http://dx.doi.org/10.5012/bkcs.2012.33.7.2359

# Rhodamine Based Fluorescent Chemosensors for $Hg^{2+}$ and its Biological Application

**Ji Young Choi, Wantae Kim,† and Juyoung Yoon***

*Department of Chemistry and Nano Science and Department of Bioinspired Science (WCU), Ewha Womans University, Seoul 120-750, Korea. *E-mail: jyoon@ewha.ac.kr*
*†Anyang Foreign Language High School, Anyang 430-013, Korea*
*Received April 1, 2012, Accepted April 21, 2012*

Two new chemosensors, rhodamine 6G derivative bearing hydroxyethyl group (**1**) and rhodamine base derivative bearing 15-crown-5 group (**2**) were synthesized and their sensing behaviors toward various metal ions were investigated by UV/Vis and fluorescence spectroscopies. Addition of $Hg^{2+}$ ion to a $CH_3CN$ solution of **1** and **2** gave visual color changes as well as fluorescent *OFF-ON* observations. Selectivity and sensitivity of **1** towards $Hg^{2+}$ are excellent enough to detect micromolar level of $Hg^{2+}$ ion, even in equeous media and biological sample (HeLa cell).

**Key Words :** Fluorescent sensor, Colorimetric sensor, Rhodamine, Hg(II) sensor, Mercury ion sensor

## Introduction

Considerable attention has been focused on fluorescent chemosensors for the selective and rapid detection of toxic heavy metal ions, such as the $Pb^{2+}$, $Cd^{2+}$ and $Hg^{2+}$ ions.[1] Among them, the $Hg^{2+}$ ion has been considered highly dangerous because both elemental and ionic mercury can be converted into methyl mercury by bacteria in the environment, which easily bioaccumulates through the food chain.[2] Therefore, there has been a high demand for the detection of the $Hg^{2+}$ ion both in environmental analysis and industrial waste treatment.[1,3]

Among non-conventional methods, the fluorescence detection method has proven to be the most convenient due to its simplicity and low detection limit.[4] Especially, rhodamine framework is an ideal model to drive *OFF-ON* fluorescent chemosensors/probes due to its structural unique property. Rhodamine derivatives with spirolactam ring are non-fluorescent and clorless, whereas ring-opening of the spirolactam gives rise to a strong fluorescence emission and pink color.[5] Moreover, the rhodamine has a long emission wavelength (over 550 nm), which is often preferred to serve as a reporting group for analyte to avoid the influence of background fluorescence (below 500 nm).[5] In this regard, several rhodamine-based chemosensors for $Hg^{2+}$, $Cu^{2+}$, $Pb^{2+}$ and $Fe^{3+}$ ions have been developed so far from our group[6] as well as others.[7] For example, two rhodamine B molecules were cojugated through a diethylenetriamine linker to produce a $Fe^{3+}$-selective chemosensor.[8] Xiang *et al.* used a rhodamine-based hydrazine bearing a salicyaldehyde binding site as a $Cu^{2+}$ amplified sensor.[9] Tae group reported a $Hg^{2+}$ chemosensor based on the rhodamine-hydrazine framework.[7l] Kwon *et al.* exploited ethylenediamine to link a rhodamine and a DPA moiety to yield a fluorescent chemosensor for $Pb^{2+}$ ion.[6i] As mentioned above, hydrazine, diethylenetriamine, ethylenediamine, and tris(2-aminoethyl)-amine moiety (tren) as a linking and binding group were widely used. Besides, 2-aminoethanol can also serve to interact with metal ions as a binding site. However, 2-aminoethanol or 2-aminomethyl-15-crown-5 has not been applied to the rhodamine-based chemosensor yet.

Herein, we report two new chemosensors, rhodamine 6G derivative bearing hydroxyethyl group (**1**) and rhodamine base derivative bearing 15-crown-5 group (**2**) as selective reporters for $Hg^{2+}$ ion. Their sensing behaviors toward $Hg^{2+}$ ions was investigated by UV/Vis and fluorescence spectroscopies. In particular, we further tested the detection ability of **1** towards $Hg^{2+}$ in aqueous media and bio sample (HeLa cell).

## Experimental Section

**Compound 1.** Under nitrogen, rhodamine 6G **3** (0.40 g, 0.84 mmol) and 2-aminoethanol (0.24 g, 1.68 mmol) were combined in 5.0 mL of ethanol (EtOH) and refluxed overnight. After cooling to the room temperature, the solvent was evaporated *in vacuo*. The residue was dissoved in $CH_2Cl_2$ (100 mL) and washed twice with water (200 mL). The $CH_2Cl_2$ layer was separated, and dried over anhydrous sodium sulfate ($Na_2SO_4$). After filtration of the sodium sulfate, the solvent was removed under reduced pressure to give **1** as brownish oil which can be crystallized in a mixture of $CH_2Cl_2$ and diethyl ether. Compound **1** was obtained as a solid in 70% yield: $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.93-7.90 (m, 1H), 7.46-7.42 (m, 2H), 7.04 (m, 1H), 6.34 (s, 2H), 6.27 (s, 2H), 4.25 (br t, 1H), 3.55 (m, 2H), 3.48 (m, 2H), 3.26-3.16 (m, 6H), 1.90 (s, 6H), 1.33-1.29 (t, 6H) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 170.3, 154.1, 151.8, 147.7, 133.0, 130.5, 128.4, 124.0, 123.1, 118.3, 105.3, 96.8, 66.2, 62.8, 44.8, 38.5, 16.9, 14.9 ppm; ESI-MS *m/z* ($M^+$) calcd 457.5, found $(M+H)^+$ 458.4, $(M+Na)^+$ 480.3, $(2M+Na)^+$ 937.7.

