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Research Article

Recognition Preference of Rhodamine Derivative Bearing Phthalimido Gly for Hg^{2+} by UV-Vis and Fluorescence Spectroscopy

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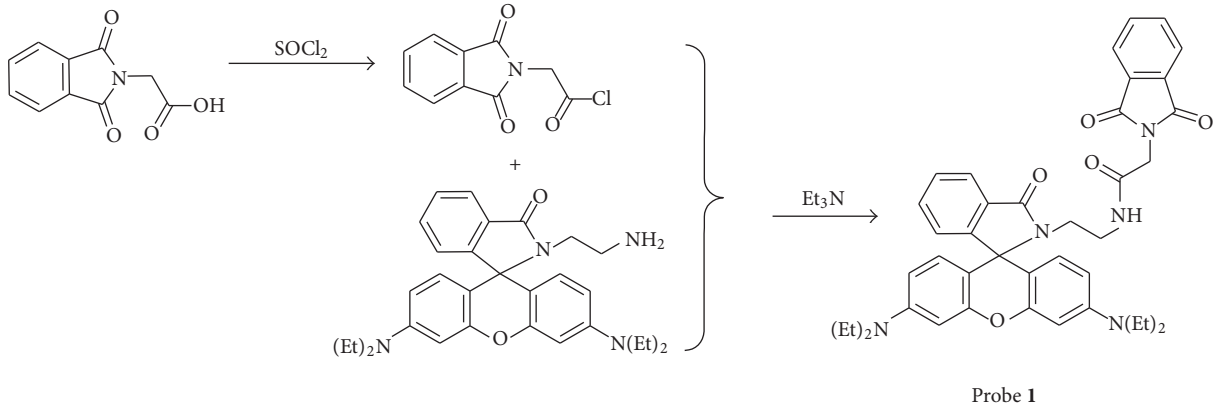
An effective Hg^{2+}-specific probe **1** was designed and prepared based on Phthalimido Gly modified rhodamine B. The sensing behavior of probe **1** was studied by UV-Vis and fluorescence spectroscopy. Probe **1** showed excellent high selectivity and sensitivity towards Hg^{2+} over commonly coexistent metal ions in neutral solution, which could be attributed to the Hg^{2+}-triggered ring opening of the spirolactam of the rhodamine moiety and the formation of a 1 : 1 **1**-Hg^{2+} complex. The limit of detection (LOD) based on $3\delta_{blank}/k$ was calculated to be 2.8×10^{-8} M, as well as an excellent linear relationship with the concentration of Hg^{2+} in the range from 0.1×10^{-6} to 1.0×10^{-6} mol/L ($R^2 = 0.98927$). In addition, the effects of pH, coexisting metal ions, and the reversibility were investigated in detail.

1. Introduction

The design and development of fluorescent chemosensors for detection of environmentally and biologically important metal cations (such as Hg^{2+}, Fe^{3+}, and Al^{3+}) are currently of significant importance [1–5]. More specifically, sensors directed toward the detection and measurement trace amounts of mercury ions which have enjoyed particular attention. The Hg^{2+} ion is considered highly dangerous because both elemental and ionic mercury can be converted into methyl mercuries by bacteria in the environment, which subsequently bioaccumulates through the food chain. Moreover, the extreme toxicity of mercury and its derivatives result from its high affinity for thiol groups in proteins and enzymes, leading to the dysfunction of cells and consequently causing health problems [6–8]. Current techniques for Hg^{2+} screening, fluorescence chemosensors offer a nondestructive and prompt detection of Hg^{2+} by a simple fluorescence enhancement (turn-on) or quenching (turn-off) response in biological, toxicological, and environmental monitoring, due to its simplicity and distinct advantages in sensitivity and selectivity to recognition of Hg^{2+} [9–14].

Among numerous chemosensors, Rhodamine B and its derivatives are a kind of excellent candidate for the construction of an off/on-type fluorescent chemosensor and well known for their desirable properties, including excellent spectroscopic properties, high extinction coefficient (>75,000 $cm^{-1}\,M^{-1}$), high fluorescence quantum yield, long absorption and emission wavelength elongated to the visible region [15–18]. The mechanism is based on the switch "off-on" of the spirocyclic moiety mediated by guest. On binding guest to the receptor, the spirocyclic form of rhodamine B which is colorless and nonfluorescent, whereas ring opening of the corresponding spirolactam induced by metal ions gives rise to strong fluorescence emission and a pink color [19–22].

