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Dye Chemosensing Effect and Characterization Based on Hydroxyl Anthracene and Naphthalene Moiety

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*In this work, we have studied the detection properties of 1,4-dihydroxyanthracene-9, 10-dione (dye **1**), 3-hydroxy-2-naphthoic acid (dye **2**) and methyl-3-hydroxy-2-naphthoate (dye **3**), which were used as dye chemosensors for the metal ion complexing. Metal binding sites in dye **1**, **2**, and **3** show similar structural characteristics. Ketone, hydroxyl and carboxyl groups provide the functions to bind the metal ions. Metal ion detection properties of these dyes were investigated by UV-Vis absorption, fluorescent emission, HOMO/LUMO energy level and potential and job's method.*

Keywords Complex ability; dye chemosensing; HOMO/LUMO; hydroxyl anthracene; hydroxyl naphthalene; Job's method

Introduction

Recently, harmful metal ion detection researches have received great attention due to their useful impacts in the areas of chemical, biological, and environmental applications. This detection skill toward metal ions is called as chemosensing technique. Chemosensors for specific chemicals based on receptor-guest complex are considered as a convenient tool in analytical chemistry. In the context of biological and environmental aspects, interesting dye chromophores and fluorophores have been reported about their colorimetric and fluorometric sensing properties [1–4]. Dye **1**, **2**, and **3** are widely used moieties in dye synthesis and the related organic chemistry, biochemistry and textile industry [5–9]. These three dyes have commonly enjoyed in synthesis and application of dye house and have selected for this study to be suitable for chemical sensing properties. In addition, these three dye molecules are very useful and easy to be applied to many kinds of research areas.

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In this work, we have focused on the feasibility of three dye molecules as an effective chemosensor for the harmful metal ion detections. The metal ion chemosensing properties of the dyes were determined by UV-Vis absorption and fluorescence emission behaviors. In addition, computational calculation determined their potential energy levels, namely HOMO and LUMO. This electron density distribution could provide the estimation of complex characteristic functions between electron rich interacting positions and electrophile metal ions [10–13].

Experimental

2.1. *Materials and Measurements*

1,4-Dihydroxyanthracene-9,10-dione (dye **1**), 3-hydroxy-2-naphthoic acid (dye **2**), and methyl-3-hydroxy-2-naphthoate (dye **3**) were purchased from Aldrich and used without further purification. Solvent was used with MeOH:water (4:1) mixture. The UV-Vis absorption spectra were measured on an Agilent 8453 spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer. HOMO and LUMO energy levels were performed by *Material Studio 4.3* program.

2.2. *Chemosensing Measurements: Absorption and Emission*

To measure optical chemosensing properties, different concentrations of dye solution were prepared, namely dye solution **1** (1.1×10^{-5} M) and dye solution **2, 3** (3.3×10^{-5} M). Measurements of UV-Vis absorption and fluorescence emission were performed by the addition of metal ions (from 8.25×10^{-7} M to 6.60×10^{-6} M of various metal ions: Hg^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Al^{2+}, and Fe^{2+}) in 2 ml of dye solutions. And then the samples were well mixed to test for 10 min using Vortex mixer.

2.3. *Job's Plot Measurements*

Using job's method, the stoichiometrical characteristics of metal complex ratio were determined. Equimolar solutions of dyes and various metal ions (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 sample mixtures were characterized at maximum absorption.

3. Results and Discussion

In this work, to detect metal ions, widely used dye moiety **1**, **2**, and **3** were selected. These compounds of dye **1**, **2**, and **3** have been enjoyed to the dye synthesis, especially mordant dye chromophores, where the expected metal ion bindings occurred and dyed. For this consideration, we were intended to apply this potential function to the metal ion detections, namely chemosensing. The optical absorption and emission properties were influenced by these complex behaviors and the corresponding findings were quite useful to use chemosensing technique. Figure 1 shows the dye structures to be used in this study.

