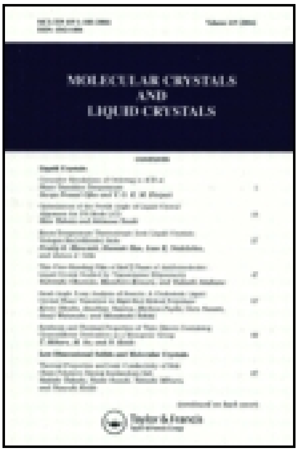

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Synthesis and Optical Determination in Rhodamine-Based Chemosensors Toward Hg^{2+}

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A new dye chemosensor molecule toward Hg^{2+} detection based on rhodamine 6G was synthesized by the condensation reaction of compound **2** *and 2-amino-5,6-dimethyl-benzimidazole. Chemosensor* **1** *showed highly selective functions toward Hg^{2+} recognition with compared to other examined metal ions. The chemical structures of all the intermediates and chemosensor* **1** *were characterized by ^1H NMR, Mass Spectrometer, and elemental analysis. Upon the addition of Hg^{2+}, chemosensor* **1** *exhibited a remarkable emission change from colorless to green fluorescence. Additionally, the absorption color change from colorless to light pink in UV-vis range was observed. However, other metal ions such as Cu^{2+}, Ag^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Fe^{2+}, and Mg^{2+} did not accompany any noticeable spectral change.*

Keywords Chemosensor; Hg^{2+}; rhodamine 6G; and 2-amino-5,6-dimethyl-benzimidazole; fluorescence; emission; color change

1. Introduction

Mercury is one of the most critical cations among various heavy metal ions because it imparts serious toxic effects [1]. In addition, mercury is one of the hazardous pollutants that cause severe environmental contaminations and human health problems [2]. Mercury can easily pass through the biological membranes, which lead malnutrition, digestive, kidney and neurological diseases such as Minamata disease even at very low concentration [3]. Therefore, rapid and simple detection technique of mercury ions has been a critical issue in biological and environmental systems. Various methods for the sensing of Hg^{2+} have been proposed [1–3]. Much effort has been paid to the development of optical chemosensors, which can selectively respond to Hg^{2+} ion [4].

Rhodamine dyes have several advantages: they have good spectroscopic properties such as long absorption and emission wavelength, large molar extinction coefficient, and high fluorescence quantum yield. Moreover, they have been applied to the study of complex biological systems as molecular probes [5]. The five-membered spirolactam structure is

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colorless. However, upon the addition of metal ions, absorption peaks within the visible range increase with accompanying ring-opened amide form [6]. This structure gives a useful method for the fluorogenic detection effects toward metal ions.

In this paper, we have designed a new chemosensor based on rhodamine 6G to achieve fluorogenic and colorimetirc recognition functions toward Hg^{2+}. Among the various metal ions, chemosensor **1** remarkably represented the enhanced detection effects with fluorescence intensity and emission color change, namely from colorless to green fluorescene in acetonitrile. And this dye chemosensor also showed absorbance responses with accompanying color changes from colorless to light pink in acetonitrile.

2. Experimental

2.1 Analysis and Measurements

^{1}H-NMR spectra were recorded on JNM-AL400-400MHz spectrometer with TMS as internal standard. UV-Vis absorbance spectra were measured on an Agilent 8453 spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301 PC fluorescence spectrophotometer equipped with a xenon discharge lamp, 1cm quartz cell. Elemental analyses were recorded on a Flash EA 1112 analyzer. Mass spectra were recorded on a JEOL MStation [JMS-700].

