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〈Research Paper〉

Electrochemical Study on Rhodamine 6G-Indole Based Dye for HOMO and LUMO Energy Levels

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Abstract: The energy levels are very important to investigate properties of organic dye materials. These values of energy levels can be calculated and compared with absorption spectra, cyclic voltammetric measurement and computer simulative calculation. In this study, absorption and emission changes were observed by complexation between rhodamine 6G based dye and mercury. This is related to spirolactam ring system of rhodamine 6G based dye. According to structural change of this dye, HOMO and LUMO energy levels were investigated and determined by their values with different approaches.

Keywords: *HOMO, LUMO, Rhodamine 6G, absorption, cyclic voltammetry*

1. Introduction

Rhodamine dyes have been received much attention and researched in various areas such as laser dyes, fluorescence standards, pigments, single-molecule imaging and imaging in living cells due to their excellent photostability and photophysical properties[1)].

Rhodamines have interesting structural characteristics of their spriolactam ring system. The structure can be changed by the reaction of metal cations. When the ring system open by metal cations, specific absorption and emission change are being operated[2)].

The energy levels such as HOMO and LUMO are related to the absorption character. In this regard, the energy levels were determined by molecular orbital and electron distribution[3,4)]. The studies of electro-chemistry, using HOMO and LUMO values, are useful for estimation of quantum chemistry calculation and redox/oxidation potential determination[5,6)].

In this study, rhodamine 6G based dye material was investigated to calculate HOMO and LUMO energy values. Two different structures of this dye can be induced by the spirolactam ring system.

All computational calculations for the energy potential and the electron distribution of HOMO and LUMO states were simulated by the program named *Material Studio 4.3 package program*. In addition, the energy potentials of reduction and oxidation were determined by cyclic voltammetric mearsurement.

2. Experimental

2.1 Rhodamine 6G Based Dye (Dye 1, Dye 1 + Hg^{2+})

The corresponding Rhodamine 6G dye was prepared and referred to the part of our previous work[7)]. The structure was shown in Figure 1. Rhodamine 6G hydrazide is prepared according to the literature method[8-10)]. Rhodamine 6G (2g, 4.18 mmol) was dissolved in 40ml MeOH. To the solution, hydrazine hydrate (2.5ml) was added dropwise, then the mixture was refluxed until the red color disappeared. After cooling to room temperature, the solution was poured into distilled water (800ml) and kept for 1day. Thereafter, the solid precipitate was filtered and dried in vacuum for 1day. Without further purification, the next step was preceded. Rhodamine 6G hydrazide (0.428g, 1.1mmol) and indole-

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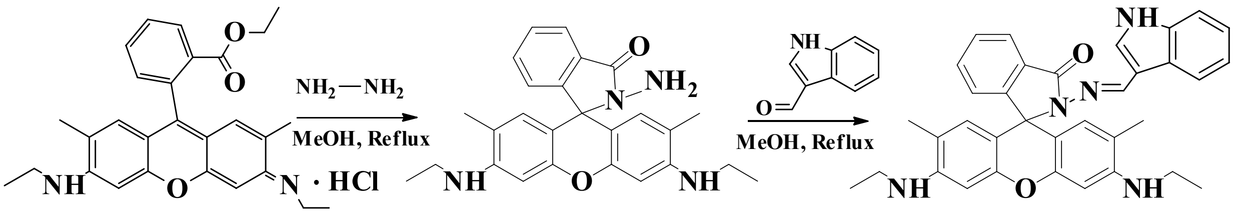


Dye 1

Scheme 1. The synthetic method for Dye 1$^{7)}$

3-carboxaldehyde (0.1596g, 1.1mmol) were refluxed in methanol with 3 drops of acetic acid. After 4hrs of stirring, white precipitates were obtained. These white solids were filtered off, washed with ethanol and dried in vaccum. The yield was 63%. ^{1}H NMR (CDCl$_3$) : 9.21 (s, 1H); 8.19 (s, 1H); 8.02-7.99 (m, 2H); 7.50-7.48 (m, 2H); 7.33-7.32 (d, 1H); 7.20-7.12 (m, 3H); 6.43 (s, 2H); 6.38-6.26 (t, 2H); 3.57-3.44 (d, 2H); 3.22-3.17 (m, 4H); 1.91-1.86 (d, 6H); 1.39-1.25(m, 6H). MS *m/z*: 555 (M$^+$).

2.2 Measurements

The spectroscopic characteristics were examined and determined using *Agilent 8453* UV-Vis 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 potentials were calculated with *Materials studio 4.3*.

