# $Hg^{2+}$-selective Fluorogenic Chemosensor Derived from 8-Aminoquinoline

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(Received February 10, 2004; CL-040158)

8-Aminoquinoline-based benzothiazole derivative **3** showed distinctive $Hg^{2+}$-selective fluoroionophoric properties over other transition metal ions. The fluorescence emission at 580 nm was completely quenched upon complexation with 100 equiv. of $Hg^{2+}$ ions in dioxane–$H_2O$ system (9:1, v/v) and the selectivity was found to be $Hg^{2+} > Cu^{2+} >$ other representative transition and heavy metal ions.

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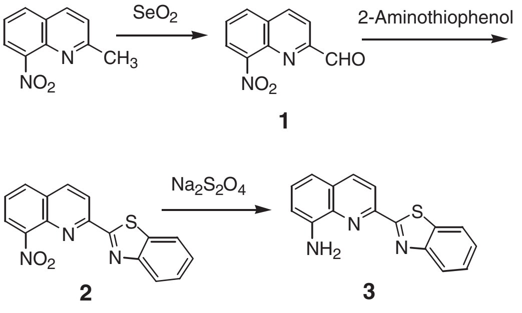
In recent years considerable effort has been given to the design and synthesis of functional molecules that could serve as sensors for the analytical detection of chemically and biologically important ionic species.[1] Especially, the detection of $Hg^{2+}$ ions has been one of the most important topics because of its extreme environmental and biological toxicities.[2] The advantages of fluorescence signaling in its intrinsic sensitivity have encouraged the development of a variety of fluorescence probes for mercury ions,[3] which would help to monitor $Hg^{2+}$ ions selectively and sensitively in many contaminated systems. A large number of quinoline derivatives have been synthesized continually because the quinoline moiety has well-defined and attractive ionophoric properties toward a variety of important metal ions. For instance, 8-hydroxyquinoline derivatives based on the well-known molecular motifs of diaza-crown ether and spyropyran are distinctive examples of $Hg^{2+}$-selective fluoroionophores.[4] In this paper, we report the synthesis of a new 8-aminoquinoline derivative having appended benzothiazole function and its $Hg^{2+}$-selective fluoroionophoric properties. The prepared compound **3** was found to exhibit $Hg^{2+}$-selective fluorogenic behavior over other tested transition and heavy metal ions in aqueous environments.

The benzothiazole derivative of 8-aminoquinoline **3** was synthesized in three steps as shown in Scheme 1. Oxidation of 2-methyl-8-nitroquinoline with $SeO_2$ in dioxane[5] afforded 8-nitro-2-quinolinecarboxaldehyde **1** (56%). Reaction of **1** with 2-aminothiophenol in the presence of acetic acid[6] gave benzothiazole **2** (52%). Reduction of the nitro derivative **2** with sodium hydrosulfite[7] afforded desired benzothiazole functionalized 8-aminoquinoline **3** in good yield (78%).[8]



**Scheme 1.**

Preliminary ion binding properties of **3** were investigated by UV–vis spectroscopy. Figure 1 shows the representative chromogenic behavior of the ionophore **3** in dioxane–$H_2O$ solution (9:1, v/v, $[\mathbf{3}] = 2.0 \times 10^{-5}$ M ($M = \text{mol dm}^{-3}$), $[M^{2+}] = 2.0 \times 10^{-3}$ M). The compound **3** showed an intense absorption band ($\lambda_{max}$) around 310 nm. Upon addition of 100 equiv. of metal ions of $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ ions (in perchlorate), the absorption behavior of the host was not significantly affected. However, the addition of $Hg^{2+}$ ions resulted in significant increase of absorption band around 367 nm with concomitant decrease in the band at 310 nm. Among the rest of tested metal ions, $Cu^{2+}$ ions also induced similar changes in absorption bands but with much lesser degree. So it is apparent that the ionophore **3** has a high selectivity for the recognition of $Hg^{2+}$ ions in dioxane–$H_2O$ solution by exhibiting chromogenic responses in decreasing order of $Hg^{2+} > Cu^{2+} >$ the rest of metal ions.

