

***Ab initio* Molecular Orbital Study of Emission Mechanism of 2,6-Bis(quinolinecarboxy)methylpyridine as Fluorescent Chemosensors for Zinc and Cadmium Ions**

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2,6-Bis(quinolinecarboxy)methylpyridine (P2Q) was synthesized as fluorescent chemosensors for metal ions. P2Q hardly shows fluorescence itself, but it showed strong fluorescence with the addition of zinc or cadmium ions ($I_{f,Zn} > I_{f,Cd}$). Therefore, the *ab initio* molecular orbital calculations (Gaussian 98) using the time-dependent density functional method with 6-31+G(d) basis set were carried out for a quinoline chromophore of P2Q and its metal complexes to investigate the emission mechanisms. The results of the molecular orbital calculations suggest that the lowest luminescent state has changed from the $n\pi^*$ to the $\pi\pi^*$ by coordinating with a metal ion.

Keywords: Ab initio molecular orbital calculation, Time-dependent DFT, Quinoline, Zinc, Cadmium, Metal ion recognition, Fluorescent chemosensor

1 Introduction

The biological importance of many metal ions is well established [1, 2]. However, some metal ions can be toxic to life when present at certain concentrations in the environment, water supplies, food chain, and industrial chemicals and products. Consequently, an intensive effort has been devoted to develop various sensory molecular receptors capable of recognizing, sensing, and selectively transporting these positively charged substrates so that the concentrations of these metal ions of commercial value can be recovered from waste solutions, and certain toxic transition metal ions in the environment can be removed [1–8]. The goal of this research is the design and construction of ion-selective sensors by assembling a specific metal ion-receptor with a subunit capable of signaling the occurrence of a receptor-substrate interaction [8]. Many kinds of crown ether type macrocyclic compounds have been used for analytical applications, such as chemical sensors [9] and spectrophotometries [10]. In the fluorimetry application, fluorescent reagents, which have two

aromatic hydrocarbon groups at both terminals of a linear polyether as an analogue of a crown ether, have also been used [11].

We have developed compounds capable of selectively responding to several metal ions [12–14]. We now wish to report the results of our study on zinc and cadmium ions recognition by 2,6-bis(quinolinecarboxy)methylpyridine (P2Q). The structural formula is shown in Figure 1. And *ab initio* molecular orbital (MO) calculations were performed for a quinoline chromophore to investigate the properties of the luminescence.

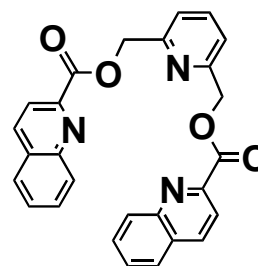


Figure 1. Structural formula of P2Q.

2 Experiment

2.1 Synthesis and measurements

P2Q was prepared from 2-Quinolinecarboxylic acid and 2,6-pyridinedimethanol in the presence of *N,N*-dicyclohexyl carbodiimide and 4-dimethylamino pyridine in dichloromethane. The fluorescence spectra were taken on a Hitachi F-4500 fluorophotometer. The fluorescence spectra measurements were carried out in an acetonitrile solution of the P2Q ($<10^{-4}$ mol dm $^{-3}$ where no intermolecular interaction was found) at room temperature, and metal salts [Ni(ClO $_4$) $_2$, Co(ClO $_4$) $_2$, Cu(ClO $_4$) $_2$, Ag(ClO $_4$) $_2$, Zn(ClO $_4$) $_2$, and Cd(ClO $_4$) $_2$] were added to the solution. To prevent any nonlinearity of the fluorescence intensity, 295nm was chosen as the excitation wavelength.