3. Results and Discussion

We measured absorption and emission spectra of the prepared Rhodamine 6G derivative to investigate its optical properties, which can be changed by adding Hg^{2+} to dye 1. Figure 1 showed that there is a specific change between dye 1 and dye 1/Hg^{2+} mixture in absorption spectrum. The new band centered at 525nm was sharply formed. In naked eye, the color of dye solution was also changed from colorless to red. In addition, the fluorescence change was also observed in Figure 2.

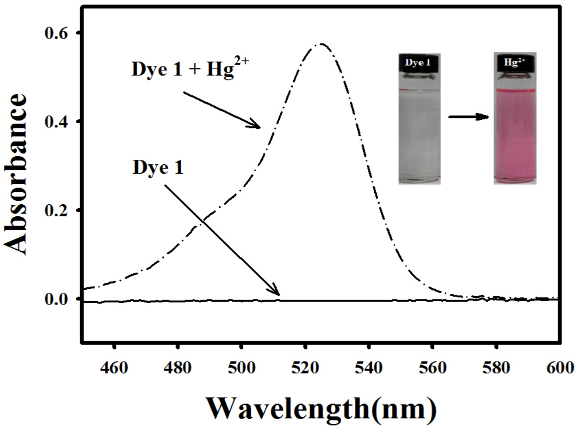


Figure 1. UV-Vis spectra of Dye 1 (10μM) upon addition of Hg^{2+} ions (10μM) in MeCN Inset: photographs of color change for dye 1 toward Hg^{2+} in MeCN.

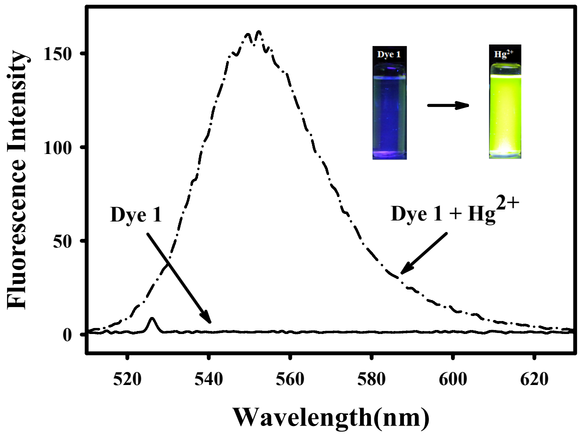
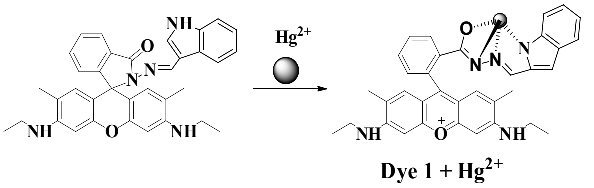


Figure 2. Fluorescence spectra of Dye 1 (10μM) upon addition of Hg^{2+} ions (10μM) in MeCN Inset: photographs of fluorescence change for dye 1 toward Hg^{2+} in MeCN.

By addition of Hg^{2+} to dye 1 solution, new fluorescence band at 552nm was appeared. The color change of fluorescent emission was demonstrated by the optical characteristics from non-fluorescence to green fluorescence.

These absorption and fluorescence changes are attributed to the complex formation of dye 1 and Hg^{2+} complex. This phenomenon can be explained by spirolactam ring system of dye 1[11,12]. The structure of dye 1 was changed in its form from closed to open ring by ligand formation bound by Hg^{2+} ion. This new open ring structure was proposed in scheme 2. This is based on Job's plot method, indicating 1:1 biding ratio between Dye 1 and Hg^{2+} as shown in Figure 3.



Scheme 2. The proposed mechanism of Dye 1+ Hg^{2+}

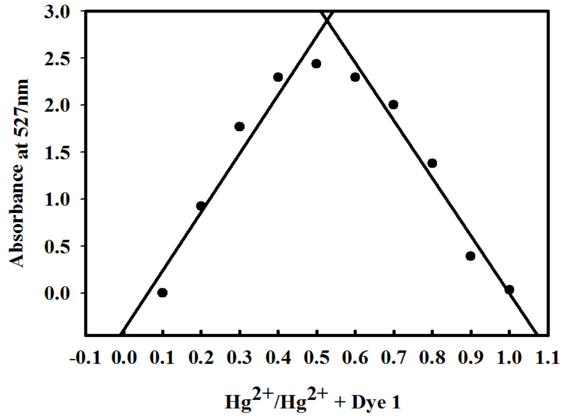


Figure 3. Job's plot method for Dye 1.

To investigate HOMO and LUMO energy levels between two different structures of dye 1 by changing the spirolactam ring system, we have measured UV-Vis absorption to obtain the band-gap energy potential, which show the energy level difference between HOMO and LUMO. As shown Figure 4 (a), (b), the band-gap energy potential values were calculated by spectroscopy, using eV = 1240 / λ from absorption edge. The band-gaps of dye 1 and dye 1/ Hg^{2+} were 2.27 eV and 2.25 eV, respectively. After mixing with dye 1 and Hg^{2+}, the value was decreased about 0.02 eV.

