〈Research Paper〉

Characteristics of HOMO and LUMO Energy Potentials toward Rhodamine 6G-Naphthaldehyde Chemosensor

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Abstract: Nowdays, the computational simulation of molecular energy potentials and the empirical evidence using electrochemical reduction/oxidation values are very significant factors to predict of molecule's energy potentials. The prepared chemosensor herein consists of spirolactam ring system in the structure, providing intra-structural change with metal cation binding. In this study, rhodamine 6G-Naphthaldehyde chemosensor was determined and compared with HOMO/LUMO energy levels by computational calculation and cyclic voltammogram method.

Keywords: chemosensor, HOMO, LUMO, Rhodamine 6G, naphthaldehyde, cyclicvoltammogram, absorption, electron distribution

1. Introduction

Electrochemistry is one of the important chemical studies to determine molecular chemical properties. In electrochemistry field, the energy level's calculation has been reported by many researchers[1,2]. These energy levels are related to HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) values. In this regard, HOMO and LUMO values have received great attention with molecular orbital and electron distributions. These values are useful for the electro-chemistry study with related to quantum chemistry calculation and redox/oxidation determination to estimate chemical potentials[3,4]. In this context, cyclicvoltammogram and computational calculation are mainly used for analyzing molecular energy levels. In this study, rhodamine 6G-Naphthaldehyde chemosensor (RNCS) was investigated by cyclicvoltammetric and computational calculation for HOMO and LUMO energy levels. In this approach, reduction and oxidation potentials were calculated and its findings were compared to the simulated energy states of the prepared chemosensor.

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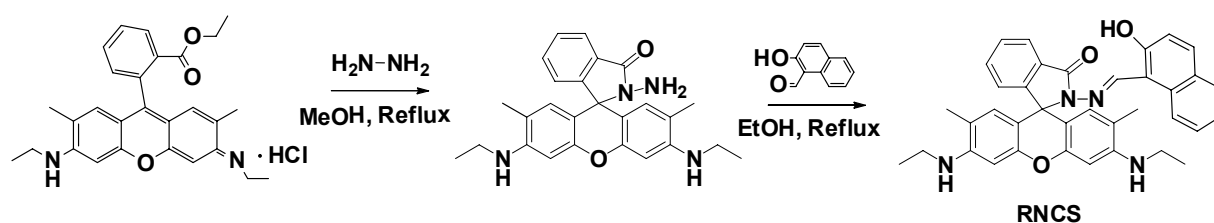Tel.: +82-42-821-6620   Fax.: +82-42-823-8870

2. Experimental

2.1 Rhodamine 6G-naphthaldehyde Chemosensor (RNCS)

The scheme was represented to the synthesis of RNCS, which was refered to the part of our previous study[5]. The outline was shown in Figure 1.

RNCS was synthesized through 2step reaction with rhodamine 6G hydrazide and 2-hydroxy-1-naphthaldehyde. Rhodamine 6G hydrazide is prepared according to the literature method[6-8]. Rhodamine 6G hydrazide (1.5mmol, 0.6437g) and 2-hydroxy-1-naphthaldehyde (1.5 mmol, 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 RNCS as 0.6620g (76% yield). ^{1}H-NMR (400MHZ, CDCl$_3$) : 12.12 (1H, s), 9.64 (1H, s), 7.89 (1H, d), 7.65 (1H, d), 7.52 (2H, t), 7.39 (2H, t), 7. 30 (1H, t), 7.14(1H, t), 6.99 (1H, t), 6.94 (1H, d), 6.32 (2H, s), 6.19 (2H, s), 3.35 (2H, s), 3.05 (4H, q), 1.72 (6H, s), 1.14 (6H, t). MS: 582 (M$^+$).

Scheme 1. The Scheme for RNCS

2.2 Measurements

Absorption and fluorescence spectra of the prepared RNCS were measured with and *Agilent 8453* spectrophotometer and a *Shimadzu RF-5301PC* fluorescent spectrophotometer, respectively. The electro-chemistry properties were examined with *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

As shown in Figure 1 and Figure 2, Absorption and emission spectra of RNCS were investigated to observe the effect of metal bindings. In absorption spectrum, there is no specific intensity with RNCS (10μM) only in absorbing behavior. Upon the addition of Cu^{2+} (10μM), strong absorption intensity appeared at 523 nm, indicating 9-folds increased intensity compared to RNCS only. In addition, emission intensity also increased by adding Cu^{2+}. It was about 40-folds. These drastic changes in absorption and emission can be explained by the spirolactam closed-open ring system[9-11]. When spirolactam ring is closed, colorless and non-fluorescence effects are observed from RNCS molecule. After adding Cu^{2+}, RNCS may react with this metal cation: consisting of ligand binding position and making spirolactam ring open. Color and fluorescence effects are increased and appeared as shown in Figure 1 and Figure 2.

