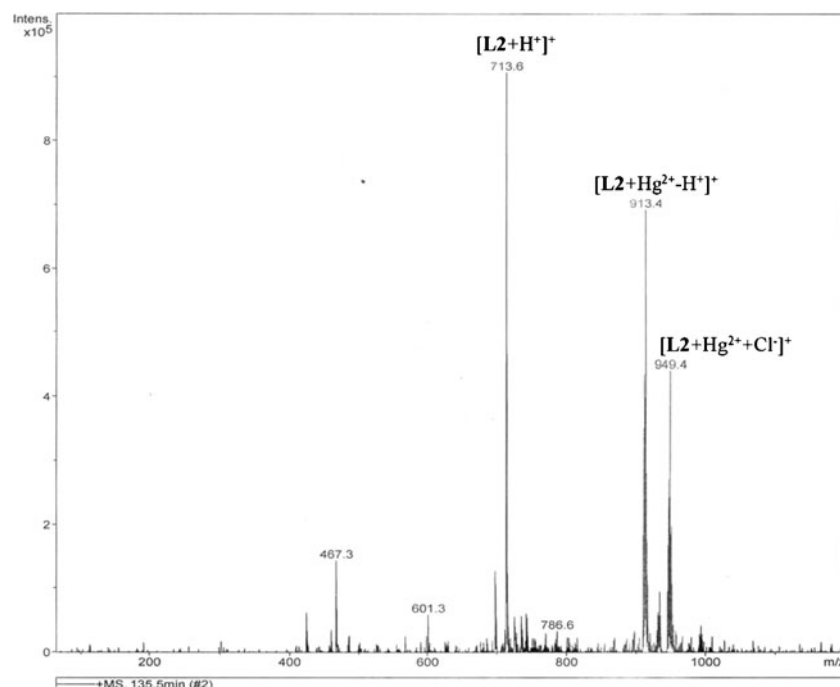
meter (Shanghai, China). ^1H and ^{13}C NMR spectra were recorded using a Bruker DTX-400 spectrometer. Samples were dissolved in CDCl_3 and placed in 5 mm NMR tubes. TMS was used as internal reference. ESI mass spectra were carried out on an HPLC Q-T of HR-MS spectrometer (Waters Micromass) by using methanol as mobile phase.

Materials

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for

chemical synthesis and analysis were purified according to standard procedures. Double distilled water was used throughout the experiment. Chloride salts of metal ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Pb^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Cr^{3+} , Hg^{2+}) and the nitrate salt of Ag^+ ions were used to evaluate the metal ion binding properties by synthesized compounds. The metal ions were prepared as 10.00 mmol/L in water solution. The stoichiometry of each compound and Hg^{2+} was determined by Job's method from the obtained absorption spectroscopic data. In the determination, the sum of concentration of Hg^{2+} and each compound

Fig. 3 ESI mass spectra (positive) of **L2** in the presence of HgCl_2 (5 equiv), indicating the formation of a 1:1 metal-ligand complex



was kept at 100 μM and the molar ratio of Hg^{2+} was changed from 0 to 1.0.

Experimental details can be found in the Supporting Information. Compounds **1** and **2** were conveniently synthesized according to the procedure as published in the literatures [25].

