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Synthesis and Characterization of Benz-X-azole Based Dye Chemosensor

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Concerns over heavy and transition metal ions such as copper, zinc and mercury are of topical interests because they are considered as highly toxic environmental pollutants. In this study, we have designed and synthesized new benz-X-azole derivatives as dye chemosensor and their selective and sensitive complex functions for heavy metal ion detection were investigated. Electron density distributions and HOMO/LUMO energy levels were computationally optimized. In addition, the formation type of metal binding complex was determined by Job's plot measurements and cyclic voltammetry were conducted to determine comparison of the energy level potentials.

Keywords Absorption; benz-X-azole; complex function; computational simulation; dye chemosensor; emission; heavy metal ion; HOMO/LUMO

Introduction

Since the first studies of the chemosensor reported on metal complex ligands such as crown ether, cryptand and spherand in the structures, many interesting works have been focused on the heavy and transition metal ions sensing [1–3]. Heavy and transition metal ions such as calcium, copper, zinc and mercury are considered to be highly dangerous metal ions in the human body and play an important role in various biologic processes and systems [4–9]. Copper and zinc are significant metal pollutants with higher concentrations in environmental systems. As well known, it is connected to serious etiology of Alzheimer's, Menke's, and Wilson's diseases [9]. Mercury is also considered to be highly toxic heavy metal ion in the biological

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systems and plays a role in the physiologic process because it can be accumulated in the organs [10–12]. Thus, the design of selective, sensitive and effective chemosensors [13] and their measurement utilizations over heavy metal cations are of great importance for chemical, biological, and environmental research areas.

In this study, we have designed and prepared of new benz-X-azole derivatives as a dye chemosensor and their heavy metal ions complex functions were examined and determined. Structures of the synthesized dye sensors **3** and **4** were identified. Metal ions detection behaviors were discussed with UV-Vis absorption and fluorescent emission optical measurements in details. Furthermore, electron density distributions and HOMO/LUMO energy levels of dye sensors **3** and **4** were computationally optimized using the density function theory (DFT) with exchange correction functional of local density approximation (LDA) based on the Perdew-Wang (PWC) set. Cyclic voltammetry measurements were carried out to examine the experimental HOMO/LUMO energy potentials.

Experimental

2.1. Analysis

Absorption spectra were examined on Agilent 8453 UV-Vis spectrophotometer. Fluorescence spectra measurements were performed on a Shimadzu RF-5301. ¹H NMR spectra were recorded on a JNM-AL400 MHz NMR instrument with TMS as internal standard and elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Electron distributions and energy potentials were calculated with Material Studio 4.3. Cyclic voltammograms were examined with a VersSTAT3 using three-electrode conventional electro chemical cell. Cyclic voltammetry experiment was run 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 100 mV/s.

2.2. Synthesis

Metal cation receptors 1 and 2 were prepared by condensing *p*-aminosalicylic acid, 6.52 mmole (0.998 g), with *o*-aminophenol and *o*-aminothiophenol 6.52 mmole (0.711 g, 0.816 g) in 20 g of polyphosphoric acid (85% phophorus pentoxide) for 3 h at 200°C. After 3 h, the reaction was quenched into ice water and stirred for 24 h. The formed precipitate solution was adjusted to the neutral pH condition using 1% sodium carbonate solution. After 3 h, the mixture was filtrated with distilled water at several times and dried in oven at 40°C. The general procedures were followed by the indicated references [14–16].

Dye 1, Yield: 23.03% (0.340 g); mp: $226.5-226.7^{\circ}$ C. Anal. Calcd for C₁₃H₁₀N₂O₂: C, 69.02; H, 4.46; N, 12.38: found; C, 69.16; H, 4.16; N, 12.81. ¹H NMR (400 MHz, CDCl₃): δ 4.00 (s, 2H), δ 6.24 (d, 1H), δ 6.28 (d, 1H), δ 7.18–7.32 (m, 2H), δ 7.42–7.50 (m, 1H), δ 7.52–7.62 (m, 1H), δ 7.30 (d, 1H), δ 11.47 (s, 1H).

Dye **2**, Yield: 38.84% (0.614 g); mp: 211–213°C. Anal. Calcd for $C_{13}H_{10}N_2OS$: C, 64.44; H, 4.16; N, 11.56; S, 13.23: found; C, 64.55; H, 4.03; N, 11.52; S, 12.62. ¹H NMR (400 MHz, DMSO-d₆): δ 5.95 (s, 2H), δ 6.18 (d, 1H), δ 6.28 (d, 1H), δ 7.34 (t, 1H), δ 7.48 (t, 1H), δ 7.64 (d, 1H), δ 7.90 (d, 1H), δ 8.04 (d, 1H), δ 11.80 (s, 1H).

