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A Selective and Sensitive "Turn-on" Fluorescent Chemosensor for Recognition of Hg^{2+} Ion in Water

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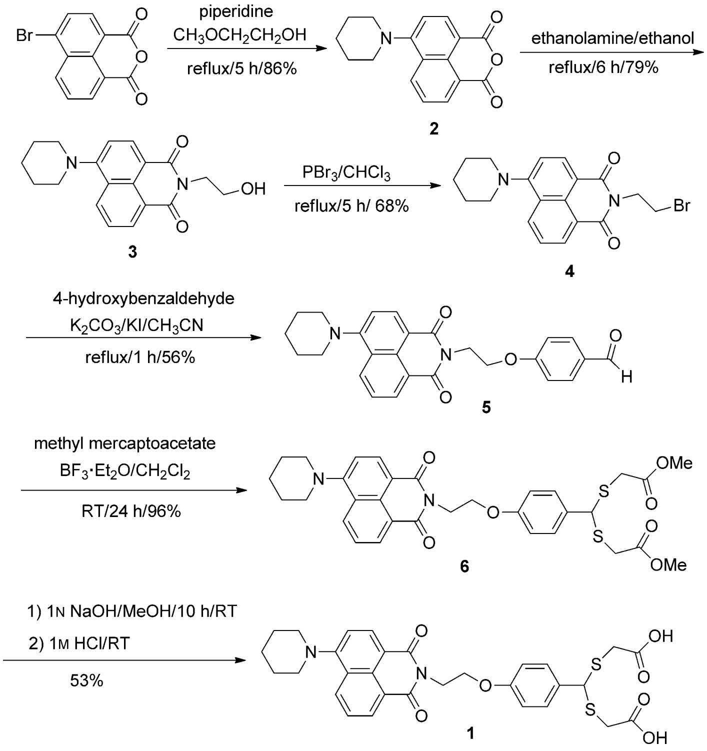
Heavy and transition-metal (HTM) ions usually play important roles in various biological systems or have an extremely toxic impact on the environment.[1] In particular, mercury ions are considered to be very dangerous environmental pollutants by bioaccumulating through the food chain when they are ingested or inhaled by human beings,[2] consequently, the development of fluorescent chemosensors for the detection of the Hg^{2+} ion over other HTM ions with excellent selectivity and sensitivity is still a challenging task.

Recently, a lot of sensors for the recognition of Hg^{2+} ion have been developed with good performance.[3] Furthermore, many attractive probes for the detection of mercury ions based on the specific mercury-promoted desulfurization reaction have also been reported.[4] More recently, another series of new interesting sensors, based on the mercury-promoted deprotection of dithioacetals groups, have been developed.[5] However, these probes for the recognition of the Hg^{2+} ion were conducted in organic solutions.[5] Meanwhile, 1,8-naphthalimides have been frequently used as the fluorophores to prepare fluorescent chemosensors for metal cations and protons in recent years.[6] Encouraged by the above-mentioned results, herein, we have designed a simple chemosensor **1** (Scheme 1) by incorporating a 1,8-naphthalimide fragment with a dithioacetal that contained two hydrophilic carboxylic groups, into a single molecular framework. We envisaged that the two carboxylic groups at the dithioacetal group would make **1** operate in aqueous solution, and therefore enable us to disclose a new highly sensitive and selective probe for the Hg^{2+} ion over other HTM ions in pure water without the requirement for additional organic solvent.



Scheme 1. Synthetic approach for chemosensor **1**.

As described in Scheme 1, 4-bromo-1,8-naphthalimide reacted with piperidine to give 4-piperidine-1,8-naphthalimide (**2**, 86 %),[7] which was further allowed to react with ethanolamine to afford **3** in a 79 % yield.[8] Then **4** was obtained in a 68 % yield by the reaction of **3** with phosphorus tribromide.[9] In the presence of K_2CO_3 and KI, subsequently, intermediate **4** was allowed to react with 4-hydroxybenzaldehyde to produce **5** in a 56 % yield,[10] which smoothly reacted with methyl thioglycolate to give **6** (96 %).[5a] Finally, the target compound **1** was obtained in a 53 % yield by hydrolysis of **6** with potassium hydroxide in a water–methanol mixture.[11] The chemical structures of compounds **1–6** were well characterized by IR spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and HRMS (see the Supporting Information).