**Compound 2.** To a solution of rhodamine B base **4** (0.355 g, 0.802 mmol) and 2-aminomethyl-15-crown-5 (1g, 4.01 mmol, purchased from Aldrich) in 1,2-dichloroethane (30

mL), phosphorous oxychloride (0.19 mL, 2 mmol) was added dropwise over 10 minutes under Ar. The solution was refluxed for 18 h. After the solvent was evaporated under reduced pressure, the crude product was purified by column chromatography ($CHCl_3$:MeOH = 30:1, v/v) to give the 216 mg of compound **2** (yield; 40%); $^1$H NMR ($CDCl_3$) δ 7.82 (m, 1H), 7.37 (dd, 2H, $J$ = 2.6 Hz and 1.9 Hz), 7.02 (m, 1H), 6.30 (m, 4H), 6.19 (dt, 2H), 6.35 (m, 4H), 6.19 (dt, 2H, $J$ = 8.9 Hz and 2.3 Hz), 3.53 (m, 10H), 3.25 (m, 19H), 1.09 (t, 12H, $J$ = 10.7 Hz); $^{13}$C NMR ($CDCl_3$) δ 168.7, 153.9, 153.7, 153.6, 149.1, 132.7, 131.6, 129.3, 128.3, 124.2, 123.0, 108.4, 106.1, 105.9, 97.9, 72.7, 71.2, 70.9, 70.8, 70.7, 70.6, 69.8, 65.5, 44.7, 44.6, 41.5, 12.9; HRMS (FAB) found $m/z$ = 696.3626 $(M + Na)^+$, calcd for $C_{39}H_{53}N_3NaO_7$= 673.3625.

## Results and Disscusion

As shown in Scheme 1, probe **1** was synthesized from rhodamine 6G (**3**) and 2-aminoethanol (0.24 g, was refluxed in ethanol (EtOH) in 70% yield. For the synthesis of probe **2**, phosphorous oxychloride was added dropwise to the solution of rhodamine B base (**4**) and 2-aminomethyl-15-crown-5 in 1,2-dichloroethane. After refluxing for 18 h, the crude product was purified by column chromatography ($CHCl_3$:MeOH = 30:1, v/v) to give the probe **2** in 40% yield. Two new compounds were fully characterized by $^1$H NMR, $^{13}$C NMR and mass spectroscopy (Experimental Section and Supporting Informations).

Figure 1 shows UV/Vis absorption and fluorescence spectra of **1** (10 μM) in $CH_3CN$ upon the addition of various metal ions, such as $Na^+$, $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, and $Ni^{2+}$ ions. All spectra was obtained at 25 °C, and the excitation wavelength ($\lambda_{ex}$) was 525 nm. From UV/Vis spectra of **1** (10 μM) (Fig. 1(a)), we clearly observed a new absorption band centered at 524 nm in the presence of 50 equiv of $Hg^{2+}$ ion. In contrast, $Fe^{2+}$ ions induced a smaller spectral change and other metal ions showed almost no spectral changes. Fluorescence changes (Fig. 1(b)) for **1** also show a similar selectivity. Among the various metal ions, addition of $Hg^{2+}$ ion resulted in a selective enhanced fluorescence at 550 nm (*OFF-ON*) even though there was a relatively smaller fluorescence enhancement with $Fe^{2+}$. Naked-eye fluorescence changes of **1** in the presence of $Hg^{2+}$ and $Fe^{2+}$ ions are also shown in insets of Figure 1. It is explicit that the binding interaction between **1** and $Hg^{2+}$ ion induces the ring-opening of spirolactam of

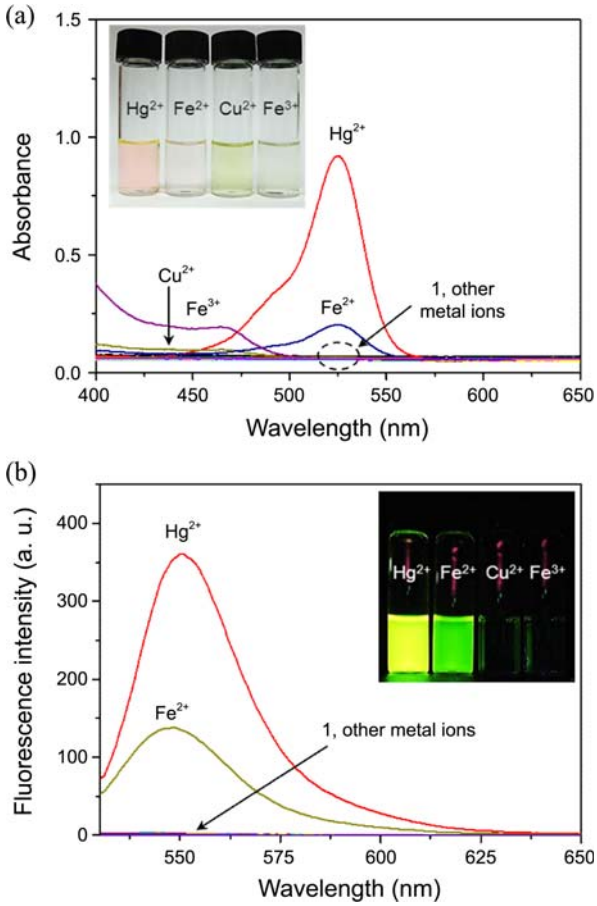
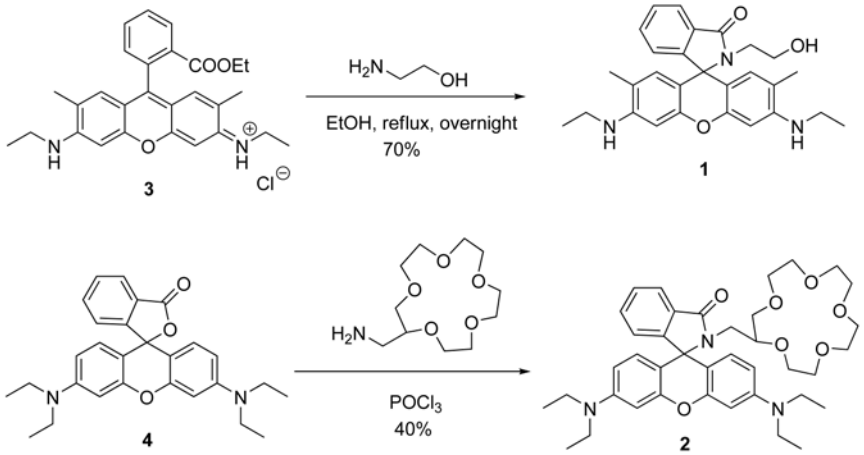



