

<Research Paper>

Study of HOMO and LUMO Energy Levels for Spirolactam Ring Moiety Using Electrochemical Approach

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Abstract: Rhodamine dyes have been studied in various scientific areas due to their excellent photophysical properties. In particular, these rhodamine dyes are one of the most famous fluorophores as signal unit in chemosensor study. This is related to spirolactam ring system in rhodamine dyes. When the spirolactam ring is closed, there is nonfluorescence and colorless. Whereas, ring-opening of the corresponding spirolactam induces strong fluorescence and color. These absorption and emission changes are related to structural changes as well as electron energy potential levels such as HOMO and LUMO values. In this study, two different structures of rhodamine 6G hydrazide depending on the spirolactam ring system were investigated using absorption measurement, electrochemical measurement and computational calculations.

Keywords: rhodamine 6G, HOMO, LUMO, absorption, cyclicvoltammetry

1. Introduction

Recently, various kinds of fluorophores such as rhodamine, coumarin, pyrene, xanthenes, squaraine, cyanine, boron dipyrromethene difluoride (BODIPY), nitrobenzofurazan have been researched in wide ranges of scientific areas¹⁾. Among these fluorophores, rhodamine dyes are one of the most used fluorophore due to their high photostability and excellent photophysical properties²⁾.

In scientific areas, rhodamine dyes have been studied for chemosensor. This is related to spirolactam ring system in the structure of rhodamine derivative³⁾. Depending on spirolactam ring system, absorption and emission properties can be observed by color and fluorescence changes in visible states. Using the theoretical background, there are so many researches have been reported using rhodamine derivatives on the subject of chemosensor^{1,3)}.

HOMO/LUMO energy levels are related to the absorption property. These energy levels were affected by molecular orbital and identifications of electron transition^{4,5)}.

In this regard, the theory is useful to apply for electrochemistry, because proton transfer functions or unshared pair/empty orbital interactions are related to HOMO and LUMO potential energy levels⁶⁾.

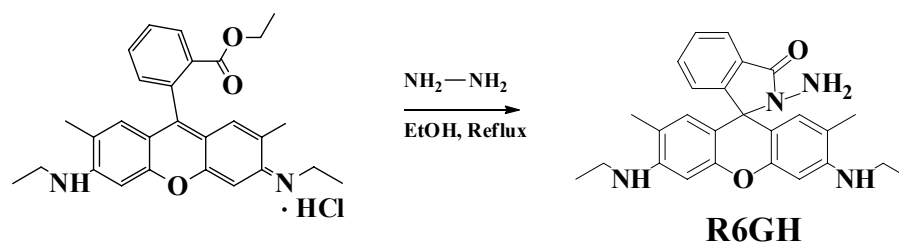
In this work, rhodamine 6G hydrazide (R6GH), one of the most used rhodamine derivatives, was investigated to determine HOMO and LUMO energy levels depending on changes of spirolactam ring system. The change of spirolactam ring in rhodamine 6G hydrazide (R6GH) was induced by Cu²⁺. Because Cu²⁺ is the high selective detection cation in published paper¹⁾. The all computational calculations for the energy potential and the electron distributions of HOMO and LUMO states were simulated using the program named *Material Studio 4.3 package program*. The energy potentials of reduction and oxidation were also determined with cyclicvoltammetric measurement.

2. Experimental

2.1 Rhodamine 6G Hydrazide (R6GH)

The rhodamine 6G hydrazide was synthesized from rhodamine 6G by a simple one step reaction as depicted in the scheme 1. The rhodamine 6G hydrazide was prepared according to literature method⁷⁻¹⁰⁾.

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Scheme 1. The synthetic method for R6GH.