Synthesis of Compound 3

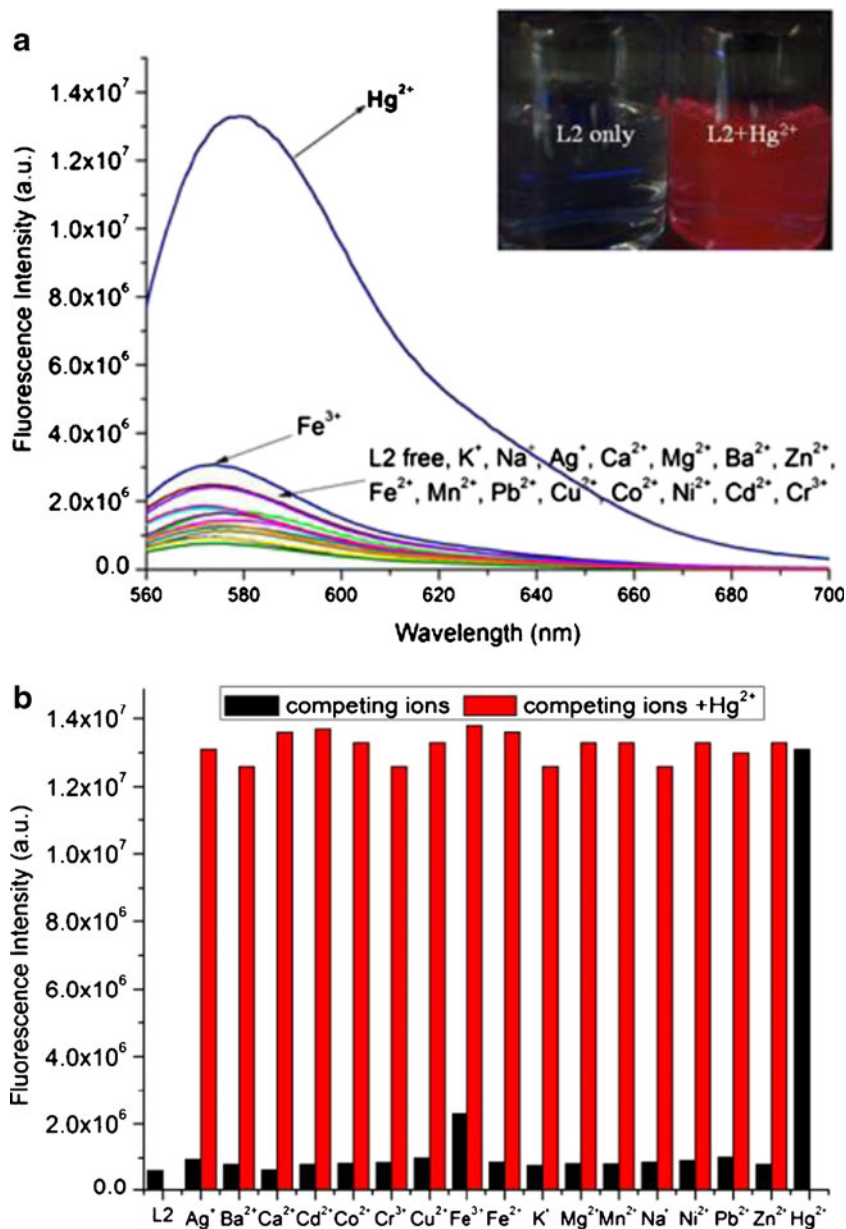
To a solution of bromoacetyl bromide (0.06 mL, 0.71 mmol) in dry dichloromethane (20 mL) was added K_2CO_3 (98 mg, 0.71 mmol). The mixture was cooled in an ice bath and then compound **2** (235 mg, 0.47 mmol) dissolved in 15 mL dry dichloromethane was added dropwise over 30 min. The reaction mixture was stirred at ice bath for about 2 h. It

was washed successively with 2 % Na_2CO_3 water solution (3×30 mL). The organic layer was dried over Na_2SO_4 and evaporated under vacuo. The residue **3** obtained was directly used for next step without further purification.

Synthesis of Compound L2

To a stirred solution of compound **3** (62 mg, 0.1 mmol) in dry toluene (30 mL), 1,4,7,10-macrocyclic polyamide (125 mg, 0.725 mmol) was added. The solution was refluxed for about 48 h under dry N_2 . The resulting solution was concentrated by evaporation and dissolved in 10 mL ethanol. Concentrated HCl was added to the solution, and the precipitated HCl salt of the unreacted cyclen was removed by filtration. The residue was

Fig. 4 **a** The fluorescence spectra of **L2** (10 μM) upon addition of 100 μM of Hg^{2+} and various other metal ions in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9/1, v/v), Inset: Fluorogenic response of **L2** (10 μM) with Hg^{2+} (10 eq.) under UV illumination (365 nm). **b** Fluorescence intensity (at 579 nm) of **L2** (10 μM) upon the addition of 100 μM Hg^{2+} in the presence of 100 μM background metal ions in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9/1, v/v), $\lambda_{\text{exc}} = 550$ nm

