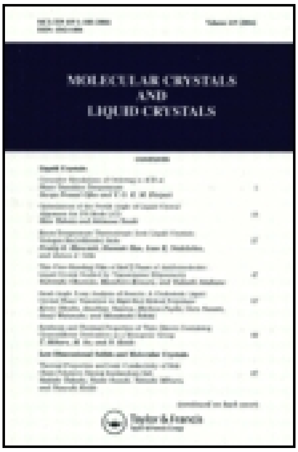

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Design, Synthesis and Optical Property of Rhodamine 6G Based New Dye Sensor

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Design, Synthesis and Optical Property of Rhodamine 6G Based New Dye Sensor

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Rhodamine dyes have been attracted to many researchers due to its excellent photophysical properties. Interesting one of these dyes is rhodamine 6G. In this study, we have designed and synthesized a strong yellowish-green fluorescent emission dye sensor based rhodamine 6G for the detection of Hg^{2+} *ions. It has noticeable properties of application for detecting and recognizing the presence of* Hg^{2+} *ions. In this regard, the optical properties of this dye sensor were intensively investigated using UV-Vis absorption, fluorescent spectrophotometer. Formation type of metal binding complex for this dye sensor was also determined by Job's plot method. Finally, computational calculation was simulated and calculated to approach for HOMO/LUMO of this dye sensor.*

Keywords Rhodamine 6G; Dye sensor; Optical property; Fluorescent; Heavy metal ions; Job's plot method; HOMO/LUMO

1. Introduction

Rhodamine dyes impart a strong fluorescent emission property and have a structural configuration of xanthene chromophore and carbonyl group in molecular structure [1–5]. There are attractive kinds of rhodamine dyes such as rhodamine 6G and rhodamine B [1–3]. These rhodamine dyes are widely applied as fluorescent sensing probes due to higher absorption and excellent fluorescence properties, quantum yields and photostability [2–4]. Their corresponding derivatives have also been applied to the wide areas such as molecular switches, thermometers and chemosensors [3–5]. Recently, various kinds of heavy metals have been caused to environmental pollution troubles. In this context, the dye sensor designed herein has been taken noticeable prospects due to its easy and convenient application benefits toward environmental pollution monitoring [1,2,4,5]. Recently, many researchers have investigated the various chemosensor materials. Rhodamine dyes are widely considered as a basic and useful substance for the promising chemosensor tool.

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Herein, we have designed and synthesized for a new dye sensor based on rhodamine 6G derivatives. This new dye sensor markedly detected Hg^{2+} ions, which showed a red color absorption and a strong yellowish-green fluorescence emission with compared to other heavy metal ions such as Cu^{2+}, Ag^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+}. Mercury is well known as one of the most toxic and dangerous metal due to its infliction for serious damage to environment and health such as central nervous and endo-crine system [6–7]. This dye sensor can provide an important role of environmental pollution monitoring caused by mercury. Detection of Hg^{2+} ions were investigated and analyzed in details. Structural analyses of this new dye sensor were identified by ^{1}H-NMR, Mass and EA. Optical sensing properties of this dye sensor were determined 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 were computationally simulated using DMol^3 program of *Materials Studio 4.3* package.

