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A selective and sensitive chemosensor for Cu^{2+} based on 8-hydroxyquinoline

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Abstract—A novel 8-hydroxyquinoline derivative **3** was synthesized. Significant fluorescent quenching was found in the presence of Cu^{2+} and Hg^{2+} with notably higher selectivity for Cu^{2+} than Hg^{2+}.

The detection of Cu^{2+} has important implications in the areas of environmental and biological analysis. Copper has been shown to be a biochemically essential metal, for example, copper–zinc superoxide dismutase's role in the enzymatic defense against oxygen toxicity.[1] Furthermore, copper has been identified as an environmental pollutant.[2]

The 8-hydroxyquinoline (8-HQ) moiety has been one of the most useful ionophores, used in a variety of investigations involving metal ion recognition.[3] In recent years, many chemosensors based on 8-HQ have been developed for sensing Zn^{2+},[4,5] Cd^{2+},[6] Pb^{2+},[7] and Hg^{2+}.[8–10] However, use of 8-HQ derivatized chemosensors for the detection of Cu^{2+} has not been developed. This letter reports a highly sensitive and selective fluorescence sensor for Cu^{2+}.

The dipyrrometheneboron difluoride (difluoroboradiaza-*s*-indacene, BODIPY) fluorescent dyes have been widely used,[11] since they have relatively high fluorescence quantum yields, good photo-stabilities, and absorption coefficients.[12–14] Long-wavelength absorption and emission have been shown to significantly reduce background absorption, background fluorescence, and light scattering. Moreover, maximal fluorescence emission was tunable to longer wavelength by extending the conjugation and rigidity of the BODIPY core.[15,16] Chemosensors that have displayed selectivity for Hg^{2+} have also shown a much more limited fluorescent change in the presence of Cu^{2+}.[8–10] Hg^{2+} has a larger atomic radius than Cu^{2+}, thus by increasing the steric hindrance around the binding site (8-HQ) it was anticipated that a significant enhancement in the selectivity for Cu^{2+} compared to Hg^{2+} would be achieved.

Based on the above observations, the sensor, **3**, which consisted of 8-HQ moiety as a binding site and BODIPY as a reporting group was designed. Compound **3** was efficiently synthesized from styrene. Compound **1** was prepared from styrene by following known procedures.[17] Reaction of **1** with methoxytetralone in the presence of NaH gave rise to **2** in 91% yield.[18] Chemosensor **3** was obtained by a one-pot three-step conversion. Condensation of 8-HQ-carbaldehyde with pyrrole **2** afforded the dipyrromethane, which was subsequently oxidized to the dipyrromethene. Subsequent treatment with BF_3–OEt_2 gave **3** (Scheme 1).[19]

Fully elaborated chemosensor **3** constitutes a flourophore with absorption (660 nm) and emission (680 nm) in the visible region, the 8-HQ also behaves as an ionophore. Chemosensor **3** had a more intense, sharper absorption band compared with a more flexible BODIPY structure.[20]

Initially, metal ion selectivity was examined in aqueous dioxane (1:1, v/v) solution. Changes of the fluorescence properties of **3** caused by various metal ions including Cu^{2+}, Hg^{2+}, K^+, Mg^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, and Cd^{2+} (10 equiv used) were measured once emission intensity was constant. Only Cu^{2+} and Hg^{2+} produced

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Keywords: 8-Hydroxyquinoline; BODIPY; Cu^{2+} ion; Chemosensor.

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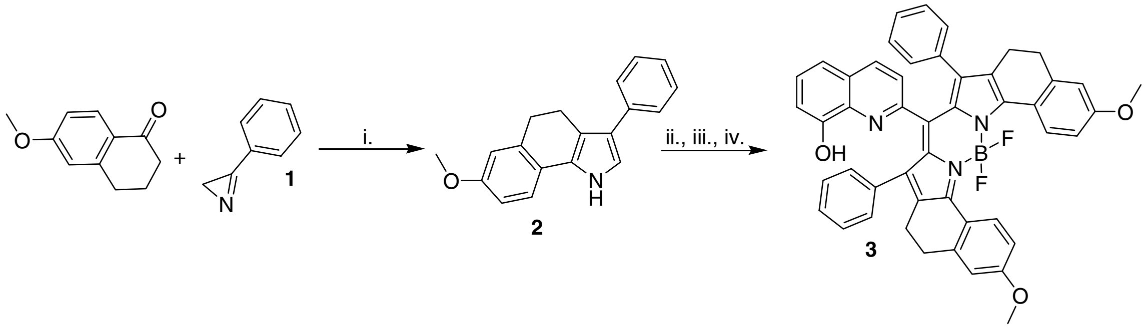

Scheme 1. Synthesis of chemosensor **3**. Reagents and conditions: (i) NaH, DMSO, 25 °C, N_2 (g), 91%; (ii) 8-hydroxyquinoline-2-carbaldehyde,TFA, DCM, 25 °C, N_2 (g); (iii) *p*-chloranil, DCM, 25 °C, N_2 (g); (iv) TEA, BF_3–OEt_2, 25 °C, N_2 (g), 25% (for ii, iii, iv).