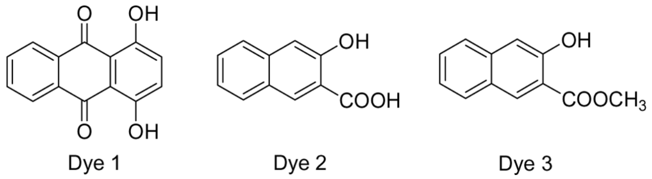
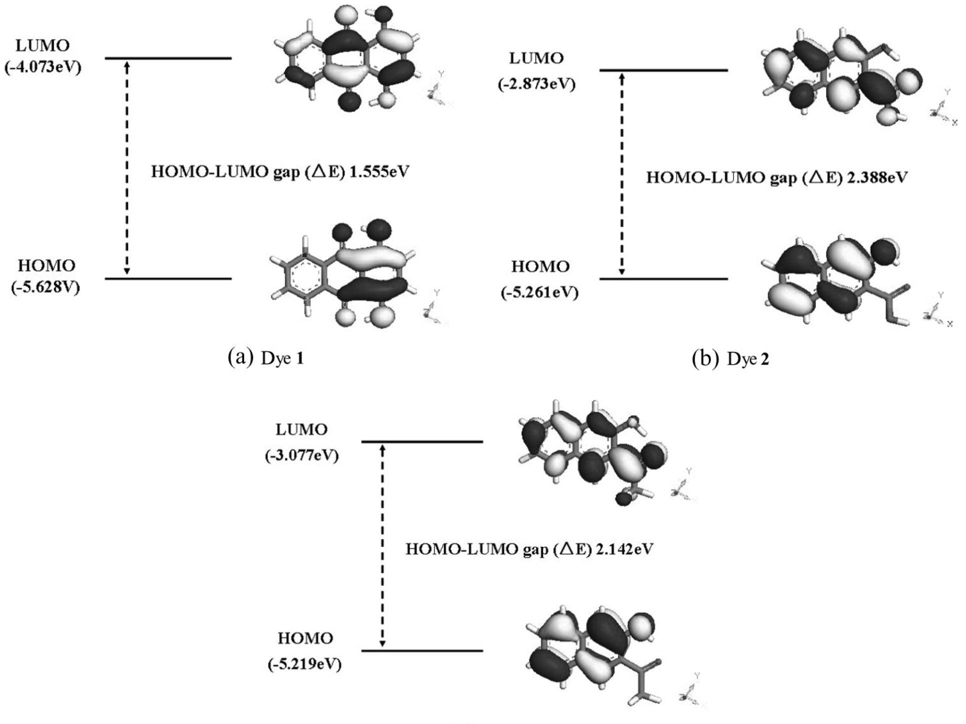


Figure 1. Dye structures used.

Metal complex efficiency and selectivity are of importance in chemosensors. Dye **1** has two metal ion binding positions. But when the first metal ion binding reaction occurs, the other metal binding site becomes inert due to the stability of this dye compound. Metal complex position in dye **2** and dye **3** is same, but only dye **2** showed the metal complexing effect. Dye **2** and **3** are different in substituents. One is carboxyl acid and the other is methyl group. Methyl group of dye **3** seems to interfere with the coordination of metal ions, which results in retardation of the metal binding reaction. In addition, the metal binding reaction, namely electrophile attack, was related to electrostatic properties and electron density distributions. We can assume the states of dye energy levels to coordinate with electrophile metal ions. Thus, HOMO and LUMO energy levels and electron density distributions were considered and displayed in Figure 2 [10,11].