Through these results, RNCS molecule can exist two different molecular structural forms by spirolactam ring system and metal ligand binding position.
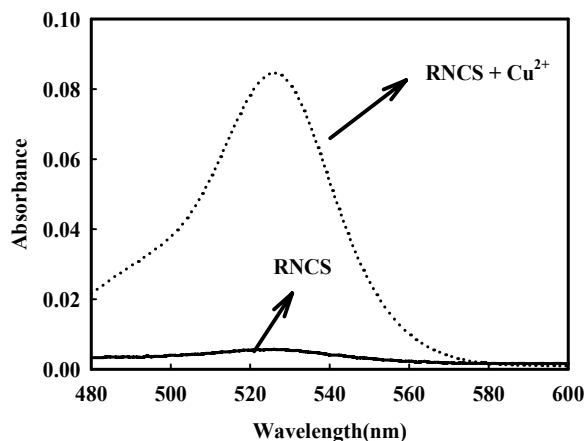
Figure 1. UV-Vis spectra of RNCS (10μM) upon addition of Cu^{2+} ions (10μM) in MeCN.
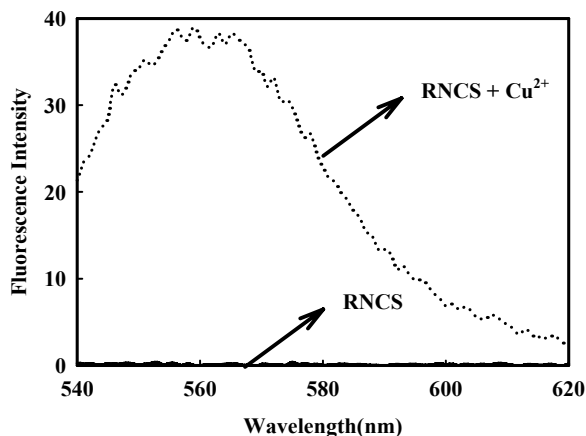
Figure 2. Fluorescence spectra of RNCS (10μM) upon addition of Cu^{2+} ions (10μM) in MeCN.

In addition, The binding ratio between RNCS and Cu^{2+} was also determined by Job's plot method as shown in Figure 3. The result indicated 1:1 ratio reaction between RNCS and Cu^{2+}. Through the result, the structure of RNCS + Cu^{2+} was proposed in scheme 2, which was introduced in the reported work[12,13].

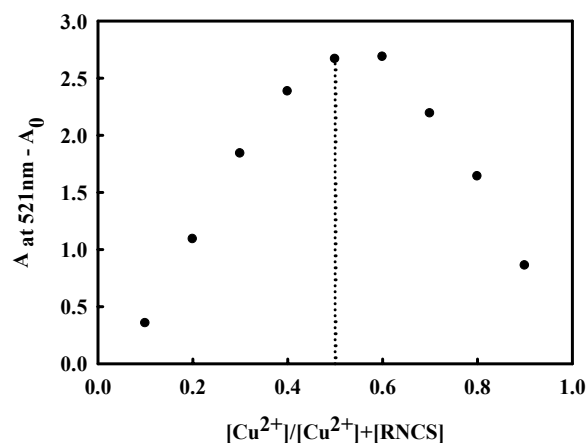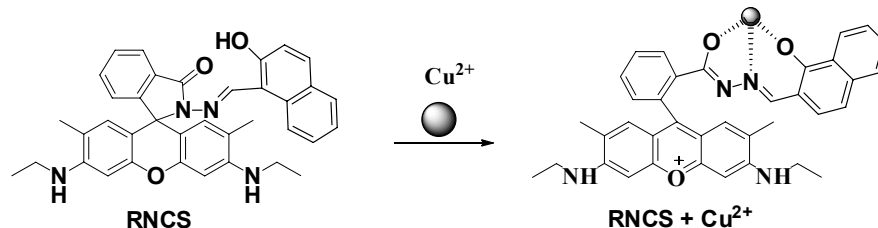In absorption and emission spectra changes of RNCS and RNCS + Cu^{2+}, it is concluded that two different

Figure 3. Job's plot method between RNCS and Cu²⁺.

structures can be transformed through closed and the open spirolactam ring system in RNCS structure. To investigate HOMO and LUMO energy levels, RNCS and RNCS + Cu²⁺ were measured by spectroscopic and cyclicvoltammetry methods.