The pK_a' of **1** was about 3.3, and the fluorescent intensity was almost a constant minimal value at pH values >4.24 in water (Figure S1, see the Supporting Information). It suggested that **1** could function over a wide range of pH values for detection. Figure 1 shows the fluorescent intensity ratio (I/I_0) of sensor **1** in the presence of Hg^{2+}, Ag^{+}, Zn^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, and Ba^{2+} ions in water. The fluorescent behavior of sensor **1** was very weak. Interestingly, only when Hg^{2+} ion was added to the pure water solution of **1**, a 155-fold increase of the fluorescent intensity was observed at 535 nm. This was because the dithioacetal of sensor **1** was deprotected by Hg^{2+} ion to give aldehyde **5**,

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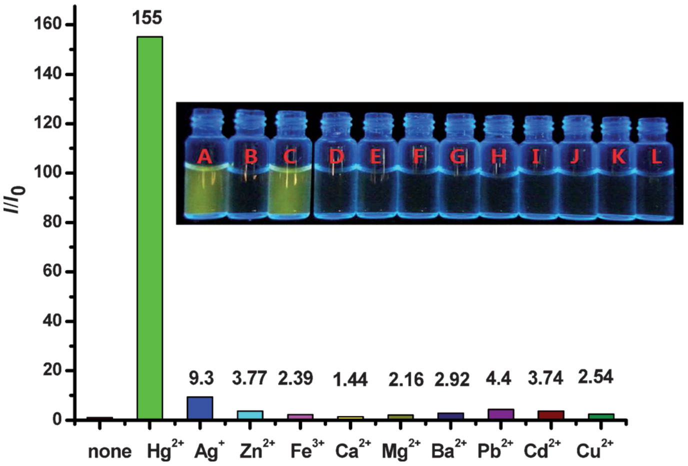

Figure 1. Fluorescent intensity ratio (I/I_0) of **1** in distilled water at 293 K in the presence of 10.0 equiv of different metal ions. Inset: Photograph of **1** in the presence of different metal ions. A: **5** (1.0×10^{-5} M); B: **1** (1.0×10^{-5} M); C–L: **1**+Hg^{2+}, Ag^{+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} (1.0×10^{-4} M).

accompanied by the transformation of weak fluorescence (colorless, inset of Figure 1) to strong fluorescence (yellow–green). However, the addition of other metal ions, namely, Ag^{+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+}, did not lead to a clear enhancement of the fluorescent intensity of **1**. The reaction time profile of **1** (1×10^{-5} M) towards Hg^{2+} (1×10^{-5} M) in water was examined in Figure S3 (in the Supporting Information), and the time for the reaction time curve to reach a stable plateau was 3 min after Hg^{2+} ion addition.

To obtain more insight into the fluorescent properties, the titration reaction curve of **1** toward the Hg^{2+} ion was investigated as shown in Figure 2. The fluorescent intensity of sensor **1** increased in response to the increase in the concentration of the added Hg^{2+} ion in water, and the titration reaction curve showed a steady increase until a plateau was reached when 1 equiv of Hg^{2+} ion was added.

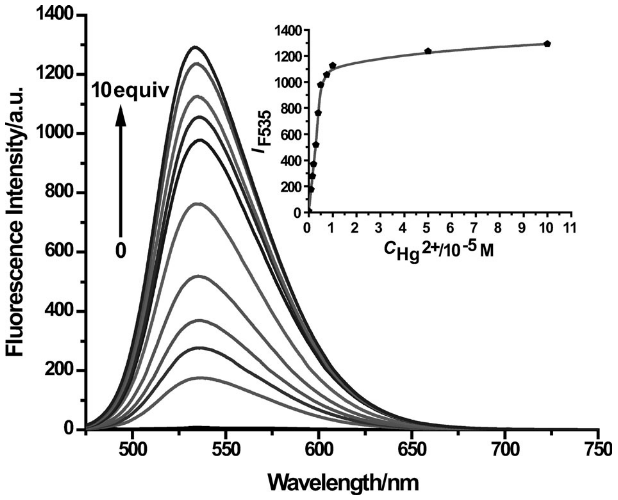

Figure 2. Fluorescence titration of **1** (1×10^{-5} M) with $Hg(ClO_4)_2$ in distilled water at 293 K. [Hg^{2+}]: 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.75, 1.0, 5.0, 10×10^{-5} M. The excitation wavelength was 416 nm and the emission intensity was measured at 535 nm.

