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# TD-DFT study on the fluorescent chemosensor for Hg<sup>2+</sup>, 2-(Benzo-d-thiazol-2-yl)quinoline

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# 1. Introduction

The development of selective and sensitive chemosensors for quantitative analysis of metal ions has become extremely important for environmental and biological applications [1–5]. In particular, the detection of  $Hg^{2+}$  has become one of the most important topics owing to the highly toxic nature of many mercury compounds [6–8]. In a recent review [9], some fluoro- and chromogenic chemodosimeters for heavy metal ions, especially the mercury(II) ion, were also summarized.

Therefore, we attempted to synthesize a new fluorescence chemosensor for the mercury ion. Recently, 2-(Benzo-d-thiazol-2-yl)quinolines (BTQs) were synthesized as fluorescent chemosensors for  $Hg^{2+}$  [10]. The structural formula of BTQ is shown in Fig. 1; the geometric (rotational) isomers are discussed below. The BTQs showed more distinctive  $Hg^{2+}$ -selective fluoroionophoric properties over the other tested metal ions. Therefore, the spectroscopic properties and the mechanisms of their luminescence become the subject of much interest.

In this paper, the metal-ion recognition of BTQ was investigated by adding  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  to an acetonitrile solution. Consequently, it was shown that BTQ had distinctive  $Hg^{2+}$ -selective fluoroionophoric properties over other tested metal ions. Furthermore, the emission maxima of the BTQ–Hg<sup>2+</sup> complexes shifted to longer wavelengths with respect to those of the other metal complexes and the BTQ itself. In the next step, the *ab initio* calculations were performed on the  $M^{2+}$ 

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# ABSTRACT

2-(Benzo-d-thiazol-2-yl)quinoline (BTQ) was synthesized and tested for its use as a fluorescent chemosensor for  $Hg^{2+}$ . The metal-ion recognition of BTQ was investigated by adding several metal ions ( $M^{2+}$ ) to a solution of BTQ in acetonitrile. The shape and intensity of the fluorescence spectra did not change upon addition of several metal ions, except for  $Hg^{2+}$  and  $Cu^{2+}$ . The time-dependent density functional calculations were carried out on BTQ and BTQ- $M^{2+}$  complexes (M = Zn, Cd, and Hg) to clarify their spectroscopic properties. The results of the calculation showed that the energy levels of the excited singlet and triplet states are similar in  $Zn^{2+}$  and  $Cd^{2+}$  complexes, whereas the  $Hg^{2+}$  complex has lower transition energy. The character of their excited states was also different between zinc and cadmium complexes with the mercury complex.

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complexes of the BTQ (M = Zn, Cd, and Hg) to clarify their molecular and electronic structures and their spectroscopic properties.

#### 2. Methods

#### 2.1. Synthesis and measurements

BTO was obtained by the reaction of 2-aminobenzenethiol with quinoline-2-carbaldehyde. The MS spectra of BTQ showed corresponding molecular ion peaks, and the NMR spectra were suitable [10]. Stock solutions of BTO were prepared by dissolving a weighed amount of BTQ in acetonitrile. The titration of BTQ ( $[BTQ] = 10 \mu M$ ,  $M = mol dm^{-3}$ ) against some metal ion solutions was performed in a spectrophotometric cell of 1 cm path length. The UV-visible spectra (between 50,000 and  $16,700 \text{ cm}^{-1}$  (200 and 600 nm, respectively)) of the resulting solutions were recorded at room temperature with a Hitachi U-2001 spectrophotometer after the addition of each of the metal salts  $(Cd(ClO_4)_2, Ni(ClO_4)_2, Zn(ClO_4)_2, Zn(Cl$  $Co(ClO_4)_2$ ,  $Ca(ClO_4)_2$ ,  $Ba(ClO_4)_2$ ,  $Cu(ClO_4)_2$ , and  $Hg(ClO_4)_2$ ). The fluorescence spectra were measured between 25,000 and 16,700 cm<sup>-1</sup> (400 and 600 nm, respectively) with a Hitachi F-4500 fluorometer using an excitation wavelength of 28,600 cm<sup>-1</sup> (350 nm). The titrations were performed with metal ions  $(1-100 \,\mu\text{M})$  as the titrant and BTQ (10  $\mu$ M) as the titrate. The metal-ion sources were identical to those used to perform the UV-visible spectroscopic studies.