2. Experimental

2.1 Measurement

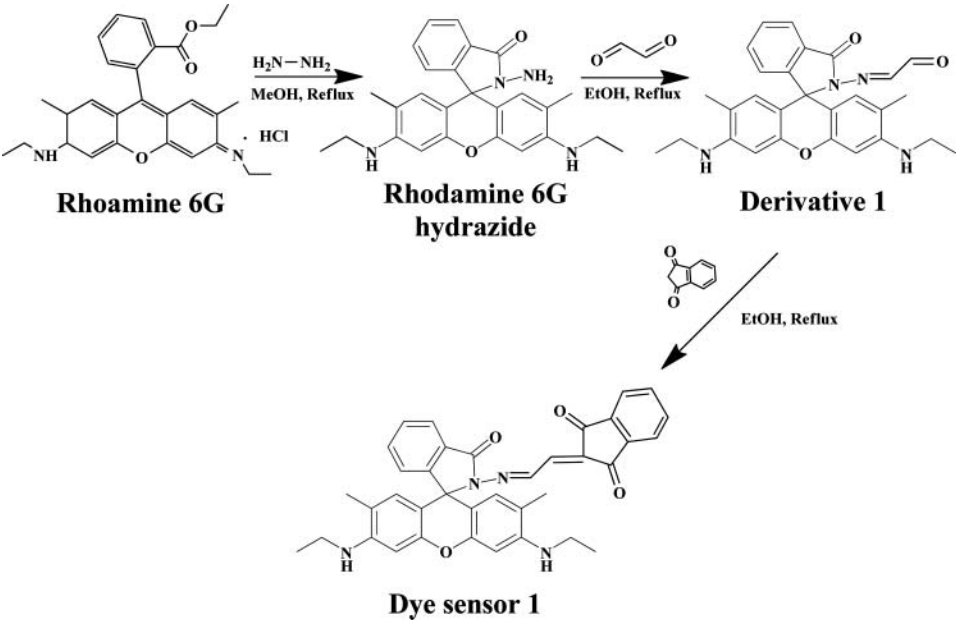
All the reagents and solvents, used for synthesis of rhodamine 6G based dye sensor 1, were purchased from Aldrich and used without further purification. Absorption and fluorescence spectra of the prepared dye sensor 1 were measured with an Agilent 8453 spectrophotometer and a Shimadzu RF-5301PC fluorescent spectrophotometer, respectively. ^{1}H NMR spectra and elemental analyses were recorded with JNM-AL400 spectrometer operated at 400 MHz NMR and a Carlo Elba Model 1106 analyzer, respectively. Mass spectra were recorded on a JEOL MStation [JMS-700]. HOMO/LUMO calculation and modeling simulation proceed with DMol^3 of *Material Studio 4.3*.

2.2 Synthesis

Rhodamine 6G, hydrazine hydrate and 1,3-indanedion were used to synthesize rhodamine 6G based dye sensor 1. As the first step, rhodamine 6G and hydrazine hydrate were reacted for rhoamine 6G hydrazide depending on described method [8–9]. As the second step, rhodamine 6G hydrazide and glyoxal were synthesized for rhodamine derivative 1 on described method [8–9]. The corresponding synthetic procedure of dye sensor 1 was illustrated in Scheme 1.

Rhodamine derivative 1 (0.4g, 0.8 mmol) and 1,3-indanedion (0.12g, 0.8 mmol) were dissolved in 50 ml of EtOH. The solution was refluxed at 70°C for 24h. After cooling to room temperature, the reaction product was filtered out and dried in vacuum. The aimed dye sensor product was obtained in 59.2% yield.

^{1}H-NMR (400MH$_Z$, $CDCl_3$) : 9.43–9.41 (d, 2H), 8.07–8.06 (d, 2H), 7.61–7.48 (m, 3H), 7.06–7.04 (d, 2H), 6.36 (s, 3H), 6.25 (s, 3H), 3.54 (s, 2H), 3.23–3.18 (m, 6H), 1.82 (m, 6H), 1.56–1.53 (d, 2H), 1.39–1.30 (t, 6H). MS *m/z*: 596 (M^+). Anal. Calculated for $C_{37}H_{32}N_4O_4$: C, 74.41; H, 5.36; N, 9.38; O, 10.72: found; C, 68.51; H, 4.98; N, 10.46; O, 10.58.



Scheme 1. Synthesis procedure of dye sensor 1.

