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An easy-to-synthesize ‘turn-on’ fluorescent sensor for the selective detection of Hg^{II}

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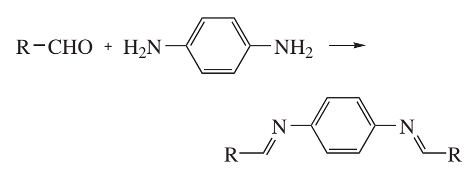
A small molecular fluorescent sensor synthesized through Schiff base reaction can be used to detect Hg^{2+} with an exclusive selectivity, high fluorescent enhancement and reversibility.

A variety of natural and anthropogenic environmental contaminants cause serious problems for human health and ecology.[1,2] Among them, mercury and mercuric salts are toxic and hazardous pollutants with recognized accumulative and persistent characters in the environment and biota, even at very low concentrations.[3] The body exposure to methylmercury leads to serious risks for human beings and other organisms,[4,5] especially a cause of prenatal brain damage and notorious Minamata disease.[6]

Thus, the development of methods for the detection of mercury with high efficiency is important. Small molecular fluorescent chemosensors that selectively respond to the target metal ions have been recognized powerful technique toward this kind of purpose. Unfortunately, most of the probes that have been prepared exhibited fluorescence quenching upon cation complexation.[7–9] That is because, like many other heavy metals, Hg^{2+} often causes fluorescent quenching *via* enhanced spin-orbit coupling associated with the heavy atom effect, which will facilitate the intersystem crossing process.[10,11] Recently, an example of a highly efficient Hg^{2+} sensor based on the seminaphthofluorescein chromophore and employing a thioether-rich metal-binding unit can afford both turn-on and single-excitation dual emission ratiometric Hg^{2+} detection in aqueous solution. However, the obtainment of the target compound experienced a tedious synthesis.[12,13] Therefore, the design of sensors that can be easily synthesized and give fluorescent enhancement upon Hg^{2+} binding is a particular challenge.[14]

On the basis of the fact that amine is an efficient ligand to mercury ion, we anchored a structure-simple receptor **1**, which contained two kinds of amino substituents. In case of being exposed to a mercury ion, one of the amine groups would integrate with the ion and a strong metal-induced intramolecular electron transfer (MICT) occurred, simultaneously a push-pull system formed (the other amine group acted as a donor and because of MICT this amine would have a very low affinity for the mercury ion), which could cause a distinct change in the optical properties (colour change and fluorescence enhancement) of the receptor.



1 R = 4-(Et$_2$N)C$_6$H$_4$
2 R = Ph

Scheme 1

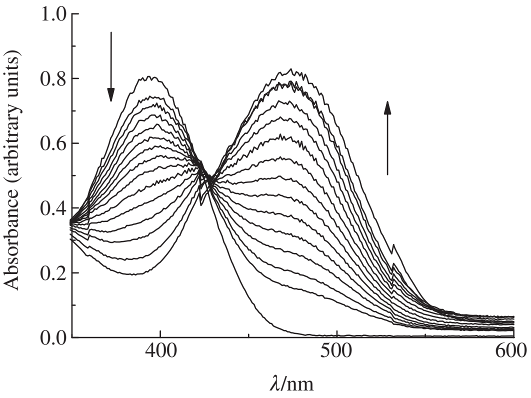


Figure 1 UV/Vis titration of **1** (1.0×10^{-5} M) in MeCN/H$_2$O (9:1 v/v) solution upon addition of Hg^{2+} (0–1.5 equiv.).

The synthesis of receptor **1** and model compound **2** is outlined in Scheme 1. Compound **1** was easily obtained in high yield through the Schiff base reaction of 4-(diethylamino)benzaldehyde and *p*-phenylenediamine in anhydrous alcohol.

From the absorbance spectra (Figure 1), upon progressive addition of Hg^{2+} to a solution of **1** in MeCN–H$_2$O (9:1 v/v, 1.0×10^{-5} M), the initial absorption band at 394 nm for free compound **1** gradually decreased with the concomitant formation of a new absorption band at 474 nm. The absorption spectrum of **1** exhibited a red shift of 80 nm with the addition of Hg^{2+}. A well-defined isosbestic point at 425 nm throughout the titration clearly indicated the existence of a two-state equilibrium; namely, one specific complex between compound **1** and Hg^{2+} formed, which was responsible for the colour change of the mixture from pale yellow to salmon pink that could be detected easily by the naked eyes. A Job’s plot (see Online Supplementary Materials, Figure S1) showed that receptor **1** formed a 1:1 complex with Hg^{2+} in the solution and the association constant K derived from the titration curve was 2.24×10^4 dm^3 mol^{-1}.

