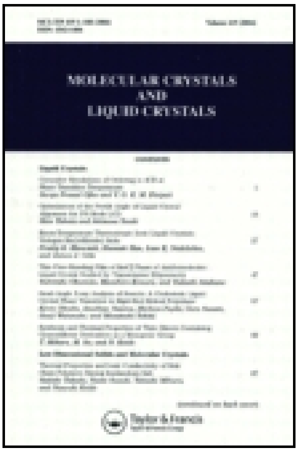

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Synthesis of 2,2-bithiophene Based Dye Sensor and Optical Properties Toward Metal Cations

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Synthesis of 2,2-bithiophene Based Dye Sensor and Optical Properties Toward Metal Cations

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We have designed and synthesized a 2,2-bithiophene-based new dye chemical sensor, and its selective and sensitive recognizing functions toward heavy metal cations were investigated. These find results were characterized using UV-Vis. spectrophotometer and spectrofluorometer. In addition, electrochemical properties were measured with cyclicvoltammetry test. Electron density distributions and HOMO/LUMO energy levels were computationally calculated and optimized. The energy levels of HOMO/LUMO were compared with computational calculation and cyclicvoltammetry measurement for each value. Finally, the formation type of metal ion bindings was determined by Job's plot measurements.

Keywords 2,2-bithiophene; cyclicvoltammetry; job's plot; metal binding; HOMO/LUMO; computational calculation; dye sensor

Introduction

Currently, various research groups have reported the colorimetric and fluorometric sensor molecules for the utilization of harmful heavy metal cation detection. For this purpose, structural characteristics with non-pair or dipolar molecular system such as cryptand, spherand, and crown ether are commonly considered. This chemosensing effect is of very importance in view point of analytical chemistry, which provides to meet the exact measurement and calculation of the harmful metal cations in chemical, environmental and biological conditions. Herein, we have focused the find the Cu^{2+} cation, Especially, Cu^{2+} detection has been considered as very important meanings due to its widespread use and essential trace element in biological systems [1–2].

Most of studies on Cu^{2+} detection sensors are focused on the design of sensor molecules providing higher sensing selectivity, which can be utilized with molecular charge transfer system, π-conjugation and powerful donor moiety. Usually, thiophene types containing fused aromatic rings, namely heteroarene, have much attention due to its various application areas such as electro photographic photoreceptors, dye-sensitized solar cells, light emitting materials, organic superconductors and so on [3]. The molecular structure containing thiophene units is very promising electron donor material. This donor moiety is important key factor in the metal complex detection because the metal binding reaction can be occurred at the electron rich site being provided by donor moieties. [3–5]

In this study, we have synthesized dye chemical sensor having thiophene molecules as a donor unit. The resulting detection properties of dye sensor were examined with UV-Vis

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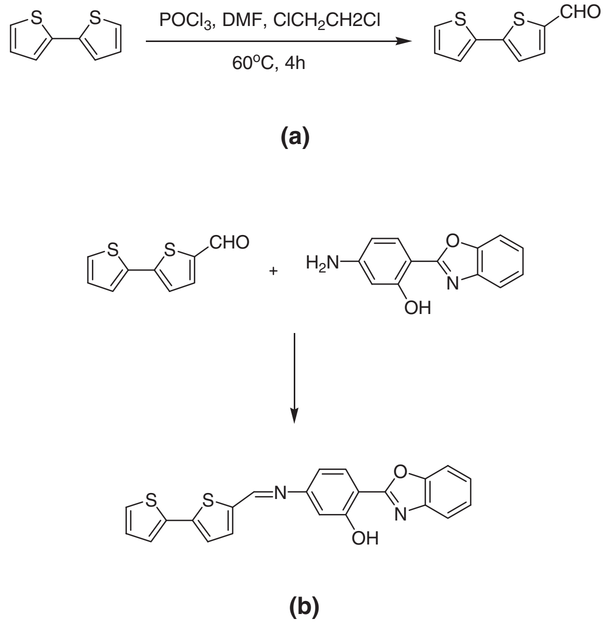
*Corresponding author. E-mail: yason@cnu.ac.kr absorption and fluorescent emission measurements. In addition, computational calculation was also carried out to determine the potential energy levels in the ground and excited states. Findings on the electron density distributions provided the estimation of complex characteristic functions between free dye-senor and metal complexed dye-sensor. All theoretically computational calculations for the energy potential and the electron distributions of HOMO/LUMO states were performed with *Material Studio 4.3 package* program [6–10]. Furthermore, we have also considered cyclicvoltammetric (CV) experiments to determine the energy potentials for the electrochemical redox potential of dye-sensor. We have used the CV oxidation onset potential of HOMO energy levels and the UV absorption fit curve calculation of band gap energy. According to this calculation we have determined the corresponding LUMO energy levels [11–14]. Finally, the complex formation types of metal detection were examined by Job's plot measurements.