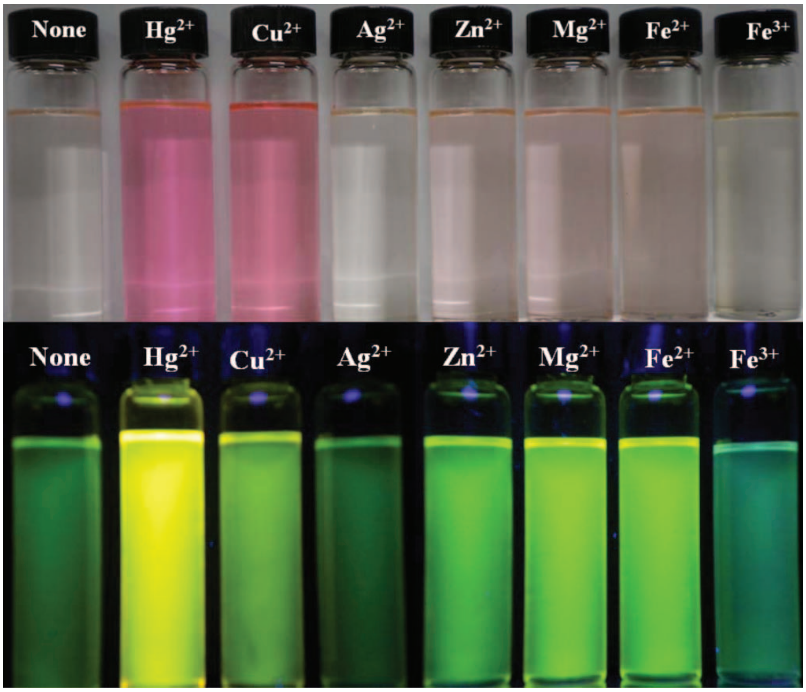


Figure 1. Photo images for absorption color (top) and fluorescence emission color changes (bottom) from the complex of dye sensor 1 (10 μM) and metal ions (10 μM) in $CHCl_3$:THF (*v/v* 9:1) such as none, Hg^{2+}, Cu^{2+}, Ag^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} (from left to right).

3. Results And Discussion

In this study, we have synthesized rhodamine 6G based dye sensor 1. To investigate sensing properties toward toxic metal ions using this dye sensor 1, dye sensor 1 (10μM) and several kinds of metal ions (10μM) such as Hg^{2+}, Cu^{2+}, Ag^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} in $CHCl_3$:THF (*v/v* 9:1) were mixed and their complex properties were optically measured. As shown in Fig. 1, this dye sensor 1 showed color change from colorless to significant red color absorption toward Hg^{2+} and Cu^{2+} ions. However, the fluorescence properties showed that this dye sensor 1 reacted with all tested metal ions and itself represented weak greenish fluorescence emission. In particular, the complex with Hg^{2+} ions displayed very strong yellowish-green fluorescence emission, which is very promising function to be used as a mercury sensing probe with this designed dye sensor 1.

UV-Vis absorption and fluorescence emission spectra are shown in Figs. 2 and 3, which show more detailed investigation on the optical sensing properties using the prepared dye sensor 1. Figure 2 shows the absorption spectral peaks of dye sensor 1 (10 μM) with several test metal ions (10 μM) in $CHCl_3$:THF (*v/v* 9:1). The dye sensor 1 shows a maximum absorption peak at 520 nm. Upon the addition of above mentioned metal ions, all of the absorption peaks slightly increased. Especially, the dye sensor 1 with Hg^{2+} showed greatly increased absorption peak with compared to other metal ions.

Figure 3 shows the fluorescence emission spectra of dye sensor 1 (10 μM) with metal ions (10 μM) in $CHCl_3$:THF (*v/v* 9:1). The dye sensor 1 represents an emission peak at 543 nm. With adding selected metal ions into dye sensor 1 solution, it showed little difference in fluorescence emission values. In particular, fluorescence emission wavelength of dye