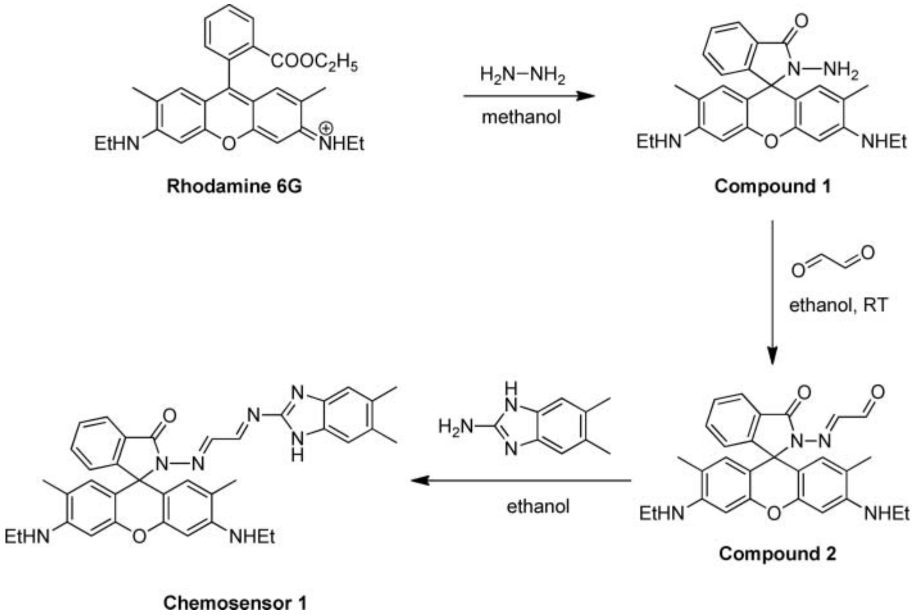
Most of reagents and rhodamine 6G dye were purchased from Aldrich Chemical Co. Ltd. and Alfa Aesar Chemical Co. Ltd. The commercially available Tris-HCl buffer solution ($pH = 7.2$) were purchased from Aldrich. Solvents were purified by standard procedures and used under moisture free atmosphere. The solutions of metal ions were prepared from their nitrate or chloride salts. All chemicals used in this work were of analytical grade and used without further purification.

2.2 Synthesis

Rhodamine 6G hydrazide (compound **1**) was synthesized in a high yield from rhodamine 6G following a literature procedure [7]. It was then reacted with glyoxal following a reported method to give compound **2** [8]. 2-amino-5,6-dimethyl-benzimidazole (0.193 g, 1.2 mmol) was reacted with compound **2** (0.562 g, 1.2 mmol) in 40 mL ethanol. The mixture was then heated at reflux for 7h and monitored by TLC. After the reaction was completed, the solution was cooled to room temperature. The precipitate so obtained was filtered and washed with cold ethanol. The crude product was purified by recrystallization from ethanol to afford chemosensor **1**. Scheme 1

2.3 Job's Method

Using job's method determination, the stoichiometrical characteristics of metal binding ratio with dye chemosensor were examined. Equimolar solutions of dye chemosensor and Hg^{2+} were mixed in different volume ratios (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0). The maximum absorption of these mixtures was characterized.



Scheme 1. The synthesis of chemosensor **1**.

3. Results and Discussion

The chemosensing effects of chemosensor **1** toward various metal ions were investigated by UV-vis spectroscopy in the acetonitrile. The concentration of chemosensor **1** was prepared by 1.0×10^{-5} M. The potential sensing function of chemosensor **1** was tested by mixing it with the metal ions such as Hg^{2+}, Cu^{2+}, Ag^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Fe^{2+} and Mg^{2+} (1.0×10^{-4} M). Hg^{2+} was the only ion that showed an absorption band at 523 nm, which corresponded to the detection work having ring-opening process of the spirolactam form

