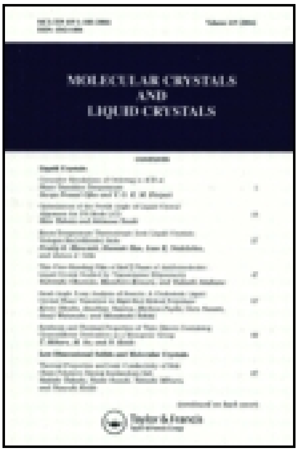

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Synthesis and Spectral Properties of a Highly Selective D-π-A Based Dye Chemosensor

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A novel chromogenic and fluorogenic dye chemosensor was computationally designed using MO theory calculation and synthesized based on donor-π-acceptor unit. This prepared dye sensor showed the selective Ni^{2+} *metal ion sensing effects in optical properties with UV-vis absorption and fluorescence emission. Dye sensor displayed evident absorption changes with* Ni^{2+} *ion and highly selective fluorescence quenching effect was determined. But it showed no significant changes upon the addition of other metal ions such as* Cd^{2+}, Na^{2+}, Mg^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Cu^{2+}, Hg^{2+} *and* Zn^{2+}

Keywords Absorption; D-π-A; dye sensor; fluorescence; metal cation; spectral properties

1. Introduction

The sensing of metal cations using dye sensor has attracted much attention owing to its application in both chemical and environmental processes [1–4]. The synthesis of chemical sensors or receptors capable of recognizing metal cations selectively continues to attract research interest. There are already many chromogenic dye sensors developed for selective recognition of different species so far due to their high selectivity, sensitivity and simplicity [5–7]. The design of chemical sensors that are sensitive towards specific target ions is a great challenge for dye chemists [8]. For various metal ions, even though there are many research reports and works are introduced [9–18] to detect Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{2+} and so on, few findings are reported for the sensing of Ni^{2+} ions. Herein, we have designed and synthesized the chromogenic and fluorephoric dye sensor to respond the presence of Ni^{2+} ions.

Intramolecular charge transfer (ICT) system based on donor-π-acceptor molecular conjugation has been widely attracted [1–7] for ions sensing, molecular switching and fluorescent labeling due to the clear changes of absorption and emission

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properties. In dye sensor **3**, we have selected 2-(3,5,5-trimethylcyclohex-2-enylidene)-malononitrile **1** as electron withdrawing acceptor and 4-(bis(pyridin-2-ylmethyl) amino)benzaldehyde **2** as electron pushing donor, which also considered as Ni^{2+} receptor. A vinyl group between the receptor (and ICT donor) and isophorone acceptor can induce longer wavelengths in absorption and fluorescence emission spectra. This paper concerns the synthesis of a dye sensor for metal ions, especially designed for Ni^{2+} ion, based on a donor-π-acceptor, intramolecular charge transfer system. And the potential function of dye sensor **3** to recognize Ni^{2+} ion, HOMO/ LUMO energy levels, electron distribution in molecular structure and the corresponding changes in its absorption/emission properties were determined.

2. Experimental

All reagents and solvents were purchased from Aldrich and were used without further purification. Mass spectra were obtained using a Shimadzu QP-1000 and ^1H NMR spectra were recorded on a Varian Inova 400 MHz FT-NMR using TMS as internal standard. UV-Vis absorption spectra were measured on an Agilent 8453 spectrophotometer whilst fluorescecne spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer. Melting points were determined using an Electrothermal IA900. 2-(3,5,5-Trimethylcyclohex-2-enylidene)-malononitrile **1** and 4-(bis(pyridin-2-ylmethyl)amino)benzaldehyde **2** were prepared using the previously described procedure [19,20].

