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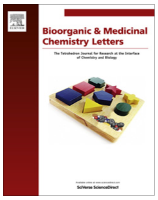

Phenanthroimidazole-based thiobenzamide as an effective sensor for highly selective detection of mercury(II)

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A B S T R A C T

Based on highly selective and irreversible Hg^{2+}-promoted desulfurization reaction, a new and simple phenanthroimidazole-type sensor was prepared and exhibited high selectivity towards Hg^{2+} ion over other metal ions, accompanied by transformation of a weakly fluorescent thioamide moiety (colorless) to a highly fluorescent amide one (blue), with a 136-fold increase in fluorescent intensity in aqueous solution with a pH span 2.57–9.12.

Mercury is considered to be a highly toxic and dangerous element for human beings because it can be bioaccumulated through the food chain and cause great damage to the nervous system even at very low concentrations.[1,2] Therefore, it is still very desirable to explore selective and sensitive chemosensors for detection of Hg^{2+} ion over other heavy and transition metal (HTM) ions. Recently, various sensors for recognition of Hg^{2+} ion over other HTM ions have been developed with good performance.[3] Additionally, many attractive probes for detection of Hg^{2+} ion based on the specific mercury-promoted desulfurization reaction have also been reported.[4] In recent years, some excellent fluorescent probes based on phenanthroimidazole subunit were prepared and showed the selective recognition of Mg^{2+},[5] Cu^{2+},[6] ClO^-,[7] cysteine and homocysteine,[8] Cu^{2+} and Cd^{2+},[9] and H_2S,[10] respectively.

As part of our ongoing research program in developing selective and sensitive chemosensors for detection of Hg^{2+} ion,[11] in this Letter we have prepared a new and simple phenanthroimidazole-type sensor **1** based on Hg^{2+}-induced transformation of the thioamide moiety to the amide one (Scheme 1). To the best of our knowledge, this is the first desulfurized probe based on a phenanthroimidazole moiety for recognition of Hg^{2+} ion in aqueous solution.

As shown in Scheme 1 and 9,10-phenanthrenequinone firstly reacted with *N*-(*n*)butyl-4-formylbenzamide to give compound **2** in a 76% yield. Then sensor **1** was obtained in a 73% yield by reaction of **2** with Lawesson's reagent.[12] The chemical structures of compounds **1** and **2** were well characterized by IR spectrometry, ^1H and ^{13}C NMR spectroscopy, and high-resolution mass spectrometry (HRMS) (see Supplementary data).

As described in Figure 1, the fluorescent intensity of **1** was a constant value when pH value was between 2.57 and 10.96. Figure 2 showed the fluorescent intensity ratio (I/I_0) of sensor **1** in the presence of Ca^{2+}, Ni^{2+}, Cs^+, Ba^{2+}, Fe^{3+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Ag^+, K^+, Co^{2+}, Zn^{2+}, and Hg^{2+} ions in CH_3CN–HEPES (0.02 M, pH = 7.0) (7/3, v/v), respectively. Meanwhile, the fluorescent intensity of compound **2** was also tested and used as the control. The fluorescent behavior of sensor **1** was very weak because its thioamide group might be a strong intramolecular quenching entity.[13] It is noteworthy that only when Hg^{2+} ion was added to the solution of **1**, a remarkably increased 136-fold of the fluorescent intensity was observed at 445 nm, accompanied with transforming a weak fluorescence (colorless, inset of Fig. 1) to a high fluorescence (blue). Whereas the addition of other metal ions such as Ca^{2+}, Ni^{2+}, Cs^+, Ba^{2+}, Fe^{3+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Ag^+, K^+, Co^{2+}, and Zn^{2+}, did not lead to a significant changes of the fluorescent intensity. The signaling mechanism is caused by the selective desulfurization of probe **1**–**2** by reaction with Hg^{2+} ion (Scheme 2), and the sulfur atom of **1** is converted to HgS with Hg^{2+} ion.[14] Evidence for the proposed transformation was supported by ^1H NMR spectra (see Supplementary data). Moreover, the reaction product **2** was also isolated from the mixture after **1** reacting with Hg^{2+} ion. As depicted in the partial ^1H NMR spectra of Figure 3, the NH (amide) proton was obviously shifted from 10.38 (**1**, (**a**)) to 8.59–8.61 ppm (**2**, (**c**), protons of benzene ring and NH were overlapped), and the ^1H NMR spectra of (**c**) was the same as that of (**b**).