# 2.2. Calculation procedure

All the *ab initio* calculations were performed by the Gaussian 03 program [11]. The molecular geometries were optimized by B3LYP



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Fig. 1. Structural formula of BTQ. (a) NS-conformer, (b) NN-conformer.

[12–14] with a 6-31G basis set for the CHNO elements, 6-31G(d) for S [15], and Stuttgart/Dresden basis set/effective-core-potential (ECP) for Zn, Cd, and Hg (using SDD keyword) [16,17]. The consistency in the calculation through the group 12 elements was preserved by using the same basis set/ECP. The excitation energies and molecular properties were calculated by a time-dependent DFT (TD-DFT) method [18–22] with a B3LYP functional and 6-31+G(d) basis set [15] for non-metal elements and SDD basis set/ ECP for metals.

According to the results of the titrating luminescence measurement, the stoichiometry of 1:1 for the BTQ-M<sup>2+</sup> complexes were assumed (vide infra, [10]). BTQ works as a bidentate chelating ligand, and the divalent metal ions M<sup>2+</sup> tested in this work usually accept four donor atoms. Therefore, some water molecules were used to fill the remaining coordinating site of the  $M^{2+}$  in the BTQ-M<sup>2+</sup> complex; the BTQ-M<sup>2+</sup>-2aq structure was assumed (aq = water molecule,  $H_2O$ ). It must be pointed out that unrealistic calculation results were obtained for the BTO-M<sup>2+</sup> complexes without these water molecules, in which the triplet states were energetically lower than the lowest singlet state that is normally called the ground state, S<sub>0</sub>. This impropriety was corrected by placing these molecules in a polar solvent or by coordinating two water molecules to the  $M^{2+}$  ion to construct the BTQ- $M^{2+}$ -2aq structure. Furthermore, BTQ has conformational isomers with the C-C bond connecting the quinoline moiety and the benzothiazole. The S-cis conformer with respect to quinoline-N and benzothiazole-S is denoted by 'NS-conformer', and S-trans as 'NN-conformer' (see Fig. 1).

### 3. Results and discussion

### 3.1. Absorption and luminescence spectra

The changes in the UV–visible absorption spectra after adding various metal ions to the solution of BTQ were observed. The absorption spectra of BTQ in acetonitrile did not show changes in shape and absorbance upon addition of the metal ions, such as  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ca^{2+}$ , or  $Ba^{2+}$ ; however, there were changes in shape and absorbance with the addition of  $Cu^{2+}$  or  $Hg^{2+}$ , and a new absorption band appeared after 28,000 cm<sup>-1</sup>. The absorption spectra of BTQ in the presence of several concentrations of Hg(ClO<sub>4</sub>)<sub>2</sub> are shown in Fig. 2; here, an isosbestic point was observed at 28,500 cm<sup>-1</sup>. Using the absorbance at 38,000 and 32,500 cm<sup>-1</sup>, titration curves were produced that show a sharp endpoint at a 1:1 ligand-to-metal ion ratio for Hg<sup>2+</sup> [10].



Fig. 2. UV-vis absorption spectra of BTQ with  $Hg^{2+}$  in acetonitrile solution at room temperature. [BTQ] = 10  $\mu$ M, [Hg<sup>2+</sup>] = 0.1-1 equiv.

Changes in the fluorescence spectra were also observed upon addition of  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Cu^{2+}$ , or  $Hg^{2+}$  to the solution of BTQ in acetonitrile. The shape and intensity of the fluorescence spectra after excitation at 28,600 cm<sup>-1</sup> did not change upon addition of  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ca^{2+}$ , and  $Ba^{2+}$ . However, the fluorescence emission of BTQ was quenched with the addition of  $Hg^{2+}$  or  $Cu^{2+}$ . The fluorescence spectra of BTQ in the presence of several concentrations of  $Hg(ClO_4)_2$  are shown in Fig. 3; here, a weak red-shifted emission maxima was also observed. In other words, the emission maxima of BTQ with  $Hg^{2+}$  was at 21,600 cm<sup>-1</sup>, while the emission maxima of free BTQ was at 24,400 cm<sup>-1</sup>.

There may be some uncertainty concerning the complex formation between BTQ and the metal ions because the UV-visible absorption spectra showed little change upon changing the metal ions, except mercury or copper. However, according to the results of the *ab initio* calculation, it could be possible that the complex



Fig. 3. Fluorescence spectra of BTQ excited at 28,600 cm<sup>-1</sup> (350 nm) with Hg<sup>2+</sup> in an acetonitrile solution at room temperature. [BTQ] = 10  $\mu$ M, [Hg<sup>2+</sup>] = 0.1–1 equiv.