Experimental

2.1 Synthesis

2,2-bihtiophene based dye sensor was synthesized. As presented in Scheme 1, mono α-aldehyde (a) was prepared by the formylation reaction at room temperature, where 12 mmol of 2,2-bithiophene and DMF were dissolved in 20 ml of 1,2-dichloroethane. After that, the reaction mixture was cooled to 0°C and 12 mmol of $POCl_3$ was then added dropwise while stirring. The reaction mixture was refluxed at 60°C for 4h. After the reaction, the mixture was poured into 100 ml of saturated sodium acetate solution and diluted with ether. The diluted solution was washed with water, saturated sodium bicarbonate solution and dried with excessive anhydrous $MgSO_4$ for overnight. The solvent was removed under



Scheme 1.

reduced pressure. The general procedures were followed by the indicated references [3]. For the next step, the dye chemosensor was obtained from the prepared intermediates of 2,2-bithiophene-5-carboxaldehyde and benzoxazole moiety. 2 mmol of 2,2-bithiophene-5-carboxaldehyde and benzoxazole moiety were dissolved in 15 ml of benzene. 5∼6 drops of piperidine was added dropwise and refluxed for 48 h. The reaction products were filtered with benzene and dried in vacuum.

(yield: 0.38g, 45%). ^{1}H-NMR (400MHz, acetone-d$_6$) δ 8.82 (s, 1H), δ 8.08 (d, 1H), δ 7.79 (m, 2H), δ 7.68 (d, 1H), δ 7.57 (m, 1H), δ 7.50 (m, 2H), δ 7.40(d, 1H), δ 7.35(s, 3H), δ 7.17(m, 1H), δ 7.00(m, 1H). MS: 402(M$^+$). Anal. Calculated for $C_{22}H_{14}N_2O_2S_2$: C, 65.65; H, 3.51; N, 6.96; S, 15.93: found; C, 66.07; H, 3.83; N, 6.82; S, 14.74.

2.2 Measurements

The spectroscopic characteristics and the fluorescence properties of the prepared dye chemosensor were examined and determined using Agilent 8453 UV-Vis spectrophotometer and Shimadzu RF-5301 spectrofluorophotometer, respectively. ^{1}H NMR spectra and elemental analyses were recorded with a JNM-AL400 spectrometer operated at 400 MHz NMR and a Carlo Elba Model 1106 analyzer, respectively. Electron distributions and energy potentials were calculated with *Material Studio 4.3* [15]. Cyclic voltammograms were examined with a *Versa STAT3* using three-electrode conventional electro chemical cell. Cyclic voltammetry test was conducted in an acetonitrile solution containing tetrabutlyammonium hexafluorophosphate electrolyte. The reference electrode, Ag/Ag$^+$ was directly immersed in the reaction cell. The working electrode was a glassy carbon. The counter electrode was a platinum wire. The scan rate was commonly 100mV/s.

2.3 Job's plot measurements

Using job's method determination, the stoichiometrical characteristics of metal binding ratio with dye sensor were examined. Equimolar solutions of dye sensor and various metal cations (Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Al^{2+} and Fe^{2+}) were mixed in different volume ratios (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0). The maximum absorption of these mixtures was characterized.

Results and Discussion

In this work, the designed dye chemosensor was synthesized using 2,2-bithiophene as a donor unit and benzoxazole dye intermediate as a signal unit. UV-Vis absorption and fluorescence emission spectra were investigated to monitor the optical changes and sensing properties of the dye sensor with various different metal cations. The UV-Vis absorption and fluorescence emission spectra of dye sensor (1×10^{-5} M) in MeOH : Water (9:1) solution with various metal cations (Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Al^{2+} and Fe^{2+}, 1×10^{-4} M) are shown in Figure 1 and 2, respectively.