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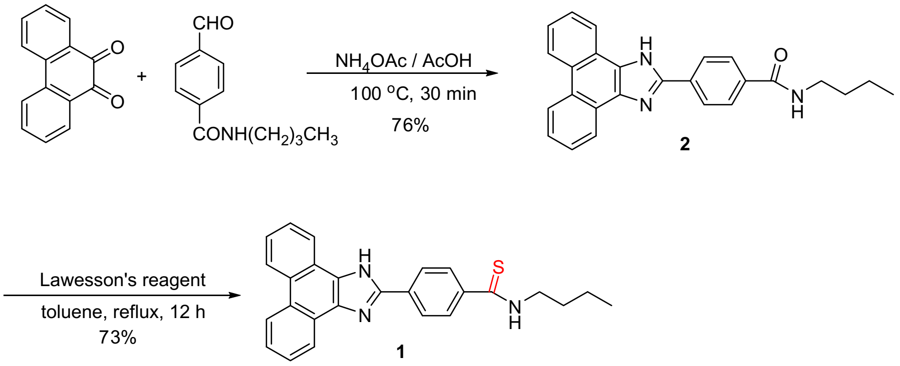

Scheme 1. Synthetic approach for probe **1**.

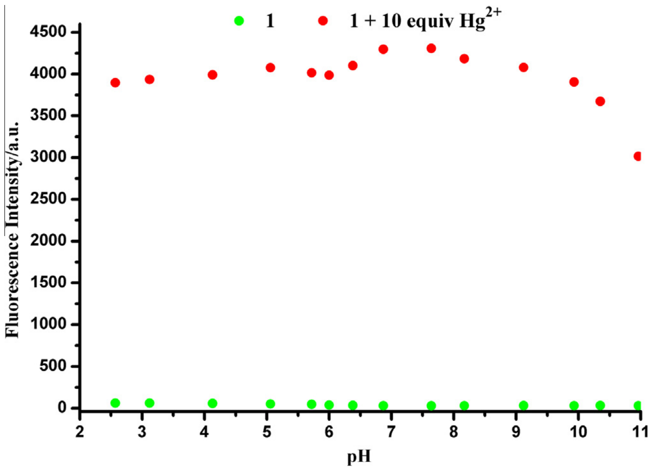

Figure 1. Fluorescence characteristics of **1** (1.0×10^{-6} M) and **1** + Hg^{2+} at 298 K in CH_3CN–H_2O (7/3, v/v) of different pH (pH adjusted by $HClO_4$ or $N^+(CH_3)_4OH^-$); λ_{ex} = 364 nm and the emission intensity was measured at 445 nm.

