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2-(Benzo-*d*-thiazol-2-yl)quinoline as a Fluorescent Chemosensor Material for Hg(II)

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2-(Benzo-*d*-thiazol-2-yl)quinoline (**BTQ**) was synthesized and tested for its use as a fluorescent chemosensor material for Hg^{2+}. We investigated the metal-ion recognition of **BTQ** by adding several metal ions (M^{2+}) to a solution of **BTQ** in acetonitrile. The shape and intensity of the fluorescence spectra with excitation at 350 nm 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+}. Furthermore, when excitation at 373 nm was used, fluorescence was not detected for pure **BTQ** and **BTQ** with Cd^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Ba^{2+}, or Cu^{2+} in acetonitrile solution, whereas fluorescence was detected for **BTQ** in the presence of Hg^{2+}. Thus, **BTQ** is well suited for use as a fluorescent chemosensor material for Hg^{2+}.
Key words: mercury ion, fluorescence, chemosensors, benzothiazol, quinoline

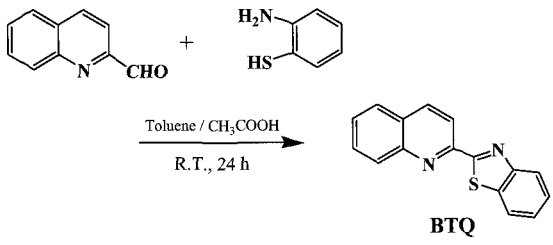
1. INTRODUCTION

The development of selective and sensitive chemosensors for quantitative analysis of metal ions has become extremely important for environmental and biological applications.[1–3] Especially, the detection of Hg^{2+} has become one of the most important topics owing to the highly toxic nature of many mercury compounds.[4–6] A number of Hg^{2+}-selective fluorescent chemosensor materials have been devised, but most of them are fluorescent "quenching" chemosensor materials.[7–8] Fluorescence quenching also occurs due to impurity contamination and leads to false results in the detection. Therefore, we attempted synthesis of a new fluorescent "emission" chemosensor for mercury ion. Recently, 2-(benzo-*d*-thiazol-2-yl)quino -line (**BTQ**) was synthesized for use as a fluorescent "emission" chemosensor material for Hg^{2+}. We here report on the results of mercury ion recognition using **BTQ**.

2. EXPERIMENTL

Synthesis

2-(benzo-*d*-thiazol-2-yl)quinoline (**BTQ**) was obtain -ed by the reaction of 2-quinolinecarbaldehyde and 2-aminobenzenethiol (Scheme 1).



Scheme 1

2-aminobenzenethiol (0.394 g, 2.50 mmol) and acetic acid (2 ml) was added to a solution of 2-quinolinecarbaldehyde (0.318 g, 2.50 mmol) in toluene (30 ml). The mixture was stirred for 24 h at room temperature. The reaction mixture was evaporated, and crystallization from dichloromethane solution afforded pure compound **BTQ** (0.150 g) in 23.2% yield. Fast atom bombardment mass spectra (FAB-MS) and ^1H NMR spectra were recorded for **BTQ** (Fig. 1).

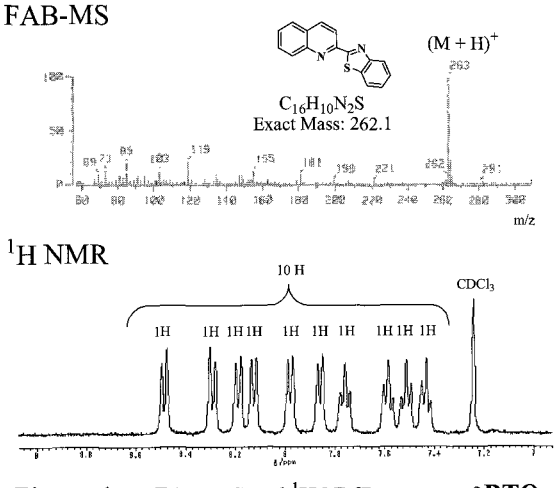


Figure 1. FAB-MS and ^1H NMR spectra of **BTQ**

2-(Benzo-*d*-thiazol-2-yl)quinoline (**BTQ**): FAB-MS m/z = 263 $(M + H)^+$; ^1H NMR ($CDCl_3$) δ = 7.4–8.6 (10 H, m, aromatic rings).