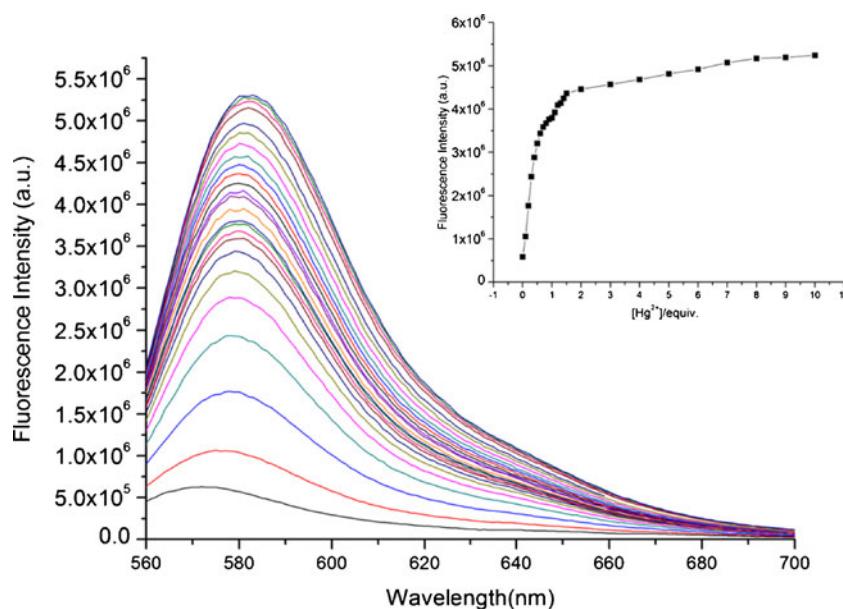


concentrated by evaporation, dissolved in 10 ml water, and washed with CHCl_3 . Aqueous NaOH solution (5 M, 15 ml) was added to the solution and extracted with CH_2Cl_2 (10 ml \times 5). The organic layer was dried over Na_2SO_4 and concentrated by evaporation. The residue was dried in vacuo at 385 K for 8 h, affording **L2** as a yellow powder. M.p: 92–94 °C. Yield of **L2**: 84 %. ^1H NMR (400 MHz, CDCl_3 , ppm): 1.17 (t, 12 H, $J=6.8$ Hz); 2.71 (m, 16 H); 3.06 (d, 4 H, $J=12.8$ Hz); 3.34 (q, 4 H, $J=6.7$ Hz); 3.68 (t, 2 H, $J=7.2$ Hz); 6.34 (m, 6 H); 7.09 (d, 1 H, $J=4$ Hz); 7.46 (s, 2 H); 8.16 (t, 1 H, $J=18.6$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 12.61, 14.17, 22.71, 29.38, 31.94, 36.72, 40.04, 43.83, 44.38, 46.12, 46.66, 47.31, 47.91, 53.51, 59.55, 73.37, 73.59, 97.68, 97.99, 98.13, 103.32, 103.83, 108.15, 123.27, 124.89, 125.01, 128.41, 128.50, 128.70, 132.38, 132.52, 137.61, 149.16, 151.49, 153.24, 171.62, 191.16. HR-MS: calcd for $[\text{C}_{40}\text{H}_{57}\text{N}_8\text{O}_2\text{S}^+]$: 713.4320. Found: 713.4324 $[\text{M}+\text{H}]^+$.

Synthesis of Compound L1

Similar method, **L1** was obtained in 65 % yield. ^1H NMR (400 MHz, CDCl_3 , ppm): 1.16 (t, 12 H, $J=6.6$ Hz); 2.95 (t, 2 H, $J=7.8$ Hz); 3.33 (q, 8 H, $J=6.9$ Hz); 3.78 (t, 2 H, $J=5.4$ Hz); 4.50 (s, 2 H); 6.20 (t, 4 H, $J=9.4$ Hz); 6.38 (s, 2 H); 6.48 (s, 1 H); 7.04 (m, 3 H); 7.51 (s, 3 H); 8.15 (d, 1 H, $J=6.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 12.54, 29.68, 39.27; 42.78, 44.39, 50.10, 73.62, 97.79, 103.39, 108.51, 120.04, 123.28, 125.23, 128.19, 128.71, 129.81, 132.85, 137.62, 137.94, 149.28, 150.98, 153.13, 166.43, 193.06. ESI-MS: m/z 609 $[\text{M}+\text{H}]^+$; HR-MS: calcd for $[\text{C}_{35}\text{H}_{41}\text{N}_6\text{O}_2\text{S}^+]$: 609.3006. Found: 609.3007 $[\text{M}+\text{H}]^+$.

Fig. 5 The fluorescence emission spectra of **L2** (10 μM) in the presence of different concentrations of Hg^{2+} (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 eq. respectively) in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9/1, v/v), $\lambda_{\text{ex}}=550$ nm. Inset: Changes in the emission intensity at 580 nm



Results and Discussion

UV–vis Spectral Responses of L2

As shown in Fig. 1, UV–vis spectrum of **L2** (10 μM) exhibited only very weak bands over 450 nm. Addition of 10 equiv Hg^{2+} into solution immediately resulted in a significant enhancement of absorbance at about 558 nm simultaneously the color change into red. Under the identical condition, no obvious response could be observed upon the addition of other ions including K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Pb^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Cr^{3+} (Fig. 1). The results demonstrated that **L2** was characteristic of high selectivity toward Hg^{2+} over other competitive metal ions.

