A Highly Selective Fluorescent Chemosensor for Hg^{2+} in Aqueous Solution

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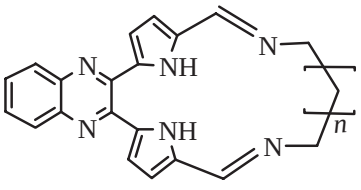
A novel selective chemosensor (quinoxaline-bridged Schiff-base macrocycle) for mercury ion has been designed and synthesized, and it exhibited a remarkable selective fluorescent quench toward Hg^{2+} in the presence of other metal ions in aqueous solution.

As mercury and its derivatives are widely used in industry and they have inherent high toxicity,[1] it is important to develop an easy mercury determination system for monitoring its concentration in polluted areas.[2] Several analytical reagents for the determination of Hg^{2+} have been reported,[3] however, most of these molecules have limitations owing to interference from other metal ions and delayed response to mercury ions. Only a few compounds have been reported to selectively detect Hg^{2+} in aqueous solutions.[4] In this paper, we reported a novel, water-soluble, highly selective fluorescent chemosensor for Hg^{2+}.

Quinoxaline-bridged macrocycles have been reported as anion sensors.[5] While known in the literature since 1911,[6] to the best of our knowledge, this particular entity has never been considered as being a possible cation fluorescent sensor. According to molecular modeling studies, we designed a simple and water-soluble chemosensor **1** (and **2**).[7] Ligand **1** (or **2**) was easily synthesized through the reaction of 2,3-bis(5-formylpyrrol-2-yl)-quinoxaline with 1,3-diaminopropane (or 1,4-diaminobutane) (Chart 1). The ionophore moiety contains nitrogen atoms, which have an affinity for soft metal (such as Hg^{2+}).[8] It is expected that the electron density of the fluorophore moiety is reduced by the electron-withdrawing effect of coordinated metal ion and that remarkable changes in the fluorescence intensity and the absorption spectra should be caused when the ionophore moiety is complexed to a metal ion.[9]

Fluoroionophores are usually disturbed by a proton in the detection of metal ions, so their low sensitivities to the operative pH are extremely important.[10] It was obtained from the fluorescence titration curve that the fluorescence intensity of ligand **1** and **2** is almost independent of pH (2.5–5.5). All of the detections of metal ions (except $FeCl_2$ and $CaCl_2$, the counter anions of the other metal salts are AcO^-) were operated in AcOH–NaOAc buffer solution (0.2 M, pH 4.5), and the fluorescence quantum yields of ligand **1** were determined by using quinin in 0.1 M H_2SO_4 ($\Phi = 0.546$) as reference.[11] The fluorescence intensity of the ligand **1** (and **2**) reaches the maximum when excited at 332 nm. In order to improve the sensitivity of the detection of the metal ions, we choose 332 nm but not 415 nm (isosbestic point) as the excitation wavelength.



$n = 1$

$n = 2$

Chart 1.

As expected, **1** has a very weak fluorescence ($\Phi_0 = 0.006$, $\lambda_{max\ (em)} = 507$ nm), and its intensity of fluorescence emission was sensitive to Hg^{2+}, Hg^{2+} could be detected at least down to 1.0×10^{-7} M when **1** was employed at 1.0×10^{-6} M. A quench of fluorescence and a blue shift were distinctly observed for **1** upon the addition of Hg^{2+} (Figure 1). Its fluorescence intensity decreased linearly with the increased concentration of Hg^{2+} ($(0.0–1.0) \times 10^{-5}$ M linearly dependent coefficient: $R^2 = 0.9923$). As shown in Figure 2, a broad absorption of ligand **1** appeared at 309 nm in aqueous solution, and its absorbance also decreased linearly with the concentration of Hg^{2+} ($(0.0–1.0) \times 10^{-5}$ M, $R^2 = 0.9955$). Meanwhile, an isosbestic point was observed. The Job curve revealed that a 1:1 complex was successively formed between the ligand **1** and Hg^{2+}. Careful analysis of the evolution of the emission spectra (Figure 1) and absorption spectra (Figure 2) showed that the complex has a very high stability constants ($Kass = (3.81 \pm 0.7) \times 10^5$, $R^2 = 0.9912$). The complexation results in a strong change of fluorescence intensity of **1** upon the addition of increasing amounts of Hg^{2+}, which might be caused by the interaction of Hg^{2+} with the lone electron pairs of the four nitrogen atoms. Experimental support substantiating the above argument has been provided

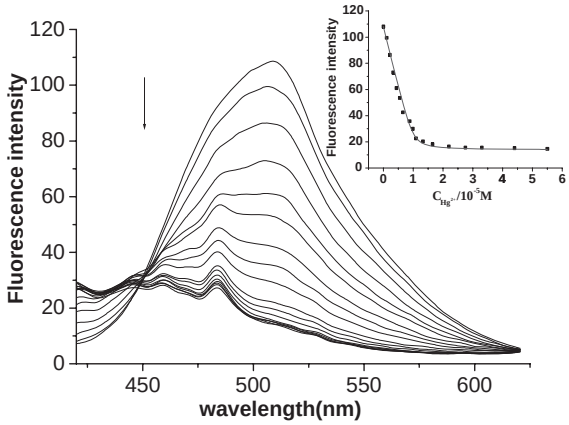


Figure 1. Fluorescence spectra of **1** (1.0×10^{-5} M) in AcOH–NaOAc solution (0.2 M, pH = 4.5) in the presence of different concentrations of Hg^{2+}, $\lambda_{ex} = 332$ nm. Inset: fluorescence intensity at $\lambda_{max\ (ex)}$ (507 nm) as a function of mercury concentration.