2.2 Computational procedure

All *ab initio* MO calculations were carried out using Gaussian 98 with Linda [15] on an HPC P4L/2.2 (Linux 2.4), a PC-cluster machine with five nodes parallel. Optimized structures were obtained by B3LYP density functional theory (DFT) with 6-31+G(d) basis set for quinoline derivative and by Hartree-Fock level calculation with 6-31G basis set for Zn $^{2+}$ complex; and total energies were estimated by B3LYP/6-31+G(d) for these structures. The singlet transition energies of the compounds were calculated at those geometries by a time-dependent DFT (TDDFT) method.

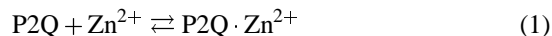
For investigating the transition energies of P2Q-Zn $^{2+}$ complex, we have used diaqua-quinolinecarboxyethyl-zinc(II) complex (QNE-Zn $^{2+}$ -aq $_2$) as a model compound, which only has a single quinoline chromophore. It is indeed that the water molecules were not necessarily in P2Q-Zn $^{2+}$, but those were added to keep the coordination structure around the Zn $^{2+}$ ion tetrahedral. The conformations of the QNE-Zn $^{2+}$ -aq $_2$ complexes were obtained by following procedure. The initial structure of the complex with zinc ion being placed near the QNE with two water molecules led to two stable structures, both of which have a C $_s$ symmetry, by HF/6-31G method. For these two structures, transition energies were estimated by using TDDFT of B3LYP/6-31+G(d). The transition energies of a QNE itself were also calculated with B3LYP/6-31+G(d) at their optimized structure.

3 Results and discussion

3.1 Fluorescence studies for metal ion recognition

When Ni $^{2+}$, Co $^{2+}$, Cu $^{2+}$ and Ag $^{2+}$ were added to an acetonitrile solution of P2Q, the fluorescence spectra were

not changed. However, the fluorescence intensity of P2Q changed greatly with the addition of Zn $^{2+}$ or Cd $^{2+}$. The fluorescence spectra of P2Q in the presence of several concentrations of Zn(ClO $_4$) $_2$ are shown in Figure 2 as a typical example. We express the metal salt interactions in terms of the equilibrium:



Also, the association constants (K) should be represented as follows:

$$\begin{aligned} K &= [\text{P2Q} \cdot \text{Zn}^{2+}] / [\text{P2Q}] [\text{Zn}^{2+}] \\ &= [\text{P2Q} \cdot \text{Zn}^{2+}] / \{ ([\text{P2Q}]_0 - [\text{P2Q} \cdot \text{Zn}^{2+}]) \\ &\quad ([\text{Zn}^{2+}]_0 - [\text{P2Q} \cdot \text{Zn}^{2+}]) \}, \quad (2) \end{aligned}$$

$$\begin{aligned} a &= (I - I_0) / (I_{\max} - I_0) \\ &= [\text{P2Q} \cdot \text{Zn}^{2+}] / [\text{P2Q}]_0. \quad (3) \end{aligned}$$

From Eqs. 2 and 3, the following equation could be derived:

$$[\text{Zn}^{2+}]_0 = a / K(1 - a) + a[\text{P2Q}]_0, \quad (4)$$

where [P2Q] $_0$ and [Zn $^{2+}$] $_0$ are the initial concentrations of P2Q and the zinc ion, I and I_0 are the observed locally excited emission intensities of P2Q in the presence and absence of the zinc ion, respectively, and I_{\max} is the observed locally excited emission intensity of P2Q and zinc ion complex. A self-written nonlinear curve-fitting computer program (Eq. 4) was used to fit the experimental titration curves. The association constant was determined from the emission-intensity changes at the emission maxima using the equation. The log K value of P2Q is 3.7.

