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Synthesis and Characterization of Quinoline-Based Dye Sensor

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Quinoline-based dye has been synthesized as a use of chemosensor for metal ions. The chemical structures and characteristics were determined by ^{1}H-NMR, EA, Computational calculation and cyclic voltammetry. The detection properties of this dye chemosensor were examined and determined using UV-Vis spectroscopy. The prepared dye showed clear detection properties for Cu^{2+} and Zn^{2+}. However, the sensing property between dye and Hg^{2+} ion was not observed. HOMO and LUMO energy levels were determined by computational calculation and electrochemical method.

Keywords: chemosensor; computational calculation; HOMO; Job's method; LUMO; quinoline-based dye

INTRODUCTION

Research developments of selective, sensitive and simple chemosensors towards metal ions have important potentials in the areas of environmental and medical applications [1–3]. Since the initial studies reported the use of chemosensors such as crown ether, cryptand and spherand, many research efforts have been focused on the detection of transition metal ions due to their toxic impacts in the areas of environmental systems [4]. Recently, a great effort has been attracted in developing "simple-to-make and naked-eye assessment tools," which was carried out using dye molecules for the use of detecting metal ions [1–4].

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The concerns over toxicity of metal ions such as mercury, copper and zinc are of growing interests because they are considered as highly toxic environmental pollutants [5–7]. Their presence in the environment even in trace concentrations causes severe health problems for long terms. Especially, mercury and copper are considered by the Environmental Protection Agency (EPA) to be highly dangerous elements due to the dangerous toxic effects [4,6–8]. In this context, the development of convenient and efficient chemosensor technique using simple dye molecules are interesting topic and strongly required.

In this work, we have synthesized quinoline-based dyes as a chemosensor for metal ions. The detection properties of this dye chemosensor compound were examined and determined. The details of metal ion detections were discussed. In addition to metal ions detection properties, the molecular orbital (HOMO and LUMO energy level) potentials of the dye sensor were also calculated and determined.

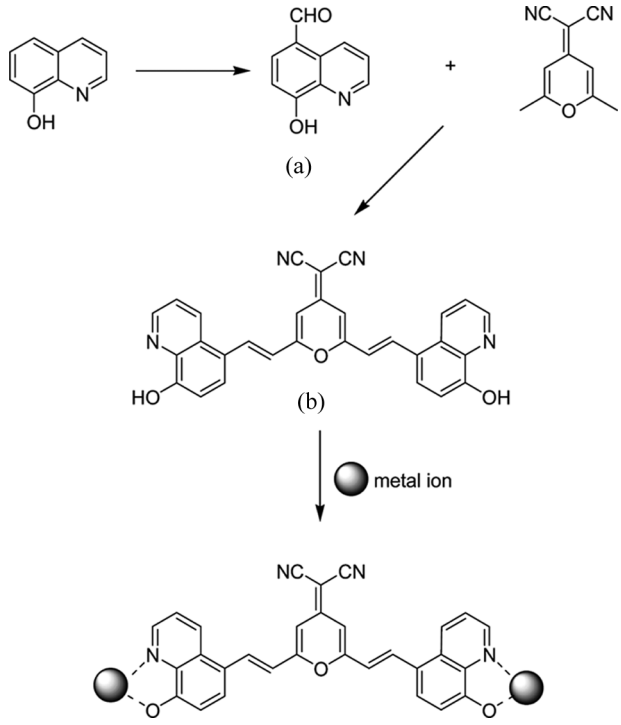
EXPERIMENTAL

Materials and Analysis

8-Hydroxyquinoline and 4-(dicyanomethylene)-2,6-dimethyl-4H-pyran were purchased from Aldrich and TCI, respectively. UV-Vis absorption spectra were recorded on Agilent 8453 spectrophotometer. ^{1}H NMR spectra were record on a JNM-AL 400 MHz NMR instrument with TMS as internal standard and elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Cyclic voltammograms were examined with a VersaSTAT3 using three-electrode conventional electrochemical cell. Cyclic voltammetry experiment was run in an acetonitrile solution containing tetrabutlyammonium hexafluorophosphate elelctrolyte. 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. The optimized geometric structure and molecular orbital were calculated with Materials studio 4.3.

