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A Rhodamine-Based Fluorescent and Colorimetric Chemodosimeter for the Rapid Detection of Hg²⁺ Ions in Aqueous Media

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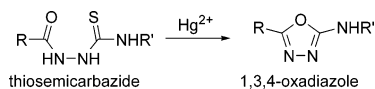
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The demand for chemosensors that are selective for specific target anions or cations is continuously increasing. Especially important in this regard are sensors that monitor toxic heavy metal ions. A great effort has gone into the development of selective fluorescent chemosensors^{1,2} due to their high sensitivity. Recently, colorimetric sensing³ of metal ions has been shown to be a less labor-intensive alternative to techniques based on fluorescence. Other fascinating devices that utilize irreversible chemical events associated with host-guest recognition have been employed as chemodosimeters for ratiometric determination of analyte concentrations. Several fluorescent chemodosimeters for metal ions, such as Cu²⁺ and Hg²⁺, have been described in the literature.⁴

Because of the strong thiophilic affinity of Hg²⁺, fluorescent changes associated with mercury-promoted desulfurization reactions, including hydrolysis,^{4a,d} cyclizations,^{4e} and eliminations,^{4f} have been used in the design of chemodosimeters for Hg²⁺. However, several significant challenges still exist in this field. For example, to drive these desulfurization reactions to completion, it is often necessary to use either elevated temperatures or excess quantities of Hg²⁺. Although being less thiophilic than Hg²⁺, other metal ions, such as Ag⁺ and Pb²⁺, can also promote the desulfurization reactions. Therefore, optimal ratiometric chemodosimeters for Hg²⁺ must possess fast response times at ambient temperature and the ability to selectively and stoichiometrically detect Hg²⁺. Finally, the dosimeters should operate in aqueous media and be sensitive enough to detect Hg²⁺ at parts per billion levels.

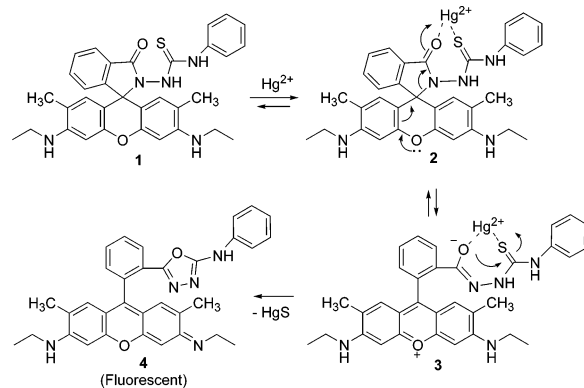
Only few fluorescence chemosensors for heavy metal ions have been designed utilizing the well-known⁵ spiro lactam (nonfluorescent) to ring opened amide (fluorescent) equilibrium of rhodamine derivatives.^{4b,6} We envisioned that coupling this process with the stoichiometric and irreversible Hg²⁺-promoted reaction of thiosemicarbazides to form 1,3,4-oxadiazoles⁷ would serve as the foundation for a novel chemodosimeter for Hg²⁺.



The rhodamine derivative **1** appeared to be ideal for this application since we anticipated that it would undergo oxadiazole formation when the thiosemicarbazide moiety is liberated by Hg²⁺-facilitated ring opening of the spirocycle grouping (Scheme 1). Below, we describe the results of studies that have led to the development of a colorimetric and fluorescent chemodosimeter system based on **1**, which is highly sensitive and selective for mercuric ions in aqueous solution.

The rhodamine derivative **1** was prepared in high yield from Rhodamine 6G by using a two-step procedure (1, NH₂NH₂·H₂O, MeOH, 95%; 2, PhNCS, DMF, 90%).⁸ This substance forms a colorless water-methanol (80/20 v/v) solution at pH 7, indicating that it exists in the spirocyclic form predominantly.⁹ Addition of mercuric ion to the solution of **1** causes instantaneous development

Scheme 1. Hg²⁺-Induced Ring Opening and Cyclization of **1**



of a pink color and a strong yellow fluorescence. This observation shows that the mercury-induced ring-opening reaction takes place rapidly at room temperature.

A fluorescence titration of Hg²⁺ was conducted using 1 μM solution of **1** in water-methanol (80/20 v/v) at pH 7. Upon addition of 1 equiv of Hg²⁺, the fluorescence intensity of the solution of **1** undergoes a ca. 26-fold increase and the emission maximum shifts from 553 to 557 nm (Figure 1). The reaction (Scheme 1) responsible for these changes reaches completion well within the time frame (<1 min) of these measurements.¹⁰ The observed fluorescence intensity was nearly proportional to the Hg²⁺ concentration. The saturation behavior of the fluorescence intensity after 1 equiv of Hg²⁺ reveals that the Hg²⁺ chemodosimeter has a 1:1 stoichiometry. Further evidence for this stoichiometry comes from the independent synthesis of **4** from **1** by using 1 equiv of Hg(ClO₄)₂ in acetonitrile at room temperature (98% yield). The compound **4** has a large molar absorptivity (log ε = 4.67) and a high fluorescence quantum yield (Φ_f = 0.52).¹¹

Similar results are obtained when different mercury salts, such as HgCl₂ and Hg(ClO₄)₂, are used. Therefore, it appears that counteranions have a negligible effect on this chemodosimeter. Moreover, various sodium salts, including NaCN, NaI, NaF, and NaOAc, do not promote any fluorescence changes under the same conditions used for the Hg²⁺ titrations.