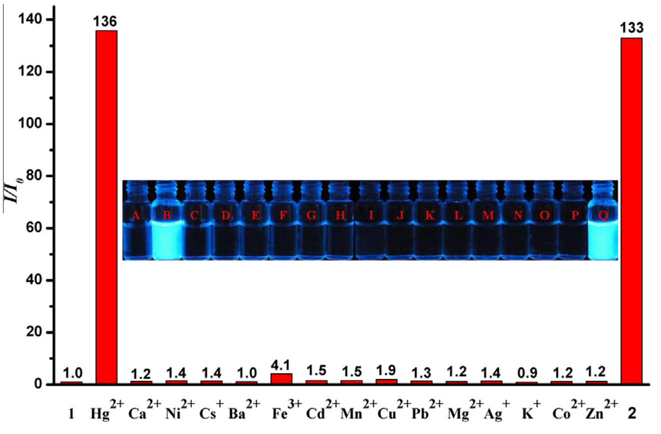

Figure 2. Fluorescent intensity ratio (I/I_0) of **1** (1.0×10^{-6} M) in CH_3CN–HEPES (0.02 M, pH = 7.0) (7/3, v/v) at 298 K in the presence of 10.0 equiv of different metal ions. Inset: photograph of **1** in the presence of different metal ions. **A**: **1** (1.0×10^{-6} M); **Q**: **2** (1.0×10^{-6} M); **B**–**P**: **1**+Hg^{2+}, Ca^{2+}, Ni^{2+}, Cs^+, Ba^{2+}, Fe^{3+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Ag^+, K^+, Co^{2+}, and Zn^{2+} (1.0×10^{-5} M); λ_{ex} = 364 nm and the emission intensity was measured at 445 nm.

The fluorescent intensity of **1** + Hg^{2+} was almost a constant value when pH value was between 2.57 and 9.12 (Fig. 1). The titration reaction curve of probe **1** toward Hg^{2+} ion was investigated as shown in Figure 4. The fluorescent intensity of **1** increased in response to the increases in the concentration of the added Hg^{2+} ion, and the titration reaction curve showed a steady increase until a plateau was reached when 7.5 equiv of Hg^{2+} ion was added.

To investigate the utility of **1** as an ion-selective fluorescent sensor for Hg^{2+} ion, as shown in Figure 5, the cross-contamination experiments were conducted in the presence of Hg^{2+} at 1×10^{-5} M mixed with other metal ions such as Ca^{2+}, Ni^{2+}, Cs^+, Ba^{2+}, Fe^{3+}, Cd^{2+}, Mn^{2+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Ag^+, K^+, Co^{2+}, and Zn^{2+} at 1×10^{-4} M, respectively. It demonstrated that the selectivity of **1** towards Hg^{2+} ion was almost not affected by other competitive ions.

In conclusion, a new, simple, and highly Hg^{2+}-selective 'turn on' phenanthroimidazole-type sensor **1** was prepared. Based on Hg^{2+}-induced transformation of a weakly fluorescent thioamide moiety (colorless) to a highly fluorescent amide one (blue), probe **1** exhibited high selectivity towards Hg^{2+} over other metal ions with a 136-fold increase in fluorescent intensity in aqueous solution over a wide-range pH value (2.57–9.12). The Hg^{2+}-promoted selective desulfurization reaction was demonstrated by the ^1H NMR spectroscopy. This study may open up new opportunity for development of phenanthroimidazole-type sensor for selective detection of Hg^{2+} ion in aqueous solution.

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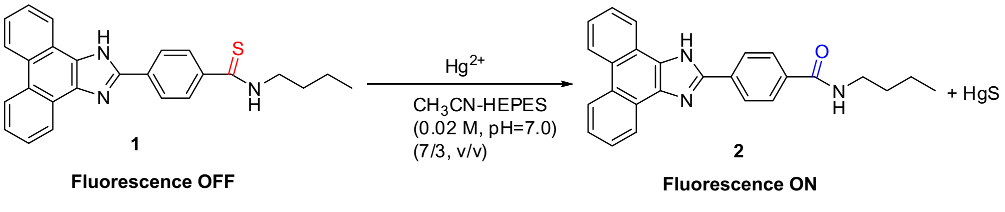
Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bmcl.2013.03.083.



Scheme 2. Selective desulfurization of probe **1**–**2** by reaction with Hg^{2+} ion.