In Figure 4 (a) and (b), absorption spectrum was determined to calculate band-gap energy by spectro-scopic: using $eV = 1240/\lambda$ from the absorption edge[14]. The band-gap of RNCS was calculated and obtained by the value of 3.01 eV. Whereas, RNCS + Cu²⁺ showed the band-gap value of 2.22 eV. This result indicated that metal binding ligand position and spirolactam ring open structure are attributable to the decrease of the band-gap value of RNCS about 0.79 eV.

Cyclicvoltammograms were carried out to calculate HOMO/LUMO energy levels of RNCS and RNCS + Cu²⁺ using oxidation/redox energy potentials. These energy potential values can be obtained from peak and onset point in Figure 5 (a) and (b). The forms of spectra for RNCS and RNCS + Cu²⁺ were also found.
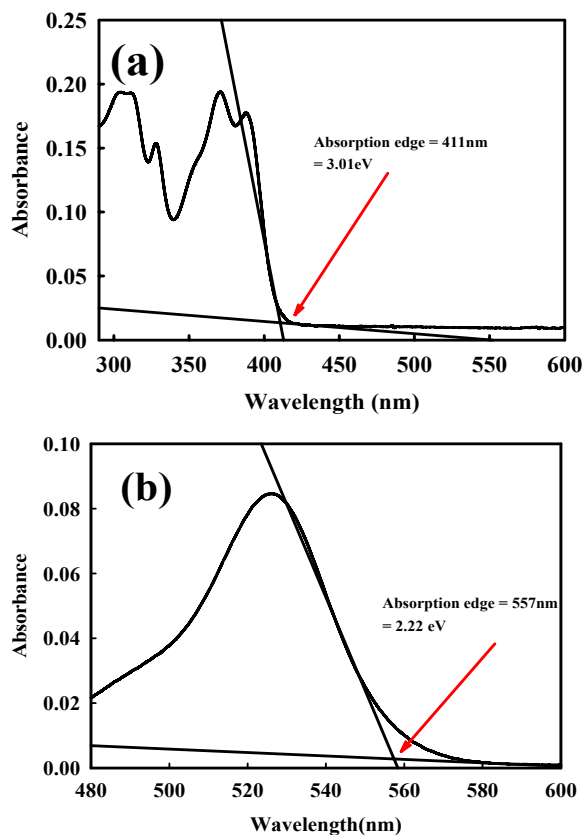

Figure 4. UV-Vis band-gap measurements : (a) RNCS (10 μM), (b) RNCS (10μM) + Cu²⁺ (10μM) in MeCN.

It is indicated that electrochemical properties are clearly affected by closed and open type structure of RNCS.

Using these two points such as peak and onset potentials, the corresponding HOMO and LUMO energy levels were calculated by the following equation (1).

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

$E_{1/2}$ (ferrocene) was assigned to 0.42V, indicating half-wave potential of ferrocene[14-16].
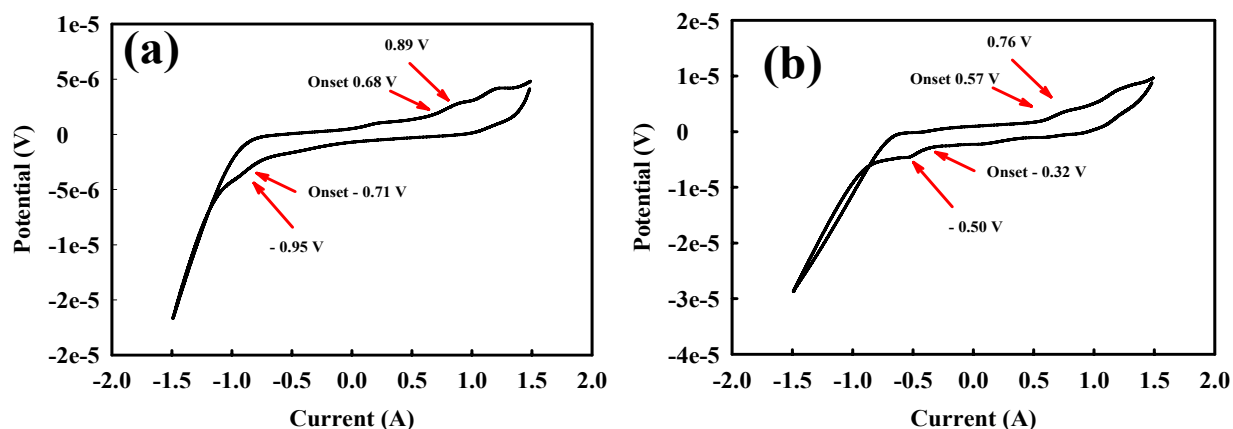

Scheme 2. Proposed scheme for RNCS + Cu²⁺

Figure 5. Cyclic voltammograms : (a) RNCS (500μM), (b) RNCS (500μM) + Cu²⁺ (500μM) in MeCN. Tetrabuty-
lammonium perchlorate was added for electrolyte.