(a) Dye **1**

(b) Dye **2**

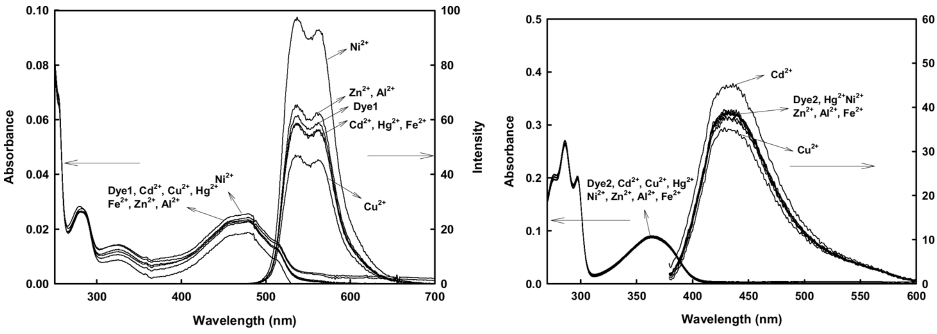
(c) Dye **3**

Figure 2. HOMO and LUMO energy levels and electron density distributions.

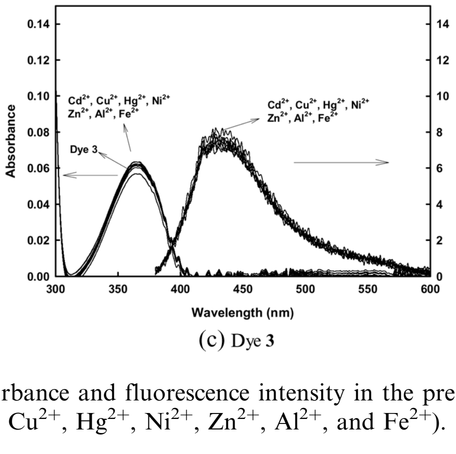
Figure 2 showed HOMO/LUMO energy levels and electron distributions of the each dyes. Metal ion complex reactions, namely electrophile bindings, could be made in electron rich HOMO state of dyes, where metal ions were complexed with dyes in stead of LUMO states. Most of the computational calculations showed that the electron density distributions were localized in the areas of ketone and hydroxyl groups, where the possibility of metal binding reactions expected. Chemical structures of dye **2** and **3** are almost same except the methyl group. Electron distributions of each dye in HOMO state are densely distributed around hydroxyl groups. Figure 2 clearly showed that electrophile metal binding reactions could occur to the electron rich positions of dyes in HOMO states.

Absorption and fluorescence emission monitoring were carried out to examine the chemosensing behaviors of dyes. Figure 3 showed that absorption and emission changes were observed by the addition of various metal ions (Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Al^{2+}, and Fe^{2+}).

Especially, dye **1** and dye **2** showed the optical changes, namely metal complex results. Dye **3** did not show any significant detection properties. Dye **1** indicated the metal ion detections for Ni^{2+} and Cu^{2+} and dye **2** provided the sensing functions for Cd^{2+} and Cu^{2+}. Thus, the dyes showed metal ion selectivity functions among tested various metal ions. More detailed sensing investigations were conducted with Ni^{2+}, Cu^{2+} for dye **1** and Cd^{2+}, Cu^{2} for dye **2** and the corresponding results were represented in Figure 4 and Figure 5.

