

A Highly Selective and Sensitive Fluorescent Chemosensor for Hg²⁺ in Neutral Buffer Aqueous Solution

Xiangfeng Guo,^{†,‡} Xuhong Qian,^{*,†} and Lihua Jia^{†,§}

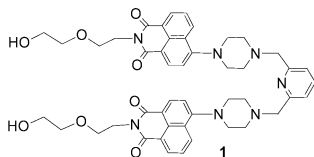
State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China, Qiqihaer University, Qiqihaer 161006, China, and Shanghai Key Laboratory of Chemical Biology, Institute of Pesticides and Pharmaceuticals, East China University of Science and Technology, Shanghai 200237, China

Received July 29, 2003; E-mail: xhqian@dlut.edu.cn

Fluorescent devices for the sensing and reporting of chemical species are currently of significant importance for chemistry, biology, and environmental science.¹ The design and synthesis of a sensitive and selective fluorescent sensor is a fundamental goal for organic and analytical chemists.² So far, the development of practical fluorescent chemosensors for many heavy and transition metal (HTM) ions is still a challenge. First, many of HTM ions are known as fluorescence quenchers via enhanced spin-orbit coupling,³ or energy or electron transfer,⁴ and the quenching is not only disadvantageous for a high signal output upon complexation but also hampers temporal separation of spectrally similar complexes with time-resolved fluorometry. Second, the most common fluorescent probes undergo nonspecific quenching with HTM analytes, such as Hg²⁺ and Cu²⁺.^{2b} Third, although HTM ions are relatively easy to chelate and detect in organic solvents, they are rather difficult to recognize directly in aqueous environments due to their strong hydrations. This limitation needs to be addressed when designing an HTM sensor for biological and environmental applications.⁵

The detection of Hg²⁺ is attracting attention,⁶ as mercury and its derivatives are widely used in industry and they have inherent high toxicity.⁷ There were some examples of fluorescent quenching chemosensors for Hg²⁺ in organic or aqueous solution.^{6a-c,8} However, there are few chemosensors with fluorescence enhancement (FE) for Hg²⁺ in organic solutions,^{2b,9} and few in aqueous solutions.^{5b,10} Most of the fluoroionophores for Hg²⁺ consist of fluorophores and macrocycle receptors^{2b,5b,6a-c,8a,9} (e.g., aza-crown ether) or the receptors containing sulfur atoms,¹⁰ and there are some fluorescent probes for Hg²⁺ designed on the basis of chemical reaction,^{11a} redox,^{11b,c} and the photodynamic principle.^{11d} The syntheses of some macrocycles are complicated or low-yielding. Therefore, novel selective chemosensors with FE for Hg²⁺ in aqueous solution become our target.

4-Aminonaphthalimide, frequently used in fluoroionophores, has desirable spectroscopic properties,¹² and we recently demonstrated that the semirigid piperazine moiety as a receptor could be used to build highly sensitive fluoroionophores of photoinduced electron transfer (PET).¹³



Herein, we designed a simple and water-soluble chemosensor **1**, which is composed of two aminonaphthalimide fluorophores and

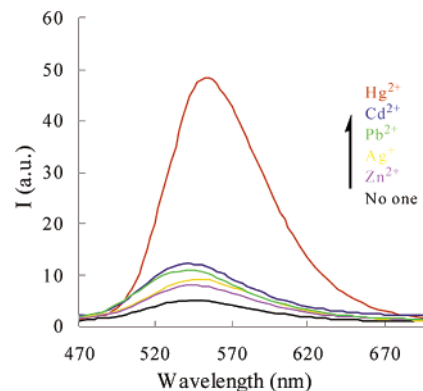


Figure 1. Fluorescence spectra of **1** (1.0×10^{-5} M) in tris-HCl (0.01 M) solution (ethanol:water = 1:9, v/v, pH = 6.98) in the presence of different metal ions (5.0×10^{-5} M), and nearly no response to some other metal ions (Mg²⁺, Ca²⁺, K⁺, Cr³⁺, Fe³⁺, Co²⁺, Cu²⁺, Ni²⁺).

