

Time-Dependent DFT Study of Emission Mechanism of 8-Hydroxyquinoline Derivatives as Fluorescent Chemosensors for Metal Ions

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8-Hydroxyquinoline derivatives (BQOH and BQCIOH) were synthesized as fluorescent chemosensors for metal ions. BQOH and BQCIOH hardly show fluorescence themselves, but they showed strong fluorescence with the addition of zinc or cadmium ions. The order of the maximum values of fluorescence intensity ($I_{f,max}$) was $BQCIOH-Zn^{2+} > BQCIOH-Cd^{2+} \gg BQOH-Cd^{2+} > BQOH-Zn^{2+}$. Therefore, the *ab initio* calculations (by Gaussian 98) using the time-dependent density functional method with 6-31+G(d) basis set were carried out on the Zn^{2+} complexes of quinoline chromophore, BQOH and BQCIOH, in order to investigate the cause of the difference in the fluorescent intensity ($BQCIOH-M^{2+} \gg BQOH-M^{2+}$, $M^{2+} = Zn^{2+}$ or Cd^{2+}). The results of the calculations showed that the T_2 state of the $[ZnBQO]^+$ lay just below its S_1 state, while that was not the case for $[ZnBQCIO]^+$.

Keywords: Time-dependent DFT, Quinoline, Metal ion recognition, Fluorescent chemosensor

1 Introduction

Molecular recognition is a subject of considerable interest because of its implications in many fields: biology, medicine, environment, etc. In particular, the detection of metal ions involved in biological processes has received considerable attention. The biological importance of many metal ions is well established [1, 2]. However, the same and other 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 [8]. We have developed compounds capable of selectively responding to several

metal ions, and performed a theoretical investigation of the excited state properties of the compounds [9–11]. We now wish to report the results of our study on zinc and cadmium ions recognition by 8-hydroxyquinoline derivatives (BQOH and BQCIOH). The structural formulas are shown in Figure 1. These compounds are found to have a novel character in that the fluorescence intensity of the chloro-substituted quinoline complex is stronger than that of the non-substituted quinoline. And then, the *ab initio* calculations were performed for a quinoline chromophore to investigate the properties of their luminescence.

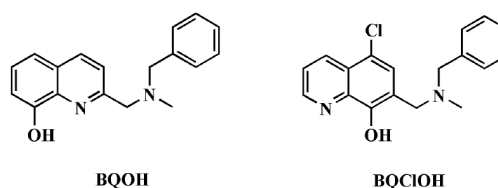


Figure 1. Structural formulas of BQOH (1) and BQCIOH (2).

2 Experiment

2.1 Synthesis and measurements

BQOH was synthesized from 8-hydroxyquinolinecarboxaldehyde and *N*-benzylmethylamine [12]. 8-Hydroxyquinolinecarboxaldehyde was prepared by the oxidation of commercially available 2-methyl-8-hydroxyquinoline with selenium dioxide in dioxane [13]. BQCIOH was from 5-chloro-8-hydroxyquinoline and *N*-benzylmethylamine [12]. The fluorescence spectra were taken on a Hitachi F-4500 fluorophotometer. The fluorescence spectra measurements were carried out in an acetonitrile solution of the BQOH and BQCIOH ($[BQOH]$ or $[BQCIOH] < 10^{-4}$ mol dm $^{-3}$ where no intermolecular interaction was found) at room temperature, and metal salts [$Zn(ClO_4)_2$, $Cd(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, $Ca(ClO_4)_2$, $Ba(ClO_4)_2$ and $Mg(ClO_4)_2$] were added to the solution. To prevent any nonlinearity of the fluorescence intensity, isosbestic points (253 or 256 nm) of the absorption spectra of BQOH and BQCIOH were chosen as the excitation wavelength.

2.2 Calculation procedure

All *ab initio* calculations were carried out by using Gaussian 98 with Linda [14] 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 6-31G basis set for quinoline derivatives and their Zn^{2+} complexes; and total energies, singlet transition energies and triplet transition energies were estimated by using a time-dependent DFT (TD-DFT) method with B3LYP/6-31+G(d) at the obtained geometries.

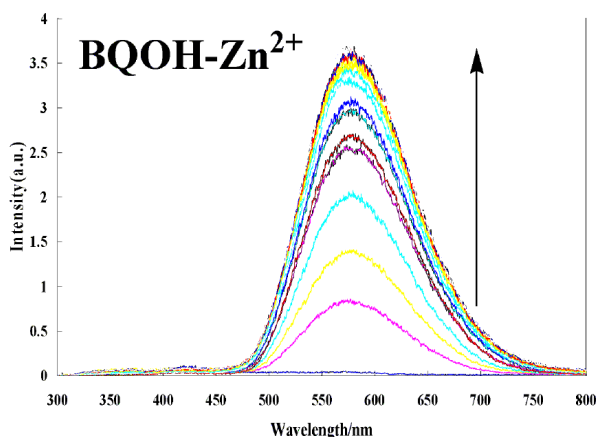


Figure 2. Fluorescence spectra of BQOH and Zn^{2+} complexes when excited at 253 nm. $[BQOH] = 1 \times 10^{-5}$ mol dm $^{-3}$. $[Zn^{2+}] = 0, 1 \times 10^{-6}, 5 \times 10^{-6}, 1 \times 10^{-5}, 2 \times 10^{-5}, 5 \times 10^{-5}, 1 \times 10^{-4}, 2 \times 10^{-4}, 5 \times 10^{-4}, 1 \times 10^{-3}$ and 1×10^{-2} mol dm $^{-3}$.

