

<Research Paper>

Synthesis and Optical Properties of Novel Chemosensor Based on Rhodamine 6G

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Abstract: The opto-functional materials have been developed as a promising research topic toward the end uses for optical materials and applications. The attractive area in this part was the design of sensor molecules for detecting harmful environmental factors. These harmful factors impart undesired effects on wide range of chemical and biological phenomenon. In this context, many researchers have studied luminescence chemosensor materials. These sensor molecules showed optical signals such as color or fluorescence change by detecting harmful environmental factors. In this study, the novel fluorescence chemosensor 1 has been designed and synthesized through reaction of rhodamine 6g hydrazide and 2-hydroxy-1-naphthaldehyde. The chemosensor 1 had been analyzed by UV-Vis and fluorescence spectrophotometer. We found that this chemosensor 1 has 'off-on' and dual type sensing properties toward Cu²⁺ and Mg²⁺.

Keywords: Rhodamine 6G, chemosensor, absorption, fluorescence, metal ions, HOMO/LUMO

1. Introduction

The copper affects in various environmental pollutions and biological processes due to its property of cycle between multiple oxidation states¹⁾. The magnesium also affects in various biological processes and environmental²⁾. Hence, sensing and monitoring for these copper and magnesium metals are important to human and environmental. Many researchers have been investigated for various kinds of chemosensor based on different chromophores and phosphors such as anthraquinone, coumarin, rhodamine³⁾. Chemosensors based on these materials plays a role as useful materials for detection of metal ions due to their selectivity and sensitivity and real-time monitoring^{4,6)}. The rhodamine dye material has been used widely to investigate chemosensors due to its excellent fluorescence property⁷⁾.

As is well-known, rhodamine derivatives provides an proper mode for the frame of new 'off-on' type fluorescence sensor based on spiro-lactam (non-fluorescent) to ring-opened amide (fluorescent) process utilized for the detection of metal ions⁸⁻¹⁰⁾.

In this study, we have designed and synthesized a

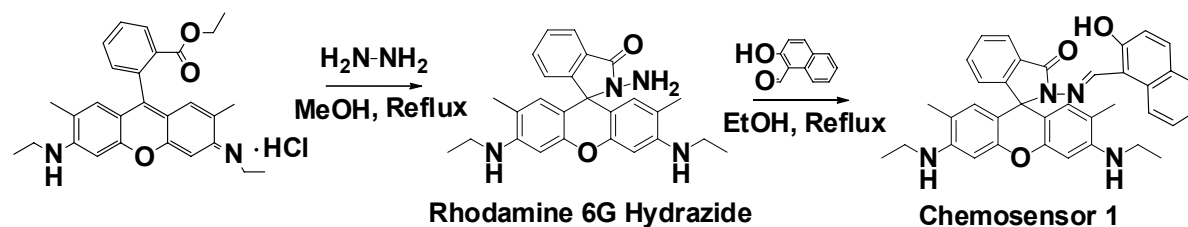
novel chemosensor based on rhodamine 6G derivatives. This novel chemosensor detected Cu²⁺ and Mg²⁺ ions, which showed yellow and green fluorescence emission visible to naked-eye with compared to other investigated metal ions. Its properties of Cu²⁺ and Mg²⁺ detection were investigated and analyzed in fine points. Structural analysis of this novel dye sensor was identified by ¹H-NMR, Mass and Elemental analysis. Optical sensing properties were investigated using UV-Vis absorption and fluorescence emission measurement.

The metal complex formation was measured by Job's plot method. Finally, electron distribution and energy level calculation such as HOMO and LUMO was computationally simulated using DMol3 program of Materials Studio 4.3 package.

2. Experimental

All the reagents and solvents, used for synthesis of rhodamine 6G based chemosensor 1, were purchased from Aldrich and used without further purification. Absorption and fluorescence spectra of the prepared novel chemosensor 1 were measured with and Agilent 8453 spectrophotometer and a Shimadzu RF-5301PC fluorescent spectrophotometer, respectively.

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Scheme 1. The synthetic route for chemosensor 1

^1H NMR spectra and elemental analyses were recorded with JNM-AL400 spectrometer operated at 400MHz NMR and a Carlo Elba Model 1106 analyzer, respectively. Mass spectra were recorded on a JEOL M Station [JMS-700]. HOMO/LUMO calculation and modelling simulation proceed with DMol³ of Material Studio 4.3. Electron distributions and energy potentials were also calculated with Material Studio 4.3.