**Figure 1.** (a) Absorption and (b) fluorescence spectra of **1** (10 μM) towards 50 equiv of various metal ions ($Na^+$, $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, and $Ni^{2+}$) in $CH_3CN$ at 25 °C. Excitation wavelength ($\lambda_{ex}$) is 525 nm.




**Scheme 1.** Synthetic schemes for **1** and **2**.

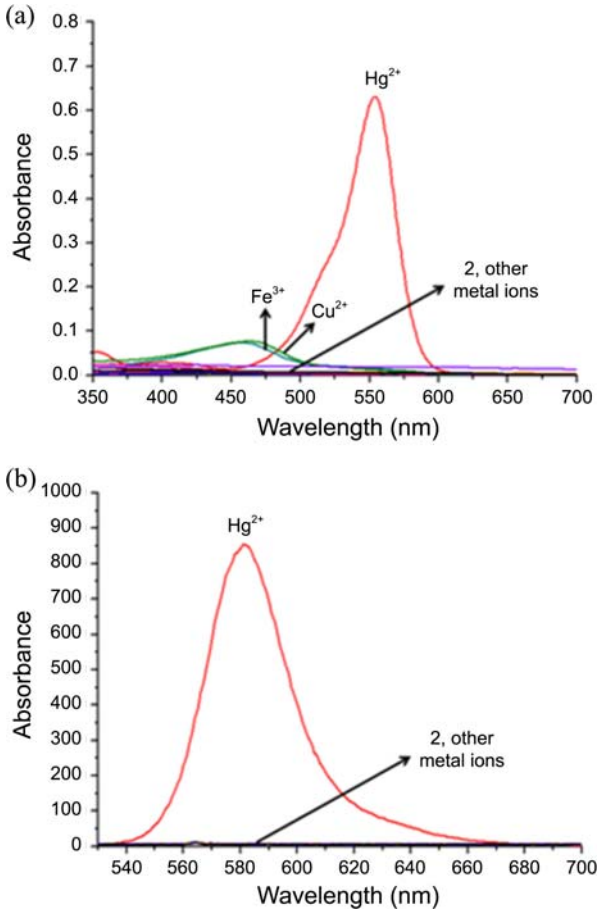



**Figure 2.** (a) Absorption spectra of **2** (10 μM) and (b) fluorescence spectra of **2** (5 μM) towards 5 equiv. of various metal ions ($Na^+$, $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, and $Ni^{2+}$) in $CH_3CN$ at 25 °C. Excitation wavelength ($\lambda_{ex}$) is 560 nm.

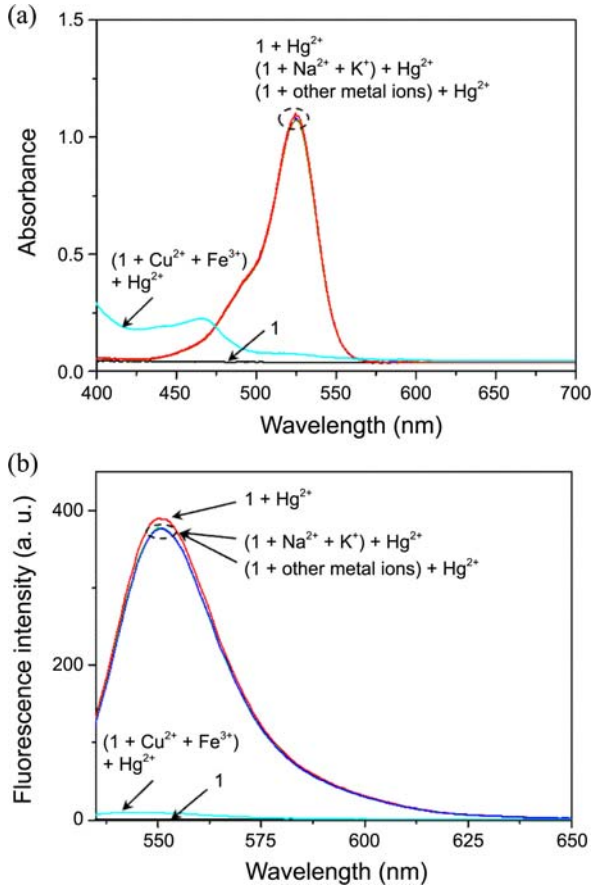



**Figure 3.** (a) Absorption and (b) fluorescence spectra of **1** (10 μM) towards $Hg^{2+}$ ions (50 equiv) in the presence of other competitive metal ions ($Na^+$ and $K^+$; $Cu^{2+}$ and $Fe^{3+}$; other metal ions including $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Pb^{2+}$, and $Ni^{2+}$) (50 equiv, respectively) in $CH_3CN$ at 25 °C. Excitation wavelength ($\lambda_{ex}$) is 525 nm.

rhoadmine framework, which is responsible for color and fluorescence changes.