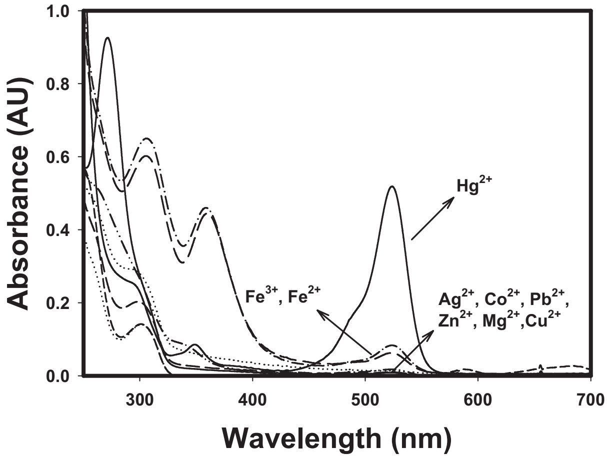


Figure 1. The absorption spectra of chemosensor **1** (1×10^{-5} M) upon the addition of various metal ions (1×10^{-4} M) in acetonitrile (10 mM Tris-HCl, pH = 7.2).

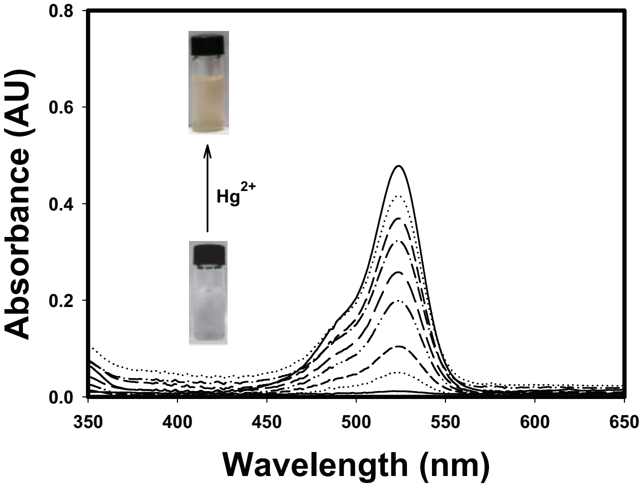


Figure 2. The absorption spectra of chemosensor **1** (1×10^{-5} M) with Hg^{2+} (0 to 8×10^{-5} M) in acetonitrile.Insert: showing the color change of absorption before and after the addition of Hg^{2+} ion.

of chemosensor **1** (Figure 1). Other metal ions did not show any noticeable absorption changes under the identical conditions.

To further investigate the sensing details of chemosensor **1** toward Hg^{2+}, the absorption response of chemosensor **1** (1×10^{-5} M) toward Hg^{2+} (1×10^{-5} M) was monitored by UV-vis absorption in acetonitrile (10 mM Tris-HCl, pH = 7.2) (Figure 2). Upon the addition of Hg^{2+} into a colorless solution of chemosensor **1**, a new absorption band at 523 nm was formed with a color change from colorless to light pink.

As shown in Figure 3, fluorescence spectra (λ_{ex} = 523nm) of chemosensor **1** (1×10^{-5} M) measured in acetonitrile with various metal ions which are Cu^{2+}, Ag^{2+},

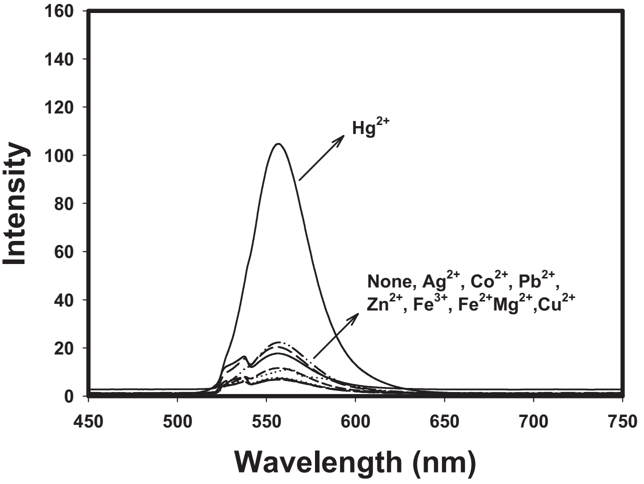


Figure 3. Emission changes of chemosensor **1** (1×10^{-5} M) upon the addition of various metal ions (1×10^{-5} M) in acetonitrile.