Rhodamine 6G (2.40g, 5mmol) was dissolved in 60mL ethanol. Excess of hydrazine hydrate (5mL) was added dropwise with vigorous stirring at room temperature. The solution was then refluxed for 6hrs. The resulting precipitate was filtered and washed by three times with ethanol. The crude product was purified by silica gel column chromatography using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ as eluent, which resulted in R6GH product as a light pink solid. $^1\text{H-NMR}$ (400MHZ, CDCl_3): 7.90-7.88 (1H, t), 7.39-7.38 (2H, m), 7.00-6.98 (1H, t), 6.32 (2H, s), 6.19 (2H, s), 3.50 (4H, br), 3.17-3.12 (4H, q), 1.85 (6H, s), 1.27-1.23 (6H, t). MS : 428 (M^+).

2.2 Measurements

All material used for the synthesis were purchased from Aldrich and Alfa Aesar companies, and which were used without further purification. $^1\text{H-NMR}$ spectra were recorded on an JEOL-AL400 operating at 400 MHz. Mass spectra were recorded on a JEOL MS-tation [JMS-700]. Absorption and fluorescent spectra were measured with Agilent 8453 and Shimadzu RF-5301PC fluorescent spectrophotometer. The electro-chemistry properties of these dyes were examined with a Versa STAT 3 using a platinum wire served as a working electrode, and Ag/Ag^+ electrode served as a reference electrode and a carbon served as a counter electrode. The scan rate was 50mV/s. The optimized geometry structure and molecular energy potential were calculated with Materials Studio 4.3.

3. Results and Discussion

To investigate the optical property of R6GH depending on the presence or the absence of target metal

ion, we measured absorption and emission spectra of the prepared R6GH with addition of Cu^{2+} ion. In Figure 1, the specific peak in visible wavelength was not appeared in the only R6GH solution. After adding Cu^{2+} , new band centered at 534nm appeared with showing color change from colorless to pink. The emission spectra also showed a similar phenomenon compared with absorption spectra as shown in Figure 2.

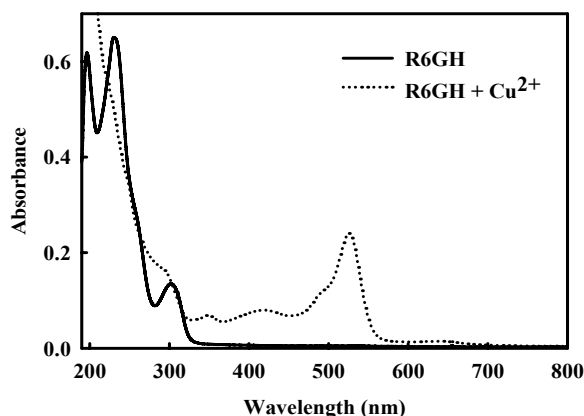


Figure 1. UV-Vis spectra of R6GH (10 μM) upon addition of Cu^{2+} ion (10 μM) in MeCN.

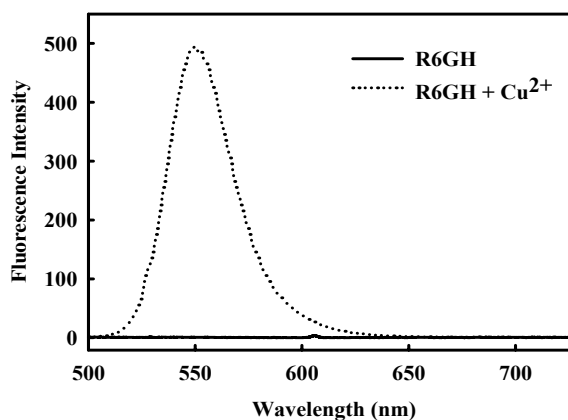


Figure 2. Fluorescence spectra of R6GH (10 μM) upon addition of Cu^{2+} ion (10 μM) in MeCN.