Consequently, the design and development of fluorescent chemosensors for monitoring the level of Hg^{2+} in environmental and biological samples have attracted a great deal of attention. Herein, we introduced a rhodamine B derivative (probe **1**) bearing Phthalimido Gly group. In our condition,



Scheme 1: Synthetic routes of the probe **1**.

probe **1** exhibited prominent absorption and fluorescence enhancements to Hg^{2+} ions with a particular selectivity and excellent sensitivity and could be used for naked-eye detection.

2. Experimental Section

2.1. Materials and Instrumentation. All solvents and reagents were purchased from commercial sources and used as received without further purification. Solutions of metal ions were prepared with metal nitrate salts. Doubly-distilled water was used for all experiments. UV-Vis spectra were obtained on a Purkinje General TU-1901 UV/Vis spectrometer. The fluorescence spectra were recorded on a Hitachi F-4500 spectrofluorimeter with a quartz cuvette (path length, 1 cm). IR data were taken in KBr disks on TENSOR37 Fourier-transform infrared spectrometer. NMR spectra were recorded on a Bruker 300 MHz spectrometer with TMS as an internal standard and $CDCl_3$ as solvent.

The stock solution of **1** (2.0 mmol/L) was prepared by dissolving the requisite amount of it in methanol. Standard test solutions were prepared by appropriate dilution of the stock solution. A solution of the nitrate salts of the respective ions Na^+, K^+, Mg^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, Zn^{2+}, Ag^+, Ba^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+} was used to evaluate the metal ion binding properties of **1** (1.0×10^{-5} M) in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES, pH = 7.0. The solution was allowed to stand for 10 min at room temperature (25°C) before the absorption/fluorescence measurement was made. For fluorescence measurements, excitation was provided at 556 nm, and emission was collected from 450 to 700 nm. The excitation and emission slit widths were 5 nm and 10 nm.

2.2. Determination of Binding Constants. The binding constant was calculated from the absorption intensity titration curves according to Benesi-Hildebrand equation as follows [23]:

$$\frac{1}{A - A_0} = \frac{1}{K_a (A_{\max} - A_0)[c]} + \frac{1}{A_{\max} - A_0}, \quad (1)$$

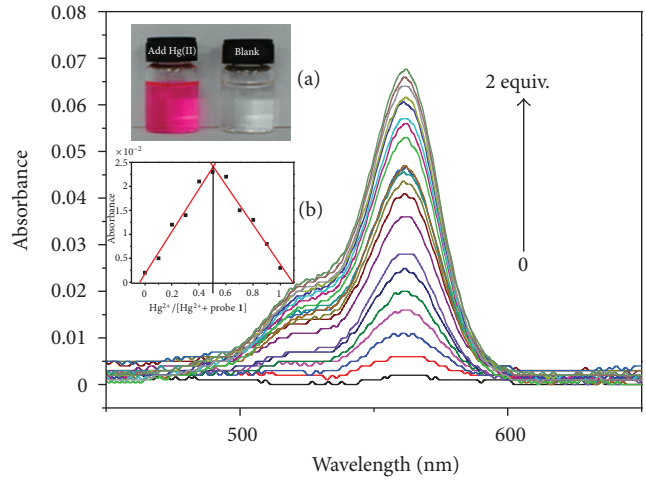


Figure 1: UV-vis absorption spectra of probe **1** (10.0 μM) in the presence of Hg^{2+} (0–2 equiv.) in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES pH = 7.0 solution at room temperature. Inset: (a) showing the change in the color of **1** (10 μM) upon addition of Hg^{2+} ions (2 equiv.); (b) Job's plot for determining the stoichiometry of probe **1** and Hg^{2+} ion by absorbance at 561 nm, the total concentration of $[Hg^{2+}] + [\mathbf{1}]$ was 10 μM.

where A and A_0 represent the absorbance of **1** in the presence and absence of Hg^{2+}, respectively, $A_{\max}$ is the saturated absorbance of **1** in the presence of excess amount of Hg^{2+}; [c] is the concentration of Hg^{2+} ion added (mol/L).