To investigate the utility of **1** as an ion-selective fluorescent chemosensor for Hg^{2+} ions, cross-contamination experiments were conducted in the presence of Hg^{2+} at a concentration of 1×10^{-5} M mixed with other metal ions, such as Ag^{+}, Zn^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+}, at a concentration of 1×10^{-4} M. As indicated in Figure 3, it clearly suggested that the selectivity of **1** towards Hg^{2+} was almost completely unaffected by other competitive ions (10 equiv).

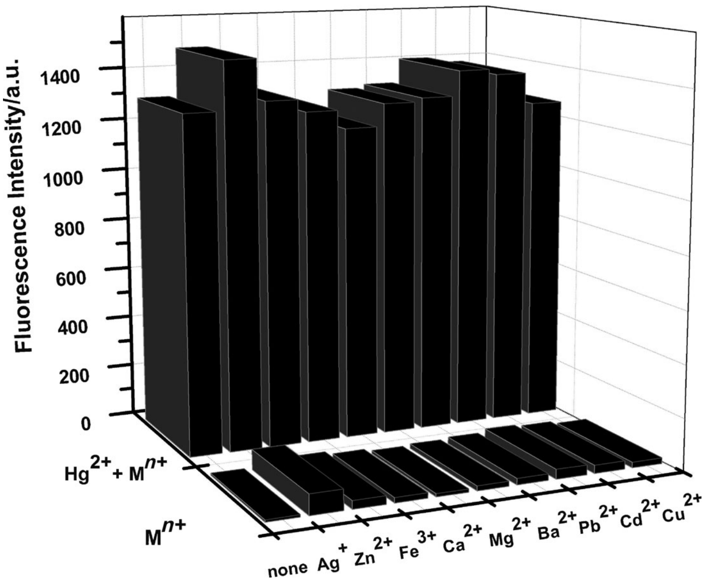

Figure 3. Results of the competition experiments between Hg^{2+} and selected metal ions in distilled water at 293 K; the concentration of Hg^{2+} was 1×10^{-5} M and that of each competing metal ions was 1×10^{-4} M; the excitation wavelength was 416 nm and the emission intensity was measured at 535 nm.

To examine the sensitivity of **1** towards Hg^{2+}, its detection limit was evaluated. As shown in Figure 4, the fluorescence titration profile of **1** (10^{-6} M) with Hg^{2+} demonstrated that Hg^{2+} could be detected at least down to 3×10^{-8} M, and the fluorescent intensity of **1** increased linearly with the concentration of Hg^{2+} $(0–1.00)\times10^{-6}$ M ($R^2=0.9951$).

As depicted in the partial ^{1}H NMR spectra in Figure 5a (sensor **1**), b (**1**+Hg^{2+}), and c (**5**, for comparison), when **1** was treated with 1.1 equiv of Hg^{2+}, the resonance of the aldehyde proton appeared similar to that in Figure 5c. Based upon the above ^{1}H NMR data, the proposed sensing mechanism was described as depicted in Figure 5d.

In summary, we have developed a new water-soluble "turn on" chemosensor with high selectivity and sensitivity for recognition of Hg^{2+} ion over other HTM ions in pure water. The sensor was designed based upon a unique and irreversible Hg^{2+}-promoted deprotection reaction of the dithioacetal by transforming a weakly fluorescent precursor

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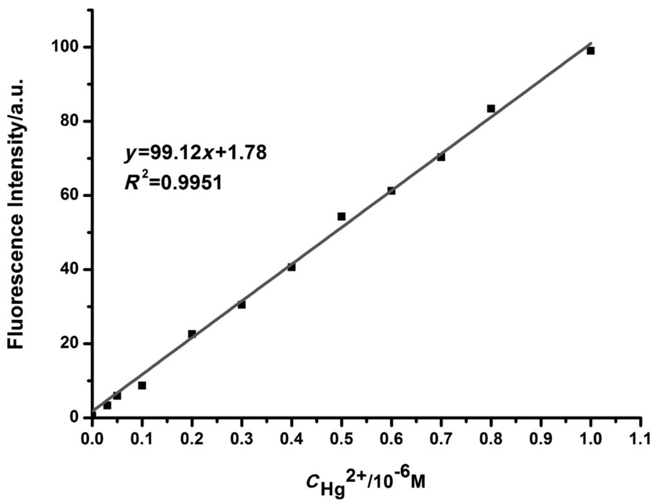

Figure 4. Fluorescence titration of **1** (1×10^{-6} M) with $Hg(ClO_4)_2$ in distilled water at 293 K. [Hg^{2+}]: 0, 0.03, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0×10^{-6} M.