Figure 2 shows UV/Vis absorption spectra of **2** (10 μM) and fluorescence spectra of **2** (5 μM) in $CH_3CN$ upon the addition of various metal ions, such as $Na^+$, $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, and $Ni^{2+}$ ions. Although $Cu^{2+}$ and $Fe^{3+}$ displayed smaller enhancements, $Hg^{2+}$ induced a selective large absorption enhancement at 554 nm. For the fluorescence change, highly selective "*OFF-ON*" fluorescence enhancement ($\lambda_{max}$ = 581 nm) was observed for $Hg^{2+}$ among the various other metal ions. Despite the selectivity of **2** for $Hg^{2+}$ comparable to that of **1**, it did not show reproducible fluorescence change in aqueous solution. The core fluorophore difference between rhodamine 6G and rhodamine base may be attributed to this different fluorescence change in aqueous solution. Therefore, further studies with $Hg^{2+}$ were examined only for probe **2**.

Further experiments for $Hg^{2+}$-selective detection of **1** were performed in the presence of other competitive metal ions (50 equiv, respectively, Fig. 3). Upon addition of 50 equiv of $Hg^{2+}$ ion, two kinds of samples containing monovalent ($Na^+$ and $K^+$ ions) or divalent ($Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Pb^{2+}$, and $Ni^{2+}$ ions) metal ions still display a dintinctively enhanced fluorescence with a new absorption band, respectively. These results indicate that **1** shows a good selectivity and sensitivity for $Hg^{2+}$ ion over other competitive metal ions ($Na^+$, $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Pb^{2+}$, and $Ni^{2+}$ ions).

Figure 4 and 5 explain the detailed absorption and fluorescence changes of **1** upon gradual additions of $Hg^{2+}$ ion. As expected, addition of small amount (8.0 μM) of $Hg^{2+}$ ion induced a new absorption band as well as a visual color change from colorless to pink. The fluorescence titration of $Hg^{2+}$ ion was conducted using 10 μM of **1** in $CH_3CN$. Upon addition of increasing concentrations (0, 0.8, 0.9, 1, 2, 2.5, 3, 5, 10, 15, 20, and 30 equiv) of $Hg^{2+}$ ion, a new emission band peaked at 549 nm increased. From these results, we noted that compound **1** is sensitive enough to detect $Hg^{2+}$ ions in a micromolar level (minimum up to 8 μM).

To confirm the stoichiometery of a binding event between **1** and $Hg^{2+}$ ion, Job's plot was conducted in $CH_3CN$ (Fig. 6). The maximum absorbance change (ΔA) was observed at 0.5 mole fraction of [**1**]/[**1**+$Hg^{2+}$], which gave a solid evidence for the formation of 1:1 complex between compound **1** and $Hg^{2+}$ ion.

To further look into an interaction between **1** and $Hg^{2+}$ ion,

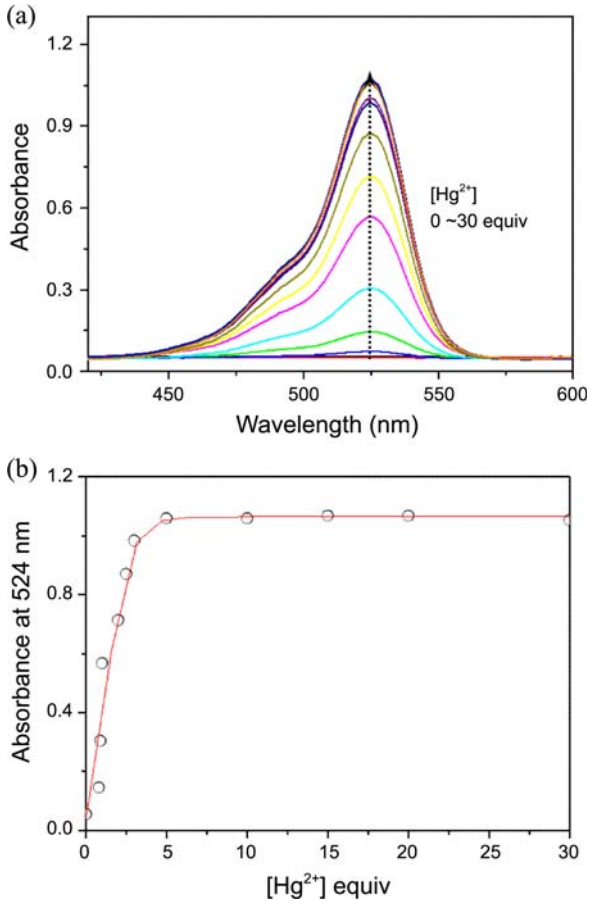



**Figure 4.** (a) Absorption spectral changes of **1** (10 μM) and (b) increase of absorbance at 524 nm in various concentrations of $Hg^{2+}$ (0, 0.8, 0.9, 1, 2, 2.5, 3, 5, 10, 15, 20, and 30 equiv) in $CH_3CN$ at 25 °C.