Measurements

The ^1H NMR spectra were recorded on JEOL α-400 spectrometer with tetramethylsilane (TMS) as the internal standard. Stock solutions of **BTQ** were prepared by dissolving a weighed amount of **BTQ** in acetonitrile. Titrations of **BTQ** ([**BTQ**] = 10 μM, M = mol · dm^{-3}) against metal ion solutions were performed in a spectrophotometric cell of

1-cm path length. UV–vis spectra (between 200 and 600 nm) of the resulting solutions were recorded at room temperature with a Hitachi U-2001 spectrophotomete after addition of each of the metal salts ($Cd(ClO_4)_2$, $Ni(ClO_4)_2$, $Zn(ClO_4)_2$, $Co(ClO_4)_2$, $Ca(ClO_4)_2$, $Ba(ClO_4)_2$, $Cu(ClO_4)_2$, and $Hg(ClO_4)_2$). Fluorescence spectra were measured between 400 and 600 nm with a Hitachi F-4500 fluorometer using excitations wavelengths of 350 or 373 nm. The titrations were performed with metal ions (1–100 μM) as a titrant and **BTQ** (10 μM) as a titrate. The metal-ion sources were identical to those used to perform the UV–vis studies.

3. RESULTS AND DISCUSSION

3.1 Absorption spectra

We examined the changes in the absorption spectra after adding various metal ions to a solution of **BTQ**. The absorption spectra of **BTQ** in acetonitrile did not show changes in shape and absorbance upon addition of Cd^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, or Ba^{2+}; however, it showed changes in shape and absorbance with the addition of Cu^{2+} or Hg^{2+}, and a new absorption band appeared after 360 nm. The absorption spectra of **BTQ** in the presence of several concentrations of $Hg(ClO_4)_2$ are shown in Fig. 2. An isosbestic point was observed at 351 nm. The titration curves produced using absorbance at 263 and 308 nm indicate a sharp endpoint at 1:1 ligand:ion ratio for Hg^{2+} as shown in the inset of Fig. 2.

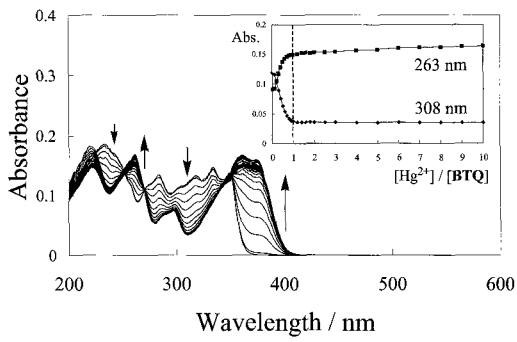


Figure 2. UV–vis absorption spectra of **BTQ** with Hg^{2+} in acetonitrile solution at room temperature: [**BTQ**] = 10 μM, Hg^{2+} = 0.1–1 equiv. The inset is the absorbance at 263 and 308 nm vs [Hg^{2+}]/[**BTQ**].