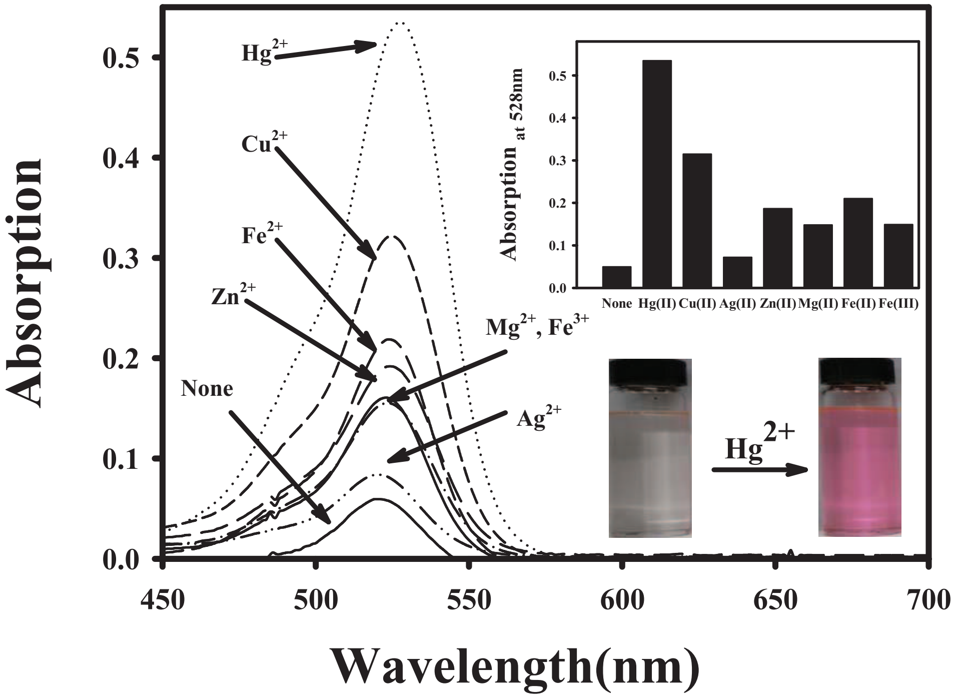


Figure 2. Absorption spectra of dye sensor 1 (10 μM) with several metal ions (10 μM) in $CHCl_3$: THF (*v/v* 9:1): inset—the absorption at 528 nm of dye sensor 1 (10 μM) to metal ions (10 μM).