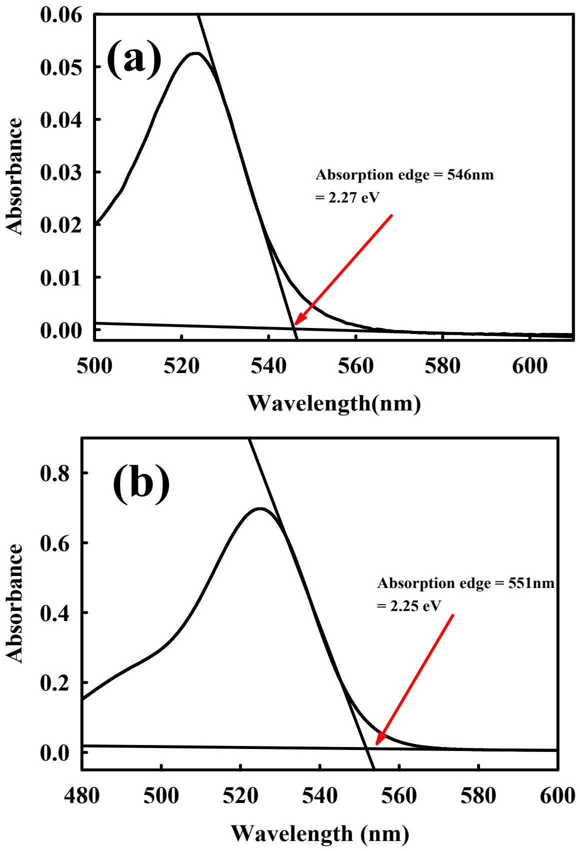


Figure 4. UV-Vis band-gap measurements : (a) Dye 1 (100μM), (b) Dye 1(50μM) + Hg^{2+}(50μM) in MeCN.

Cyclic voltammograms were also investigated to calculate the HOMO and LUMO Energy levels. Two factors of obtaining peak and onset potentials from spectra were considered for calculation of HOMO and LUMO energy levels. In Figure 5 (a) and (b), Oxidation peak and onset potentials were clearly observed. These spectra showed the different potential positions, indicating that different structures may exist, showing different electrochemical behaviors.

$$\text{HOMO (or LUMO) (eV)} = -4.8 - (E_{peak\ /\ onset} - E_{1\ /\ 2\ (Ferrocence)}) \cdots\cdots\cdots (1)$$

The following peak potential and onset potential in Figure 5 were used for HOMO and LUMO energy level calculations with equation (1)[13-15]. $E_{1/2\ (Ferrocence)}$ values of 0.42V were applied in the equation (1). Oxidation values of onset and peak potentials for Dye 1 were obtained as -4.94 eV and -5.15 eV, respectively.

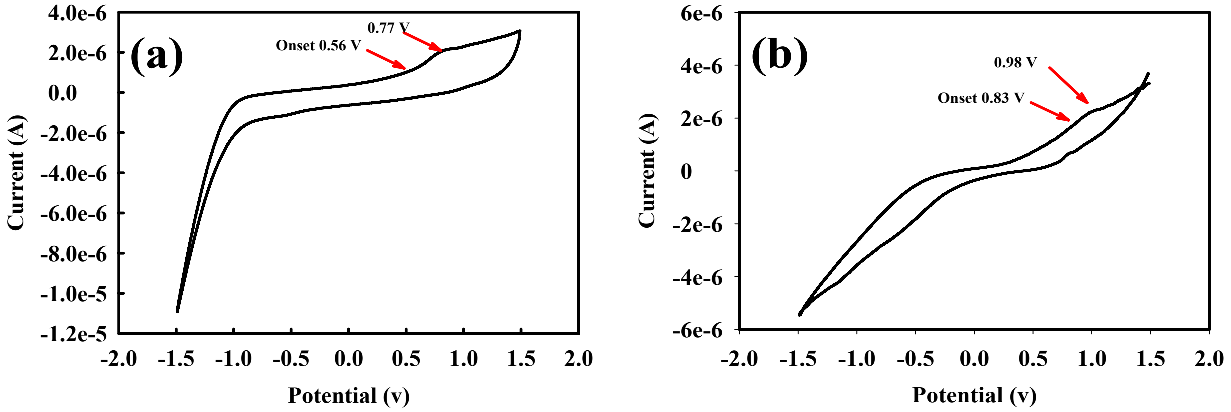


Figure 5. Cyclic voltammograms : (a) Dye 1(100μM), (b) Dye 1(500μM) + Hg^{2+}(500μM) in MeCN. Tetrabutylammonium Perchlorate was added for electrolyte.