3.2 Fluorescence spectra

We examined the changes in the fluorescence spectra upon addition of Cd^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, or Hg^{2+} to a solution of **BTQ** in acetonitrile. The shape and intensity of the fluorescence spectra after excitation at 350 nm did not change upon addition of Cd^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, and Ba^{2+}. The fluorescence spectra of **BTQ** in the presence of several concentrations of $Ba(ClO_4)_2$ are shown in Fig. 3a as a typical example. On the other hand, the fluorescence emission of **BTQ** was quenched with the addition of Hg^{2+} or Cu^{2+} as shown in Fig. 3b and 3c. A red shift of the emission maxima was also observed

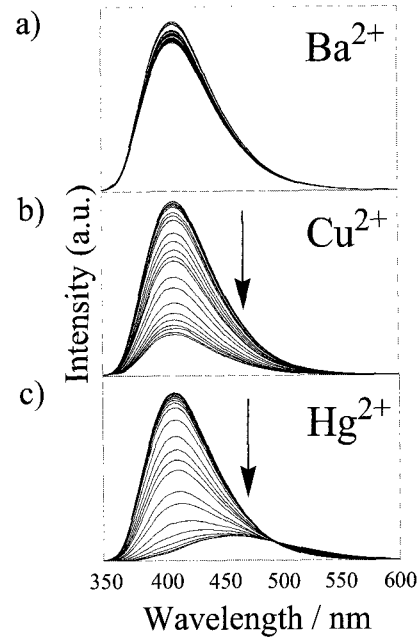


Figure 3. Fluorescence spectra of **BTQ** excited at 350 nm with Ba^{2+}, Cu^{2+}, and Hg^{2+} in an acetonitrile solution at room temperature: [**BTQ**] = 10 μM, Ba^{2+}, Cu^{2+}, or Hg^{2+} = 0.1–10 equiv.

when $Hg(ClO_4)_2$ was added to the solution. Although the emission maximum of free **BTQ** was at 410 nm, the emission maximum of **BTQ** with Hg^{2+} was at 463 nm.

Next, fluorescence spectra were measured using 373 nm as the excitation wavelength, because **BTQ**-Hg^{2+} complex and **BTQ**-Cu^{2+} complex can be selectively excited. Pure **BTQ** and **BTQ** with Cd^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, or Ba^{2+} in acetonitrile solution did not show fluorescence, because there are no absorption bands at 373 nm. The **BTQ**-Cu^{2+} complex also did not show fluorescence in spite of having an absorption band at 373 nm. However, the **BTQ**-Hg^{2+} complex showed fluorescence (Fig. 4).

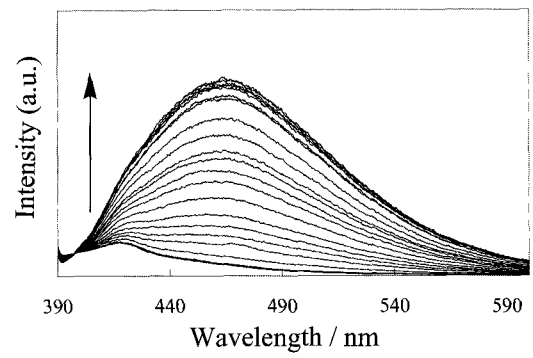


Figure 4. Fluorescence spectra of **BTQ** excited at 373 nm with Hg^{2+} in an acetonitrile solution at room temperature: [**BTQ**] = 10 μM, Hg^{2+} = 0.1–10 equiv.

The association constant (K) was determined from

the fluorescence change at 463 nm using the program NMRTIT.[9] The value of log K of the **BTQ**-Hg^{2+} complex was 4.4.

4. CONCLUSIONS

A fluorescent chemosensor material (**BTQ**) for Hg^{2+} was synthesized by a one-step facile reaction of 2-quinolinecarbaldehyde and 2-aminobenzenethiol. The shape and intensity of the fluorescence spectra with 350-nm excitation did not change upon the addition of Cd^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, or Ba^{2+}. However, the fluorescence emission of **BTQ** was quenched with the addition of Hg^{2+} or Cu^{2+}. Furthermore, when fluorescence spectra were measured using 373-nm excitation, only the **BTQ**-Hg^{2+} complex exhibited fluorescence. Thus, by choosing a suitable excitation wavelength, **BTQ** can be used as not only a fluorescent "quenching" chemosensor but also a fluorescent "emission" chemosensor for recognition of Hg^{2+}.

5. ACKNOWLEDGEMENTS

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