Synthesis of Dye Sensor 3

2-(3,5,5-Trimethylcyclohex-2-enylidene)-malononitrile **1** (0.31 g, 1.65 mmol) and 4-(bis(pyridin-2-ylmethyl)amino)benzaldehyde **2** (0.5 g, 1.65 mmol) were dissolved in 1-propanol (10 ml) with piperidine (0.1 ml) as catalyst and refluxed for 4 h. After which, the reaction mixture was cooled down to room temperature. Via column chromatography (silica, ethlyacetate/ethanol, 40/1. v/v), the desired product was obtained in 50% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (s, 6H), 2.35 (s, 2H), 2.49 (s, 2H), 4.86 (s, 4H), 6.75 (m, 4H), 6.91 (d, J = 15.88, 1H), 7.28 (m, 5H), 7.65 (t, J = 7.84, 2H), 8.57 (d, J = 3.84, 2H). $M^+ = 471$. mp: 173°C.

3. Results and Discussion

Dye sensor **3** was designed and synthesized readily from commercially available starting materials using a one-step reaction (Fig. 1). Due to its well-defined intramolecular

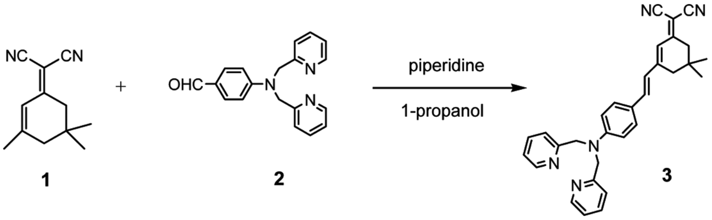
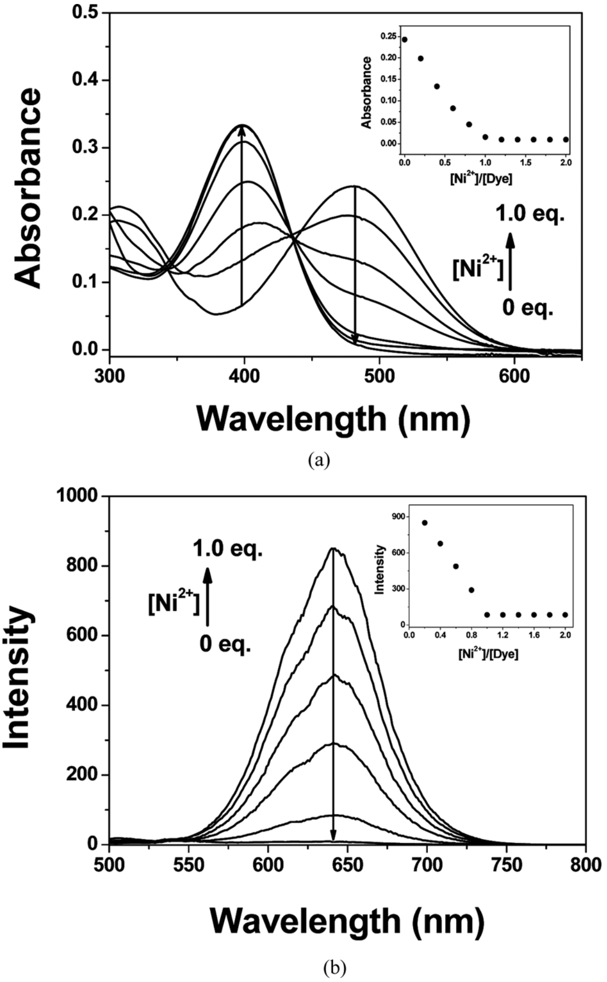


Figure 1. Synthetic route for dye sensor **3**.

charge transfer theory, donor-π-acceptor structure that contains an electron rich donating (N) atom, it was anticipated that dye sensor **3** could function as a host molecule for the recognition of metal cations via coordinating interaction. This was investigated by adding various metal cations (Cd^{2+}, Na^{2+}, Mg^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+} and Ni^{2+}) to a 1×10^{-5} mol solution of dye sensor **3** in CH_3CN and recording the changes in absorption and emission spectra that occurred during the titration of the solution of dye sensor **3** with between 0 and 1.0 equiv of Ni^{2+} cation.