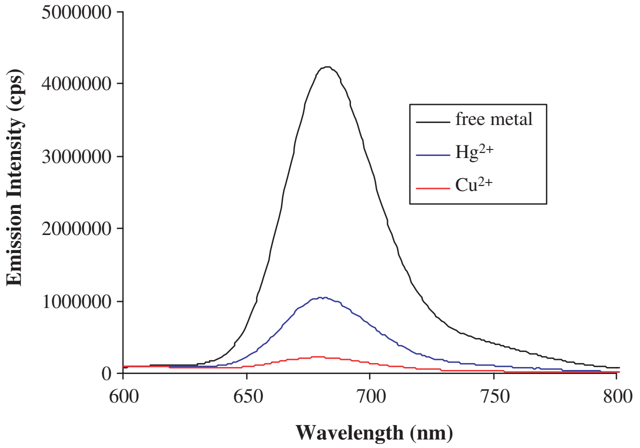

Figure 1. Fluorescence emission spectra of **3** (5.0×10^{-6} M) in an aqueous dioxane (1:1, v/v) solution in the presence of different metal ions (5.0×10^{-5} M). Excitation wavelength is 550 nm. Emission wavelength is 680 nm.

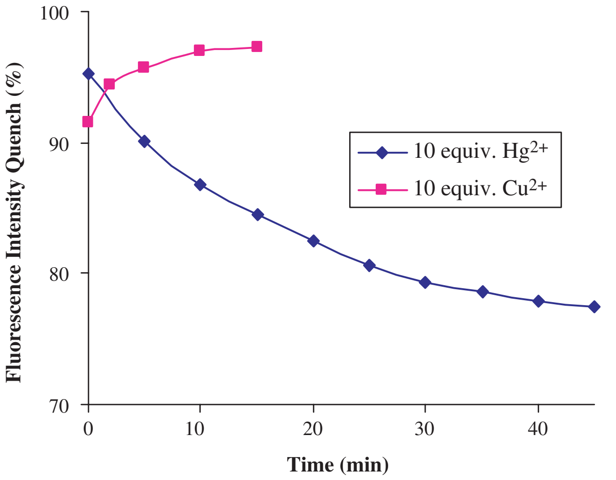

Figure 2. Fluorescence intensity of **3** (5.0×10^{-6} M) in an aqueous dioxane (1:1, v/v) solution in the presence of Cu^{2+} and Hg^{2+} (5.0×10^{-5} M). Excitation wavelength is 550 nm. Emission wavelength is 680 nm.

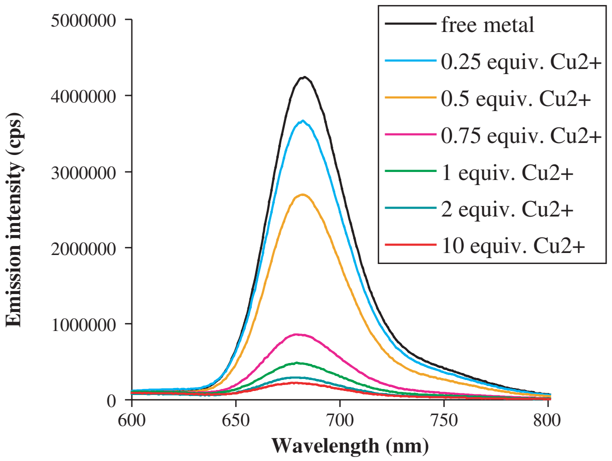

Figure 3. Fluorescence emission spectra (excitation at 550 nm) of **3** (5.0×10^{-6} M) in an aqueous dioxane (dioxane:water = 1:1, v/v) solution in the presence of different concentrations of Cu^{2+}.

significant changes in the fluorescent spectra of **3** (Fig. 1). More significantly, as expected, the fluorescent quenching induced by Cu^{2+} (quenched 97% by 10 equiv) was more pronounced in the fluorescent quenching induced by Hg^{2+} (quenched 77% by 10 equiv).

Interestingly, the fluorescence emission intensity of **3** in the presence of Hg^{2+} increased over 45 min whilst in the presence of Cu^{2+} fluorescence emission intensity decreased over 15 min (Fig. 2). This suggests that the complex of compound **3** with Hg^{2+} is not very stable, possibly due to the steric hindrance of Hg^{2+} with the phenyl functionality of **3**.

The sensitivity of the fluorescence emission response of **3** toward Cu^{2+} was subsequently examined under the same conditions with various Cu^{2+} concentrations (Fig. 3). The sensor exhibited high sensitivity as low as sub-millimolar concentration. The association constant of **3** with Cu^{2+} was determined as 3.11×10^5 (assuming the formation of 1:1 complex[8,21]).

In summary, a novel chemosensor (**3**) based on 8-HQ was designed and synthesized. Compound **3** showed no sensitivity to numerous metal ions (K^+, Mg^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, and Cd^{2+}). However, **3** has displayed higher sensitivity for Cu^{2+} than Hg^{2+} in an aqueous dioxane solution, which has taken advantage of the conformationally restricted and sterically hindered BODIPY core.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.01.091.

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