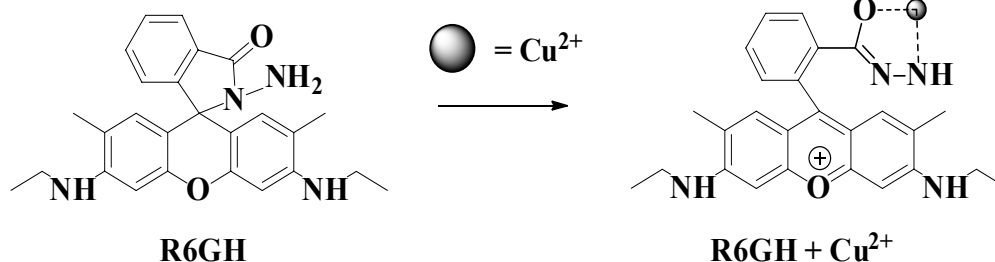
In only R6GH solution, there is no noticeable peak with showing non-fluorescence. Upon addition of Cu^{2+} , emission intensity was drastically increased about 500 folds, showing that new band centered at 549nm appeared. Fluorescence color was also changed to green fluorescence. These changes, such as absorption and emission indicated that the structure of R6GH was changed to the open structural formation by complexation with Cu^{2+} .

The above results are related to spiro lactam ring system, because spiro ring opening reaction have induced absorption and emission changes³⁾. In general, rhodamine derivative showed a color change and strong fluorescence by activation of a carbonyl group in a spiro lactam moiety. On the basis of theoretical background and references^{9,11)}, the promising mechanism of $\text{R6GH} + \text{Cu}^{2+}$ was depicted in Scheme 2 is

With respect to the above results, we investigated band-gap energy and HOMO/LUMO energy potential levels of R6GH and $\text{R6GH} + \text{Cu}^{2+}$ respectively. Three experimental methods were progressed such as absorption measurement, cyclic voltammogram and computational calculation method. And these results are compared together.

First of all, the band-gap energy of respective R6GH and $\text{R6GH} + \text{Cu}^{2+}$ was investigated by using absorption measurement as shown in Figure 3 (a) and (b). 3.80eV and 2.23eV were obtained for the band-gap energy of R6GH and $\text{R6GH} + \text{Cu}^{2+}$ respectively. These values were calculated by following equation (1).

$$eV = 1240 / \lambda \text{ from absorption edge} \dots\dots\dots (1)$$



Scheme 2. The probable mechanism of $\text{R6GH} + \text{Cu}^{2+}$.

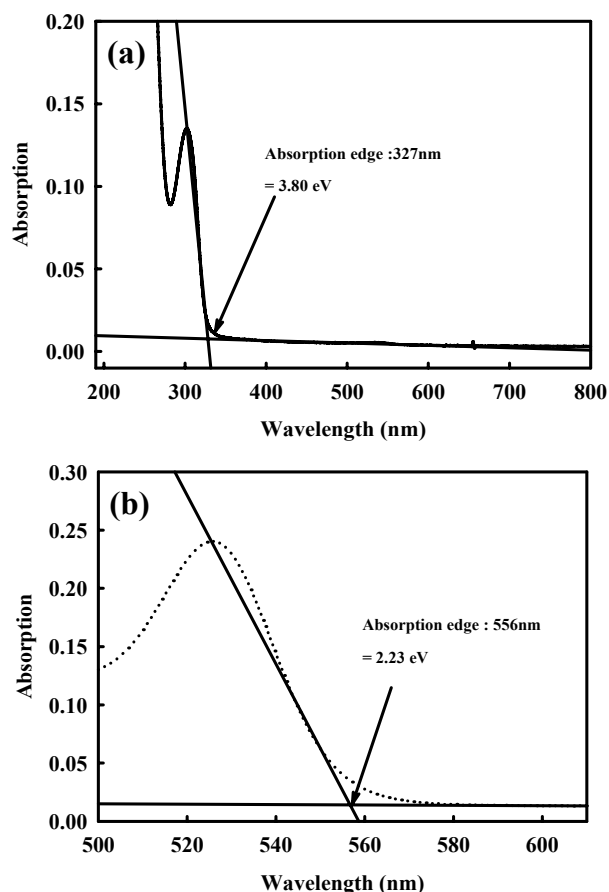


Figure 3. UV-Vis band-gap measurements : (a) R6GH (10 μM), (b) R6GH (10 μM) + Cu^{2+} (10 μM) in MeCN.