3 Results and discussion

3.1 Fluorescence studies for metal ion recognition

Very weak fluorescences were observed for both BQOH and BQCIOH at $\lambda_{max} = 418$ nm and 545 nm, respectively. When Co^{2+} , Ni^{2+} , Cu^{2+} , Ca^{2+} , Ba^{2+} and Mg^{2+} were added to an acetonitrile solution of BQOH, the fluorescence spectra were not or slightly changed. However, the fluorescence intensity of BQOH changed greatly with the addition of Zn^{2+} or Cd^{2+} ; the fluorescence spectra for both metal complexes were observed to be red-shifted at $\lambda_{max} = 550$ nm. The fluorescence spectra of BQOH in the presence of several concentrations of $Zn(ClO_4)_2$ are shown in Figure 2 as a typical example. Though a similar enhancement in intensity was observed for BQCIOH whose fluorescence was seen at $\lambda_{max} = 540$ -550 nm with the addition of Zn^{2+} or Cd^{2+} , the fluorescence intensity of metal complexes was very different from the case of BQOH. The maximum values of the fluorescence intensity ($I_{f,max}$) of the metal complexes are shown in Figure 3. The order of the $I_{f,max}$ was $BQCIOH-Zn^{2+} > BQCIOH-Cd^{2+} \gg BQOH-Cd^{2+} > BQOH-Zn^{2+}$.

These are very interesting results in that the fluorescence intensity of the chloro-substituted quinoline complex is stronger than that of the non-substituted one, though a substituted chlorine atom is usually thought to be a potential intramolecular-sensitizer. It is also pointed out that the intensities of the absorption bands of $BQOH-Zn^{2+}$ and $BQCIOH-Zn^{2+}$ were not so different from each other, in energies and intensities. In order to investigate the mechanisms of enhanced fluorescence by chlorine substitution, *ab initio* calculations were carried out.

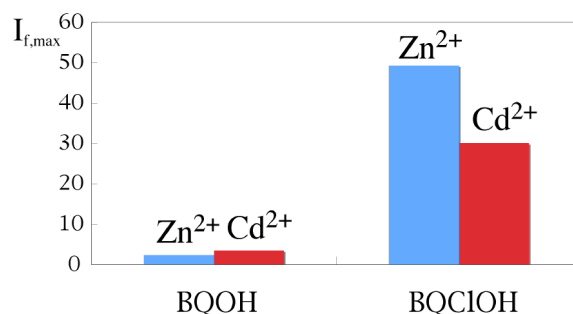


Figure 3. The maximum values of fluorescence intensity ($I_{f,max}$) of $BQOH-M^{2+}$ and $BQCIOH-M^{2+}$ ($M^{2+} = Zn^{2+}$ or Cd^{2+}).

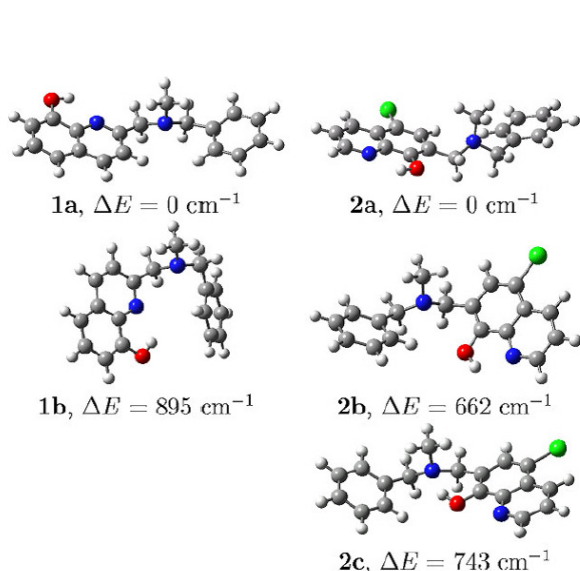


Figure 4. Optimized molecular structures of BQOH (1) and BQClOH (2).