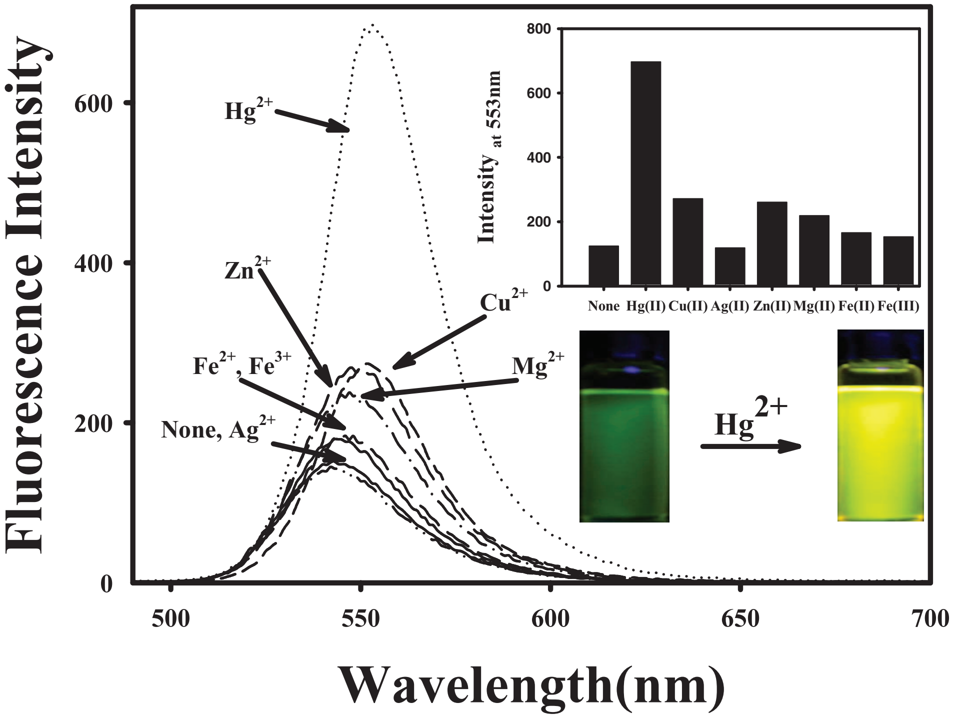


Figure 3. Fluorescence emission spectra of dye sensor 1 (10 μM) with several metal ions (10 μM) in $CHCl_3$:THF (*v/v* 9:1): inset—the fluorescence intensity at 553 nm of dye sensor 1 (10 μM) to metal ions (10 μM).

sensor 1 with binding Hg^{2+} showed slight red shift to 553 nm and also displayed a dramatic increase of its emission intensity having yellowish-green fluorescence.

As a useful function of common sensor, its selective detection ability to compete with other subjecting metal ions is of importance [10–11]. In this regard, we have also monitored the influence of the presence of other metal ions to the dye sensor 1 and Hg^{2+}.

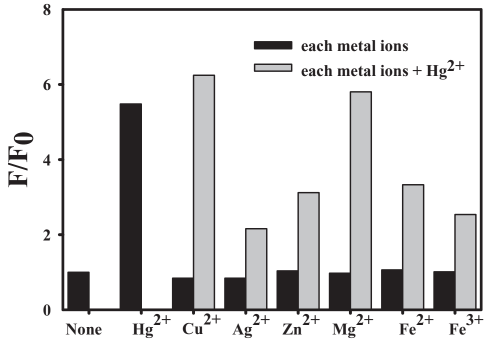


Figure 4. Fluorescence emission spectra of dye sensor 1 (1 μM) with 1 μM of several metal ions (black bar) and selectivity function for the competition of Hg^{2+} and other metal ions mixture (1 μM) (grey bar) in $CHCl_3$:THF (*v/v* 9:1), respectively.