2.3. Synthesis of Probe **1**. (See Scheme 1). RhE was synthesized from rhodamine B by reaction with ethylenediamine in ethanol following a published procedure in a yield of 70% [24]. **1** was prepared by one-step of rhodamine ethylenediamine with Phthalimido Gly chloride at 0–5°C. Briefly, rhodamine ethylenediamine (1.88 g, 4 mmol) was dissolved in 20 mL dichloromethane in a 100 mL flask. An excess of triethylamine was added and 15 mL dichloromethane solution of Phthalimido Gly chloride (0.89 g, 4 mmol) was added to this solution. The reaction mixture was stirred 2 h

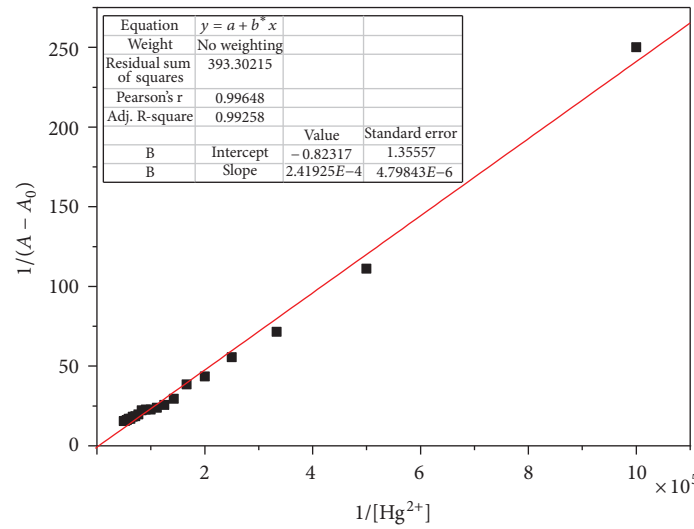


Figure 2: Benesi-Hildebrand plot (absorbance at 561 nm) of probe **1**, assuming 1 : 1 stoichiometry for association between **1** and Hg^{2+}.

at 0–5°C. After drying under reduced pressure, and pale yellow solid was observed. The target compound was further purified by column chromatography with CH_3OH/CH_2Cl_2 (1 : 5 v : v) to give 1.5 g of **1** in 78% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.92 (dd, 2H), 7.80 (dd, 2H), 7.39–7.49 (m, 3H), 7.07 (dd, 1H), 6.30–6.37 (m, 6H), 4.29 (s, 2H), 3.29–3.34 (m, 12H), 1.16 (t, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.19, 167.87, 166.16, 153.79, 153.17, 148.96, 133.96, 132.84, 132.55, 130.11, 128.43, 128.04, 123.86, 123.47, 122.68, 108.46, 104.49, 97.74, 65.67, 44.38, 41.55, 40.76, 39.29, 12.57. IR (KBr, ν/cm^{-1}): 3396, 3001, 2863, 1632, 1613, 1546, 1221, 1117, 996.

3. Results and Discussion

3.1. UV-Vis Spectral Characteristics. Like most of the spirocycle rhodamine B derivatives, due to its spirolactam form, the absorption spectra of free **1** (1.0×10^{-5} M) remained colorless and exhibited very weak absorbance from 450 to 650 nm and found to be very stable in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES pH = 7.0 solution system for more than one week. Upon incremental addition of Hg^{2+} ($0-2.0\times10^{-5}$ M) to probe **1** solution (1.0×10^{-5} M), the peak around 561 nm was formed and its intensity increased gradually with increasing Hg^{2+} concentrations (Figure 1), suggesting the formation of the ring-opened form of **1**. Moreover, the titration solution exhibited an obvious and visual color change from colorless to pink, which could be easily detected by the "naked-eye" (Figure 1, inset (a)).

For further determination the stoichiometry between Hg^{2+} and **1**, Job's plot analyses were also used. According to the continuous variations with a total concentration of $[Hg^{2+}] + [\mathbf{1}]$ as 1.0×10^{-5} M. (Figure 1, inset (b)). When the molar fraction of Hg^{2+} was 0.5, the absorbance exhibited a maximum, which demonstrates the 1 : 1 complex between **1** and Hg^{2+}.

When assuming a 1 : 1 stoichiometry for the probe **1**-Hg^{2+} complexation, the association constant (K_a) of the probe **1** with Hg^{2+} was determined using the Benesi-Hildebrand equation. Plotting of $1/(A - A_0)$ versus $1/[Hg^{2+}]$ showed a linear relationship (Figure 2), which indicates that probe **1** is bounded with Hg^{2+} in a 1 : 1 binding stoichiometry, and association constant (K_a) is being calculated as 6.78×10^4 M^{-1}.