Rhodamine 6G based dye compound was synthesized through 2step reaction with rhodamine 6G hydrazide and 2-hydroxy-1-naphthaldehyde. The scheme was shown in Figure 1. Rhodamine 6G hydrazine is prepared according to the literature method¹¹⁻¹⁷.

Rhodamine 6G Hydrazide (1.5mmol, 0.6437g) and 2-hydroxy-1-naphthaldehyde (0.258mmol, 0.2582g) were dissolved in absolute EtOH.

The mixture solution was mixed and added 3 drops of acetic acid. After 8h, reaction mixture cooled to room temperature, yellow precipitate was filtered off, washed with EtOH. Obtained solid was recrystallized from MeCN/Water to give chemosensor 1 as 0.6620g (76% yield).

$^1\text{H-NMR}$ (400MHz, CDCl_3) : 9.78 (1H, s), 8.04(1H, t, $J=4.4\text{Hz}$), 7.80 (1H, d, $J=8.8\text{Hz}$), 7.66 (2H, t, $J=7.2\text{Hz}$), 7.54 (2H, q, $J=4.7\text{Hz}$), 7.44 (1H, t, $J=7.6\text{Hz}$), 7.14 (1H, t, $J=4.4\text{Hz}$), 7.09 (1H, d, $J=9.0\text{Hz}$), 6.47 (2H, s), 6.33 (2H, s), 3.50 (2H, s), 3.20 (4H, q, $J=6.8\text{Hz}$), 1.87 (6H, s), 1.29 (8H, t, $J=7.1\text{Hz}$). MS: 582 (M^+).

3. Results and Discussion

3.1 UV Vis and fluorescence spectra response of chemosensor 1

We measured UV-Vis and fluorescence spectra to further investigate the selectivity of chemosensor 1 for the result as shown Figure 1.

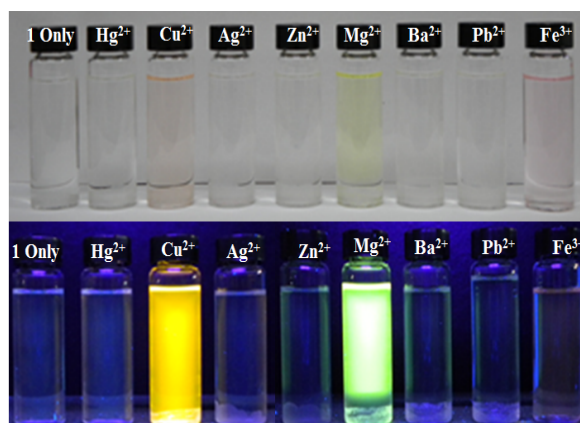


Figure 1. The picture of absorption (top) and fluorescence (bottom) change of chemosensor 1 (10 μM) to various metal ions (10 μM) in MeCN (Tris-HCl pH 7.2).

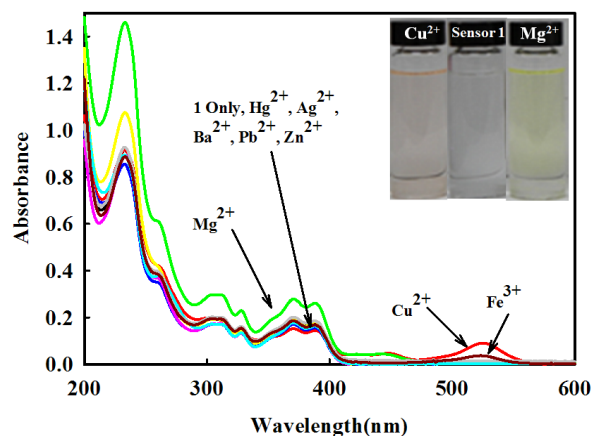


Figure 2. UV-Vis spectra of chemosensor 1 (10 μM) upon addition of different metal ions (10 μM) in MeCN (Tris-HCl pH 7.2). Inset: photographs of color change for sensor 1 toward Cu^{2+} and Mg^{2+} in MeCN (Tris-HCl pH 7.2).

