The rhodamine 6G hydrazide was synthesized from rhodamine 6G by a simple one step reaction as depicted in the scheme 1. The rhodamine 6G hydra-
dize was prepared according to literature method7-10)
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 CH2Cl2/MeOH as eluent, which resulted in R6GH product as a light pink solid. 1H-NMR (400MHz, CDCl3) : 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. 1H-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 electrochemistry 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 Cu2+ ion. In Figure 1, the specific peak in visible wavelength was not appeared in the only R6GH solution. After adding Cu2+, 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.
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 spirolactam ring system, because spiro ring opening reaction have induced absorption and emission changes$^{3) }$. In general, rhodamine derivative showed a color change and strong fluorescence by activation of a carbonyl group in a spirolactam moiety. On the basis of theoretical background and references$^{9,11}$, the promising mechanism of R6GH + Cu$^{2+}$ was depicted in Scheme 2.

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

First of all, the band-gap energy of respective R6GH and R6GH + 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 R6GH + Cu$^{2+}$ respectively. These values were calculated by following equation (1).

\[ eV = \frac{1240}{\lambda} \text{ from absorption edge} \]  

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

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

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

\[ \text{Scheme 2. The probable mechanism of R6GH + Cu}^{2+}. \]
were observed in these spectra. To calculate HOMO values using these obtained onset and peak potential values, the following equation (2) used. $E_{1/2}$ (Ferrocence) values of 0.42V were applied in equation $^6, ^12, ^13$.

$$\text{HOMO (eV)} = -4.8 - (E_{\text{peak-onset}} - E_{1/2 \text{ (Ferrocence)}}) \quad \ldots (2)$$

Through calculation with equation (2), HOMO values of both R6GH and R6GH + Cu$^{2+}$ were calculated. In the case of the use of peak values, -5.08eV and -5.32eV were respectively evaluated for R6GH and R6GH + Cu$^{2+}$. 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 + Cu$^{2+}$. Depending on $E_{\text{peak-onset}}$ values, the results showed differences and were related to the structural change of spirolactam ring due to complexation of R6GH and Cu$^{2+}$.

Finally, HOMO and LUMO energy levels and electron distributions of R6GH and R6GH + Cu$^{2+}$ 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](image)

**Figure 4.** Cyclicvoltammograms : (a) R6GH (50μM), (b) R6GH (1μM) + Cu$^{2+}$ (1μM) in MeCN. Tetrabutylammonium perchlorate was added for electrolyte.

![Figure 5](image)

**Figure 5.** HOMO/LUMO energy levels and electron distributions for R6GH and R6GH + Cu$^{2+}$. 
bases set was used to calculate the energy level of the frontier molecular orbits14-16). When the electron distribution of HOMO and LUMO states were compared, electrons were moved from xanthene part to spirolactam and hydrazide part in R6GH. On the other hand, electron distributions were localized in spirolactam 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, cyclic voltammogram 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 spirolactam ring system in R6GH structure. With absorption measurement, cyclic voltammetry 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