The band-gap energy of R6GH was decreased by 1.07eV compared with $\text{R6GH} + \text{Cu}^{2+}$, which indicated that the structural change of spiro lactam ring due to the complexation of R6GH and Cu^{2+} might affect to the band-gap energy.

Cyclic voltammogram was also investigated to obtain HOMO and LUMO values using onset and peak potentials from cyclic voltammogram spectra. As shown in Figure 4 (a) and (b), only oxidation potential values

were observed in these spectra. To calculate HOMO values using these obtained onset and peak potential values, the following equation (2) used. $E_{1/2}$ (Ferrocene) values of 0.42V were applied in equation^{6,12,13}.

$$\text{HOMO (eV)} = -4.8 - (E_{\text{peak/onset}} - E_{1/2} (\text{Ferrocene})) \dots\dots\dots (2)$$

Through calculation with equation (2), HOMO values of both R6GH and R6GH + Cu²⁺ were calculated. In the case of the use of peak values, -5.08eV and -5.32eV were respectively evaluated for R6GH and R6GH + Cu²⁺. In the same way, HOMO values with using onset values were also obtained.

These values are -4.96eV and -5.23eV for each R6GH and R6GH + Cu²⁺. Depending on $E_{\text{peak/onset}}$ values, the results showed differences and were related to the structural change of spiro lactam ring due to complexation of R6GH and Cu²⁺.

Finally, HOMO and LUMO energy levels and electron distributions of R6GH and R6GH + Cu²⁺ were computationally simulated with *Materials Studio 4.3 suite* in Figure 5. This program is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof function of generalized gradient approximation level with double numeric polarization

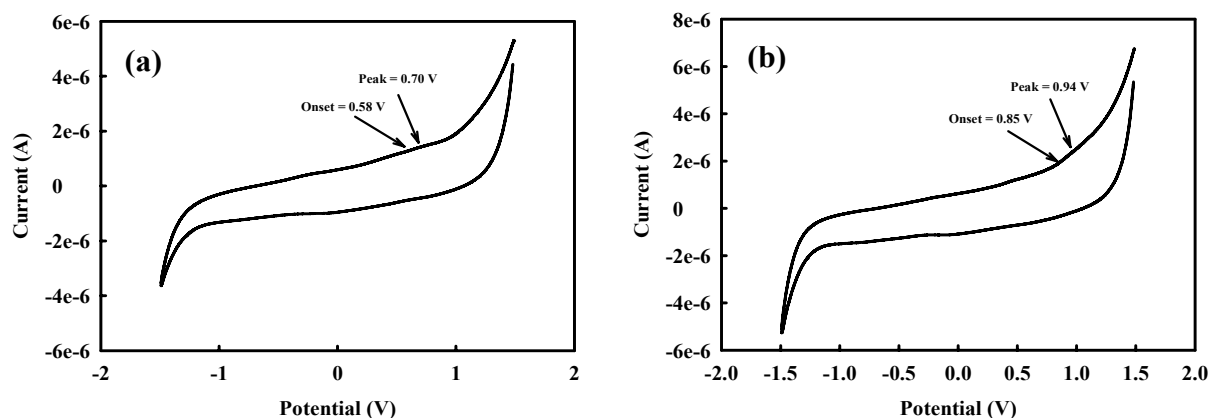


Figure 4. Cyclic voltammograms : (a) R6GH (50 μ M), (b) R6GH (1 μ M) + Cu²⁺ (1 μ M) in MeCN. Tetrabutylammonium perchlorate was added for electrolyte.