Dye chemosensors 3 and 4 were obtained using the prepared metal ion receptor dyes 1 and 2. The general procedures were described in the reported references [14–16]. Terephthalaldehyde (0.1 mmole, 0.013 g) and metal ion receptor dyes 1 and 2 (0.2 mmole, 0.045 g, 0.048 g) were stirred in 5 ml of benzene. $5 \sim 6$ drops of piperidine was added during the reaction. Reflux was continued for 2 days. The reaction was cooled to room temperature and the reaction product was filtrated using benzene at several times and dried in vacuum [17].

Dye **3**, Yield: 34.80% (0.019 g); mp: $226.5-226.7^{\circ}$ C. Anal. Calcd for $C_{34}H_{22}N_4O_4$: C, 74.17; H, 4.03; N, 10.18: found; C, 73.69; H, 4.10; N, 9.45. ¹H NMR (400 MHz, CDCl₃): δ 4.29 (s, 4H), δ 6.89 (s, 6H), δ 7.51 (s, 6H), δ 8.05 (s, 4H), δ 10.14 (s, 2H).

Dye 4, Yield: 33.98% (0.020 g); mp: 211–213°C. Anal. Calcd for $C_{34}H_{22}N_4O_2S_2$: C, 70.08; H, 3.81; N, 9.62; S, 11.01: found; C, 70.09; H, 4.04; N, 9.18; S, 10.95. ¹H NMR (400 MHz, CDCl₃): δ 5.29 (s, 4H), δ 6.99 (s, 6H), δ 7.51 (s, 6H), δ 8.05 (s, 4H), δ 10.11–10.14 (d, 2H).

2.3. Absorption and Fluorescence Emission

Absorption and fluorescence measurements were performed by the addition from 0 to 2 equiv. of different metal cations (Cu^{2+} , Zn^{2+} , and Hg^{2+}) in 3 ml of dye sensor (3 and 4) solutions (1.0×10^{-4} M). After being well mixed for 30 sec using Vortex mixer, the absorption and fluorescence spectra were examined and determined.

For Job's plot measurements, equimolar solution of dyes and metal ions $(1.0 \times 10^{-4} \text{ M} \text{ in acetonitrile})$ was prepared. And the dye sensors and metal ions were then 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 monitored.

Results and Dicussion

In this work, *p*-aminosalicylic acid and *o*-aminophenol (and *o*-aminothiophenol) were used to synthesize the benz-X-azole dye derivatives as metal cation receptors. After this reaction, the synthesized benz-X-azole dye intermediates 1 and 2 were reacted with terephthalaldehyde to produce dyes 3 and 4 as a dye chemosensor for the use of metal ion detections. Using these dyes, characterization studies and metal ion detection properties were investigated to examine the feasibility for the use of dye chemosensor purposes. These dyes 3 and 4 show promising chemical structures to be used for metal binding reactions, namely dye chemosensing complex, where electron rich groups or atoms such as nitrogen, sulfur and hydroxyl groups can be utilized to be binding sites for this detection purpose. The structures of prepared dyes 3 and 4 are shown in Figure 1.

The metal cation complex ability and optical property of dye chemosensors **3** and **4** $(1.0 \times 10^{-4} \text{ M})$ with different metal ions $(\text{Cu}^{2+}, \text{Zn}^{2+}, \text{ and Hg}^{2+})$ were investigated by UV-Vis absorption measurements. The changes in UV-Vis absorption spectra of dye sensors **3** and **4** upon the addition of different metal ions in the chloroform are shown in Figure 2(a) and (b), respectively. Figure 2 displays that the optical absorption behaviors of dye **3** were changed by the addition of three metal cations, but dye **4** had selectively responded to Cu^{2+} ions. The complex sensing ability of these dye sensors **3** and **4** specially showed the recognition function to Cu^{2+} ions among other metal. With increasing concentration of Cu^{2+} to the solution of dye sensor **3**, the absorption intensity peak at 390 nm gradually decreased, and a new



Figure 1. Synthetic routes for dye chemosensor.



Figure 2. UV-Vis absorption spectra changes of dye sensors 3 (a) and 4 (b) $(1.0 \times 10^{-4} \text{ M})$ in the presence of 2 equiv. molar of metal cations and more detailed titration with Cu²⁺ in CHCl₃.

peak at 330 nm sharply increased with an isobestic point at 360 nm. In the case of dye sensor 4, the isobestic point at 380 nm was clearly observed. The absorption intensity of a new peak at 350 nm increased dramatically and a peak at 390 nm decreased with increasing concentration of Cu^{2+} .