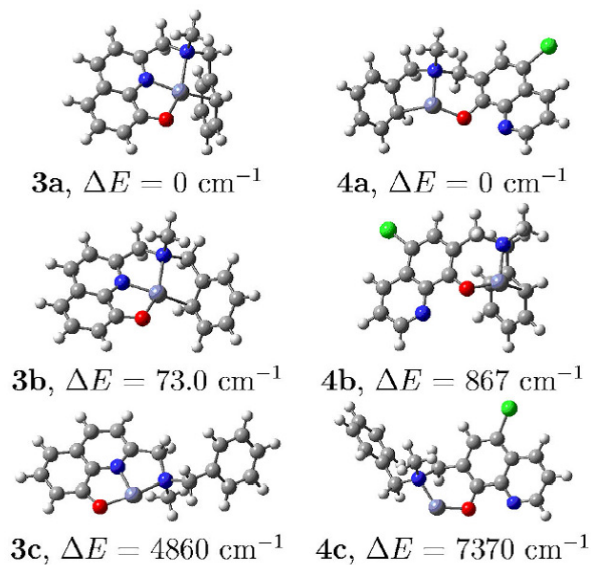


Figure 5. Optimized molecular structures of [ZnBQO]⁺ (3) and [ZnBQClO]⁺ (4) complexes.

3.2 The *ab initio* calculations

Ab initio calculations for quinoline derivatives at some conformations were carried out. And then, the zinc complexes with metal-to-ligand ratio of 1:1 were used to investigate the geometry and the electronic structure by DFT calculation. Some of the optimized structures with the energy differences (ΔE) from that of the most stable conformation are shown in Figure 4 and Figure 5. The obtained excited state energies for the S_1 , T_1 , and T_2 states and the oscillator strength for the S_0 - S_1 transition are summarized in Table 1; and the energy diagrams of **3a** and **4a** are illustrated in Figure 6.

These results are very interesting in that the T_2 energy of **3a** is just below the energy of its S_1 state, on the other

hand the T_2 state of **4a** lies highly above its S_1 state. A similar situation was also encountered for all other conformations of **3b**, **3c**, **4b**, and **4c**; the calculated results for these conformations were also shown in Table 1. According to the energy gap law, these results suggest that the inter-system crossing rate from S_1 to T_2 is faster in **3a** than that in **4a**. This result means that the chlorine-substitution on the quinoline chromophore enables the changing of its energy levels, and then it enhances the fluorescence intensity of the quinoline derivatives-metal complex. The larger oscillator strength in **4a** may also contribute to its strong fluorescence intensity, though the absorbance of its corresponding band was weak in our experimental results.

Table 1. The excited state energies (E) and oscillator strengths (f).

	1a	1b	2a	2b	2c	
$E(S_1) / \text{cm}^{-1}$	29789	27953	27882	24946	29066	
f	(0.0331)	(0.0123)	(0.0179)	(0.0040)	(0.0623)	
$E(T_1) / \text{cm}^{-1}$	20618	11957	19657	19292	19702	
$E(T_2) / \text{cm}^{-1}$	29501	27641	27950	24935	28505	
	3a	3b	3c	4a	4b	4c
$E(S_1) / \text{cm}^{-1}$	20100	21615	19535	14230	14255	10105
f	(0.0024)	(0.0263)	(0.0046)	(0.0580)	(0.0416)	(0.0431)
$E(T_1) / \text{cm}^{-1}$	16334	16658	17043	12749	12833	6936
$E(T_2) / \text{cm}^{-1}$	19886	21116	18850	19703	20514	15432

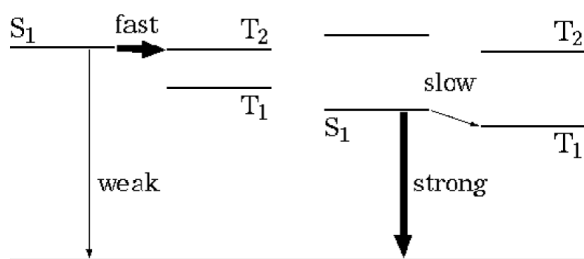


Figure 6. Energy diagrams of **3a** (left) and **4a** (right).

4 Conclusion

BQOH and BQClOH hardly show fluorescence themselves, but they showed strong fluorescence with the addition of zinc or cadmium ions. The order of the $I_{f,max}$ was $BQClOH-Zn^{2+} > BQClOH-Cd^{2+} \gg BQOH-Cd^{2+} > BQOH-Zn^{2+}$. Therefore, *ab initio* calculations (by Gaussian 98) using TD-DFT method with 6-31+G(d) basis set were carried out for the Zn^{2+} complexes of the quinoline chromophore, BQOH and BQClOH, to investigate the difference in the fluorescent intensity.

The results of the calculations showed that the T_2 state of the $[ZnBQO]^+$ was lying just below the S_1 state which reduced the fluorescent intensity; while for the $[ZnBQClO]^+$ such was not the case. In other words, when the energy levels of a compound are in the case like this, the changing of their energy levels by some chemical modification on the emissive chromophore makes possible enhancement of the fluorescent intensity for a chemosensor of metal ions.

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