To further investigate the interaction of Hg^{2+} and **L2**, an ultraviolet titration experiment was carried out (Fig. 2). To determine the stoichiometry of the mercury–ligand complex, Job’s method for absorbance measurement was applied. As shown in Fig. 2 inset, the absorbance reached a maximum when the ratio of $[\text{Hg}^{2+}]/\{[\text{Hg}^{2+}]+[\text{L2}]\}$ was 0.5, indicating a 1:1 stoichiometry of the Hg^{2+} to **L2** in the complex. To confirm the stoichiometry between **L2** and Hg^{2+} ion, ESI-MS analysis was conducted. As shown in Fig. 3, Mass peaks at m/z 913.4 corresponding to $[\text{L2}+\text{Hg}^{2+}-\text{H}^+]^+$ (calcd=913.4) and m/z 949.4 corresponding to $[\text{L2}+\text{Hg}^{2+}+\text{Cl}^-]^+$ (calcd=949.3) were clearly observed when 5 equiv of Hg^{2+} was added to **L2**, which gave a remarkable evidence for the formation of the 1:1 complex of Hg^{2+} with **L2**.

Fluorescence Spectral Responses of L2

As shown in Fig. 4a, **L2** (10 μM) showed a very weak fluorescence in the absence of metal ions. When 10 equiv.

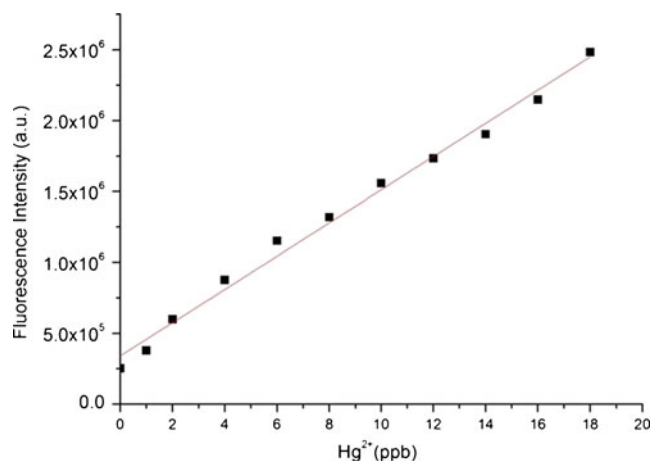


Fig. 6 The fluorescence intensity at 579 nm of compound **L2** (0.1 μM) as a function of the Hg^{2+} concentration (0–20 ppb) in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9/1, v/v), $\lambda_{\text{ex}}=550$ nm

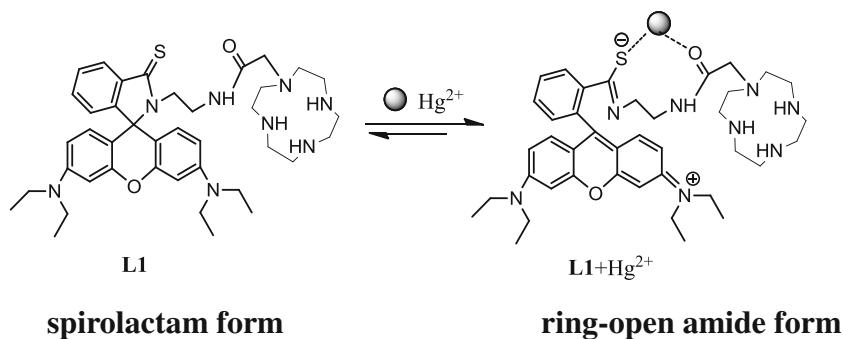
metal ions of Zn^{2+} , Mg^{2+} , Ca^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , Mn^{2+} , Fe^{3+} , Ba^{2+} , Ni^{2+} , Fe^{2+} , K^+ , Ag^+ , Co^{2+} , Cr^{3+} and Na^+ were added, no obvious changes on fluorescence intensity and color could be observed. However, under the same conditions, the addition of Hg^{2+} (10 equiv.) resulted in a remarkably enhancement of fluorescence (17-fold) at 579 nm. This strongly suggested that **L2** can serve as a high sensitivity for Hg^{2+} . Moreover, the enhancement in fluorescence intensity resulting from the addition of Hg^{2+} is not influenced significantly by the addition of the background metal ions (Fig. 4b).