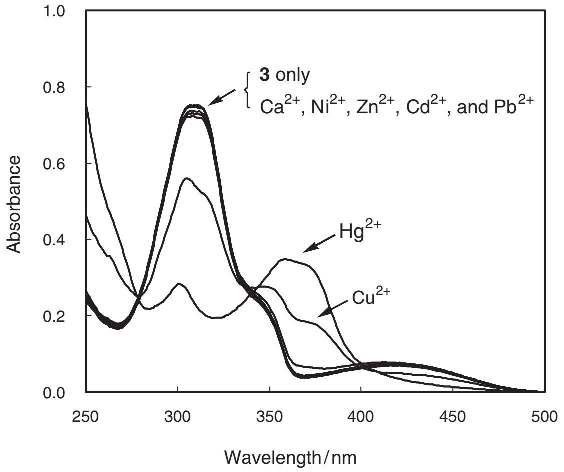


**Figure 1.** UV–vis absorption spectra of free **3** and **3** in the presence of metal ions in dioxane–$H_2O$ (9:1, v/v). $[\mathbf{3}] = 2.0 \times 10^{-5}$ M. $[M^{2+}] = 2.0 \times 10^{-3}$ M.

Based on the observations of the $Hg^{2+}$-selective chromogenic behaviors, we next investigated the fluorogenic behaviors of **3** for the $Hg^{2+}$-selective sensing applications. In dioxane–$H_2O$ (9:1, v/v) solution, the free ionophore **3** ($1.0 \times 10^{-5}$ M) showed an intense fluorescence around 580 nm ($\lambda_{ex} = 340$ nm). Upon interaction with metal ions, the emissions of **3** centered at 580 nm were significantly affected and $Hg^{2+}$ ions exhibited the most effective quenching efficiency (Figure 2). The quenching efficiency of $Hg^{2+}$ and $Cu^{2+}$ ions are found to be larger than 98% and 41% with 100 equiv. of added metal ions, respectively. Other metal ions showed not so significant, at best less than 5%, quenching efficiency. The effect of pH was also checked and the fluorescence intensity of **3** was not so affected upon the addition of up to 1000 equiv. of $HClO_4$.

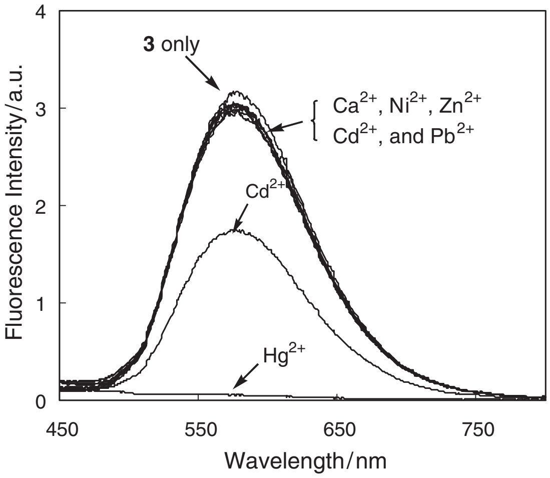


**Figure 2.** Fluorescence spectra of free **3** ($\lambda_{ex} = 340\,nm$) and **3** in the presence of 100 equiv. of metal perchlorate in dioxane–$H_2O$ (9:1, v/v). [**3**] $= 1.0 \times 10^{-5}$ M.