3.2. Fluorescence Spectral Characteristics. The sensing behavior was investigated by the fluorescence measurement in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES pH = 7.0 solution upon excitation at 556 nm. As shown in Figure 3(a), upon the gradual addition of Hg^{2+} ($0-2 \times 10^{-5}$ mol/L), an emission band peaked at 581 nm significantly increased in fluorescence intensity. The titration reaction curve showed a steady and smooth increase until a plateau was reached (15.0 μM Hg^{2+}), The chemosensor exhibited very efficient fluorescence responding, which is attributed to the formation of **1**-Hg^{2+} complex as a result of which the nonfluorescent spirocyclic form of the receptor get opened leading to the formation of strongly fluorescent ring-opened amide form.

In addition, to see its practical applicability, the detection limit of **1** for Hg^{2+} was evaluated. The fluorescence intensity of **1** (1.0×10^{-5} mol/L) at 581 nm was found to increase linear relationship with the concentration of Hg^{2+} in the range of 0.1×10^{-6} to 1.0×10^{-6} mol/L (R^2 = 0.98927) (Figure 3. inset(a)). The detection limit is then calculated to be 2.8×10^{-8} M based on $3\delta_{blank}/k$ [25], where δ_{blank} is the standard deviation of the blank measurements, k is the slope between fluorescence intensity versus sample concentration. The results indicated that probe **1** is sensitive enough to detection of trace mercury ion in the environment.

Probe **1** coordinates with Hg^{2+} in a 1 : 1 stoichiometry. This is confirmed by a Job's plot (Figure 3, inset (b)). A maximum emission intensity was showed when the molecular fraction of Hg^{2+} was close to 0.5, which indicated