From Figure 1 and Figure 2, the dye sensor showed the higher selective detection toward Cu^{2+} cations. As Figure 1 and Figure 2 show, upon the addition of Cu^{2+} to the solution of the prepared dye sensor, the absorption band at 390 nm progressively decreased in intensity and a weak new peak at 470 nm appeared; an isobestic point at 430 nm also developed. The appearance of this isobestic point suggests that at least one stable dye sensor-Cu^{2+} metal cation species is present in solution and is indicative that a stable complex formed between dye sensor and Cu^{2+}. In the case of fluorescence emission band at

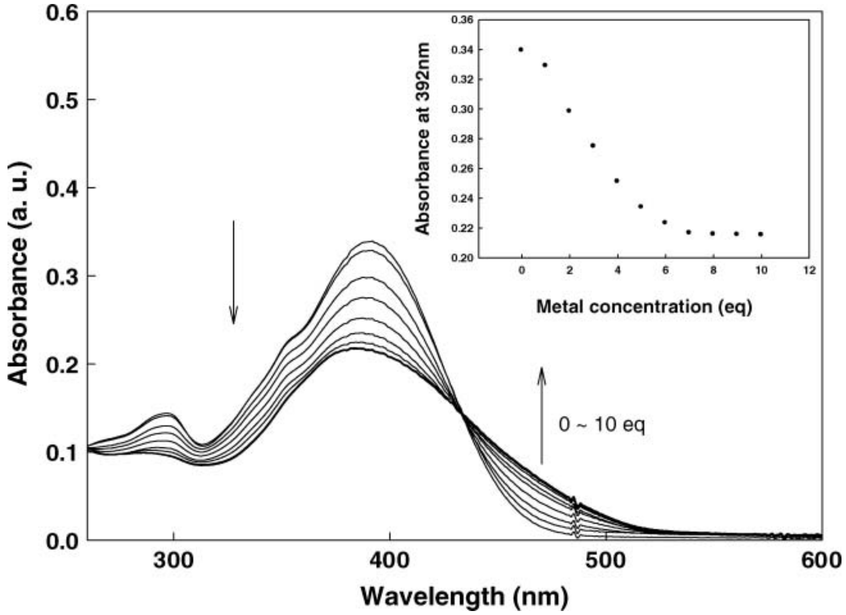


Figure 1. UV-Vis. absorption of dye sensor (1.0×10^{-5} M) in MeOH: water (9:1) solution with Cu^{2+}.

445 nm gradually increased with the addition of Cu^{2+} cations. Usually, this metal binding reaction occurs, the fluorescence intensity is enhanced due to the effect of MLCT (metal to ligand charge transfer) system. However, none of the other metal cations investigated, namely Cd^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Al^{2+} and Fe^{2+} had any noticeable effect on absorption and emission, as shown in Figure 3 and Figure 4.

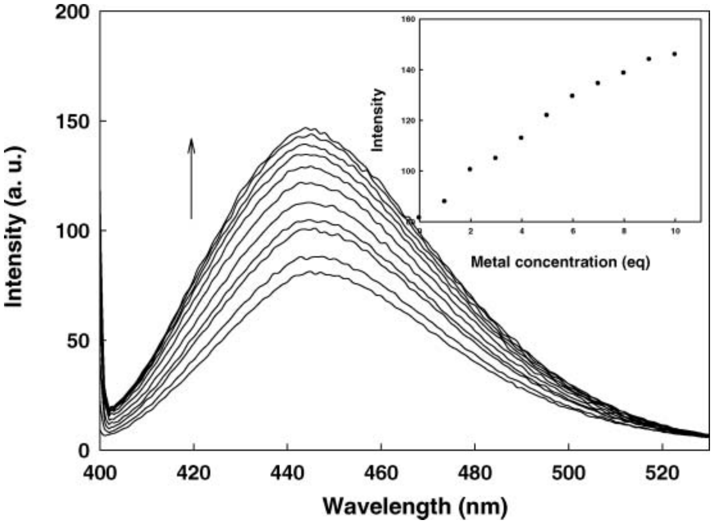


Figure 2. Fluorescence spectra of dye sensor (1.0×10^{-5} M) in MeOH : water (9:1) solution with Cu^{2+}.