Table 1
Energy levels $(E/cm^{-1})$ and oscillator strengths $(f)$ for BTQ-M(II)-2aq complexes.

State	Free base <sup>c</sup>		Zn(II)		Cd(II)		Hg(II)	
	NS	NN	NS	NN	NS	NN	NS	NN
$\Delta_{\rm f} E^{\rm a}$	-	-	-	-1435	-	-1176	-	-1244
S <sub>0</sub> <sup>b</sup>	-	2301.55	-	-9001.51	-	-7442.70	-	-6178.53
S1	28960.1	29572.3	25266.9	23315.9	21012.4	23780.45	14413.9	18160.4
$(f_1)$	(0.2900)	(0.6183)	(0.3249)	(0.0329)	(0.0224)	(0.0263)	(0.0044)	(0.0000)
S <sub>2</sub>	29925.6	30136.1	25909.8	24249.9	23012.6	24704.0	17069.9	19376.7
$(f_2)$	(0.3475)	(0.0096)	(0.0248)	(0.0591)	(0.0074)	(0.0991)	(0.0277)	(0.0000)
S <sub>3</sub>	31008.8	30220.0	26409.8	25129.8	23643.3	24894.3	17653.9	20519.6
(f <sub>3</sub> )	(0.0377)	(0.0006)	(0.0477)	(0.5066)	(0.0151)	(0.0030)	(0.0217)	(0.0000)
S <sub>4</sub>	32247.7	30988.6	28181.8	31366.1	26465.47	25425.8	22890.0	23519.9
$(f_4)$	(0.0007)	(0.0260)	(0.0274)	(0.0001)	(0.2528)	(0.4667)	(0.0001)	(0.0271)
S <sub>5</sub>	35376.3	34626.2	30382.9	32004.1	27417.2	26129.1	25043.5	24473.3
(f <sub>5</sub> )	(0.2442)	(0.0008)	(0.0044)	(0.0172)	(0.0189)	(0.0034)	(0.1274)	(0.1147)
$T_1$	19778.3	19434.7	18430.6	16878.8	18205.5	17272.4	13630.8	17258.7
$T_2$	23520.7	23964.3	20271.9	19572.7	20211.4	19931.6	14467.2	17761.1
$T_3$	25885.6	26148.496	23909.5	19829.1	21587.4	20105.8	16745.7	19190.4
$T_4$	28435.9	26216.2	25623.4	25590.4	21933.4	24631.4	19175.0	19803.3
$T_5$	29602.2	29601.4	27597.9	29052.1	23560.3	25984.0	20865.6	19899.3



Fig. 4. Optimized structures of BTQ-M<sup>2+</sup>-2aq complexes.

formation makes little change in the spectra upon changing the metal ions other than mercury (*vide infra*). Regardless of whether or not several metal ions make a coordination complex with BTQ, it is clear that  $Hg^{2+}$  and BTQ form a complex in the 1:1 manner [10]; this result indicates that BTQ showed distinctive  $Hg^{2+}$ -selective fluoroionophoric properties over other tested metal ions.

# 3.2. Ab initio calculation

The calculated transition energies and oscillator strengths are summarized in Table 1. A series of the optimized structures of the BTQ– $M^{2+}$ –2aq complexes (M = Zn, Cd, Hg) are depicted in Fig. 4, in which these complexes have tetrahedral coordination structures for all metal ions.

For the BTQ molecule two conformers are possible (see Fig. 1), and each conformer gives rise to a different type of the coordination complex. The energy of  $S_0$  in the table shows the energy differences ( $\Delta E/cm^{-1}$ ) between the NS-conformer and the NNconformer of each compound in the ground state. It is interesting that the NS-conformer has lower energy than the NN-conformer in BTQ ( $\Delta E = 2302 \text{ cm}^{-1} = 27.53 \text{ kJ/mol}$ ), while the NN-conformer is more stable compared to the NS-conformer in all the BTQ-M<sup>2+</sup>–2aq complexes. According to the hard-soft-acid-base (HSAB) theory, the heavier metal ion, Hg<sup>2+</sup>, is preferred over the soft donor atom, S, and vice versa. However, in our results, the Hg<sup>2+</sup> complex has a more stable conformation with the NN-conformer, which is also true for the  $Zn^{2+}$  and  $Cd^{2+}$  complexes. Furthermore, it is remarkable that the optimized structure of the BTQ-M<sup>2+</sup> complexes shows that the NS-conformation makes a distortion or twist between the quinoline-thiazole bond (Fig. 4). The dipole moment of BTO is 1.39 Debve in the NS-conformer, which is smaller than the 2.31 Debve for the NN-conformer. In addition, the NN-conformer has steric hindrance in sulfur and hydrogen, such that the BTQ in the NS-conformer is slightly more stable. These properties are very similar to 2,2'-bipyridine in that the S-trans form is stable because of the steric hindrance between the hydrogens at the 3,3'position. While in the metal complexes of the BTQ, the NN-conformers are stable because  $\pi$ -electron conjugation-systems in planar BTQ are broken in the NS-conformers. This means that the lone-pair or the orbital lobe of the sulfur is directed toward a tilted angle with the in-plane and/or perpendicular to the five-membered ring. Because the C–S–C angle is approximately 90°, the sulfur has  $sp^3$  hybridization rather than  $sp^2$ .