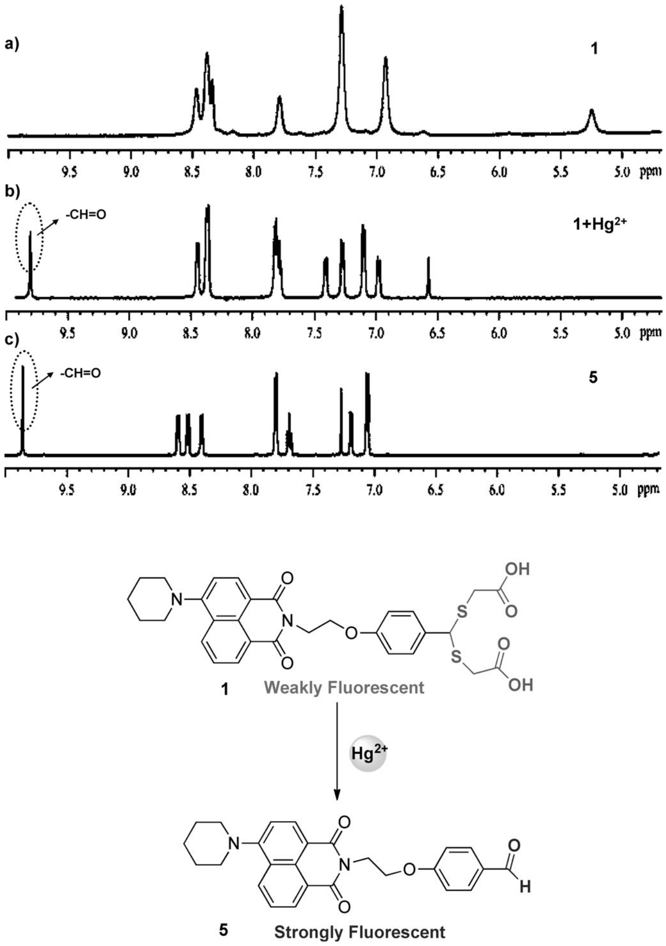

Figure 5. Partial ^{1}H NMR spectra of **1** (a), complex (**1**+1.1 equiv of Hg^{2+} in [D_6]DMSO (b), **5** in $CDCl_3$ (c), and the sensing mechanism of **1** with Hg^{2+} ion (d).

(colorless) to a highly fluorescent aldehyde product (yellow–green) with a 155-fold increase in fluorescent intensity. Moreover, **1** could behave as a fluorescent sensor over a wide range of pH values for the detection of Hg^{2+}. Based on its good water solubility, and highly selective and sensitive response to Hg^{2+}, this probe could be used to determine Hg^{2+} ion concentrations in aqueous environments. These results will encourage us to design more chemosensors for other specific ions in water.

Acknowledgements

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Keywords: dithioacetals · fluorescence · mercury · sensors

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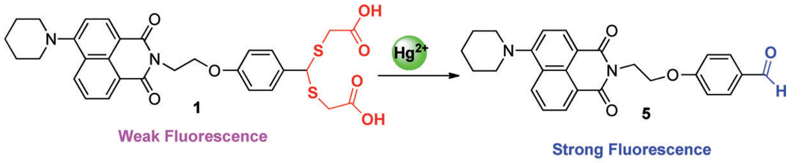
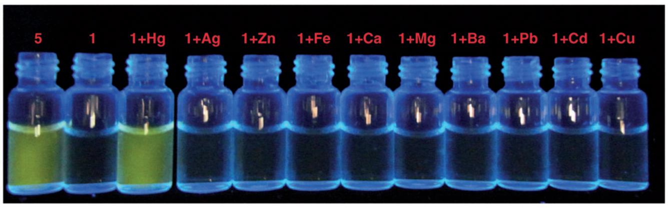
Fluorescence

*H. Dai, Y. Yan, Y. Guo, L. Fan, Z. Che, H. Xu** .... ▮▮▮▮–▮▮▮▮

A Selective and Sensitive "Turn-on" Fluorescent Chemosensor for Recognition of Hg^{2+} Ion in Water





Based upon highly selective and irreversible Hg^{2+}-promoted deprotection of the dithioacetal reaction, a new water-soluble "turn on" fluorescent chemosensor **1** was prepared and exhibited high selectivity and sensitivity towards the Hg^{2+} ion over other heavy and transition-metal ions in pure water by transforming a weakly fluorescent precursor (colorless) to a highly fluorescent aldehyde (yellow–green; see figure) with a 155-fold increase in fluorescent intensity.

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