Synthesis of 2-(2,6-Bis((E)-2-(8-Hydroxyquinolin-5-Yl)vinyl)-4 H-Pyran-4-Ylidene)malononitrile (HQM Dye)

As presented in Scheme 1(a), 8-hydroxyquinoline (0.035 mol, 5 g) were added in 20 ml of ethanol and refluxed. After 30 min, aqueous sodium hydroxide was added. Six ml of chloroform was then slowly dropwised over 1 h reaction. Reflux was continued for 18 h. Ethanol and excess chloroform was evaporated. The reaction mixture was poured into 125 ml of ice water and this solution was adjusted to the



SCHEME 1 Synthetic route of HQM dye.

acidic pH condition using hydrochloric acid. After 3 h, the mixture was filtrated, dried and purified using column chromatography (hexane: dichloromethane = 1:2 v/v) [9]. Yield: 17.32%; Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09. Found; C, 69.14; H, 4.14; N, 7.99. ^{1}H NMR (400 MHZ, $CDCl_3$): δ7.29 (s, 1H), δ7.65-7.67 (t, 1H), δ7.99-8.01 (d, 1H), δ8.86 (s, 1H), δ9.67-9.69 (d, 1H), δ10.14 (s, 1H).

Synthesis of quinoline-based dye sensor was shown in Scheme 1(b). To the mixture of 4-(dicyanomethylene)-2,6-dimethyl-4H-pyran (0.5 mmole, 0.086 g) and 5-formyl-8-hydroxyquinoline (1.0 mmole, 0.173 g) were mixed in 10 ml of 1-propanol and stirred. Five or six drops of piperidine were dropwised during the reaction. Reflux was continued for 2 days. The reaction was cooled to room temperature and the mixture was filtrated with 1-propanol at several times and dried in vacuum [10]. Yield: 14.26%; Anal. Calcd for $C_{30}H_{18}N_4O_3$: C, 74.68; H, 3.76; N, 11.61. Found; C, 74.56; H, 3.89; N, 11.96. 1H NMR (400 MHZ, $CDCl_3$): δ6.57 (s, 1H), δ6.64 (s, 2H), δ6.73 (s, 3H), δ7.52 (s, 1H), δ7.59 (s, 1H), δ8.10 (s, 4H), δ8.51 (s, 1H), δ8.85 (s, 5H).

3. RESULTS AND DISCUSSION

In this work, 5-formyl-8-hydroxyquinoline and 4-(dicyanomethylene)-2,6-dimethyl-4H-pyran were used to produce 2-(2,6-bis((E)-2-(8-hydroxyquinolin-5-yl)vinyl)-4H-pyran-4-ylidene)malononitrile (HQM dye) chemosensor for detecting metal ions. The sensing properties between this HQM dye sensor and three metal ions (Hg^{2+}, Cu^{2+} and Zn^{2+}) were investigated by UV-Vis spectrophotometer. The metal ions sensing properties of the dye were shown in Figure 1. The detection properties of HQM dye showed towards Cu^{2+} and Zn^{2+} ions. The characteristic strong UV-Vis absorption peak of HQM dye at 420 nm decreased with increasing concentration of Zn^{2+} and Cu^{2+} ions. At the same time, a new UV-Vis absorption peak of HQM dye appeared at 485 nm. The addition of metal ions to the HQM dye solution and its corresponding metal binding reaction resulted in a 65 nm red shift of absorption