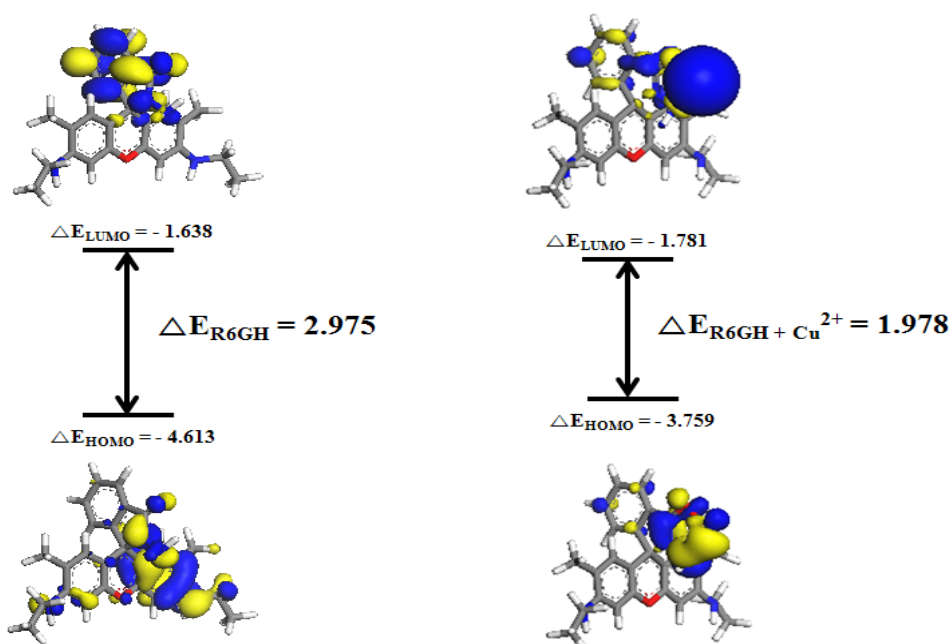


Figure 5. HOMO/LUMO energy levels and electron distributions for R6GH and R6GH + Cu²⁺.

Table 1. HOMO/LUMO and band-gap energy potential

Type	Onset (eV)			Peak (eV)			Computational Calculations (eV)		
	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
R6GH	-4.96	-1.16	3.80	-5.08	-1.28	3.80	-4.613	-1.638	2.975
R6GH + Cu ²⁺	-5.23	-3.00	2.23	-5.32	-3.09	2.23	-3.759	-1.781	1.978

bases set was used to calculate the energy level of the frontier molecular orbitals¹⁴⁻¹⁶. When the electron distribution of HOMO and LUMO states were compared, electrons were moved from xanthene part to spiro-lactam and hydrazide part in R6GH. On the other hand, electron distributions were localized in spiro-lactam and amine part in R6GH + Cu²⁺ complexation.

Based on the above results, three obtained results, namely HOMO and LUMO, band-gap energy values for R6GH and R6GH + Cu²⁺ obtained from absorption, cyclicvoltammogram and computational calculation, were compared as shown in Table 1. The results indicated that HOMO and LUMO values calculated from onset potential are closer than the values calculated from peak potential being compared with computational calculations. The result may propose that onset potential calculation is more accurate than peak potential calculation.

4. Conclusions

In this work, rhodamine hydrazide (R6GH) was synthesized and investigated for its optical properties and HOMO/LUMO values. In optical properties, complexation between R6GH and Cu²⁺ ion leads to the enhancement of absorption and emission intensity in visible wavelengths. This is related to the change of spiro-lactam ring system in R6GH structure. With absorption measurement, cyclicvoltammetry and computational calculations, HOMO and LUMO values were determined and compared. The results proposed that onset potential calculation is more accurate than peak potential calculation. In addition, these results from electrochemical approaches were considered to compare more detailed characteristics of the designed molecules.