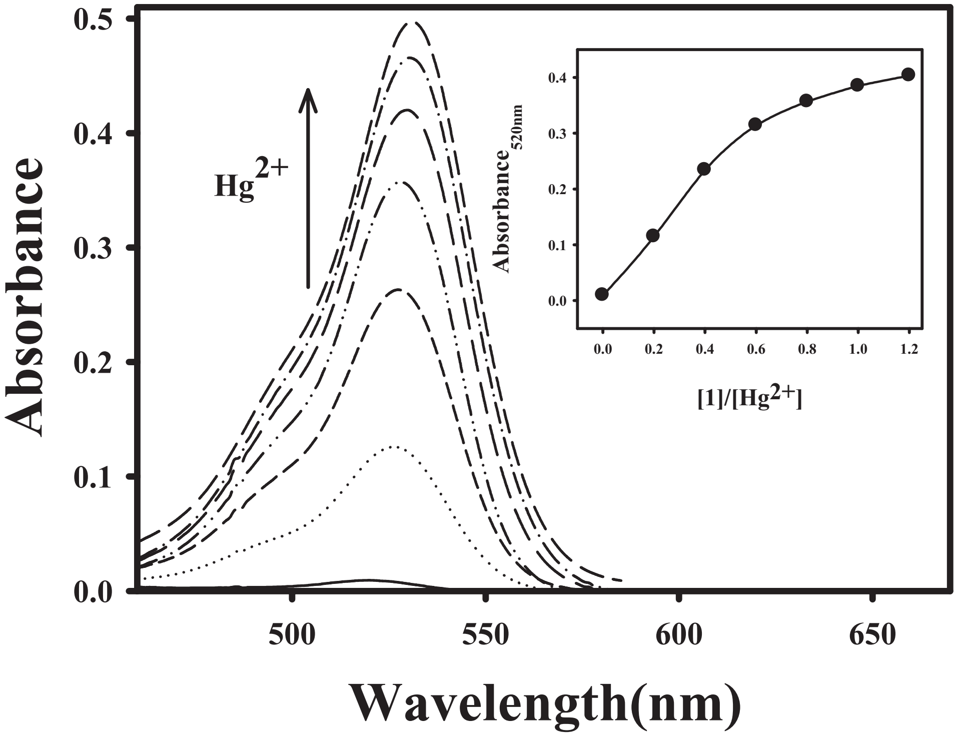


Figure 5. Absorption response at 520 nm of dye sensor 1 (10 μM) with different mole concentrations (0–12 μM) of Hg^{2+} in $CHCl_3$:THF (*v/v* 9:1).

Dye sensor's selectively recognizing potentials toward Hg^{2+} competing with other metal ions were shown in Figure 4. When 1 μM of Hg^{2+} was added into the solutions of dye sensor 1 having each metal ion, the fluorescence intensity for the detection of Hg^{2+} was not intervened by the presence of Cu^{2+} and Mg^{2+}. Whereas, the fluorescence intensity for the detection of Hg^{2+} was slightly quenched by the presence of Ag^{2+}, Zn^{2+}, Fe^{2+} and Fe^{3+}. However, from this finding, it can be proposed that this designed dye sensor 1 showed very promising selectivity function toward harmful Hg^{2+} ions in the circumstance of the presence of other metal ions [12–13].

Figure 5 shows the absorption response with different mole concentrations of Hg^{2+}. With increasing Hg^{2+} concentrations, maximum absorption value of dye sensor 1 gradually increased at 520 nm. Figure 6 also shows the fluorescence emission response with different mole concentrations of Hg^{2+}. With increasing Hg^{2+} concentrations, maximum fluorescence emission intensity remarkably increased at 552 nm. The results show that this dye sensor 1 can be applied as quantitatively useful chemosensing probe toward the aimed Hg^{2+} detection.

Furthermore, we investigated the binding ratio between dye sensor 1 and Hg^{2+} using the Job's method [14]. For the measurement of Job's plot method, various molar ratios between dye sensor 1 and Hg^{2+} metal ions (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0) in $CHCl_3$:THF (*v/v* 9:1) were prepared. The relationship between maximum absorption peaks versus various mole fractions is shown in Fig. 7. From the findings, dye sensor 1 exhibited that the mole fraction was close to 50%. In this regard, these results indicate 1:1 complex stoichiometry composition between dye sensor 1 and Hg^{2+} ions.