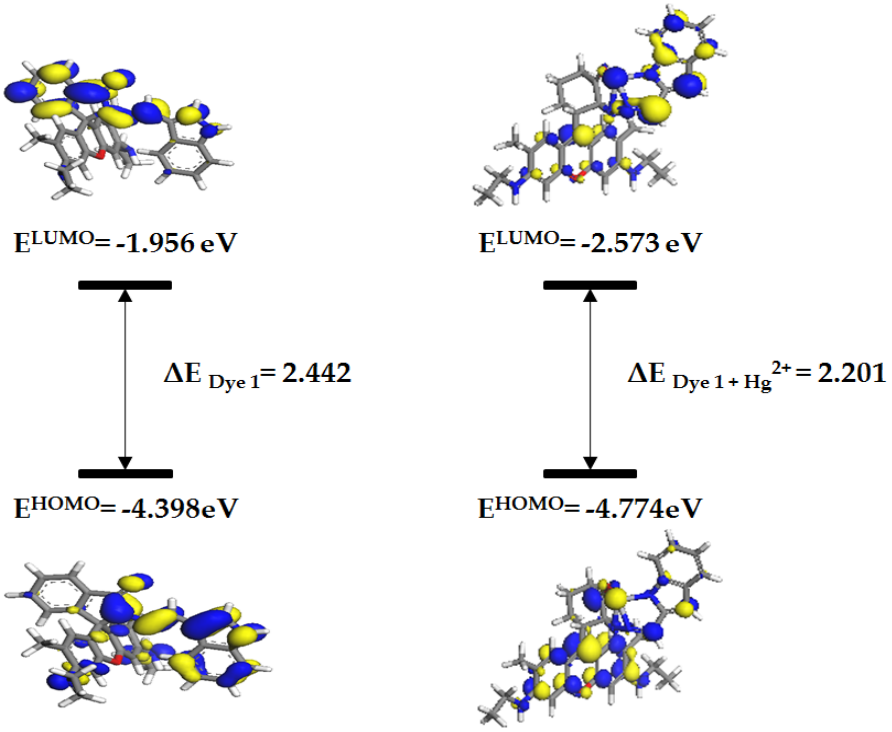


Figure 6. HOMO/LUMO energy levels and electron distributions for Dye 1 and Dye 1 + Hg^{2+}.

The same values of Dye 1/Hg^{2+} were also obtained as each -5.21 eV and -5.36 eV. These are related to HOMO energy levels. Through the results, there are little differences between the calculated values from each peak and onset potentials. However, these two values are useful for determination and analysis of electrochemical properties for Dye 1 and Dye 1/Hg^{2+}.

In addition, HOMO and LUMO energy levels and electron distributions of Dye 1 and Dye 1/Hg^{2+} were computationally simulated as shown in Figure 6. The dye 1 has been simulated with Materials Studio 4.3 suite of program which is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof function of generalized gradient approximation level with double numeric polarization bases set was used to calculate the energy level of the frontier molecular orbits[16-18)]. In Dye 1, electron localization was moved from xanthine and indole-3-carboxaldehyde to a unit of rhodamine 6G.

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

Sample	Onset (eV)			Peak (eV)			Computational Calculations (eV)		
Type	HOMO	LUMO	△E	HOMO	LUMO	△E	HOMO	LUMO	△E
Dye 1	-4.94	-2.67	2.27	-5.15	-2.88	2.27	-4.398	-1.956	2.442
Dye 1 + Hg^{2+}	-5.21	-2.96	2.25	-5.36	-3.11	2.25	-4.774	-2.573	2.201

The dye 1/Hg^{2+} showed different electron denstity localization compared with Dye 1. In Indole-3-carboxaldehyde part, considerable electron localization was induced in HOMO and LUMO states. There was no specific change in xanthene.

Based on the above results, computational calculated and electrochemically determined levels were energy levels were compared and shown in Table. 1. The results showed that the values of onset potential are closer than the obtained values from peak potential compared with computational calculations. This may propose that onset potential calculation is more accurate than peak potential calculation.

4. Conclusions

In this study, we investigated the electrochemical study for two different structures of rhodamine 6G based dye derivative. These structures were formed by the spirolactam ring close-open system.

The electrochemical properties and computational calculations were examined and compared for obtaining HOMO/LUMO energy levels. According to the change of structure for dye 1, these energy levels were changed, indicating that molecular structure can affect to HOMO/LUMO energy levels.

It is also proposed that onset potential calculation is more accurate than peak potential calculation and its effective approaches were compared to consider more detailed characteristics of the designed molecules.

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