The transition energy levels of BTQ in the NS-conformation and those of the BTQ– $M^{2+}$  complexes with two water molecules are shown in Fig. 5; note that only the lowest five levels of the singlet and triplet states are depicted. The solid bar at each singlet energy level indicates the oscillator strength of an individual transition from the ground state. Detailed values are shown in Table 1. The observed electronic absorption/emission spectra can be interpreted using the results of the *ab initio* calculation.

The lowest singlet-excited state of BTQ, S<sub>1</sub> at 28,960 cm<sup>-1</sup>, is characterized as a  $\pi\pi^*$  transition, which is constructed mainly from the HOMO(68)–LUMO(69) transition; note that the word "molecular orbital" means Kohn–Sham orbital in this context. The lowest  $n\pi^*$  transition of MO(65)–LUMO(69) appears at 32,248 cm<sup>-1</sup> as S<sub>4</sub>, for which the MO(65) has a lone pair of nitrogen at the quinoline ring and has some contribution from the lone pairs of another nitrogen and sulfur (Fig. 6).

The results show that the lowest singlet-excited state, S<sub>1</sub>, for all complexes under study is lowered by forming a metal complex. The energy levels of the first three singlet states and their oscillator strengths match well in Zn<sup>2+</sup> and Cd<sup>2+</sup> complexes; the first four triplet states match as well. It is very interesting that the S<sub>1</sub> level of the Zn<sup>2+</sup> complex is similar to that of the Cd<sup>2+</sup> complex but is not similar to the Hg<sup>2+</sup> complex. Moreover, the S<sub>n</sub> levels with large oscillator strengths have nearly the same energy through Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup> complexes (*ca.* 25,000 cm<sup>-1</sup>), which are  $\pi\pi^*$  transitions (*vide infra*). These results coincide with the observed electronic absorption spectra in the visible region; a new absorption band can be measured by adding metal salts to BTQ, and a similar change was observed for all the Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup> salts (Fig. 2).

As well as the energy levels, the properties of the excited states of the metal complexes are also interesting. The excited states of  $S_1-S_3$  of the  $Zn^{2+}$  complex have  $\pi\pi^*$  character; these states are created by the various combination of the transitions from HOMO(87),



**Fig. 5.** Transition energy diagram of BTQ- $M^{2+}$ -2aq complexes.  $M^{2+}$  = metal free,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ . The lowest five levels are shown for both singlet (S) and triplet (T) states of the complexes; and the bold part of the singlet level indicates the oscillator strength.



Fig. 6. Selected MOs of BTQ as NS-conformer.

MO(86), and MO(85) to LUMO(88) (Fig. 7). However, in the Hg<sup>2+</sup> complex, the lowest three excited states have ligand-to-metal charge-transfer (LMCT) character; those states consist of the transition of HOMO(87)–LUMO(88), MO(86)–LUMO(88), and MO(85)–LUMO(88), respectively, for which the LUMO(88) has mainly a central metallic character. The S<sub>4</sub> of the Hg<sup>2+</sup> complex is constructed by the transitions from HOMO(87), MO(86), and MO(85) to next-LUMO(89), which are  $\pi\pi^*$  transitions (Fig. 8).

When the Hg<sup>2+</sup> ion was added to the solution of BTQ, the luminescence spectrum was very different from those that added other



Fig. 7. Selected MOs of BTQ–Zn<sup>2+</sup>–2aq as NN-conformer.