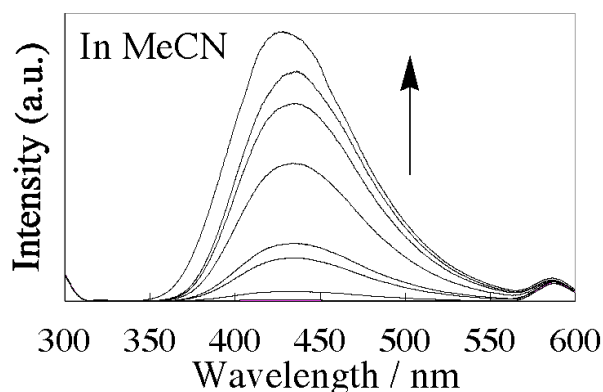


Figure 2. Fluorescence spectra of P2Q and Zn $^{2+}$ complexes when excited at 295nm. [P2Q] = 1×10^{-5} mol dm $^{-3}$. [Zn $^{2+}$] = 1×10^{-6} , 5×10^{-6} , 1×10^{-5} , 2×10^{-5} , 5×10^{-5} , 1×10^{-4} , 2×10^{-4} , 5×10^{-4} , 1×10^{-3} and 1×10^{-2} mol dm $^{-3}$.

Table 1. Transition energies (λ) and oscillator strengths (f) of the excited states of QNE and its Zn^{2+} complex.

Conformer	a			b		
	λ / nm	f	assignment	λ / nm	f	assignment
state 1	312.60	0.0011	A'', $n\pi^*$	320.70	0.0010	A'', $n\pi^*$
state 2	308.06	0.0277	A', $\pi\pi^*$	307.96	0.0270	A', $\pi\pi^*$
state 3	284.97	0.0643	A'	284.24	0.0654	A'
state 4	283.93	0.0001	A''	266.32	0.0001	A''
state 5	250.16	0.0001	A''	252.87	0.0000	A''
state 6	231.55	0.9354	A'	231.69	0.8606	A'
Conformer	c			d		
	λ / nm	f	assignment	λ / nm	f	assignment
state 1	387.46	0.0195	A', $\pi\pi^*$	378.81	0.0209	A', $\pi\pi^*$
state 2	306.45	0.1685	A', $\pi\pi^*$	321.45	0.0000	A'', LMCT
state 3	304.12	0.0001	A'', LMCT	301.72	0.1424	A', $\pi\pi^*$
state 4	260.93	0.0000	A'', LMCT	283.42	0.0002	A'', $n\pi^*$
state 5	250.57	0.5073	A', $\pi\pi^*$	276.12	0.0000	A'', LMCT
state 6	240.94	0.0002	A'', $n\pi^*$	245.68	0.4834	A'

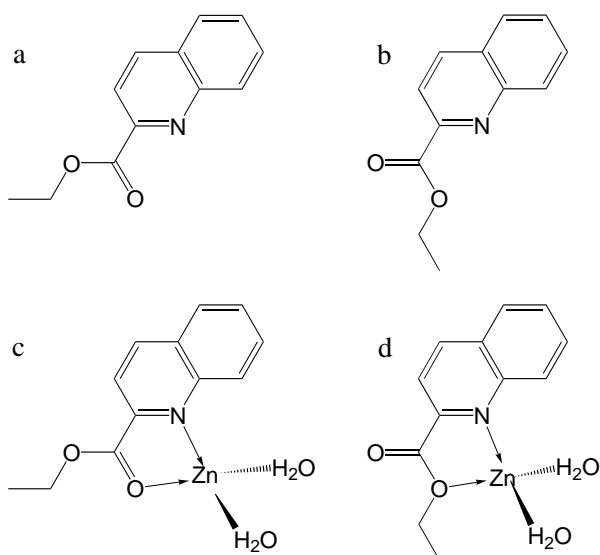


Figure 3. Conformations of QNE and QNE-Zn^{2+} -aq₂.

3.2 The *ab initio* molecular orbital calculations

The conformations of QNE and their zinc complexes are shown in Figure 3. Note that all of these structures are characterized as having C_S symmetry. Rotation of C(carboxyl)-C(quinoline) gave two stable conformers for QNE. The conformer-b was 572 cm^{-1} more stable than conformer-a (see Figure 3). According to the conformers of QNE, it is interesting that two conformers of the Zn^{2+} complex were also obtained, where one of them has a carbonyl oxygen as a donor atom and the other has an etheric oxygen. Naturally, in the ground state, the former is calculated to be more stable than the latter ($\delta E(S_0) = 5955\text{ cm}^{-1}$).