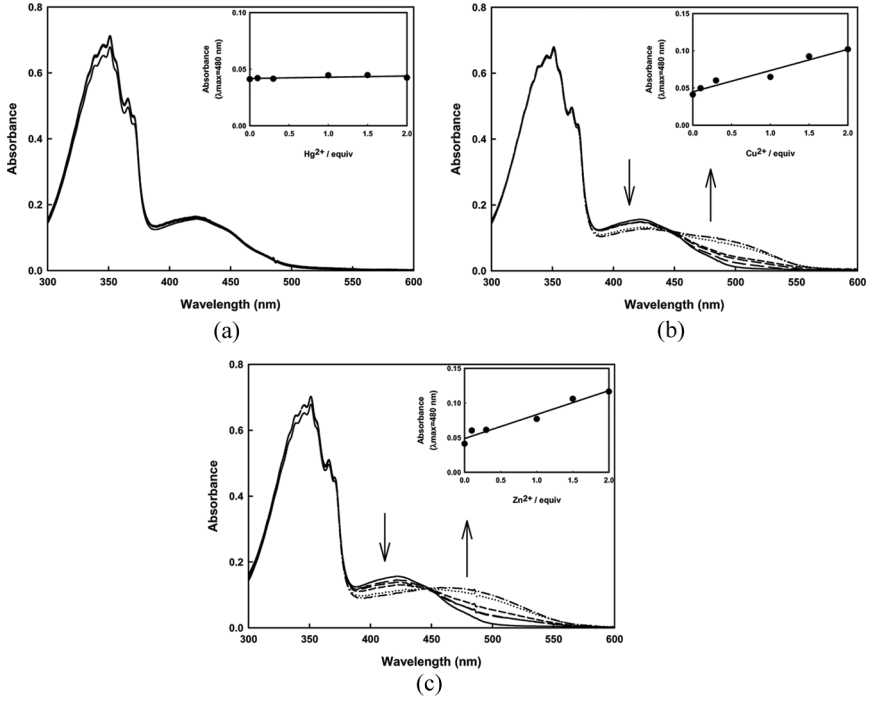


FIGURE 1 UV-Vis absorption spectra of HQM dye (1.0×10^{-4} M) titrated with metal ions in chloroform (a) Hg^{2+} (0–2 equiv), (b) Cu^{2+} (0–2 equiv), (c) Zn^{2+} (0–2 equiv).

maximum. According to this finding, 'naked-eye' detection can be possible by the distinct color change of the solution (Fig. 2). Therefore, without resorting to any expensive instrumental uses, the simple-to-use diagnostic tool for the detecting metal ions, namely dye chemosensor was positively considered from this HQM dye. However, the sensing property between HQM dye and Hg^{2+} ions cannot be observed.

Another spectrophotometric technique such as Job's method [12–14] was conducted to determine the form of the complex structures. In Job's method, equimolar solutions of HQM dye and metal ions (1.0×10^{-4} M in chloroform) were prepared. HQM dye and metal ion solution were prepared in different volume ratio (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 investigated by UV-Vis spectroscopy. The maximum absorption peak over mole fraction of the metal ions is shown in Figure 3. From the Job's plot result, it is found that one molecule of HQM dye complexes with two metal ions (Cu^{2+} and Zn^{2+}) [12,13].

The structural geometry and molecular orbital level of HQM dye were computationally optimized with Materials studio 4.3. Figure 4 shows that electron density distribution in HOMO state is mainly localized in 5-formyl-8-hydroxyquinoline moieties and electron density in LUMO state is moved to 4-(dicyanomethylene)-2,6-dimethyl-4H-pyran moieties after excited. HOMO and LUMO energy was calculated -5.17 eV and -3.45 eV, respectively.

The oxidation and reduction potential values were also used to determine HOMO and LUMO energy levels. Cyclic voltammogram of

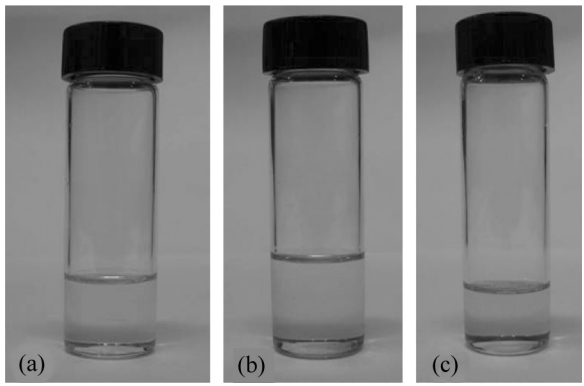


FIGURE 2 The images of HQM dye with metal ions (a) Hg^{2+}, (b) Cu^{2+}, and (c) Zn^{2+}.

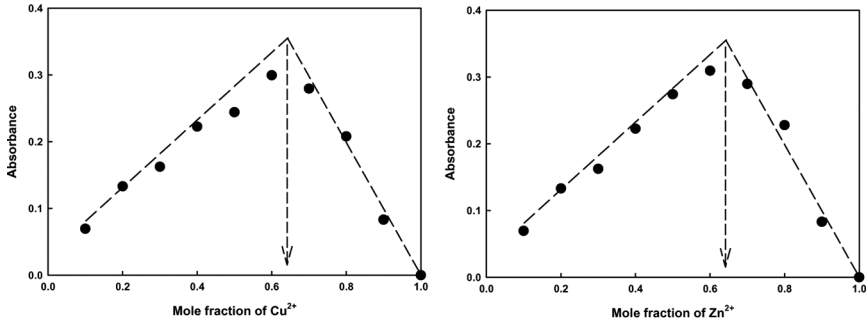


FIGURE 3 Job's method plot of HQM dye for Cu^{2+} and Zn^{2+} ions.