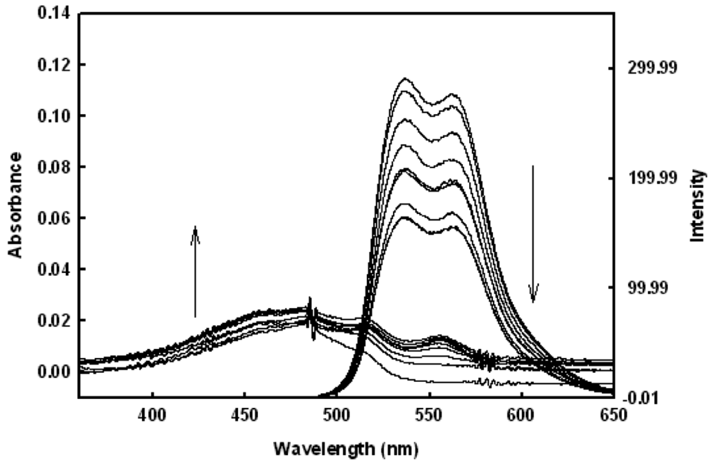


(a) Dye **1** (b) Dye **2**

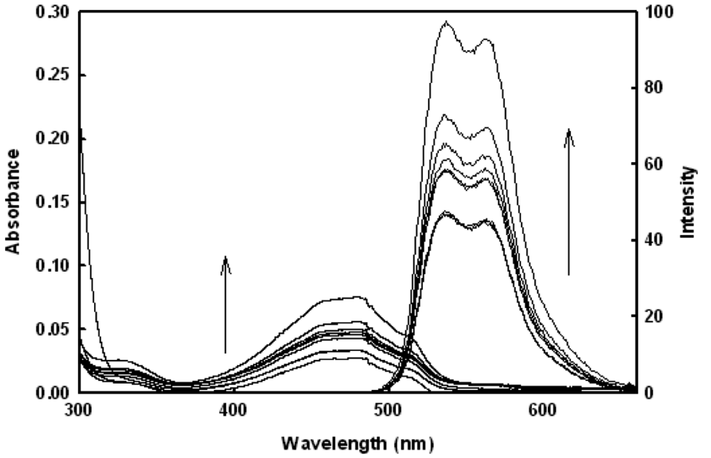


(c) Dye **3**

Figure 3. UV-Vis absorbance and fluorescence intensity in the presence of 6.60×10^{-6} M of each metal ions (Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Al^{2+}, and Fe^{2+}).



(a) Dye **1** with Cu^{2+}

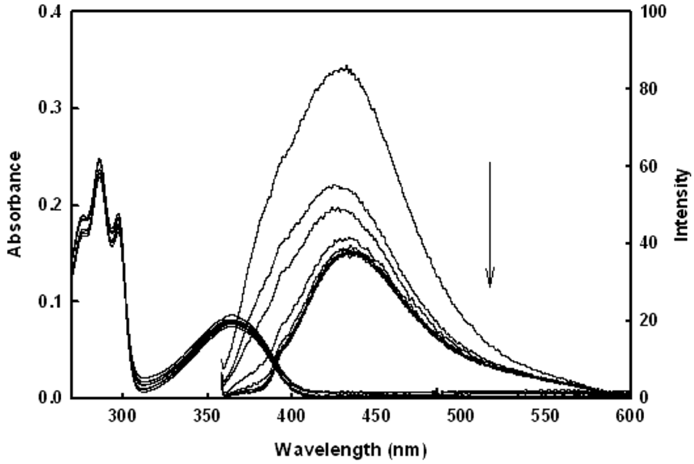


(b) Dye **1** with Ni^{2+}

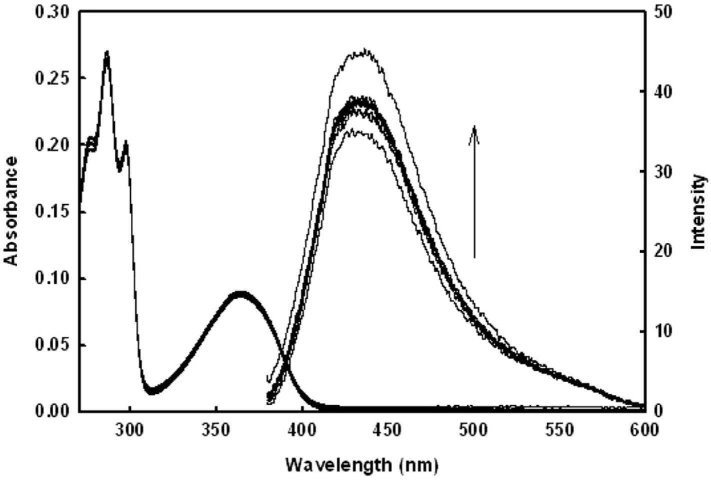
Figure 4. Absorption and fluorescence spectra of dye **1**: metal ion concentrations from 8.25×10^{-7} M to 6.60×10^{-6} M and dye concentration 3.30×10^{-5} M in methanol:water (4:1).