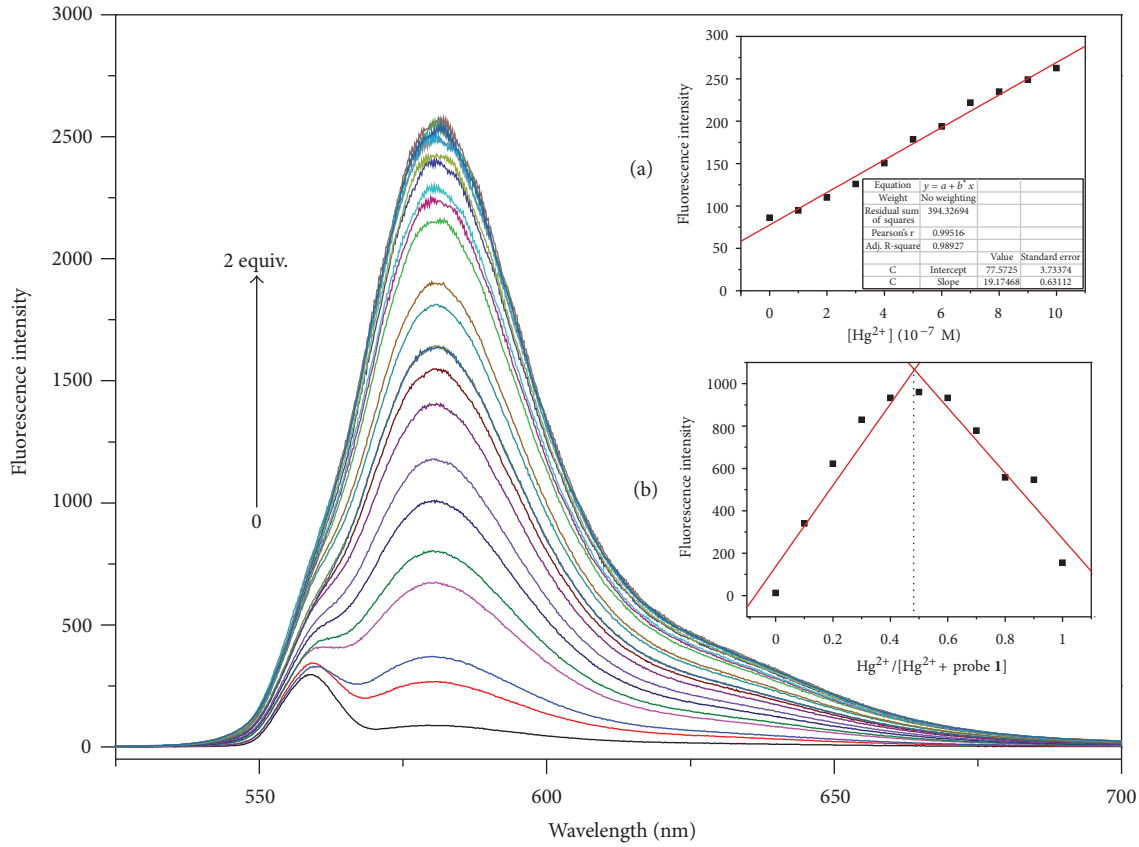


Figure 3: Fluorescence emission spectra of **1** (10.0 μM) in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES pH = 7.0 solution in the presence of increasing concentration of Hg^{2+} (0–2 equiv.) with an excitation of 556 nm. Inset: (a) fluorescence intensity of solution 1 versus the concentration of Hg^{2+} in the low concentration range (0.1×10^{-6} to 1.0×10^{-6} mol/L); (b) Job's plot according to the method for continuous variations, indicating the 1 : 1 stoichiometry for **1**-Hg^{2+}, the total concentration of [Hg^{2+}] + [**1**] was 10 μM.

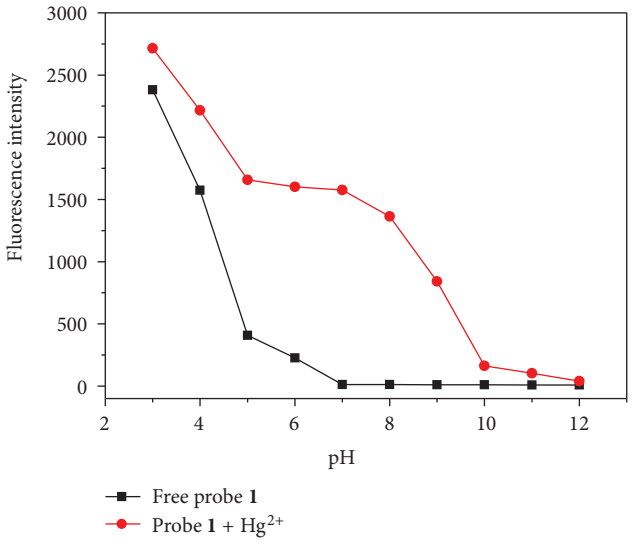


Figure 4: The effect of pH on the fluorescence (557 nm) of **1** in C_2H_5OH-water (4 : 6, v/v) solution, the pH was modified by adding 75% $HClO_4$ or NaOH (10%). Excitation: 556 nm, emission: 581 nm.

the 1 : 1 complex formation between **1** and Hg^{2+} with a total concentration of 1.0×10^{-5} M.

3.3. Effect of pH Value. To study the practical applicability, the sensitivity of the Hg^{2+} fluorescent probe **1** toward variations in the sample pH was examined in the absence and presence of the Hg^{2+} ion. Figure 4 clearly indicates that the free **1**, which has weak fluorescence between pH 7.0 and 12.0. However, the fluorescence intensity become strong when pH value below 7.0. It is due to that the ring opening of rhodamine took place for the strong protonation. Under identical condition, while addition of the Hg^{2+} ion, **1** showed a meaningful response between pH 5.0 and 9.0, because it can lead to a remarkable increase of fluorescence. Finally, in order to eliminate the influence of pH, the HEPES buffer system, at a physiological pH value 7.0, was chosen for the fluorescence intensity determination.

3.4. Selectivity and Completion. Selectivity is an important parameter to evaluate the performance of a chemosensor. As shown in Figure 5, the absorbance and fluorescence spectra changes of Rh-G caused by Hg^{2+} and various competitive