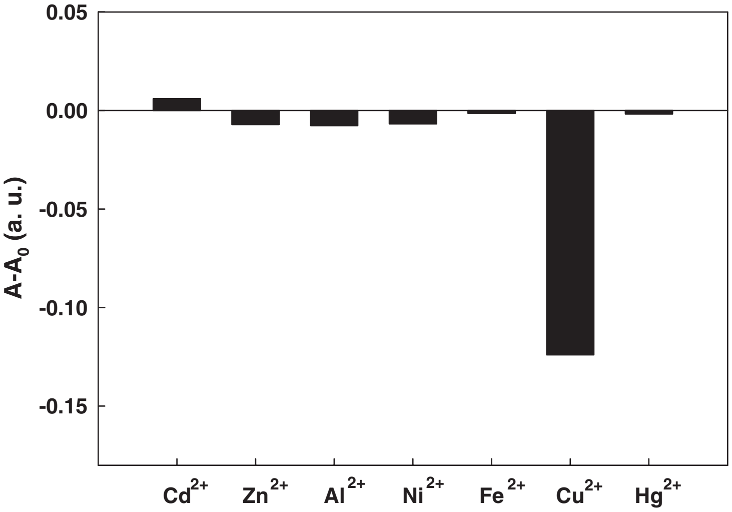


Figure 3. Effects of metal cations on UV-Vis absorption of dye sensor (1.0×10^{-5} M) in MeOH: water (9:1) solution (A and A_0 are the absorbance in the presence and the absence of metal ions, respectively at 390 nm).

Metal complexing behavior can be considered as electrophile attack reaction to the dye sensor molecules. This result is related with electrostatic properties and electron distributions through the dye sensor molecules. Thus, it is possible to predict the binding position with dye sensor and Cu^{2+} cations. The complex position is an electron rich binding group in the dye sensor molecule, namely nitrogen and hydroxyl group. Thus, electron energy levels and distributions of the dye sensor were further examined by molecular orbital calculations,

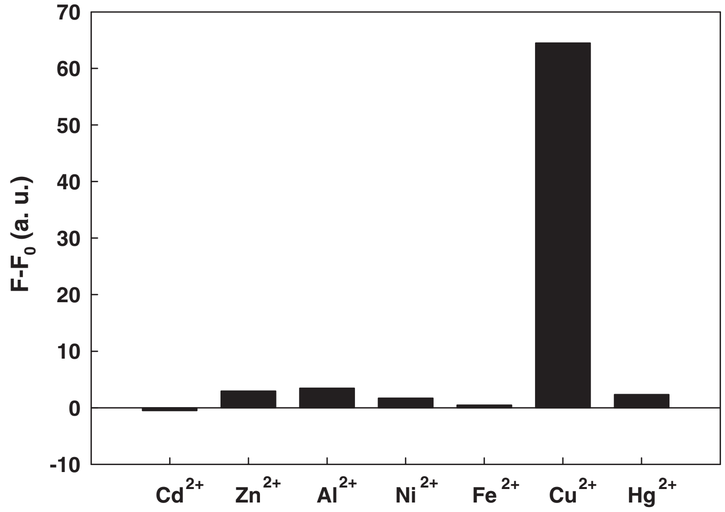


Figure 4. Effects of metal cations on fluorescence intensity of dye sensor (1.0×10^{-5} M) in MeOH: water (9:1) solution (F and F_0 are the emission in the presence and the absence of metal ions, respectively at 445 nm).