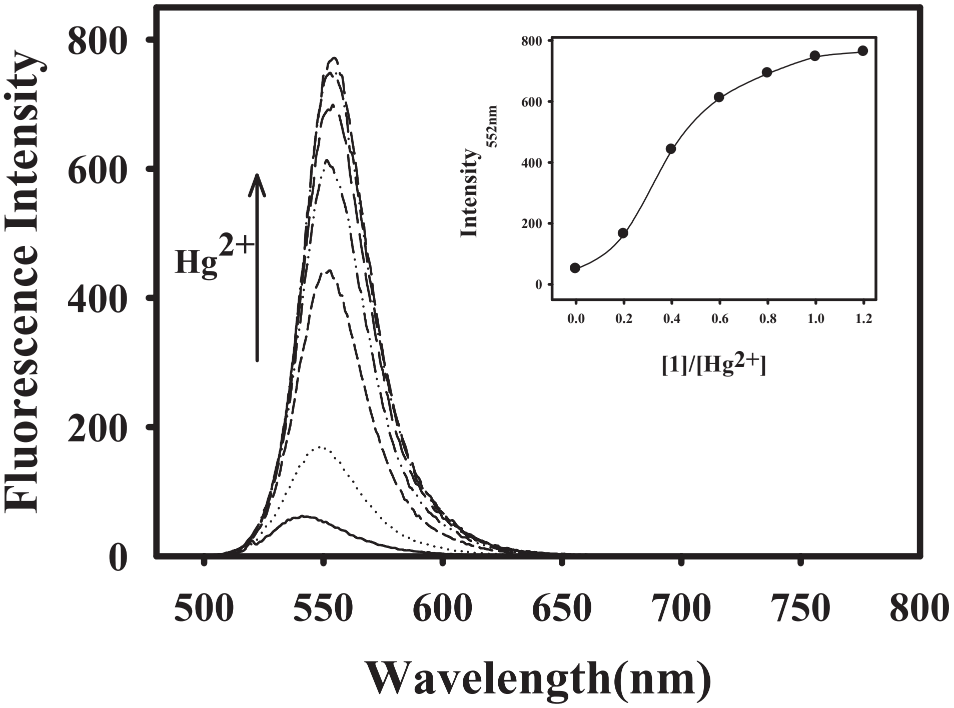


Figure 6. Fluorescence response at 552 nm of dye sensor 1 (10 μM) with different mole concentrations (0–12 μM) of Hg^{2+} in $CHCl_3$:THF (*v/v* 9:1).

Finally, we computationally calculated electron distributions and HOMO/LUMO energy levels of dye sensor 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 orbits [15–17]. Figure 8 shows the calculated electron distributions and its HOMO and

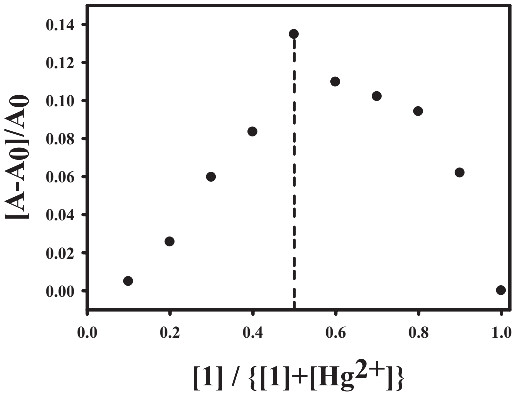


Figure 7. Job's Plot for dye sensor 1 with Hg^{2+}.

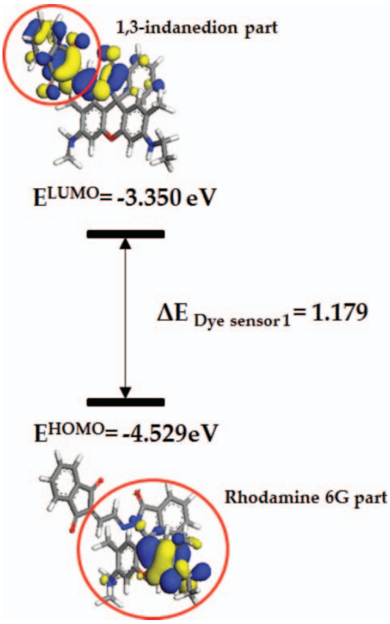


Figure 8. Electron distributions and HOMO/LUMO energy levels of dye sensor 1.

LUMO energy levels of dye sensor 1. With considering HOMO and LUMO states, most of electrons moved from xanthene chromophore within rhodamine 6G to 1,3-indanedion part through this dye sensor 1. This interesting characteristic can be explained by intramolecular charge transfer system of dye sensor 1.

4. Conclusions

In this study, we designed and synthesized rhodamine 6G based dye sensor 1. Sensing properties of this dye sensor 1 was determined with various kinds of heavy metal ions such as Hg^{2+}, Cu^{2+}, Ag^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+}. Especially, dye sensor 1 showed significant sensing properties toward Hg^{2+}:colorless to red absorption and colorless to yellowish green fluorescence emission. Binding configuration between dye sensor 1 and Hg^{2+} revealed to 1:1 stoichiometry complex from Job's plot method. HOMO/LUMO energy potential was calculated and the movement of electron density distribution was simulated with energy excitation.

Acknowledgments

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