the HQM dye (1.0×10^{-3} M) in acetonitrile with 0.05 M $TBAPF_6$ (Tetrabutylammonium hexafluorophosphate) was carried out and its result was shown in Figure 5. From the graph, this HQM dye exhibited one oxidation and one reduction curve. In addition, the HOMO and LUMO energy level of HQM dye can be determined by

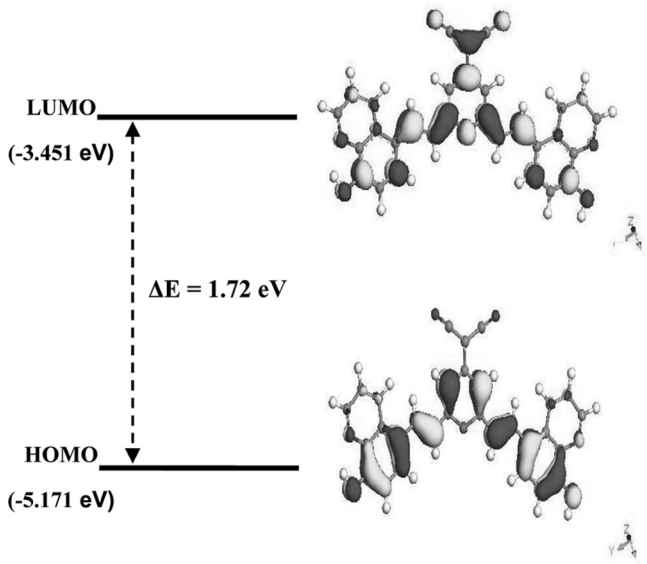


FIGURE 4 Fully optimized HOMO and LUMO energy levels and geometry of HQM dye.

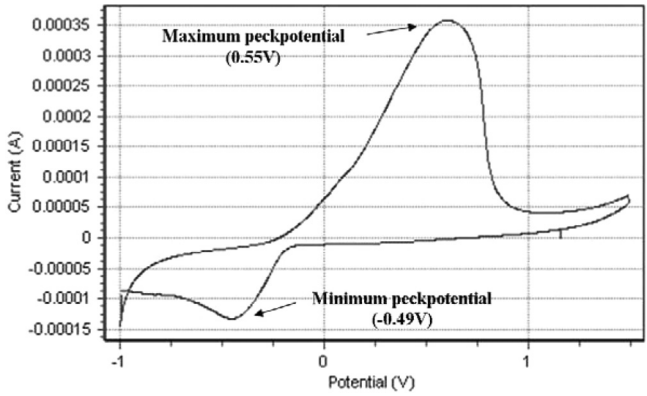


FIGURE 5 Cyclic Voltammogram of HQM dye in acetonitrile (0.05 M $TBAPF_6$, Ag/Ag^+ reference electrode and scan rate 100 mV/s).

experimental data of maximum peak potential (0.55 V) and minimum peak potential (−0.49 V). The HOMO and LUMO energy levels were calculated using the formula [14]:

$$\text{HOMO (or LUMO)(eV)} = -4.8 - (E_{\text{peakpotential}} - E_{1/2}(\text{Ferrocene}))$$

where, $E_{\text{peakpotential}}$ and $E_{1/2}$(Ferrocene) are the maximum and the minimum peak potential of HQM dye and the half-wave potential of Ferrocene (0.42 V), respectively. Using the formula, HOMO and LUMO energy levels were calculated by −4.93 eV and −3.89 eV, respectively.

4. CONCLUSIONS

In this context, a new chromogenic chemosensor based on quinoline moiety was synthesized. It showed sensitive detection function for Cu^{2+} and Zn^{2+} by UV-Vis absorptions and color changes. An obvious color change from yellow to orange was clearly observed with naked-eye detection. In other words, the synthesized HQM dye chemosensor can be used as a naked-eye sensor for Cu^{2+} and Zn^{2+} without resort to any spectroscopic instrumentation. The molecular orbital (HOMO and LUMO energy level) was also calculated by Materials studio 4.3 and cyclic voltammograms. The energy levels of HQM dye was determined by −5.171 eV (HOMO)/−3.451 eV (LUMO) using computational optimization and −4.93 eV (HOMO)/−3.89 eV (LUMO) using cyclic voltammograms, respectively. Thus, it is proposed that

HOMO and LUMO energy levels show the similar characteristic patterns from the both values of computational calculation and electrochemical redox potential measurement. The synthesized compound, namely HQM dye could be utilized as a simple sensing material for the analysis of toxic metal ions such as Cu^{2+} and Zn^{2+} ions in chemical, environmental and biological systems.

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