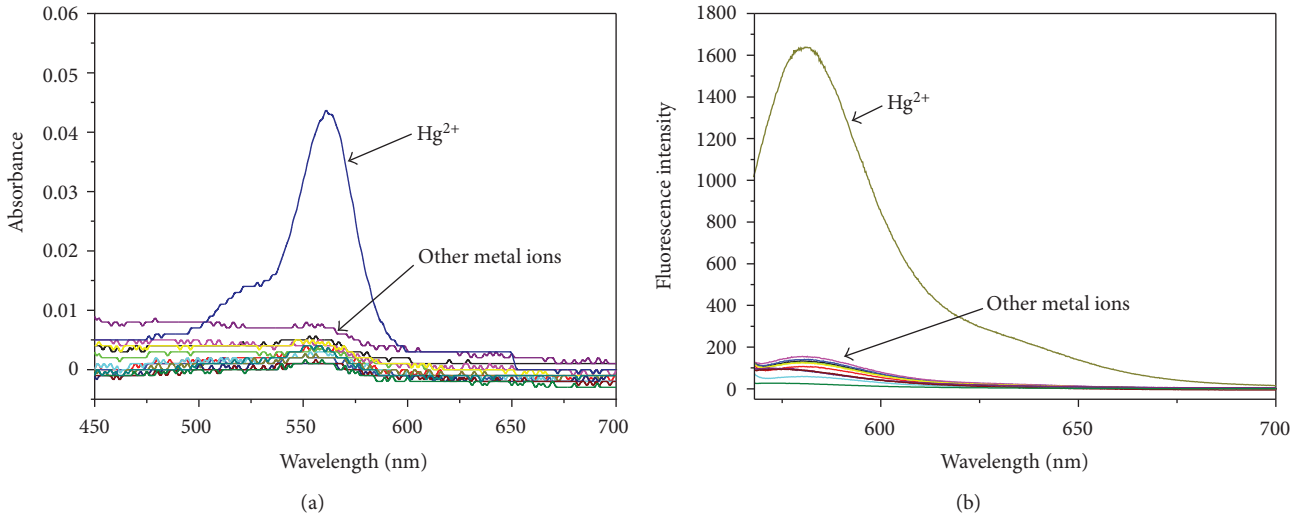


Figure 5: UV-vis spectra (a) and fluorescent spectra (b) of **1** (10.0 μM) in the presence of 1.0 equiv. Hg^{2+} and 10 equiv. other metal ions (Na^+, K^+, Mg^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, Zn^{2+}, Ag^+, Ba^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+}) in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES pH = 7.0 solution.

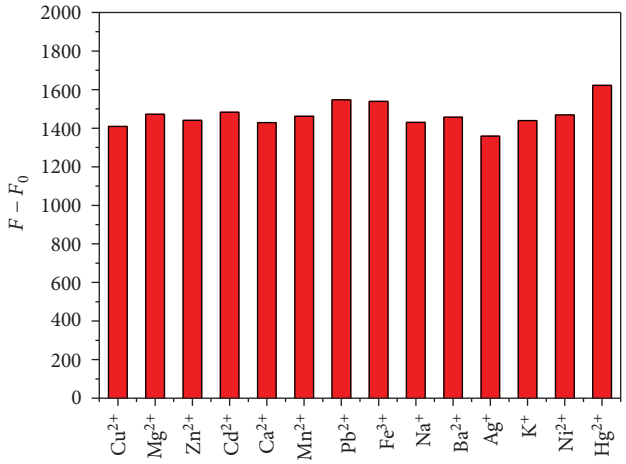


Figure 6: Competition of **1** (10.0 μM) for Hg^{2+} (1.0 equiv.) upon addition of other metal ions (10.0 equiv.) in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES pH = 7.0 solution. $\Delta F = F - F_0$, (F_0 and F were the fluorescence intensity of **1** in the absence and presence of Hg^{2+}). Excitation: 556 nm, emission: 581 nm.

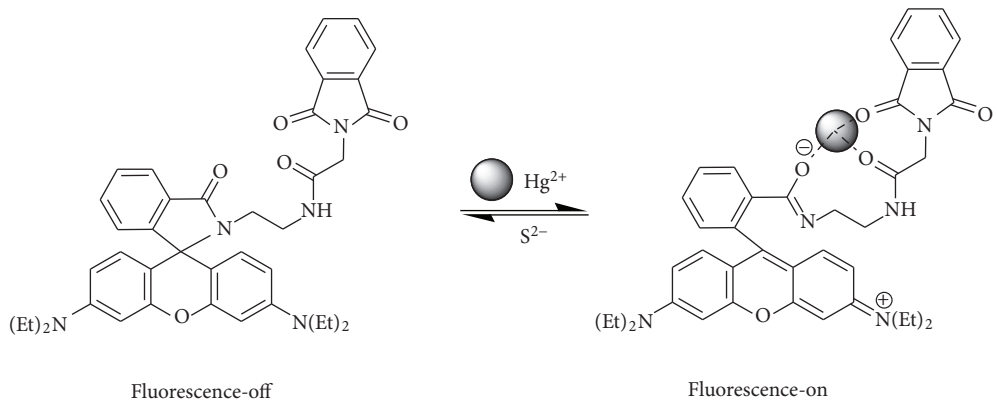
metal ions, such as Na^+, K^+, Mg^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, Zn^{2+}, Ag^+, Ba^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, and Ni^{2+}.From UV-vis spectra of probe **1** (10 μM), the free **1** remained colorless and did not exhibit apparent absorption above 561 nm in C_2H_5OH-water (4 : 6, v/v) buffered with HEPES pH = 7.0 solution. Upon addition of 1.0 equiv. of Hg^{2+}, we can clearly observe a new absorption band centered at 561 nm. The fluorescence spectra were obtained by excitation of the rhodamine fluorophore at 556 nm. Among various competitive metal ions, **1** showed significant fluorescence enhancements with Hg^{2+} only. In contrast, other metal ions developed no significant absorption and fluorescence intensity changes under the identical conditions. These results indicate that probe **1** has a remarkable selectivity towards Hg^{2+} and could serve as a "naked-eye" chemosensor selective for Hg^{2+} in the aforementioned buffer solution.