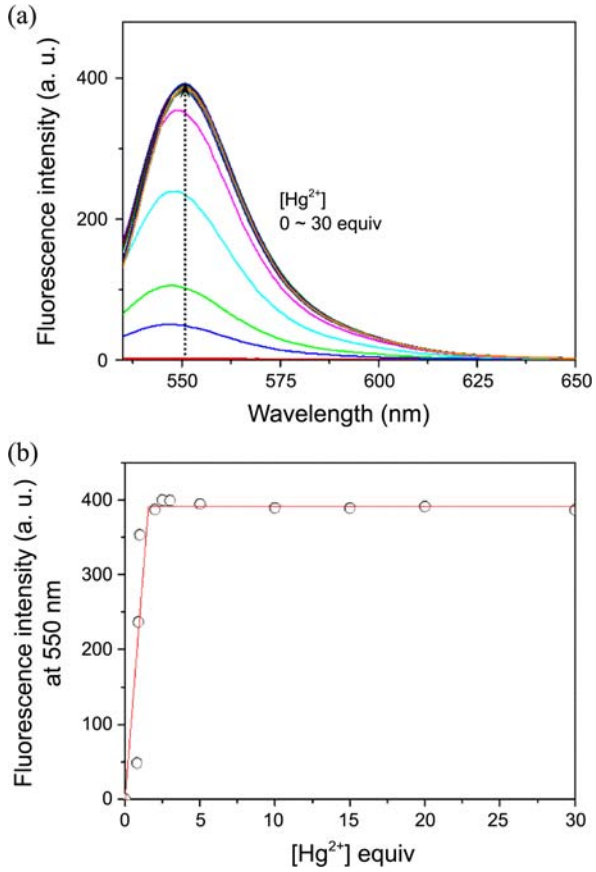



**Figure 5.** (a) Fluorescence spectral changes of **1** (10 μM) and (b) increase of fluorescence intensity at 524 nm in various concentrations of $Hg^{2+}$ (0, 0.8, 0.9, 1, 2, 2.5, 3, 5, 10, 15, 20, and 30 equiv) in $CH_3CN$ at 25 °C. Excitation wavelength ($\lambda_{ex}$) is 525 nm.

upon addition of $Hg^{2+}$ ion to the solution of **1**, ethylenediaminetetraacetic acid was added, and then UV/Vis absorption and fluorescence spectral changes were measured. Ethylenediaminetetraacetic acid (EDTA) is widely used as a chelating agent for metal ions because of its role as a hexadentate ligand. In the presence of 50 equiv of $Hg^{2+}$ ion, **1** exhibits a new absorption at 524 nm and a strongly enhanced fluorescence at 550 nm. On the other hands, as seen in Figure 7, upon addition of EDTA (1 and 10 mM, respectively) to a mixture of **1** and $Hg^{2+}$ ion, the absorption (524 nm) and the fluorescent emission (550 nm) band significantly decreased. In addition to this, color chang was also observed from pink to colorless. This is obviously because the $Hg^{2+}$ ion in **1**•$Hg^{2+}$ complex is encapsulated by EDTA, thus giving free **1** and EDTA•$Hg^{2+}$ complex, which is responsible for the dual color (pink → coloress) and fluorescence (ON-OFF) changes. These results firmly support that the binding interaction between **1** and $Hg^{2+}$ ion is non-covalent and reversible reaction.

Based on the results shown in Figure 7 in conjunction with those in Figures 2-6 we concluded that $Hg^{2+}$ ion binding causes the spirolactam ring-opening of the rhodamine to give a fluorescence and a color change of **1**. Thus, as seen in Figure 8, we proposed the binding mechanism of **1** for $Hg^{2+}$ ion.

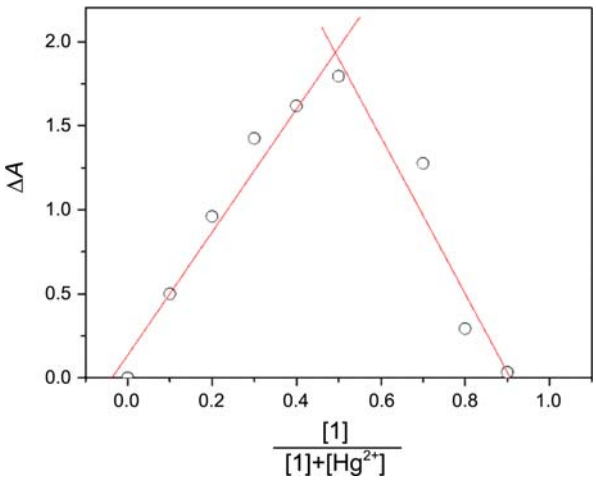



**Figure 6.** Job's plot of **1** (50 μM) with $Hg^{2+}$ ions (50 μM) in $CH_3CN$; $\Delta A$ is absorbance changes at 525 nm.

Figure 9 shows UV/Vis absorption and fluorescence spectra of **1** (10 μM) in 27% of PBS buffer at pH 7.4 upon addition of various competitive metal ions, such as $Na^+$, $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, and $Ni^{2+}$ ions. As seen in Figure 9, the probe **1** is still sensitive to detect $Hg^{2+}$ ions in aqueous condition (Fig. 9(b)). The color change of **1** was also observed in the presence of