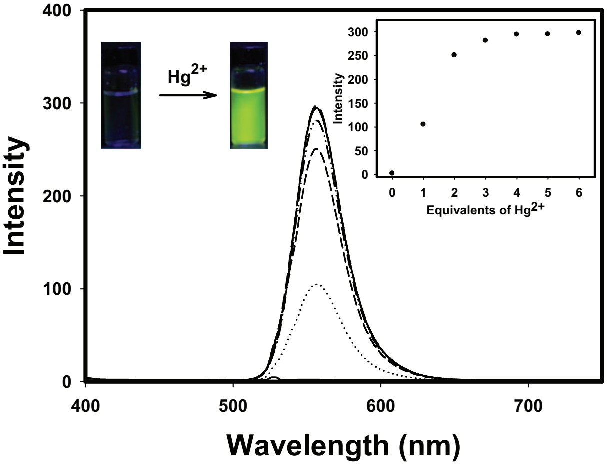


Figure 4. Fluorescence intensity changes of chemosensor **1** (1×10^{-5} M) in upon the addition of Hg^{2+} (0 to 6×10^{-5} M). Insert: showing the colorchange of emission before and after the addition of Hg^{2+} ion (left). Change of emission intensity according to equivalents of Hg^{2+} (right).

Co^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Fe^{2+}, and Mg^{2+} (1×10^{-5} M). Chemosensor **1** without metal ions showed a very weak fluorescence at 557 nm; however, Hg^{2+} addition created a remarkably enhanced green fluorescence at 557 nm. Cu^{2+}, Fe^{3+}, and Fe^{2+} also induced an emission results, but the all of intensity were very small.

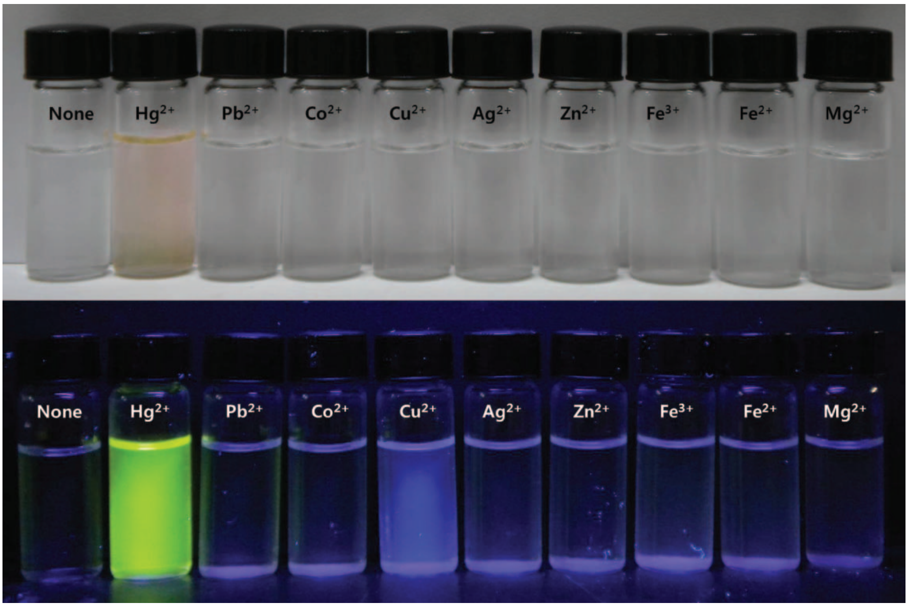


Figure 5. Absorption changes (top) of chemosensor **1** (1×10^{-5} M) with various metalions (5×10^{-5} M) and fluorescence changes (bottom) of chemosensor **1** (1×10^{-5}) with various metalions (1×10^{-5} M) in acetonitrile.