Figure 2 shows the emission spectra of sensor **1** at various Hg^{2+} concentrations. A gradual increase in the fluorescent intensity was observed with the addition of Hg^{2+}, which may be attributed to the formation of a complex between compound **1** and Hg^{2+}, as mentioned above.

To investigate selectivity for Hg^{2+}, the influence of various metal ions on the fluorescence behaviour of compound **1** was studied. Upon the addition of 1.5 equiv. of other metal ions including Fe^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+} and Ag^{+}, all emission responses except for Hg^{2+} showed the fluorescence quenched to a certain degree, even chemically

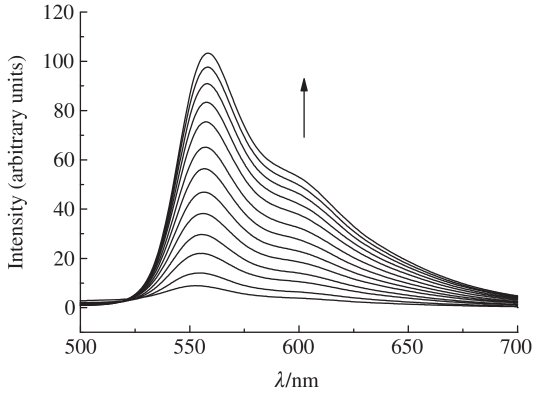


Figure 2 Fluorescence response of **1** (1.0×10^{-5} M) in MeCN/H_2O (9:1 v/v) solution upon addition of Hg^{2+} (0–2.0 equiv.), λ_{ex} = 370 nm.

closely related metal ions, such as Cd^{2+} and Cu^{2+}, did produce obvious fluorescence quenching (Figure 3).

On the other hand, the reversibility of the binding between receptor **1** and Hg^{2+} was also expectant. On addition of thiourea to the solution of **1**·Hg^{2+}, the colour of the solution was found to recover pale yellow quickly (see Supporting Information). At the same time, the fluorescence returned to the original degree, which explained that the adduct **1**·Hg^{2+} decomplexed immediately against thiourea. The reason is that the complexing ability between thiourea and Hg^{2+} is stronger than that between compound **1** and Hg^{2+}.

As receptor **1** contains both imine and aniline groups, the compound might integrate Hg^{2+} on either imine or aniline sites. In order to understand, which nitrogen combine Hg^{2+} to form the complex, model compound **2** was designed and synthesized, which only contained imine. In the titration of compound **2** with Hg^{2+}, no significant variation could be found in both the fluorescence intensity and absorbance (see Online Supplementary Materials, Figures S2 and S3), from which it could be concluded that the binding site in sensor **1** was the aniline group rather than the imine.

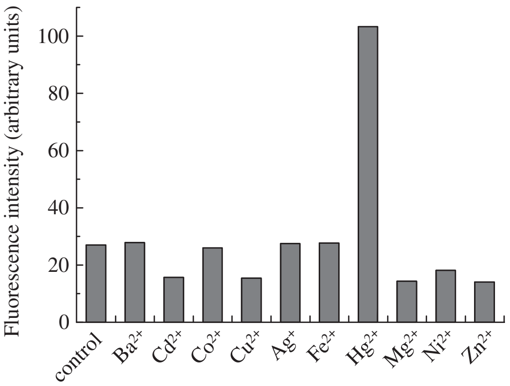


Figure 3 Fluorescence response of **1** in MeCN/H_2O (9:1 v/v, 1.0×10^{-5} M) solution in the presence of 1.5 equiv. of different metal ions, λ_{ex} = 370 nm.

In summary, a structure-simple sensor that gives selective fluorescent enhancement for mercury ion was described. The Schiff base reaction made the obtaining of the sensor escaping from a tedious synthesis. Upon binding with Hg^{2+}, a strong push-pull system formed and the colour change could easily be detected by naked eyes. Experiments with corresponding model compound showed the binding site in sensor **1** located in the aniline group. We believe such design strategies like using structure-simple, electron-rich compounds and MICT effects to avoid tedious synthesis will be helpful in the design of other kinds of sensors for specific ions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.09.013.

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