a nonmacrocycle receptor of 2,6-bis(aminomethyl) pyridine. **1** can adopt a semirigid V-shaped conformation, which might be able to selectively bind with a metal ion,¹⁴ and nitrogen atoms of 2,6-bis(aminomethyl)pyridine were both the ion receptor and the quencher of PET. When a target species is bound with the receptor, the two fluorophores are turned to the "on" state, so **1** is more sensitive than the corresponding chemosensor with one fluorophore. In addition, the two hydrophilic 2-(2-hydroxyethoxy)ethyl groups at imide moieties make **1** operate in aqueous solution. The results show that **1** displays a highly selective and sensitive response of FE toward Hg²⁺ in neutral buffer aqueous solution.

1 was easily synthesized through the reaction of 2,6-bis-(chloromethyl)pyridine and *N*-[2-(2-hydroxyethoxy)ethyl]-4-piperazino-1,8-naphthalimide, which is prepared from the corresponding 4-bromo-1,8-naphthalimide and piperazine.

Fluoroionophores are usually disturbed by a proton in the detection of metal ions, so their low sensitivities to the operative pH are extremely important.^{5a} It was obtained from the fluorescence titration curve that the p*K*_a' of **1** is about 5.2, and the fluorescence intensity is almost a constant minimal value when pH > 6.5 in a mixed solution of ethanol and water (1:9, v/v). Therefore, all of the detections of metal ions were operated in the mixed solution containing tris-HCl (0.01 M, pH 6.98), and the fluorescence quantum yields were determined by using *N*-butyl-4-butylamino-1,8-naphthalimide in absolute ethanol ($\Phi = 0.81$) as a reference.¹⁵

As expected, **1** showed a very weak fluorescence ($\Phi_0 = 0.007$, $\lambda_{\text{max(em)}} = 548$ nm) (Figure 1), and its fluorescence was slightly influenced by the addition of Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Cr³⁺, Ca²⁺, K⁺, and Mg²⁺, respectively. A small enhancement in fluorescence was detected upon the addition of Cd²⁺ ($\Phi/\Phi_0 = 2.8$, $\lambda_{\text{max(em)}} = 547$ nm), Pb²⁺ ($\Phi/\Phi_0 = 2.4$, $\lambda_{\text{max(em)}} = 546$ nm), Ag⁺ ($\Phi/\Phi_0 =$

[†] Dalian University of Technology.

[‡] Qiqihaer University.

[§] East China University of Science and Technology.

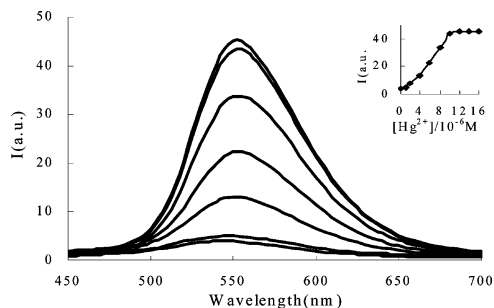


Figure 2. Fluorescence spectra of **1** (1.0×10^{-5} M) in tris-HCl (0.01 M) solution (ethanol:water = 1:9, v/v, pH = 6.98) in the presence of different concentrations of Hg^{2+} . Inset: fluorescence intensity at $\lambda_{\text{max(em)}}$ as a function of mercury concentration.

2.7, $\lambda_{\text{max(em)}} = 548$ nm), and Zn^{2+} ($\Phi/\Phi_0 = 1.6$, $\lambda_{\text{max(em)}} = 546$ nm), respectively. However, a much higher FE ($\Phi/\Phi_0 = 17.4$, $\lambda_{\text{max(em)}} = 556$ nm) and a red shift of about 8 nm were observed for **1** upon addition of Hg^{2+} by comparison with that of only **1** in the solution. The red shift may be due to the intramolecular excimer formation that is caused by the decrease in the distance between two fluorophores when mercury ion is bound. The results indicate that the selectivity of **1** for Hg^{2+} is very high. It was noticed that only d^{10} ions of $-\text{Hg}^{2+}$, $-\text{Cd}^{2+}$, $-\text{Pb}^{2+}$, $-\text{Ag}^{+}$, and $-\text{Zn}^{2+}$ display FE, as this kind of ion usually does not introduce low-energy metal-centered or charge-separated excited states into the molecule, so that the energy-transfer or electron-transfer processes cannot usually occur.¹⁶