Attempts were made to estimate the transition energies by using a configuration interaction with single excitation (CIS) scheme and a time-dependent Hartree-Fock (TDHF) approach. However, both methods have led to a $\pi\pi^*$ as the lowest singlet excited state for QNE, which is not an acceptable result. Then the more sophisticated method, TDDFT, was used. When two water molecules of the ligand were removed, ligand-to-metal charge-transfer (LMCT) transitions were observed in the near IR region, which were not acceptable as well. The transition energies, oscillator strengths and their assignments (or characters) are summarized in Table 1.

Calculated transition energies of QNE show very good agreement with the observed absorption spectra of P2Q in the UV-visible region (λ_{max}/nm ($\epsilon/\text{cm}^{-1}\text{M}^{-1}$): 237 (79200), 270 (11000), 290 (10100), 320 (4400)). Both conformer-a and conformer-b have nearly the same transition energies and oscillator strengths, with $n\pi^*$ being the lowest excited state where the non-bonding orbital is coming from the nitrogen of the quinoline and $\pi\pi^*$ the second lowest.

In the next step, forming a metal complex has made a dramatic change in the energy levels of the excited states, regardless of the structure of the conformer. The lowest excited state was $\pi\pi^*$ being located more than 50 nm longer from the $n\pi^*$ band of QNE; and some new LMCT bands appeared. Furthermore, $n\pi^*$ band was shifted to the higher energy region at 240-280 nm. Consequently, the results of the TDDFT calculation suggested that the allowed transition band exists for the QNE-Zn^{2+} -aq₂ complex at the region lower than the lowest $n\pi^*$ state of QNE. Indeed, when adding zinc ion to the P2Q, the absorption band at $\sim 300\text{ nm}$ was observed to be red-shifted and/or a new luminescent band at $\sim 450\text{ nm}$ could be seen.

4 Conclusion

P2Q hardly shows fluorescence itself, but it showed strong fluorescence with the addition of zinc or cadmium ions ($I_{f,Zn} > I_{f,Cd}$). Therefore, *ab initio* molecular orbital calculations (Gaussian 98) using the time-dependent density functional method with 6-31+G(d) basis set were carried out for a quinoline chromophore of P2Q and its metal complexes to investigate the emission mechanisms. The results of the molecular orbital calculations suggest that the lowest luminescent state has changed from the $n\pi^*$ to the $\pi\pi^*$ by coordinating with a metal ion. Actually, there are few Zn^{2+} or Cd^{2+} -selective analytical reagents available. P2Q will become a good fluorescent chemosensor for Zn^{2+} and Cd^{2+} .

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非経験的分子軌道計算による亜鉛・カドミウムイオン用蛍光性 化学センサー 2,6-Bis(quinolinecarboxy)methylpyridine の 発光メカニズム

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2,6-Bis(quinolinecarboxy)methylpyridine (P2Q) を、金属イオン用蛍光性化学センサーとして合成した。P2Q は殆ど蛍光を示さない系であるが、亜鉛或はカドミウムイオンが存在すると蛍光を示すことがわかった ($I_{f,Zn} > I_{f,Cd}$)。そこで、P2Q-亜鉛錯体の発光メカニズムについて、時間依存密度汎関数法による非経験的分子軌道計算を用いて調べた (Gaussian 98, 6-31+G(d))。その結果、P2Q は、亜鉛イオンと錯形成することによって、最低励起状態が $n\pi^*$ から $\pi\pi^*$ に変わり、蛍光を発するようになることが示唆された。

キーワード：非経験的分子軌道計算, 時間依存密度汎関数法, キノリン, 亜鉛, カドミウム, 金属イオン認識, 蛍光センサー