As Figure 2 shows, upon the addition of Ni^{2+} to the solution of dye sensor **3**, the absorption band at 396 nm progressively increased in intensity and a peak at 479 nm decreased; an isobestic point at 432 nm also developed. The appearance of this isobestic point in absorption band changes suggests that at least one stable dye-Ni^{2+} cation species is present in solution and is indicative that a stable complex formed between dye sensor **3** and Ni^{2+}. However, none of the other cations investigated,



(a)

(b)

Figure 2. Effect of Ni^{2+} cation concentration on the absorbance and emission intensity of a 1×10^{-5} mol solution of dye sensor **3** in CH_3CN.

namely Cd^{2+}, Na^{2+}, Mg^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Cu^{2+}, Hg^{2+} and Zn^{2+} had any noticeable effect on absorption, as shown in Figure 3.

When Ni^{2+} cations and the dye sensor formed a complex via the –N electron donors of the 4-(bis(pyridin-2-ylmethyl)amino)benzaldehyde, the large intramolecular charge transfer system within dye sensor **3**, namely the donor-acceptor electron stream, was changed, resulting in the observed changes in UV-Vis absorption and fluorescence emission.

In the context of the ability of dye sensor **3** to act as a fluorescence sensor toward metal cation detection, the marked quenching of fluorescence emission imparted by Ni^{2+} cations (Fig. 2) can be explained on the basis that, as a result of the formation of an −N, coordination binded complex between Ni^{2+} and dye sensor **3**, both the intramolecular charge transfer system and the excited state were greatly modified, resulting in reduced fluorescence emission. When a fluorophore acceptor contains an electron-donating group, e.g., amino group, conjugating to a fluorophore unit, it undergoes ICT from the donor to the fluorophore acceptor on light excitation, which shows a red-shifted emission. If the donor receptor is coordinated with metal ion, the amino group loses its donating ability [19]. Thus, the ICT is inhibited and the emission is quenched. This observation is in well agreement with the UV-Vis absorption behavior (Fig. 2) insofar as, colorimetric changes due to the coordination binding of −N, which is directly influenced by the chromophore and the fluorophore, have been employed in the design of a chemosensor for Ni^{2+} cation.

For the interpretation of the complexation and electronic structure of dye sensor **3**-Ni^{2+}, the quantum chemical $DMol^3$ approach was used. All the theoretical calculations were performed by $DMol^3$ program in the Materials Studio 4.2 package [21,22] which is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof (PBE) function of generalized gradient approximation (GGA) level [23] with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbital. The optimized dye sensor **3**-Ni^{2+} bidentate

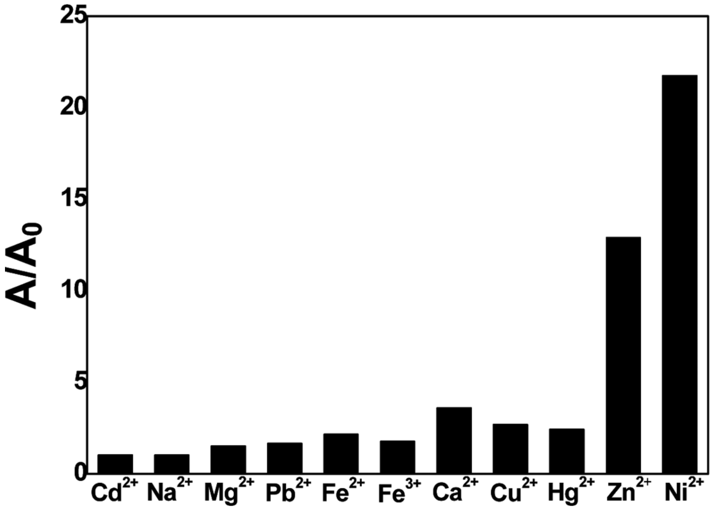


Figure 3. Comparison of absorption ratio for various cations (A and A_0 are the absorbance in the presence and the absence of metal cations, respectively at 396 nm).