Figure 3 illustrates the changes in fluorescence spectra of **3** upon addition of increasing amount of $Hg^{2+}$ ions. The effective quenching behavior of **3** was well evidenced by the observation of larger than 90% of total quenching was induced by the addition of 20 equiv. of $Hg^{2+}$ ions. The titration results suggest that the formation of **3**–$Hg^{2+}$ complex in 2:1 stoichiometry and the association constants ($K_{assoc}$) estimated by the nonlinear curve fitting[9] were found to be $6.1 \times 10^7\,M^{-2}$ and $2.1 \times 10^5\,M^{-2}$ for $Hg^{2+}$ and $Cu^{2+}$, respectively. From the concentration dependent plot, the detection limit[10] of **3** for $Hg^{2+}$ ions was also estimated to be $3 \times 10^{-5}$ M. To investigate the possibility of practical application, the competitive experiments of the $Hg^{2+}$ ion selectivity of **3** in the presence of other common interfering metal ions (100 equiv. each of background metal ions of $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ in their perchlorate salts) were further carried out. Although somewhat residual quenching due to the presence of large amount of background metal ions was observed, the fluoroionophore **3** showed a clear $Hg^{2+}$ dependent quenching behavior, which implies that the prepared compound can be used for the analysis of $Hg^{2+}$ ions in the presence of other common interfering metal ions in aqueous media. The formation of **3**–$Hg^{2+}$ complexes in 2:1 stoichiometry was further supported by the Job's plot[11] employing the UV–vis and $^1$H NMR titrations. The mass spectrum of **3** obtained under competitive condition with a mixture of $Hg(ClO_4)_2$ and other metal perchlorates ($Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$) in *m*-nitrobenzyl alcohol (*m*-NBA) also showed a prominent peak at $m/z = 755.26$ corresponding to the complex of $[2\cdot\mathbf{3} + Hg\text{–}H]^+$.

In conclusion, we have developed a new selective and sensitive fluorescent probe for $Hg^{2+}$ ions by appending benzothiazole function to 8-aminoquinoline. The ionophore exhibited a highly selective signaling for $Hg^{2+}$ ions in the presence of common interfering metal ions, which is useful for the analysis of $Hg^{2+}$ ions in biological and environmental systems.

This work was kindly supported by KRF (2003-041-C20167, SKC).

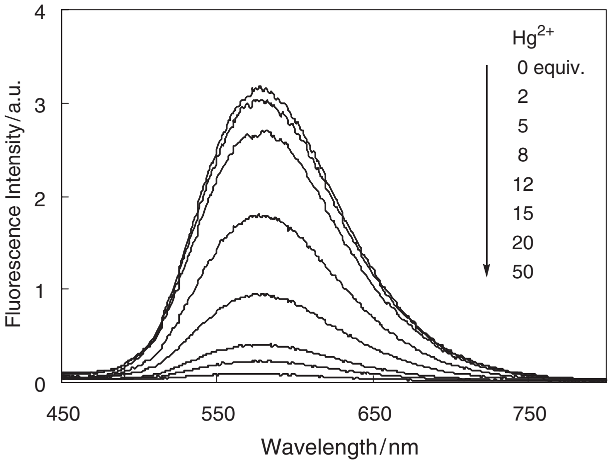


**Figure 3.** Fluorescence spectra of **3** in dioxane–$H_2O$ (9:1, v/v) upon the addition of $Hg^{2+}$ ions ($\lambda_{ex} = 340\,nm$). [**3**] $= 1.0 \times 10^{-5}$ M.

## References and Notes

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8 Selected data for **1**. Yield: 56%. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 10.20 (s, 1H), 8.55 (d, $J = 7.8$ Hz, 1H), 8.19–8.13 (m, 3H), 7.79 (t, $J = 8.1$ Hz, 1H). HRMS (EI): Calcd for $C_{10}H_6N_2O_3$ ($M^+$) 202.0378. Found 203.0386. For **2**. Yield: 52%. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.64 (d, $J = 8.7$ Hz, 1H), 8.40 (d, $J = 8.7$ Hz, 1H), 8.15–8.07 (m, 3H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.66 (t, $J = 7.8$ Hz, 1H), 7.54–7.46 (m, 2H). HRMS (EI): Calcd for $C_{16}H_9N_3O_2S$ ($M^+$), 307.0415. Found 307.0407. For **3**. Yield: 78%. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J = 8.5$ Hz, 1H), 8.19 (d, $J = 8.5$ Hz, 1H), 8.12 (d, $J = 8.7$ Hz, 1H), 7.96 (d, $J = 8.7$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 7.4$ Hz, 1H), 5.11 (s, 2H). HRMS (EI): Calcd for $C_{16}H_{11}N_3S$ ($M^+$) 277.0674. Found 277.0655.

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Published on the web (Advance View) May 17, 2004; DOI 10.1246/cl.2004.702