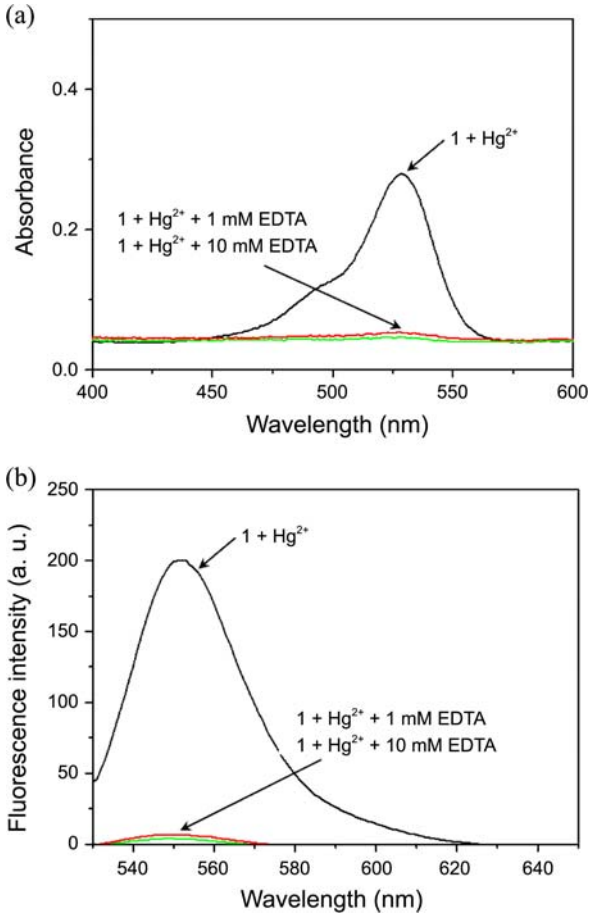



**Figure 7.** (a) Absorption and (b) fluorescence spectra of **1**•$Hg^{2+}$ (10 μM) upon addition of EDTA (1.0 and 10 mM, respectively) in $CH_3CN$ at 25 °C. Excitation wavelength ($\lambda_{ex}$) is 525 nm.

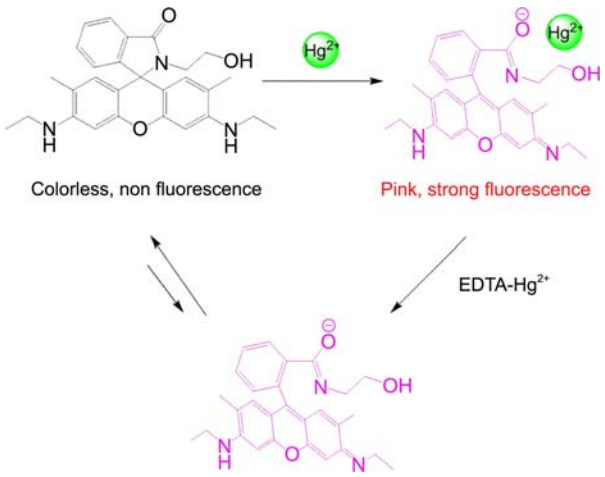



**Figure 8.** Proposed binding mechanism of **1** and $Hg^{2+}$ ions.

$Hg^{2+}$ ion (Fig. 9(a) inset). More interestingly, as seen in Figure 9(b), the selectivity of **1** toward $Hg^{2+}$ ions is better than that of **1** in $CH_3CN$. As previously mentioned, addition of $Fe^{2+}$ ion also gave the similar UV/Vis absorption and fluorescence spectral changes of **1** in $CH_3CN$ (see Fig. 1). However, in aqueous condition, the $Fe^{2+}$ ion induced no significant absorption and fluorescence changes of **1**.

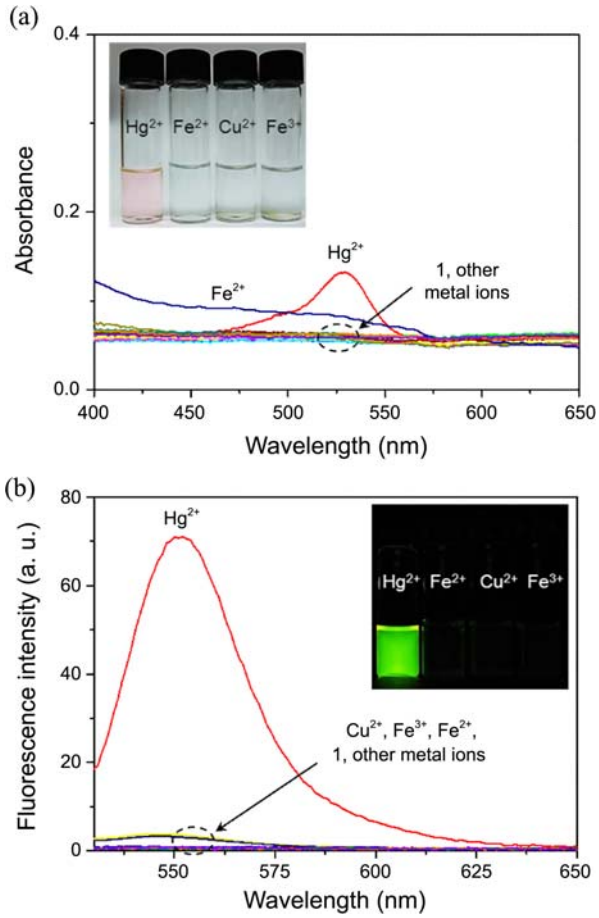



**Figure 9.** (a) Absorption and (b) fluorescence spectra of **1** (10 μM) towards 50 equiv of various metal ions ($Na^+$, $K^+$, $Ca^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, and $Ni^{2+}$) in 27% of PBS buffer at pH 7.4 (25 °C). Excitation wavelength ($\lambda_{ex}$) is 525 nm. All spectra were acquired 1 h after addition of metal ions.