Fig. 8. Selected MOs of BTQ-Hg<sup>2+</sup>-2aq as NN-conformer.

cations. The transition energy diagram depicted in Fig. 5 shows that the energy levels of the  $Zn^{2+}$  and  $Cd^{2+}$  complexes were similar to each other; however, that of Hg<sup>2+</sup> was different from the others. The former two have triplet states lying apart from the S<sub>1</sub> state, such that a nonradiative decay process may be prohibited in these cases. Whereas in the latter case, the lowest singlet state approaches the lower triplet states. Then, its luminescence is decreased in intensity and is red-shifted in wavelength. Another possible interpretation of the experimental results would be that BTQ does not make a coordination complex with Zn<sup>2+</sup> or Cd<sup>2+</sup> ions, while only Hg<sup>2+</sup> makes a BTQ-Hg<sup>2+</sup>-2aq complex, which leads to the change in the spectra. However, it cannot be explained from our calculations that Hg<sup>2+</sup> takes precedence to form a complex with BTQ over the other metal ions because the complex formation energies of these ions estimated by the following equation were comparable with each other (see Table 1):

$$\Delta_{\rm f} E = E_{\rm complex} - (E_{\rm M^{2+}} + E_{\rm BTQ} + 2 \times E_{\rm water}),$$

where *Es* are the total electronic energies of each compound.

Finally, it may be necessary to comment on a failure of TD-DFT in the excited state calculations. It is known that TD-DFT sometimes produces spurious charge-transfer excited states for large molecules or long-range charge-transfer systems [23,24], although DFT is one of the most powerful and successful quantum chemical tools for investigating molecular and electronic structures. The systems under study,  $BTQ-M^{2+}-2aq$ , are not as large as the systems in the literature discussed above, and the moieties of the electron donor and accepter have some orbital overlap, which does not indicates "long-range". However, the low-lying LMCT states for BTQ-M<sup>2+</sup>-2aq were investigated by configuration interaction singles (CIS and CIS(D)) [25–27] to confirm the TD-DFT results. The results of the HF calculation show that excited energy levels and the character of MOs around the HOMO and LUMO were coincident within all three complexes (M = Zn, Cd, Hg), while in the results by DFT, the Hg<sup>2+</sup> complex had different properties from the other two complexes (Figs. 5, 7, and 8). It seems that this HF result does not directly indicate a failure of the DFT calculation because DFT usually provides more reliable electronic structure in metal complexes than does HF. In fact, the orbital energies of LUMO(88) and next-LUMO(89) of the  $\rm Hg^{2+}$  complex given by HF were very close (almost 1/10 order) with respect to the  $Zn^{2+}$  complex case, and the lowest LMCT state of the  $Hg^{2+}$  complex was only about 1000 cm<sup>-1</sup> above the ligand-centered S<sub>1</sub> state (by CIS(D) calculation). Therefore, it would be difficult for the HF level calculation to provide an accurate estimation for the electronic structures of the compound including heavy metal elements; further progress is required in this region.

# 4. Conclusion

The metal-ion recognition of BTQ was investigated by adding several metal ions ( $M^{2+}$ ) to a solution of BTQ in acetonitrile. The shape and intensity of the fluorescence spectra did not change upon addition of several metal ions, including Cd<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ca<sup>2+</sup>, and Ba<sup>2+</sup>. However, the fluorescence emission of BTQ was quenched with the addition of Hg<sup>2+</sup> or Cu<sup>2+</sup>, and a red shift of the emission maxima was observed when Hg<sup>2+</sup> was added to the solution. While the emission maxima of free BTQ was at 24,400 cm<sup>-1</sup>, the emission maxima of BTQ with Hg<sup>2+</sup> was at 21,600 cm<sup>-1</sup>.

The *ab initio* calculations using the time-dependent density functional method with a 6-31+G(d) basis set and ECP for metals were carried out on the zinc, cadmium, and mercury complexes of BTQ. Then, the source of the spectroscopic properties shown above was investigated. The results of the calculation showed the following: (1) all the metal complexes calculated are more stable for the NN-conformer rather than NS-conformer, while BTQ itself has lower energy for the NS-conformer; (2) the energy levels of the excited singlet and triplet states are similar in the Zn<sup>2+</sup> and Cd<sup>2+</sup> complexes, while the Hg<sup>2+</sup> complex has lower transition energies than others; and (3) the character of the excited states were also different between the zinc and cadmium complexes with the

mercury complex, and the S<sub>1</sub> of the former is a  $\pi\pi^*$  transition, while that of the latter is LMCT.

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