As shown in Figure 2, without metal ions, chemosensor 1 scarcely showed an absorption at 500~600nm. Upon addition of different metal ions, the chemosensor 1 with Cu^{2+} and Fe^{3+} showed absorptions. Absorption peak of Cu^{2+} was higher than other metal ions at 525nm. Absorption peak of Fe^{3+} also showed

minor increase. As shown in Figure 3, without metal ions, chemosensor 1 showed non fluorescence. Upon addition of different metal ions, Cu^{2+} and Mg^{2+} only showed orange and green fluorescence at 567nm and 509nm, respectively. Toward Cu^{2+} and Mg^{2+} , we expect that this chemosensor 1 for absorbance and emission changes are due to spirolactam ring structure. When spirolactam ring closed, it shows colorless and non-fluorescence.

However, color and fluorescence appear when spirolactam ring open¹⁴. Through former researches, this chemosensor 1 can be turn 'off-on' type and dual type chemosensor toward Cu^{2+} and Mg^{2+} ¹⁵.

3.2 Cu^{2+} and Mg^{2+} titration of chemosensor 1

The chemosensor 1 showed properties of detecting Cu^{2+} and Mg^{2+} . In this regard, we also investigated titration of Cu^{2+} and Mg^{2+} with chemosensor 1.

As shown in Figure 4, upon addition of Cu^{2+} , the absorption intensity increased at 529nm peak. The absorption wavelength was red shifted from 388nm to 529nm. Absorption intensity of the peak decreased at 388nm and absorption intensity at 529nm was enhanced. This enhancement was saturated with over 6 equiv. Mg^{2+} titration was also shown similar results with Cu^{2+} titration. Upon addition of Mg^{2+} , the absorption also increased at 448nm. The absorption wavelength was red-shifted from 388nm to 448nm. The color change from colorless to yellow was shown with 60nm red shift. The increase was saturated with over 16 equiv.

As shown in Figure. 5, upon addition of Cu^{2+} , the emission also increased at 557nm. This increase was saturated with over 6 equiv. Upon addition of Mg^{2+} , the emission increased at 510nm. The increase was saturated with over 30 equiv. These results indicate that the chemosensor 1 has a property of application for quantitatively useful detection probe toward Cu^{2+} and Mg^{2+} .

3.3 Job's Plot Method

We investigated the binding ratio between chemosensor 1 toward each Cu^{2+} and Mg^{2+} using the Job's method¹⁸.

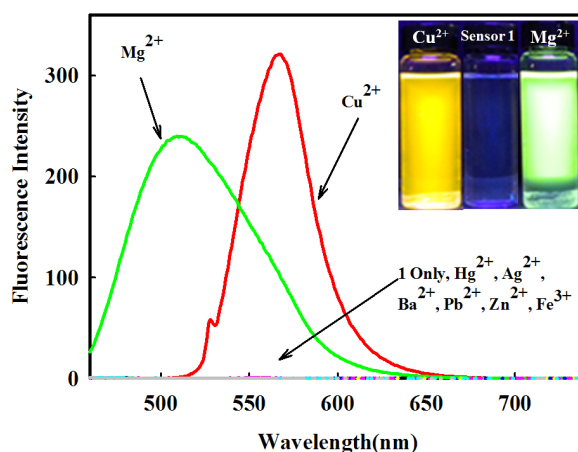


Figure 3. Fluorescence spectra of chemosensor 1 ($10\mu\text{M}$) upon addition of different metal ions ($10\mu\text{M}$) in MeCN (Tris-HCl pH 7.2). Inset: photographs of fluorescence change for sensor 1 toward Cu^{2+} and Mg^{2+} in MeCN (Tris-HCl pH 7.2).