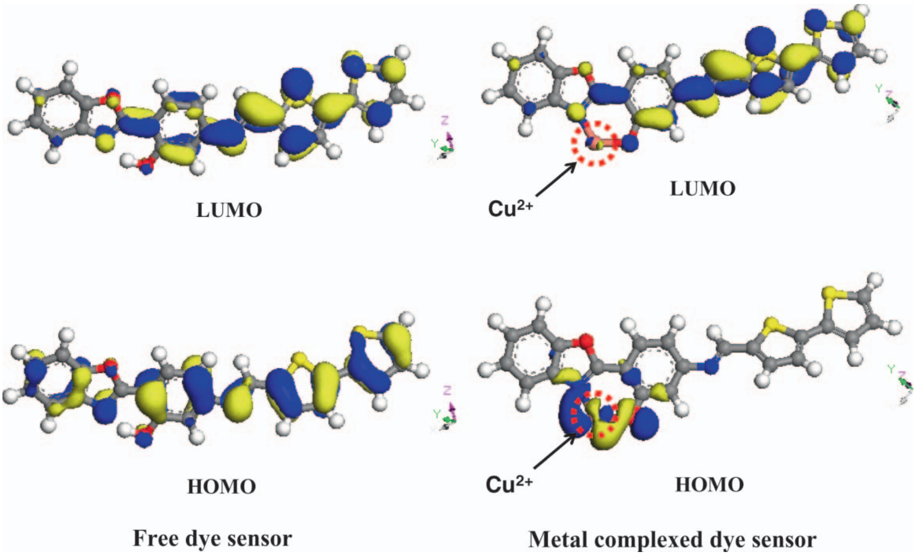


Figure 5. Electron density distributions of dye sensor.

which were based on the density functional theory (DFT) level using the exchange correction functional of the generalized gradient approximation (GGA), employing the *Materials Studio 4.3* suite of programs.

The resulting computational calculation indicated that the energy levels of free dye sensor were HOMO (−5.170 eV) and LUMO (−3.113 eV) and the energy levels of metal complexed dye sensor were HOMO (−4.811 eV) and LUMO (−3.131 eV), respectively.

HOMO energy of free dye sensor showed the delocalized electron distribution. In contrast, the electron distribution of HOMO energy in metal complexed dye sensor was localized in the area of Cu^{2+} cation biding legand (Figure 5).

Further electrochemical properties were calculated with cyclicvoltammetry (CV) measurement. Using CV measurement, we have found the oxidation peak at 0.845 V(onset, free dye sensor) and 0.908 V(onset, metal complexed dye sensor). The resulting cyclicvoltammogram was summarized in Figure 6.

In addition, the energy potentials of oxidation onset peak and absorption band gap were used to calculate empirical HOMO/LUMO energy levels. The following equation was used [11].

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

The resulting cyclicvoltammetry calculation showed that the energy levels of free dye sensor were HOMO (−5.225 eV) and LUMO (−2.538 eV) and the energy levels of metal complexed dye sensor were HOMO (−5.288 eV) and LUMO (−2.773 eV), respectively.

The comparison of computational calculation and experimental determination showed the similar values of HOMO and LUMO energy levels (Table 1 and Figure 7). Thus, the computational calculation results can be used as good supporting data for the analysis of electrochemical properties.

Finally, we have determined the binding ratio between dye sensor and Cu^{2+} metal cations using the Job's method [16]. For Job's plot measurements, 1×10^{-5} M of dye

Table 1. HOMO and LUMO values of dye sensor

	Computationally calculated values			Cyclicvoltammetry values		
Dye sensor	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
Free dye sensor	−5.170	−3.113	2.057	−5.225	−2.538	2.687
Metal complexed dye sensor	−4.811	−3.131	1.680	−5.288	−2.773	2.515