Figure 3(a) and (b) show that the fluorescence emission changes of dye sensors **3** and **4** upon the addition of Cu^{2+} ions. Similar to absorption changes, dye sensors **3** and **4** were recognized with Cu^{2+} , the fluorescence emission gradually increased. With increasing with concentration of Cu^{2+} to the solution of dye sensors **3** and **4**, the intensity of fluorescence emission band at 460 nm and 520 nm greatly increased, respectively. The prepared dye sensors **3** and **4** were effectively and



Figure 3. Fluorescence spectra of dye sensors 3 (a) and 4 (b) $(1.0 \times 10^{-4} \text{ M})$ titrated with Cu²⁺ in CHCl₃.



Figure 4. Job's plots for dye sensors 3 (a) and 4 (b).



Figure 5. Electron density distributions and HOMO/LUMO energy levels of dye sensors 3 (a) and 4 (b).

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selectively complexed with Cu^{2+} ions, where the functions of dye chemosensor were promisingly observed and confirmed.

To estimate and judge the complex formation type of dye sensor-metal cation, Job's plot [18] was used. In Job's plot, the ratio of maximum absorption peak versus mole fraction of the metal ions was 0.6 to 0.7, which was concluded to be 1:2 complex type of binding. The job's plot findings showed these characteristics in Figure 4. As previously shown in the Figure 1, metal ions might be bound to nitrogen (or sulfur) and hydroxyl group in metal ion receptor sites of dye sensor molecules.

Electron density distributions and molecular energy potential levels of dye sensors **3** and **4** were computationally simulated by *Material studio 4.3* and the corresponding results were illustrated in Figure 5. Figure 5 shows that the electron density distributions are mainly localized in benz-X-azole moieties in HOMO and the electrons are densely distributed in terephthalaldehyde moiety in LUMO. Metal cations, namely



Figure 6. Cyclic voltammetry diagrams of dye sensors 3 (a) and 4 (b) in acetonitrile.

Dye sensors	Computationally calculated values			Cyclic voltammetry obtained values		
	НОМО	LUMO	ΔΕ	НОМО	LUMO	ΔΕ
3 4	-5.18 -5.28	$-3.43 \\ -3.55$	1.75 1.73	$-5.03 \\ -5.13$	$-2.33 \\ -2.40$	2.70 2.73

Table 1. Summary of HOMO/LUMO values of dye sensors 3 and 4

electrophiles, may attack to the electron rich HOMO states, where the complexes between dye sensors and metal cations can be coordinated. In other words, dye sensing functions can be utilized in electron rich HOMO levels. This theory also well matched with the electron density distributions in Figure 5. In HOMO levels, rich electron distributions were localized in benz-X-azole binding sites having nitrogen (or sulfur) and hydroxyl group, where the complexes were proceeded.

Figure 6 shows that the cyclic voltammograms of the dye sensors **3** and **4** in acetonitrile solution containing a dye concentration of 1.0×10^{-3} M with 0.05 M TBAPF₆. Using the maximum peak potentials, HOMO energy levels were calculated [19]. The LUMO energy levels were also calculated by the band-gap energy from UV-Vis absorption fit curve.

$$HOMO(orLUMO)(eV) = -4.8 - (E_{peakpotential} - E_{1/2}(Ferrocene))$$

Where $E_{peakpotential}$ and $E_{1/2}$ (Ferrocene) is the maximum (minimum) peak potential of dyes and the half-wave potential of Ferrocene (0.42 V), respectively. The obtained electrochemical results were in agreement with observed theoretical calculation values. The summaries are listed in Table 1.

Conclusions

We have designed and synthesized the new dye chemosensors **3**, **4** and even though dye **3** and **4** showed metal recognition, especially selective and sensitive complex properties of dye **4** for harmful metal cations were interested. The dye sensors **3** and **4** showing complex ability can be effectively recognized with Cu^{2+} , where UV-Vis absorption and fluorescence emission spectra were sharply changed. These dye sensors **3** and **4** formed 1:2 complexes with metal ions because dye sensors **3** and **4** have two metal complex legands in the molecular structures. The results were also confirmed by Job's plot measurements. Electron density distribution and HOMO/LUMO energy levels were computationally simulated and the corresponding results were considered to estimate the metal binding positions in dye sensor molecules. In addition, calculated and experimented HOMO/LUMO energy levels were compared and the results were well matched. Thus, the synthesized new dye sensors can be utilized as chemosensors for the detection of metal cations in environmental and biological research areas.

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