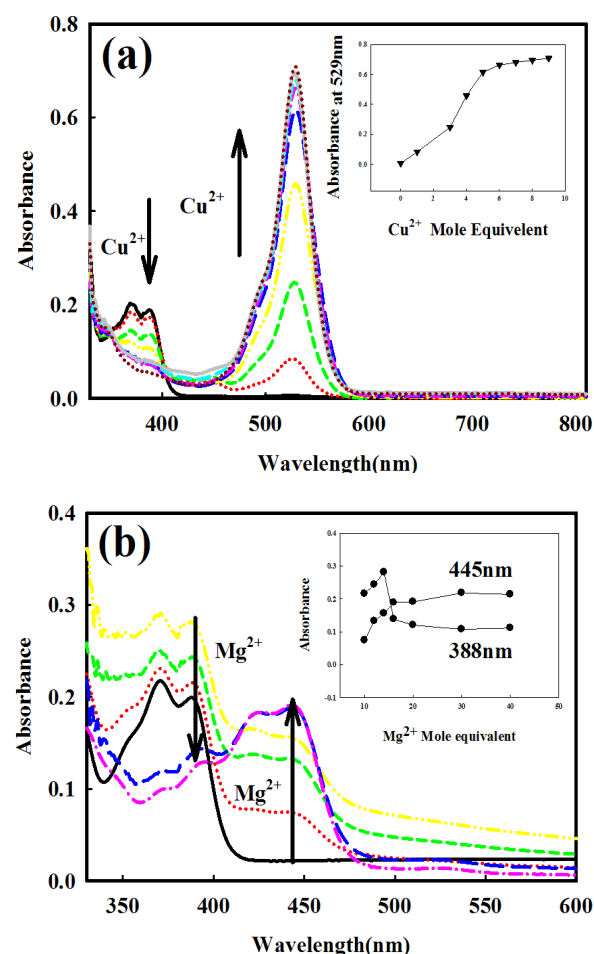


Figure 4. UV-Vis spectra of chemosensor 1 ($10\mu\text{M}$) upon addition of different mole concentrations for (a) Cu^{2+} ($10\mu\text{M}$) and (b) Mg^{2+} ($10\mu\text{M}$) in MeCN (Tris-HCl pH 7.2). Inset: The non-linear graph of absorbance spots toward (a) Cu^{2+} and (b) Mg^{2+} .

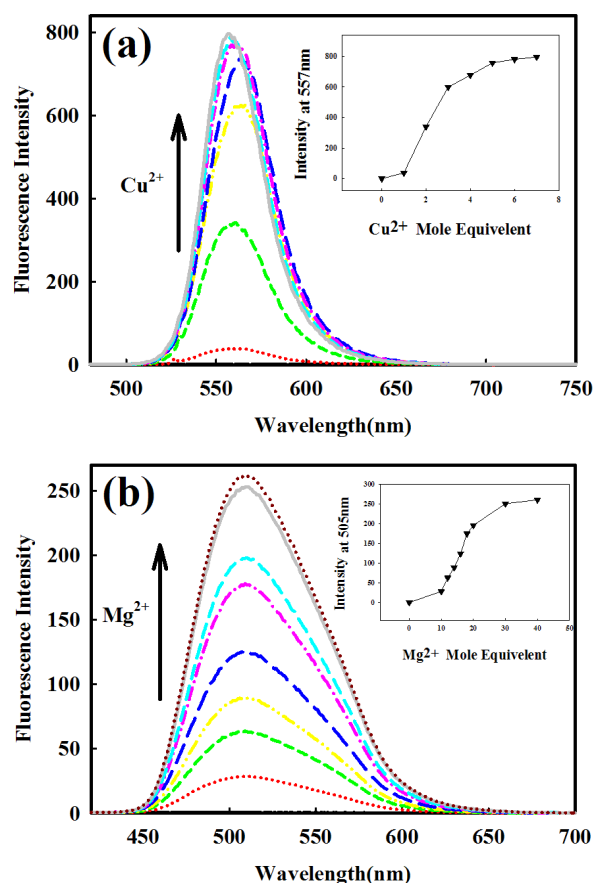


Figure 5. Fluorescence spectra of chemosensor 1 (10 μM) upon addition of different mole concentration for (a) Cu²⁺ and (b) Mg²⁺ (10 μM) in MeCN (Tris-HCl pH 7.2). Inset: the non-linear graphs of fluorescence intensity spots toward (a) Cu²⁺ and (b) Mg²⁺.

The relationship between maximum absorption peaks versus various mole fractions is shown in Figure 6.

From the findings with Cu²⁺, chemosensor 1 exhibited that the mole fraction was close to 50%.