To further investigate the binding stoichiometry of **L2** and Hg^{2+} ion, a fluorescence titration experiment was carried out. An increase of fluorescence intensity of **L2** could be observed with gradual addition of Hg^{2+} ion (Fig. 5). The increment saturated after adding 1.0 equiv of Hg^{2+} (Fig. 5, inset), this also indicating a 1:1 stoichiometry of the Hg^{2+} to **L2** in the complex.

The Detection of Hg^{2+}

Generally, one of the most important and useful applications for a fluorescent chemosensor is the detection of metal ions, especially for heavy metals. The limit of the chemosensor

Scheme 2 Proposed mechanism for the fluorescence enhancement of **L2** upon the addition of Hg^{2+}



for Hg^{2+} ion has been tested. When **L2** was employed at 0.1 μM in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9/1, v/v, pH 7.0), the fluorescent intensity of **L2** was proportional to the concentration of Hg^{2+} added (Fig. 6). The detection limit was measured to be 1.0 ppb, establishing that **L2** was capable of distinguishing safe and toxic levels of Hg^{2+} in drinking water according to the U.S. (EPA) standard (2 ppb).

Mechanism

Cyclen (1,4,7,10-tetraazacyclododecane) is good hydrophilic groups and can coordinate strongly with many transition metal cations. In order to improve target compound's water solubility, we introduce 1,4,7,10-macrocyclic polyamide into rhodamine. It is well-known that cyclen coordinates with one metal cation in organic media. Many metal cation can coordinate with cyclen, but the binding constant is low [29–31]. In aqueous media, coordination of cyclen nitrogens with the Hg^{2+} may weaker than that with water. As compound **L2** contained a macrocycle and an "S" group, based on the coordination of Hg^{2+} to the S atom, we assumed that **L2** may display a more fluorescence enhancement.

Considering the behaviors of absorption and fluorescence spectra, the turn-on response of **L2** may be explained by the spirocycle open-close mechanism. The free probe **L2** is the spirocyclic form, which is colorless and non fluorescent, whereas the coordination of Hg^{2+} leads to the spirocycle opening, resulting in an appearance of visible absorption and fluorescence. According to our knowledge [24], we propose a plausible mechanism which is illustrated in Scheme 2. In order to certify this binding model, we designed and synthesized compound **L1** which contained an imidazole group, and the colorimetric and fluorescent results of **L1** confirmed this binding model. The ultraviolet titration experiment, fluorescence titration experiment and ESI-MS all indicated a 1:1 stoichiometry of the Hg^{2+} to **L1** or **L2**. That means the imidazole or cyclen group has no coordination with Hg^{2+} ion.

The little discrepancy in recognizing Hg^{2+} of **L1** and **L2** may duo to the different solubility of cyclen (1,4,7,10-tetraazacyclododecane) and imidazole in water. As the macrocycle had a better solubility than imidazole in water,

and this may display a beneficial effect to the sensing effect of **L2** with Hg^{2+} in aqueous media.

Another direct evidence was obtained by comparing the IR spectra of **L2** and **L2**- $\text{Hg}(\text{II})$ in KBr disks, and the results were shown in Figs. S13 and S14. The peak at $1,671\text{ cm}^{-1}$, which corresponds to the amide carbonyl($\text{C}=\text{O}$) absorption drastically shifted to lower frequency upon the addition of excess $\text{Hg}(\text{II})$, indicating that the carbonyl oxygen coordinated with Hg^{2+} .

Further, it was of great interest to investigate the reversible binding nature of the sensor. To demonstrate the reversibility of **L2**, KI (10 eq.), as a strong affinity for Hg^{2+} , was introduced into the solution containing **L2** (10 μM) and Hg^{2+} (100 μM). Upon the addition of KI, the color of the mixture of **L2** and Hg^{2+} changed from red to colorless and the fluorescence intensity was decreased, indicating that Γ sequestered Hg^{2+} of the mixture, liberated the free **L2** (Fig. S12). Thus, **L2** can be classified as a reversible chemosensor not a chemodosimeter for Hg^{2+} ions.

Conclusion

In conclusion, we have developed two efficient rhodamine thiospirolactam-based fluorescent reversible chemosensor for Hg^{2+} . They exhibited a strong fluorescence enhancement upon addition of Hg^{2+} while showing almost no response to other cations. The significant changes in the fluorescence color could be used for naked-eye detection, the limit of detection of **L2** for Hg^{2+} in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9/1, v/v) was found to be 1 ppb. They may therefore be applicable as rhodamine-based turn-on type fluorescent chemosensors for Hg^{2+} .

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