After confirming the utility of probe **1** in aqueous solution, Next, we investigated any possibility whether **1** is applicable to $Hg^{2+}$ detection in bio system by using confocal microscopy. For this study, we prepared HeLa cell which is the most commonly used human cell line derived from cervical cancer cells. As indicated in Figure 10(a), when HeLa cells were only treated with 5.0 μM of **1**, no fluorescence was observed. Upon treatment of 50 μM of $Hg^{2+}$ ion to the cells pre-treated with **1**, green fluorescence emission was observed, which can be attributed to the spirolactam ring-opening of **1** (Fig. 10(c)).

Figure 11 displays fluorescence spectra of the observed green emission in cells (red circled region A-D in Fig. 11). The emission band centered at 550 nm is in accordance with that of **1** in the presence of $Hg^{2+}$ ion. These results clearly indicate that probe **1** is sensitive enough to detect $Hg^{2+}$ ion in biological sample.

## Conclusions

In current study, we synthesized two new rhodamine based probes **1** and **2**, which showed selective colorimetric

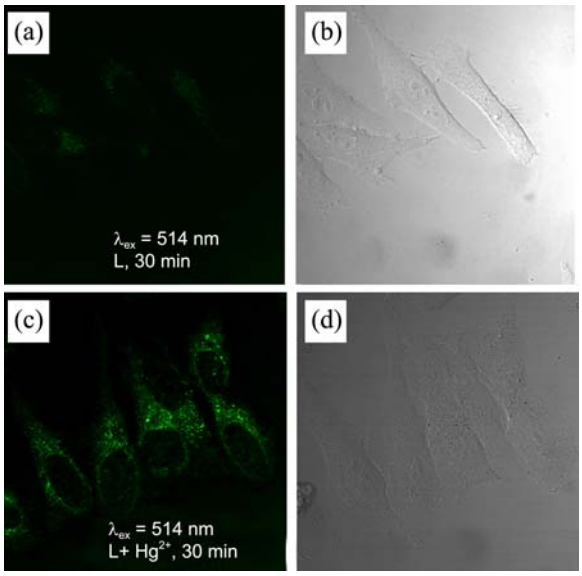



**Figure 10.** Confocal microscopy images of HeLa cells incubated with **1** (5 μM) before (a) and after (c) addition of $Hg^{2+}$ (50 μM) for 30 min. (b) and (d) are bright-field image. The fluorescence emission was collected at 540-600 nm upon excitation at 514 nm.

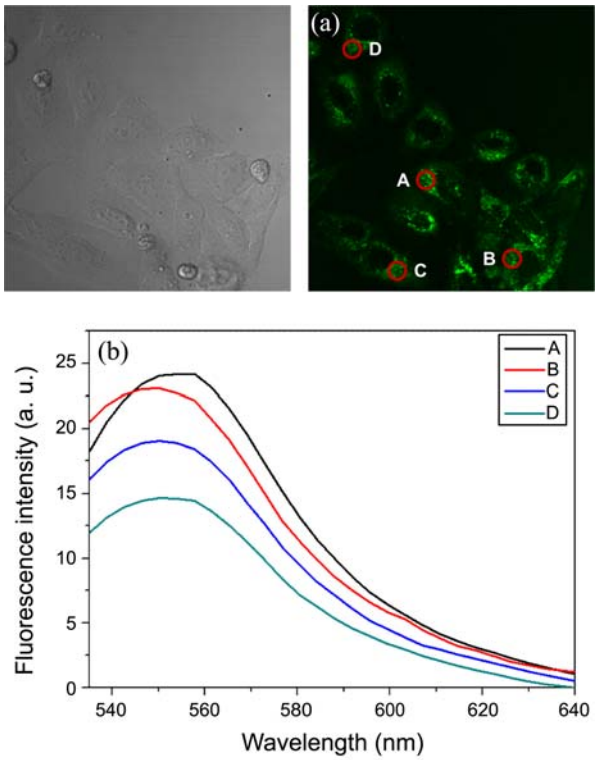



**Figure 11.** Confocal microscopy image of **1** (5 μM) in HeLa cells treated with $Hg^{2+}$ (50 μM). (b) Fluorescence spectra from the red circled region (A-D) in (a).

and fluorimetric changes with $Hg^{2+}$ among the various metal ions in $CH_3CN$. Especially, probe **1** exhibits a high selectivity toward $Hg^{2+}$ over other metal ions in organic and aqueous solutions with micromolar level detection limit. Futhermore, probe **1** also functions $Hg^{2+}$ sensing in HeLa cells. Hence, synthesis of **1** and its selective and sensitive $Hg^{2+}$ detection both in organic and aqueous solutions can give a potential guideline in biological or environmental application-oriented sensor research.