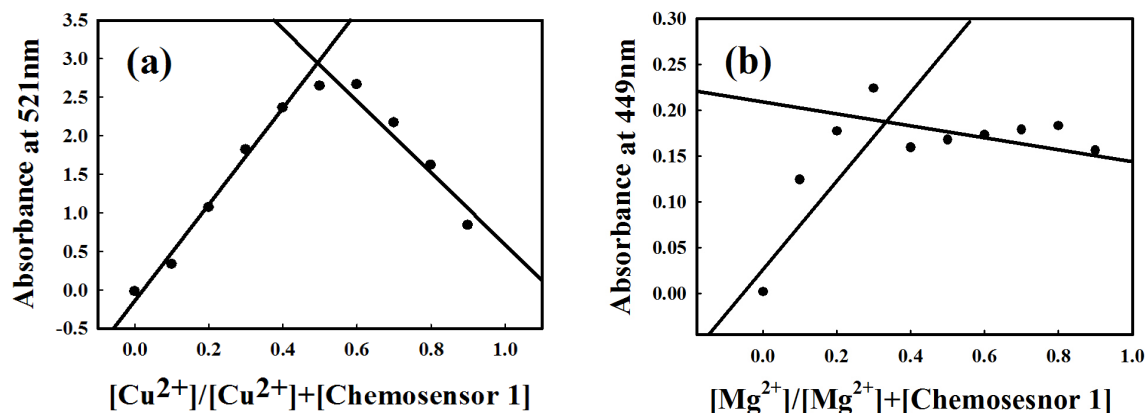


Figure 6. Job's plot method of chemosensor 1 (10 μM) with addition of different mole concentrations for (a) Cu²⁺ and (b) Mg²⁺ (10 μM) in MeCN (Tris-HCl pH 7.2).

In this regard, Result for Cu²⁺ indicated 1:1 complex stoichiometry composition between chemosensor 1 and Cu²⁺ ions. However, Result for Mg²⁺ showed that the mole fraction was close to 33% and indicated 2:1 complex stoichiometry composition between chemosensor 1 and Mg²⁺.

3.4 The calculation of electron distributions and HOMO/LUMO energy levels with DMol³ of Material Studio 4.3

We computationally calculated to investigate electron distributions and HOMO/LUMO energy levels of chemosensor 1.

It has been simulated with Material Studio 4.3 suite of program which is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof (PBE) function of generalized gradient approximation (GGA) level with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbitals¹⁹⁻²¹. As shown in Figure 7, chemosensor 1 was calculated electron distributions and its HOMO/LUMO energy levels of chemosensor 1.

The ΔE value was finally calculated 2.235 eV. HOMO and LUMO states were showed that electron distributions moved from xanthene part to spiro lactam and 2-hydroxy-1-naphthaldehyde parts in structure of chemosensor 1. This indicates that chemosensor 1 has interesting property of intra molecular charge transfer system.

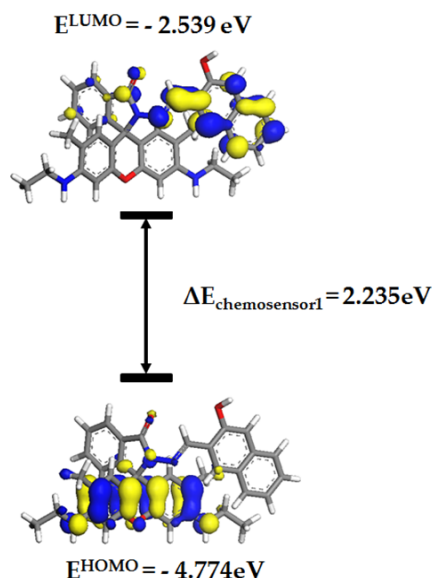


Figure 7. Electron distributions and HOMO/LUMO energy levels of chemosensor 1.

4. Conclusions

In this study, we have designed and synthesized novel chemosensor 1. This chemosensor 1 showed significant absorption and fluorescence response toward Cu^{2+} and Mg^{2+} . The binding ratios of chemosensor 1 toward Cu^{2+} and Mg^{2+} were also investigated by Job's plot method. HOMO/LUMO energy potential was calculated and the electron density distribution was simulated with energy excitation.

Above investigated results indicated that chemosensor 1 is 'off-on' and dual type sensing material for Cu^{2+} and Mg^{2+} .

Acknowledgment

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