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References

1. X. Chen, T. pradhan, F. Wang, J. S. Kim, and J. Yoon, Fluorescent Chemosensors Based on Spiro-roring-Opening of Xanthenes and Related Derivatives, *Chemical Reviews*, **112**(3), 1910(2012).
2. M. Beija, C. A. M. Afonso, and J. M. G. Martinho, Synthesis and Applications of Rhodamine Derivatives as Fluorescent Probes, *Chem. Soc. Rev.*, **38**(8), 2410(2009).
3. Y. K. Yang, K. J. Yook, and J. Tae, A Rhodamine-Based Fluorescent and Colorimetric Chemosensometer for The Rapid Detection of Hg²⁺ Ions in Aqueous Media, *J. Am. Chem. Soc.*, **127**(48), 16760(2005).
4. G. B. Ferreira, E. Hollauer, N. M. Comerlato and J. L. Wardell, An Experimental and Theoretical Study of The Electronic Spectra of Tetraethylammonium [bis(1,3-dithiole-2-thione-4,5-dithiolato) M(III)] and Tetraethylammonium [bis(1,3-dithiole-2-one-4,5-dithiolato) M(III)] (M = Sb or Bi), *Spectrochim. Acta Part A*, **71**(1), 215(2008).
5. C. N. Ramachadran, D. Roy, and N. Sathya-murthy, Host-Guest Interaction in Endohedral Fullerenes, *Chem. Physic. Lett.*, **461**, 87(2008).

6. Y. S. Kim, S. H. Kim, T. K. Kim, and Y. A. Son, Characteristics of HOMO and LUMO Potentials by Altering Substituents: Computational and Electrochemical Determination, *Textile Coloration and Finishing*, **20**(5), 41(2008).
7. S. P. Wu, T. H. Wang, and S. R. Liu, A Highly Selective Turn-On Fluorescent Chemosensor for Copper(II) Ion, *Tetrahedron*, **66**(51), 9655(2010).
8. Z. Zhang, Y. Zheng, W. Hang, X. Yan, and Y. Zhao, Sensitive and Selective Off-On Rhodamine Hydrazide Fluorescent Chemosensor for Hypochlorous Acid Detection and Bioimaging, *Talanta*, **85**(1), 779(2011).
9. H. Li, J. Fan, F. Song, H. Zhu, J. Du, S. Sun, and X. Peng, Fluorescent Probes for Pd²⁺ Detection by Allylidene-Hydrazone Ligands with Excellent Selectivity and Large Fluorescence Enhancement, *Chem. Eur. J.*, **16**, 12349(2010).
10. J. S. Bae, S. Y. Gwon, and S. H. Kim, Anthraquinone-Carbamodithiolate Assembly as Selective Chromogenic Chemosensor for Fe³⁺, *Textile Coloration and Finishing*, **25**(1), 13(2013).
11. Y. Xiang, A. Tong, P. Jin, and Y. Ju, New Fluorescent Rhodamine Hydrazone Chemosensors for Cu(II) with High Selectivity and Sensitivity, *Organic Letters*, **8**(13), 2863(2006).
12. H. S. Lee and J. H. Kim, Measurement of Physical Properties of Conducting Polymers, *Polymer Sci. Technol.*, **18**, 488(2007).
13. Y. S. Kim, J. I. Shin, S. Y. Park, K. Jun, and Y. A. Son, Electrochemical Studies on Heptamethine Cyanine Dyes, *Textile Coloration and Finishing*, **21**(5), 35(2009).
14. B. Delley, An All-Electron Numerical Method for Solving The Local Density Functional for Polyatomic Molecules, *J. Chem. Phys.*, **92**(1), 508(1990).
15. B. Delley, From Molecules to Solids with the DMol³ Approach, *J. Chem. Phys.*, **113**(18), 7756(2000).
16. A. D. Boese and N. C. Handy, A New Parametrization of Exchange-Correlation Generalized Gradient Approximation Functionals, *J. Chem. Phys.*, **114**(13), 5497(2001).