Absorption and fluorescence emission of dye **1** were measured at 479 nm and 535 nm, respectively. In the case of dye **2**, the wavelength of absorption and emission were 370 nm and 505 nm, respectively. Absorption spectra of dye **2** did not indicate any changes, but fluorescence intensity was changed by dye-metal complex bindings. Dye **1** showed higher selective functions to nickel ions, which resulted in great fluorescence enhancement. Dye **2** displayed slight fluorescence enhancement for cadmium ions. In the case of copper sensing, fluorescence emission spectra decreased with both of dye **1** and dye **2**. The detection properties for all applied metal ions were summarized in Figure 6.

Fluorescence emission spectra of the dye **1** increased with the addition of nickel ions and decreased with copper ions. In the case of dye **2**, increasing properties with cadmium ions and decreasing properties with copper ions were determined. Their corresponding relationships were represented in Figures 7 and 8.



(a) Dye **2** with Cu^{2+}



(b) Dye **2** with Cd^{2+}

Figure 5. Absorption and fluorescence spectra of dye **2**: metal ion concentrations from 8.25×10^{-7} M to 6.60×10^{-6} M and dye concentration 3.30×10^{-5} M in methanol:water (4:1).

Fluorescence enhancement can be explained by MLCT (metal to ligand charge transfer) system, when the metal binding reaction occurred. However, copper ions showed fluorescence quenching effect. Theoretically, this characteristic proposes the complex ability of dye **1** and **2** with copper ions, which is not so large and causes to fluorescence quenching result [14]. The metal ion size and electron withdrawing power can be also considered with this effect.

Finally, we determined the composition of the metal binding form using the Job's method [13]. For Job's plot measurements, 5×10^{-5} M of dye **1** and 1.65×10^{-4} M of metal ions were prepared and then various molar ratios of dyes and metal ions (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0) were measured. The relationship for maximum absorption peak versus mole fraction of the metal ions is summarized in Figure 9. From the findings, dye **1** exhibited that the molecular

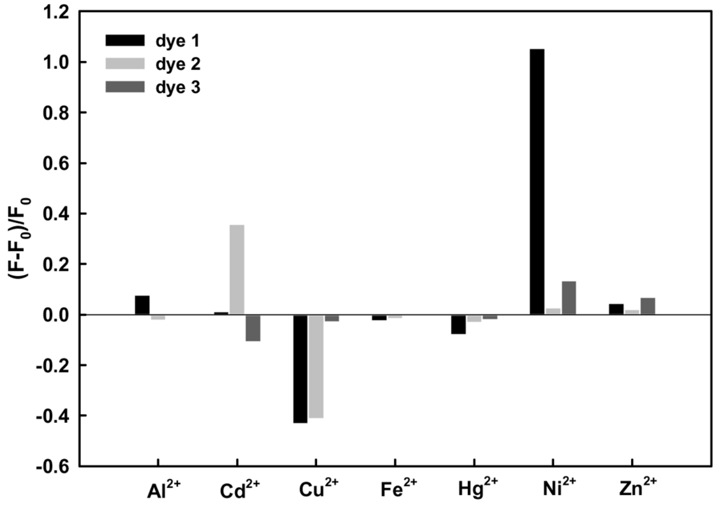


Figure 6. Effects of metal ion detection.