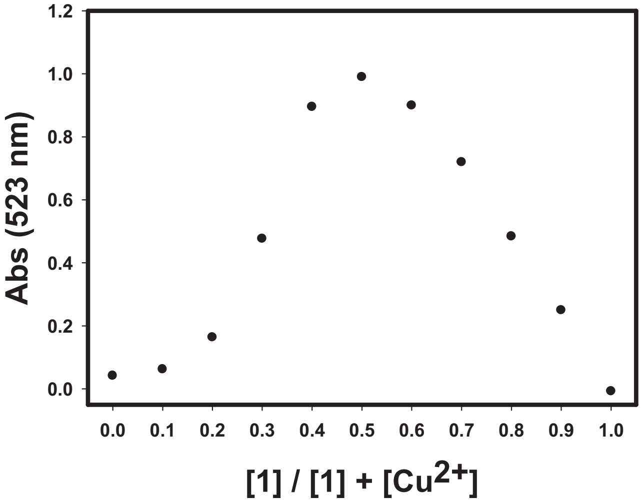


Figure 6. Job's plot monitored at 523 nm: the total concentration of $[Hg^{2+}]+[\mathbf{1}]$ was 5.0×10^{-5} M.

To validate the interaction of chemosensor **1** and Hg^{2+}, fluorescence titration of chemosensor **1** with Hg^{2+} (0 to 6×10^{-5} M) was carried out. Upon the addition of Hg^{2+}, emission at 557 nm increased. The fluorescence emission color changed from colorless to green with increasing Hg^{2+} amount. As shown in Figure 4 (insert), the emission intensity increased with increasing Hg^{2+} amount up to 4 equiv., but there was no more increase from 4 equiv.

Photograph images for the promising sensing effects toward various tested metal ions represent that the designed dye chemosensor herein showed the remarkable sensing selectivity potentials toward Hg^{2+}. It showed absorption and fluorescence color changes of chemosensor **1** (Figure 5).

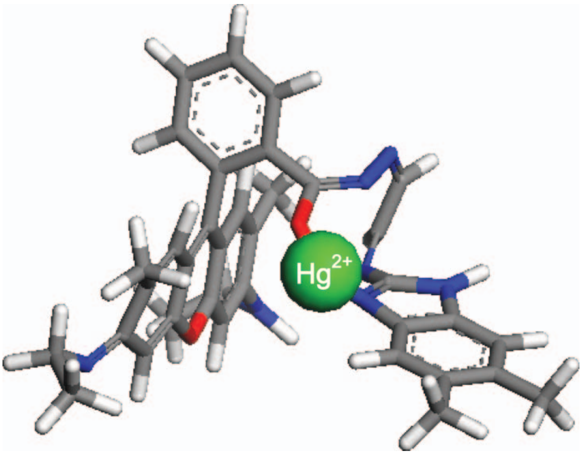


Figure 7. Calculated modeling structure for interaction between chemosensor **1** and Hg^{2+}.

Additionally, we determined the binding ratio between chemosensor **1** and Hg^{2+} using the Job's method [9]. The results proved the 1:1 binding stoichiometry of chemosensor **1** toward Hg^{2+} with a total concentration of [Hg^{2+}]+[**1**] at 5.0×10^{-5} M. The absorbance demonstrated a maximum value when the molar fraction of Hg^{2+} was 0.5, which represented the 1:1 binding stoichiometry between chemosensor **1** and Hg^{2+} (Figure 6).

Furthermore, to study the metal binding position, the molecular modeling calculation based on DMol^3 program is performed [10–12].The CPK model of the energy-minimized structure of chemosensor **1** with Hg^{2+} are shown in Figure 7, which shows the recognition of chemosensor**1** with Hg^{2+} to form a stable complex.

4. Conclusions

In conclusion, we synthesized and characterized a new chemosensor **1** based on rhodamine 6G which could specifically recognize Hg^{2+} in acetonitrile. An obvious color change from colorless to light pink was observed by the naked eyes. Furthermore, its selectivity toward Hg^{2+} with compared to other metal ions was very remarkable. It also showed significant sensing responses in fluorescence changes with accompanying color changes from colorless to green emission in acetonitrile.

Acknowledgment

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