$E^{LUMO} = - 0.561\,eV$ $E^{LUMO} = - 2.485\,eV$

$\Delta E_{RNCS} = 7.75eV$ $\Delta E_{RNCS+Cu^{2+}} = 3.172eV$

$E^{HOMO} = - 8.311eV$ $E^{HOMO} = - 5.657eV$
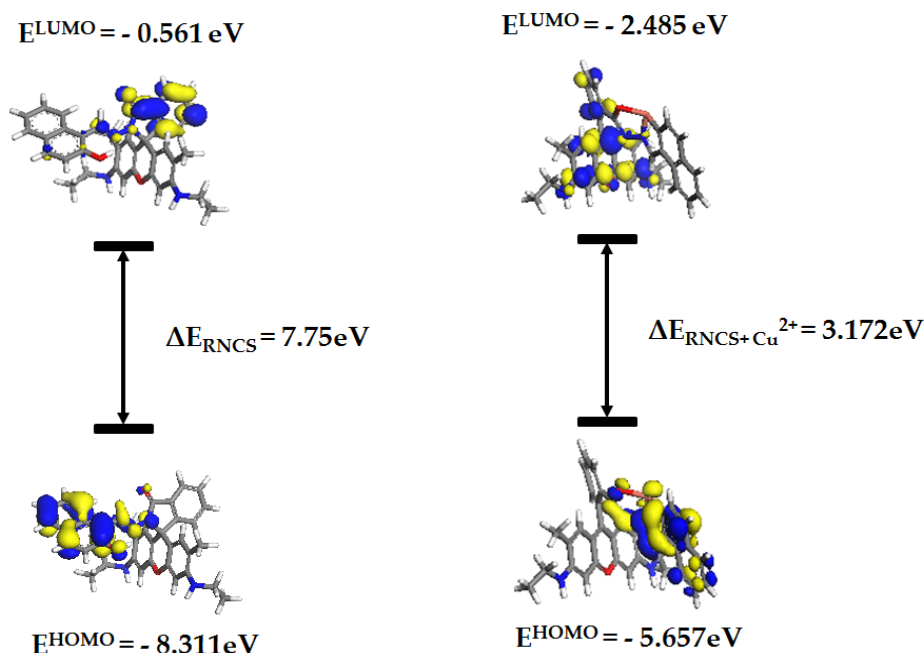
Figure 6. HOMO/LUMO energy levels and electron distributions for RNCS and RNCS + Cu²⁺.

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

Sample	Onset (eV)			Peak (eV)			Computational Calculations (eV)		
Dye	HOMO	LUMO	△E	HOMO	LUMO	△E	HOMO	LUMO	△E
RNCS	-5.06	-2.05	3.01	-5.27	-3.43	1.84	-8.311	-0.561	7.75
RNCS + Cu²⁺	-4.95	-2.73	2.22	-5.14	-3.88	1.26	-5.657	-2.485	3.172

From the result of calculations as shown in Table 1, little differences were observed by the calculated values between the peak and onset potentials, respectively.

However, these values obtained from each different potentials play an important role to investigate electrochemical properties for RNCS and RNCS + Cu²⁺.

Electron distributions and energy levels of HOMO

and LUMO states were also simulated and calculated in Figure 6. In RNCS, electron density localization was significantly shifted from xanthene to hydroxy-naphthaldehyde in HOMO and LUMO states. This electron distribution was also shown with a similar pattern in RNCS + Cu^{2+}, showing that electrons were moved from rhodamine 6G part to naphthaldehyde.

With the above results obtained from spectroscopic, cyclicvoltammograms and computational calculations, the resulting potential energy values were compared in Table 1. The onset potential values are much closer to the computational calculated values. This result indicated that the calculated values obtained from onset potentials can be more useful to determine HOMO and LUMO energy levels.

4. Conclusions

In this work, structural changes of RNCS induced by spirolactam closed-open ring system were investigated with the electrochemical approach. By analyzing spectroscopy, cyclicvoltammetry and computational calculation, band-gap and HOMO/LUMO energy levels were obtained and compared. The result indicated that the closed-open molecular structure can affect to its electrochemical properties and onset potentials are more useful approaches than peak potentials to calculate HOMO/LUMO energy levels.

Acknowledgment

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