Moreover, in order to verify the high selectivity of **1** toward Hg^{2+}, competition experiments in the presence of miscellaneous competitive metal ions (above mentioned) were conducted. The enhancement in fluorescence intensities resulting from the addition of the Hg^{2+} was hardly influenced by the subsequent addition of excess metal ions (Figure 6). It is likely that the addition of Hg^{2+} induces the carbonyl oxygen atom of spirolactam to coordinate with Hg^{2+} resulting in the opening of spirolactam ring that leads to the development of pink colour and enhancement in fluorescence intensity.

3.5. The Reaction Mechanism and Reversible. The chemosensor is the most likely to chelate with Hg^{2+} via its three oxygen on the three carbonyl groups (Scheme 2). To test whether the proposed complex could be reversed, we added Na_2S to the solutions of **1**-Hg^{2+} species. Upon addition of Na_2S, fluorescent emission intensity of the system was quenched (Figure 7), and the color of the mixture of **1** and Hg^{2+} changed from pink to almost colorless, indicating that Na_2S replaced the receptor **1** to coordinate Hg^{2+}. Thus, these findings indicated that probe **1** can be classified as a reversible chemosensor for Hg^{2+}.

4. Conclusions

In summary, we have synthesized a new rhodamine-based probe **1** linked with Phthalimido Gly for the detection of Hg^{2+} ions, which displayed Hg^{2+} via a 1 : 1 binding mode enabled the spirolactam ring (nonfluorescence) to the ring-opened amide (fluorescence), a desirable "off-on" mode. Moreover, its fluorescence intensity was enhanced in a linear



Scheme 2: Proposed possible binding mode of probe **1** with Hg^{2+}.

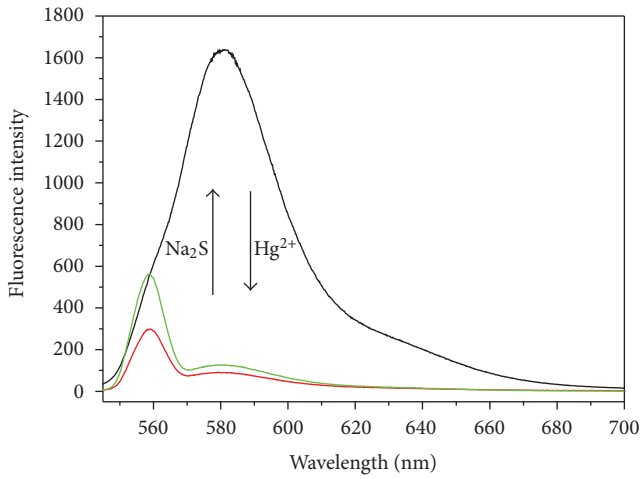


Figure 7: The emission spectra of **1** (10.0 μM C_2H_5OH-water solution 4 : 6, v/v pH = 7.0) in the presence of 1 equiv. of Hg^{2+} and 5 equiv. of Na_2S.

fashion with a Hg^{2+} concentration from 0.1×10^{-6} to 1.0×10^{-6} mol/L, with a detection limit of 2.8×10^{-8} M. Thus, probe **1** also enables the "naked-eye" detection of Hg^{2+} over other commonly coexistent metal ions (even those that exist in high concentration).

Acknowledgments

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