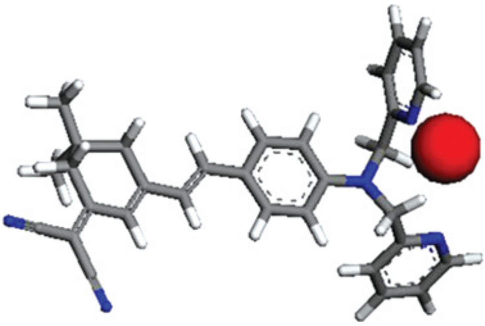


Figure 4. Optimized structure of dye sensor **3**-Ni^{2+} complex.

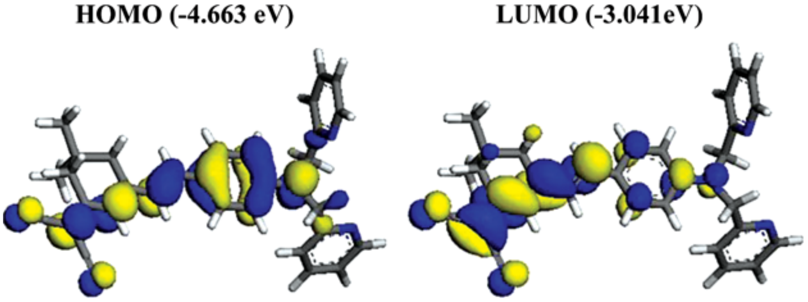


Figure 5. Electron distribution of HOMO and LUMO energy levels of dye sensor **3**.

structure is shown in Figure 4; Ni^{2+} cation is bridged between two nitrogen atoms in electrong donor unit.

Figure 5 shows the calculated structural energy levels of dye sensor **3** and the electron distribution of its HOMO and LUMO. Comparison of the electron distribution in the frontier MOs reveals that HOMO-LUMO excitation moved the electron distribution from 4-(bis(pyridin-2-ylmethyl)amino)benzaldehyde to the isophorone moiety, which shows a strong migration of intramolecular charge-transfer characteristic of dye sensor **3**. Therefore, the electron donating moiety of 4-(bis(pyridin-2-ylmethyl)amino)benzaldehyde in HOMO energy level is important for effective complexation with Ni^{2+} in this system. As a result, the complexation of Ni^{2+} to nitrogen atoms reduces the electron density on the nitrogen atoms and lowers the electron donating ability of 4-(bis(pyridin-2-ylmethyl)amino)benzaldehyde.

4. Conclusions

A novel, chromogenic and fluorescent dye senor based on 4-(bis(pyridin-2-ylmethyl)-amino)benzaldehyde as donor unit and 2-(3,5,5-trimethylcyclohex-2-enylidene)malononitrile as acceptor unit exhibited marked changes in UV-Vis absorption peak and fluorescence emission intensity upon the addition of Ni^{2+} ion. Dye sensor displayed evident spectral changes with Ni^{2+} ion and highly selective fluorescence quenching effect was determined. But it showed no significant changes upon the addition of other metal ions such as Cd^{2+}, Na^{2+}, Mg^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Cu^{2+}, Hg^{2+} and Zn^{2+}. For the interpretation of the complexation and electronic structure of dye sensor **3**-Ni^{2+}, the optimized dye sensor **3**-Ni^{2+} bidentate structure is bridged between two nitrogen atoms in electron donor unit. For the electron distribution of its HOMO and LUMO, HOMO-LUMO excitation has changed the electron distribution from 4-(bis(pyridin-2-ylmethyl)amino)benzaldehyde to the isophorone moiety, which shows a strong migration of ICT characteristic of dye sensor **3**.

Acknowledgment

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