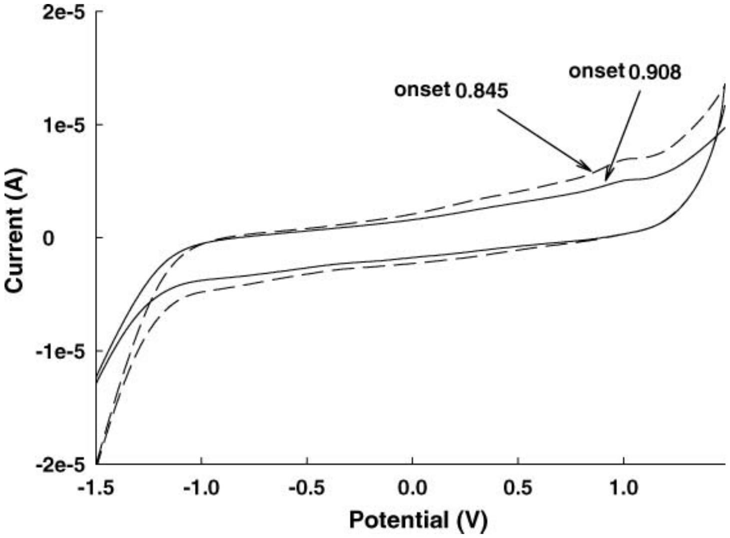


Figure 6. Cyclicvoltammogram of dye sensor in acetonitrile

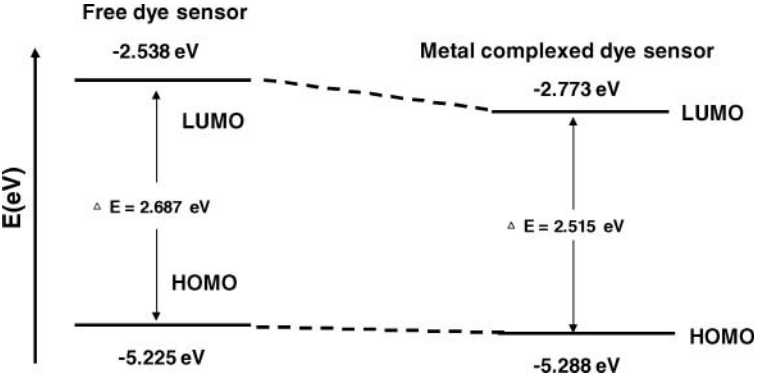


Figure 7. HOMO and LUMO energy levels of dye sensor

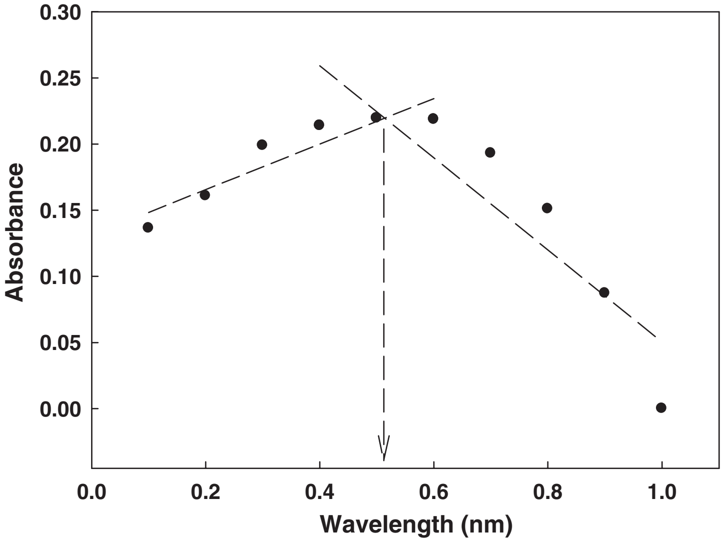


Figure 8. Job's plots for the binding ratio of dye sensor and Cu^{2+}.

sensor and 1×10^{-4} M Cu^{2+} cations were prepared using various molar ratios of dye sensor and Cu^{2+} cations (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0). The relationship between maximum absorption peak and mole fraction of Cu^{2+} cations is displayed in Figure 8. From the findings, dye sensor exhibited that the molecular fraction was close to 50%, which indicated 1:1 complex composition between dye sensor and Cu^{2+} cations.

Conclusions

In this work, the designed dye chemosensor was synthesized using 2,2-bithiophene as a donor unit and benzoxazole intermediate as a signal unit. UV-Vis absorption and fluorescence emission spectra were investigated to monitor the optical changes and sensing properties of the dye sensor with various different metal cations (Cd^{2+}, Zn^{2+}, Al^{2+}, Ni^{2+}, Fe^{2+}, Hg^{2+}). The dye sensor showed the higher selective detection toward Cu^{2+} cations. The comparison of computational calculation and experimental determination showed the similar values of HOMO and LUMO energy levels. Thus, the computational calculation results can be used as good supporting data for the analysis of electrochemical properties. From the Job's method, dye sensor exhibited that the molecular fraction was close to 50%, which indicated 1:1 complex composition between dye sensor and Cu^{2+} cations.

Acknowledgment

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