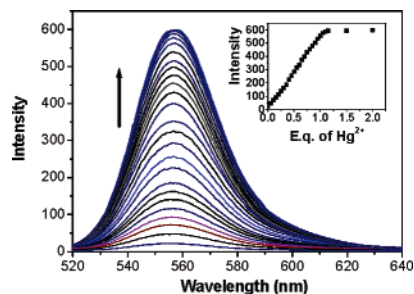


Figure 1. Fluorescence response of **1** (1 μM) upon addition of Hg²⁺ in water-methanol (80/20 v/v) at pH 7 (excitation at 500 nm).

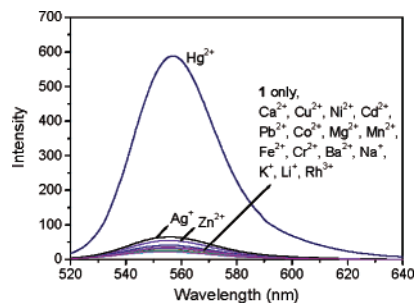


Figure 2. Fluorescence spectra (excitation at 500 nm) of **1** (1 μM) in water–methanol (80/20 v/v) at pH 7 in the presence of 1 equiv of Hg^{2+} , Ag^+ , Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , Li^+ , K^+ , Na^+ , Rh^{3+} , Cr^{2+} .

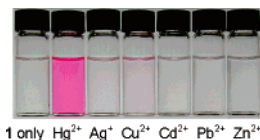


Figure 3. Color changes of **1** (10 μM) upon addition of Hg^{2+} , Ag^+ , Cu^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} (1.0 equiv) in water–methanol (80/20 v/v).

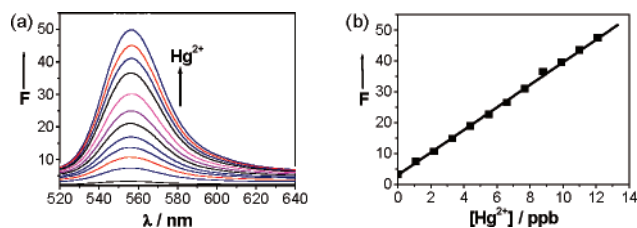


Figure 4. (a) Fluorescence emission changes of **1** (10^{-7} M) upon additions of Hg^{2+} (by 1 ppb) in water–methanol (80/20 v/v) at 25 $^{\circ}\text{C}$. (b) The fluorescence intensities at 556 nm.

Changes in the fluorescence properties of **1** caused by other metal ions, including Ag^+ , Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Mg^{2+} , Ca^{2+} , Ba^{2+} , Li^+ , K^+ , Na^+ , Rh^{3+} , Cr^{2+} , were also measured. Fluorescence spectra of solutions of **1** (1 μM), recorded within 5 min after the addition 1 equiv of each of these metal ions, are displayed in Figure 2. Only Ag^+ and Zn^{2+} ions promote small fluorescence intensity changes,¹² while other metal ions did not cause any significant changes under identical conditions. The selectivity observed for Hg^{2+} over other ions is remarkably high. In addition, the enhancement in fluorescence intensity resulting from addition of Hg^{2+} is not influenced by subsequent addition of other metal ions. Finally, while the colorless to pink color change associated with the reaction of **1** with Hg^{2+} is readily detectable visually, no significant color changes are promoted by other metal ions (Figure 3).

To see practical applicability, the detection limit of this new chemodosimeter system was evaluated. The fluorescence titration profile of **1** (10^{-7} M) with Hg^{2+} , shown in Figure 4, demonstrates that detection of Hg^{2+} is at the parts per billion level.¹³ Under these conditions, the fluorescence intensity of the solution of **1** was nearly proportional to the amount of Hg^{2+} added (Figure 4b).

In summary, the investigation described above has resulted in the development of a highly selective and sensitive chemodosimeter for Hg^{2+} ion in aqueous solution. The system, which utilizes an irreversible Hg^{2+} -promoted oxadiazole forming reaction of rhodamine derivative **1**, is monitored by colorimetric and fluorescence intensity changes that respond instantaneously at room temperature in a 1:1

stoichiometric manner to the amount of Hg^{2+} . The selectivity of this system for Hg^{2+} over other metal ions is remarkably high, and its sensitivity is below 2 ppb in aqueous solutions. The findings suggest that this method will serve as the foundation of practical chemodosimeters for rapidly determining Hg^{2+} concentrations in aqueous environments.

Acknowledgment. This work was supported by the Center for Bioactive Molecular Hybrids (CBMH) at Yonsei University.

Supporting Information Available: Experimental procedures for the synthesis, spectral data, and copies of ^1H NMR and ^{13}C NMR of **1** and **4**, data for UV–vis and fluorescence titrations of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) The spirocyclic form was confirmed by ^{13}C NMR spectra. The spiro carbon peak appeared at 67.0 ppm. According to the pH titration, compound **1** retained the spirocyclic form in the pH range of 4–14. Below pH 4, the fluorescence intensity increased, which implies that ring opening is occurring. Compound **1** is stable as a solid and a solution for several days.
- (10) Typical desulfurization reactions used in known Hg^{2+} chemodosimeters require elevated temperatures and/or relatively long reaction times.
- (11) The fluorescence quantum yield was calculated using Rhodamine 6G ($\Phi_f = 0.94$ in EtOH) as a reference (Fischer, M.; Georges, J. *Chem. Phys. Lett.* **1996**, *260*, 115–116).
- (12) Fluorescent intensities promoted by Ag^+ increased gradually over an 8 h period.
- (13) The EPA standard for the maximum allowable amount of Hg^{2+} in drinking water is 2 ppb.

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