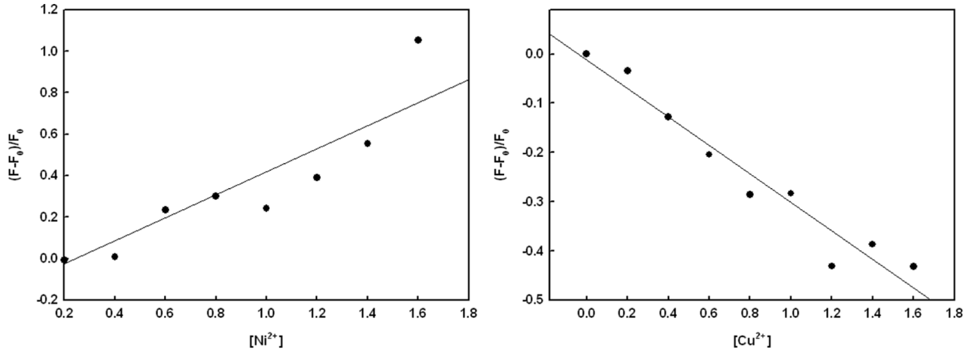


Figure 7. Plots of dye **1** and metal ions with a function of fluorescence.

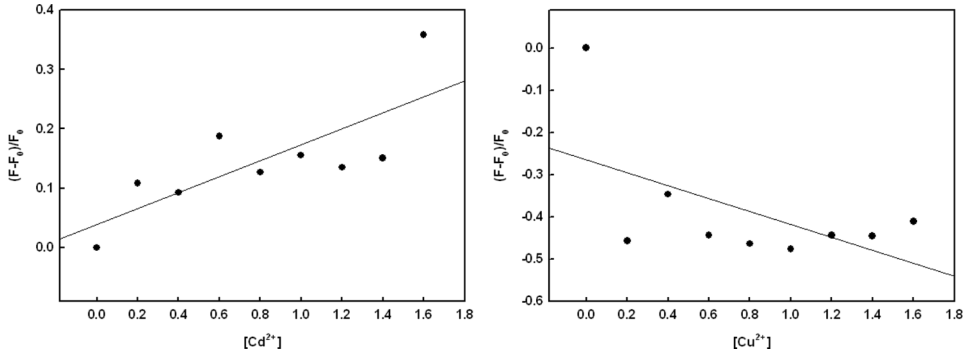


Figure 8. Plots of dye **2** and metal ions with a function of fluorescence.

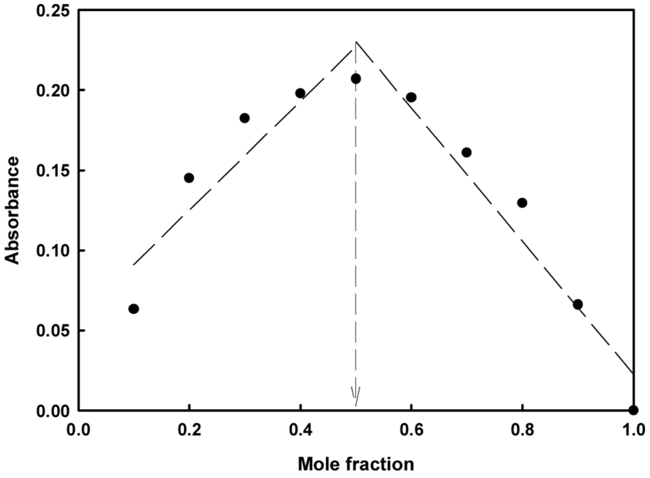


Figure 9. Plot of Job's method for dye **1**.

fraction was close to 50%, which indicated 1:1 complex composition between dye **1** and metal ions.

4. Conclusions

In this study, we investigated the effects of dye molecular chemosensing behaviors. It showed sensitive and selective sensing properties for Ni^{2+}, Cd^{2+}, and Cu^{2+}. These detection bindings were formed by 1:1 stoichiometry complex type with subjected metal ions. Dye **2** was not observed by absorption changes upon addition of metal ions. But fluorescence intensity indicated the effective binding functions. Thus, these dye molecules showed their sensing properties with fluorometric sensings and selectivity functions.

Acknowledgments

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