The selective and sensitive signal response of **1** toward Hg^{2+} is preserved in the buffer aqueous solution in both emission and absorption. Its fluorescence intensity increased linearly with the concentration of Hg^{2+} ($(0.1-1.0) \times 10^{-5}$ M, linearly dependent coefficient: $R^2 = 0.9827$) up to a mole ratio ($\text{1}/\text{Hg}^{2+}$) of 1:1, and there it remained (Figure 2). The complexation resulted in a strong change of **1** in its absorption intensity upon the addition of increasing amounts of Hg^{2+} , which might be caused by the interaction of Hg^{2+} with the lone electron pair of the 4-nitrogen at the naphthalimide. Its absorption decreased linearly with the concentration of Hg^{2+} ($(0.0-1.0) \times 10^{-5}$ M, $R^2 = 0.9901$) up to a ratio ($\text{1}/\text{Hg}^{2+}$) of 1:1, and there it remained.¹⁷ This behavior is also diagnostic for the formation of a complex with 1:1 stoichiometry of **1** and Hg^{2+} , and the associated constant is 1.7×10^5 .

Furthermore, Hg^{2+} could be detected at least down to 1.0×10^{-8} M when **1** was employed at 1.00×10^{-6} M in 0.001 M tris-HCl buffer aqueous solution, and its fluorescence intensity also increased linearly with the concentration of Hg^{2+} ($(0.00-1.00) \times 10^{-6}$ M, $R^2 = 0.9912$) up to a mole ratio ($\text{1}/\text{Hg}^{2+}$) of 1:1, and there it remained as well.

To explore further the utility of **1** as an ion-selective fluorescence chemosensor for Hg^{2+} , the competition experiments were conducted in the presence of Hg^{2+} at 1.0×10^{-5} M mixed with Ca^{2+} , Fe^{3+} , Co^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , Cr^{3+} , Zn^{2+} , Ca^{2+} , Pb^{2+} , Cd^{2+} , K^{+} , and Ag^{+} at 5.0×10^{-5} M, as well as the mixture of the metal ions,^{18a} respectively; no significant variation in its fluorescence intensity (1.0×10^{-5} M) was found by comparison with that without the other metal ions besides Hg^{2+} . Moreover, no obvious interference was observed in its fluorescence while performing the titrations with Hg^{2+} in the different mixtures of metal ions.^{18b} The above results implied that its selectivity for Hg^{2+} was remarkable.

In summary, a simple and water-soluble PET chemosensor **1** for recognition of heavy metal ions was designed and synthesized easily, and it displays high selectivity and sensitivity for Hg^{2+} by FE in neutral buffer aqueous solution.

Acknowledgment. We acknowledge the National Natural Science Foundation of China, the Natural Science Foundation Heilongjiang Province, the National Key Project for Basic Research (2003CB114400), and the Shanghai Education Commission for partial support of this work.

Supporting Information Available: Synthetic details, molecular model, and spectroscopy data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (17) For the absorption spectra details, see the Supporting Information.
- (18) (a) Metal ions (such as NO_3^- or Cl^- salts) besides Hg^{2+} used for the studies were Ca^{2+} , Fe^{3+} , Co^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , Cr^{3+} , Zn^{2+} , Ca^{2+} , Pb^{2+} , Cd^{2+} , K^{+} , Na^{+} , and Ag^{+} in tris-HCl buffer aqueous solution (see the Supporting Information). (b) The different mixtures of metal ions were Ca^{2+} , Fe^{3+} , Co^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , and Cr^{3+} ; Zn^{2+} and Ca^{2+} ; Zn^{2+} , Ca^{2+} , and Pb^{2+} ; and Zn^{2+} , Ca^{2+} , and Cd^{2+} , respectively (see the Supporting Information).

JA037604Y