**Acknowledgments.** This work was supported by the Ewha Global Top5 Grant 2011 of Ewha Womans University.

## References

1. Kim, H. N.; Ren, W. X.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2012**, *41*, 3210.
2. Maya, C.; Jimenez, B.; Schwartzbrod, J. *Environ. Res.* **1998**, *78*, 118.
3. Nolan, E. M.; Lippard, S. J. *Chem. Rev.* **2008**, *108*, 3443.
4. (a) Zhang, J. F.; Zhou, Y.; Yoon, J.; Kim, J. S. *Chem. Soc. Rev.* **2011**, *40*, 3416. (b) Zhou, Y.; Yoon, J. *Chem. Soc. Rev.* **2012**, *41*, 52. (c) Quang, D. T.; Kim, J. S. *Chem. Rev.* **2010**, *110*, 6280. (d) Zhou, Y.; Xu, Z.; Yoon, J. *Chem. Soc. Rev.* **2011**, *40*, 2222. (e) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419. (f) Chen, X.; Tian, X.; Shin, I.; Yoon, J. *Chem. Soc. Rev.* **2011**, *40*, 4783. (g) Cho, D. G.; Sessler, J. L. *Chem. Soc. Rev.* **2009**, *38*, 1647. (h) Do, J. H.; Kim, H. N.; Yoon, J.; Kim, J. S.; Kim, H.-J. *Org. Lett.* **2010**, *12*, 932. (i) Kim, G.-J.; Kim, H.-J. *Tetrahedron Lett.* **2010**, *51*, 185. (j) Hong, S.-J.; Yoo, J.; Kim, S.-H.; Kim, J. S.; Yoon, J.; Lee, C.-H. *Chem. Commun.* **2009**, 189. (k) Kim, S. K.; Kim, H. N.; Xiaoru, Z.; Lee, H. N.; Lee, H. N.; Soh, J. H.; Swamy, K. M. K.; Yoon, J. *Supramolecular Chem.* **2007**, *19*, 221.
5. (a) Chen, X.; Pradhan, T.; Wang, F.; Kim, J. S.; Yoon, J. *Chem. Rev.* **2012**, *112*, 1910. (b) Kim, H. N.; Lee, M. H.; Kim, H. J.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2008**, *37*, 1465.
6. (a) Wang, F.; Nam, S.-W.; Guo, Z.; Park, S.; Yoon, J. *Sensor & Actuat. B: Chem*. **2012**, *161*, 948. (b) Kim, H. N.; Nam, S.-W.; Swamy, K. M. K.; Jin, Y.; Chen, X.; Kim, Y.; Kim, S.-J.; Park, S.; Yoon, J. *Analyst* **2011**, *136*, 1339. (c) Kim, S. K.; Swamy, K. M. K.; Chung, S.-Y.; Kim, H. N.; Chung, Y. S.; Yoon, J. *Tetrahedron Lett.* **2010**, *51*, 3286. (d) Chen, X.; Baek, K.-H.; Kim, Y.; Kim, S.-J.; Shin, I.; Yoon, J. *Tetrahedron* **2010**, *66*, 4016. (e) Jou, M. J.; Chen, X.; Swamy, K. M. K.; Kim, H. N.; Kim, H.-J.; Lee, S.-g.; Yoon, J. *Chem. Commun.* **2009**, 7218. (f) Chen, X.; Nam, S.-W.; Jou, M. J.; Kim, Y.; Kim, S.-J.; Park, S.; Yoon, J. *Org. Lett.* **2008**, *10*, 5235. (g) Swamy, K. M. K.; Ko, S.-K.; Kwon, S. K.; Lee, H. N.; Mao, C.; Kim, J.-M.; Lee, K.-H.; Kim, J.; Shin, I.; Yoon, J. *Chem. Commun.* **2008**, 5915. (h) Kwon, J. Y.; Jang, Y. J.; Lee, Y. J.; Kim, K.-M.; Seo, M.-S.; Nam, W.; Yoon, J. *J. Am. Chem. Soc.* **2005**, *127*, 10107. (i) Chen, X.; Jou, M. J.; Lee, H.; Kou, S.; Lim, J.; Nam, S.-W.; Park, S.; Kim, K.-M.; Yoon, J. *Sensors and Actuat. B: Chem.* **2009**, *137*, 597.
7. (a) Zhang, J. F.; Zhou, Y.; Yoon, J.; Kim, Y.; Kim, S. J.; Kim, J. S. *Org. Lett*. **2010**, *12*, 3852. (b) Lee, Y. H.; Lee, M. H.; Zhang, J. F.; Kim, J. S. *J. Org. Chem.* **2010**, *75*, 7159. (c) Shi, W.; Sun, S.; Li, X.; Ma, H. *Inorg. Chem.* **2010**, *49*, 1206. (c) Du, J.; Fan, J.; Peng, X.; Sun, P.; Wang, J.; Li, H.; Sun, S. *Org. Lett.* **2010**, *12*, 476. (e) Wang, C.; Tao, S.; Wei, W.; Meng, C.; Liu, F.; Han, M. *J. Mater. Chem.* **2010**, *20*, 4635. (f) Chatterjee, A.; Santra, M.; Won, N.; Kim, S.; Kim, J. K.; Kim, S. B.; Ahn, K. H. *J. Am. Chem. Soc.* **2009**, *131*, 2040. (g) Yang, Y.-K.; Ko, S.-K.; Shin, I.; Tae, J. *Org. Biomol. Chem.* **2009**, *7*, 4590. (h) Huang, W.; Song, C.; He, C.; Lv, G.; Hu, X.; Zhu, X.; Duan, C. *Inorg. Chem.* **2009**, *48*, 5061. (i) Zhang, X.; Xiao, Y.; Qian, X. *Angew. Chem. Int. Ed.* **2008**, *47*, 8025. (j) Wu, J. S.; Hwang, I. C.; Kim, K. S.; Kim, J. S. *Org. Lett.* **2007**, *9*, 907. (k) Lee, M. H.; Wu, J.-S.; Lee, J. W.; Jung, J. H.; Kim, J. S. *Org. Lett.* **2007**, *9*, 2501. (l) Yang, Y.-K.; Yook, K.-J.; Tae, J. *J. Am. Chem. Soc.* **2005**, *127*, 16760. (m) Dujols, V.; Ford, F.; Czarnik, A. W. *J. Am. Chem. Soc.* **1997**, *119*, 7386.
8. Xiang, Y.; Tong, A. *Org. Lett.* **2006**, *8*, 1549.
9. Xiang, Y.; Tong, A.; Jin, P.; Yong, J. *Org. Lett.* **2006**, *8*, 2863.