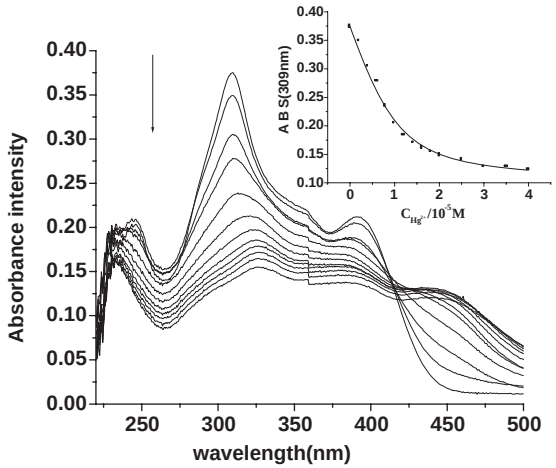


Figure 2. UV–vis spectra of **1** (1.0×10^{-5} M) in AcOH–NaOAc solution (0.2 M, pH = 4.5) in the presence of different concentrations of Hg^{2+}. Inset: absorbance intensity at λ_{max} (309 nm) as a function of mercury concentration.

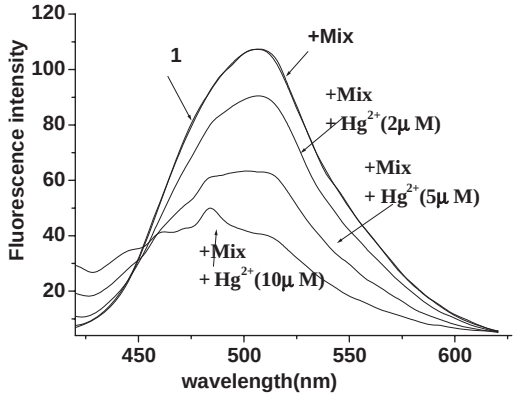


Figure 3. Fluorescence spectra of **1** (1.0×10^{-5} M) in AcOH–NaOAc solution (0.2 M, pH = 4.5) in the presence of different metal ions (5.0×10^{-5} M), $\lambda_{ex} = 332$ nm, nearly no response to some other metal ions (Cu^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, and Ca^{2+}).

by X-ray crystallography data.[12] When the amino group interacts with the Hg^{2+}, the latter reduces the electron-donating character of amino group and together with a decrease of the extinction coefficient.[13]

To further explore 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 different concentration mixed with Cu^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, and Fe^{2+} at 5.0×10^{-5} M. As shown in Figure 3, the addition of a mixture of other metal ions (Cu^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, and Fe^{2+}, each 5.0×10^{-5} M) did not alter the shape or the intensity of the fluorescence. In contrast, the fluorescence spectra was sensitive to the presence of Hg^{2+} ions, and its intensity decreased as the Hg^{2+} concentration increased. No interference was observed in its fluorescence while performing the titrations with Hg^{2+} in the mixtures of these metal ions. The above results indicated that the ligand **1** has remarkable selectivity for Hg^{2+}. We measured the change in emission behavior of ligand **2** with Hg^{2+}, the ligand **2** also has the high selectivity toward Hg^{2+}.

In summary, a novel and water-soluble chemosensor **1** (and **2**) for recognition of Hg^{2+} was designed and synthesized easily by us, and it displays high selectivity for Hg^{2+} by fluorescence in buffer solution.

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7 Selected data: for **1**: yellow solid, yield 92%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.07–8.04 (dd, $J = 3.5, 3.5$ Hz, 2H, quinoxaline), 7.86 (s, 2H, –HC=N), 7.68–7.65 (dd, $J = 3.5, 3.2$ Hz, 2H, quinoxaline), 7.59 (d, $J = 3.8$ Hz, 2H, pyrrole H), 6.96 (d, $J = 4.1$ Hz, 2H, pyrrole H), 3.97 (t, 4H, $J = 5.4$ Hz, =N–CH_2–CH_2), 2.14 (br, 2H, =N–CH$_2$–CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.09, 145.94, 144.53, 140.28, 131.58, 129.20, 128.74, 121.59, 117.46, 55.16, 29.70. IR (KBr): 2937–2832 (m), 1647 (s), 1604 (s), 1469 (s), 1299 (s), 1015 (s), 805 (w), 770 (s), 685 (s) cm^{-1}. FAB-MS m/z 355 $(M + H)^+$. Anal. Calcd for $C_{21}H_{18}N_6$: C, 71.17; H, 5.12; N, 23.7%. Found: C, 71.10; H, 5.14; N, 23.67%. For **2**: yellow solid, yield 89.4%. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.05–8.01 (dd, $J = 3.5, 3.5$ Hz, 2H, quinoxaline), 7.89 (s, 2H, –CH=N), 7.67–7.64 (m, 4H), 6.97 (d, $J = 3.8$ Hz, 2H, pyrrole H), 3.72 (br, 4H, =N–CH_2–CH$_2$), 2.04 (br, 4H, =N–CH$_2$–CH_2). ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.56, 146.36, 144.23, 140.25, 131.11, 129.06, 128.62, 123.04, 117.47, 56.01, 28.83. IR (KBr): 2937–2832 (m), 1647 (s), 1604 (s), 1469 (s), 1299 (s), 1015 (s), 805 (s), 770 (s), 685 (s) cm^{-1}. FAB-MS m/z: 369 $(M + H)^+$. Anal. Calcd for $C_{22}H_{20}N_6$: C, 71.72; H, 5.47; N, 22.81%. Found: C, 71.06; H, 5.48; N, 22.76%.

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