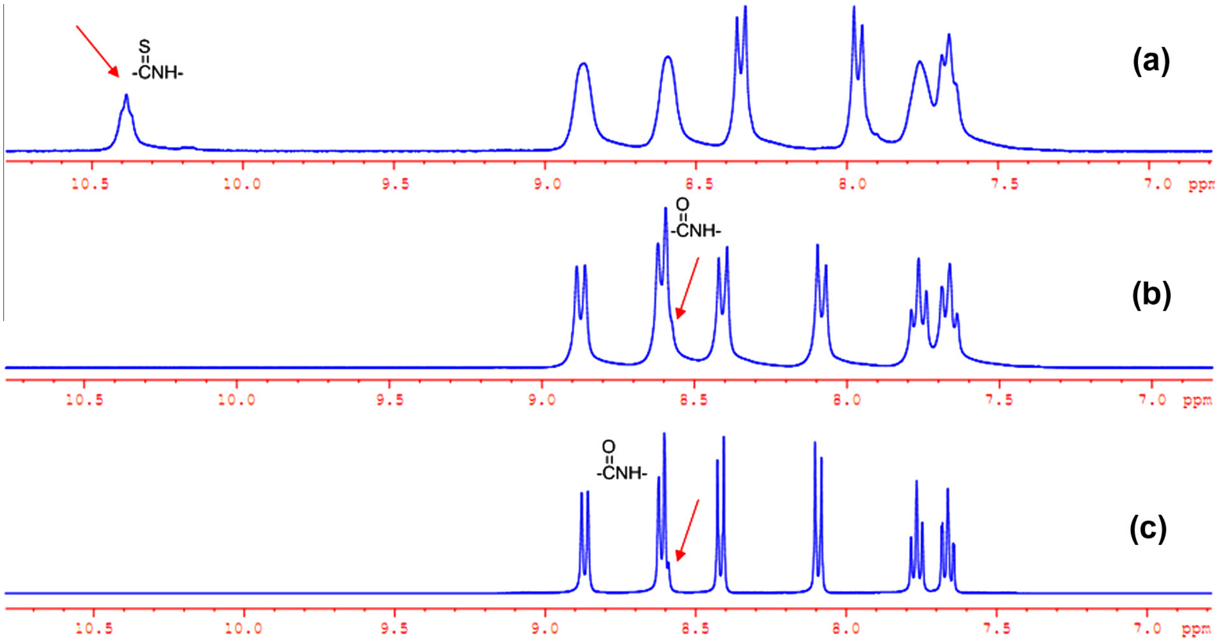


Figure 3. Partial ^{1}H NMR spectra of **1** (a), **2** (b), and isolated compound **2** from **1** reacting with Hg^{2+} ion (c).

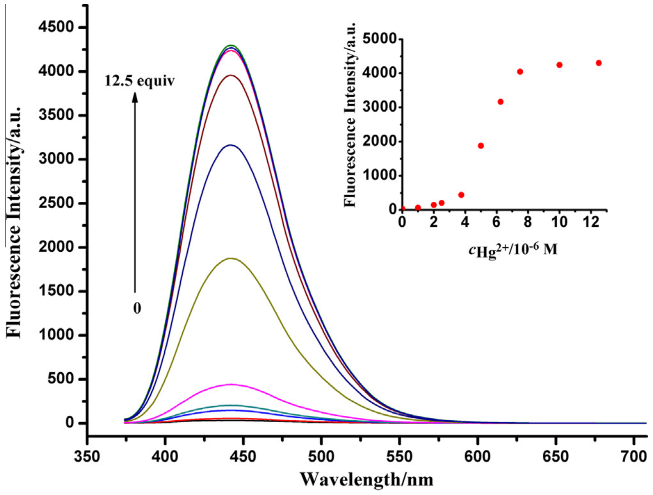


Figure 4. Fluorescence titration of **1** (1.0×10^{-6} M) with Hg^{2+} in CH_3CN–HEPES (0.02 M, pH = 7.0) (7/3, v/v) at 298 K; [Hg^{2+}]: 0, 1, 2, 2.5, 3.57, 5, 6.25, 7.5, 10, 12.5 × 10^{-6} M; λ_{ex} = 364 nm and the emission intensity was measured at 445 nm.

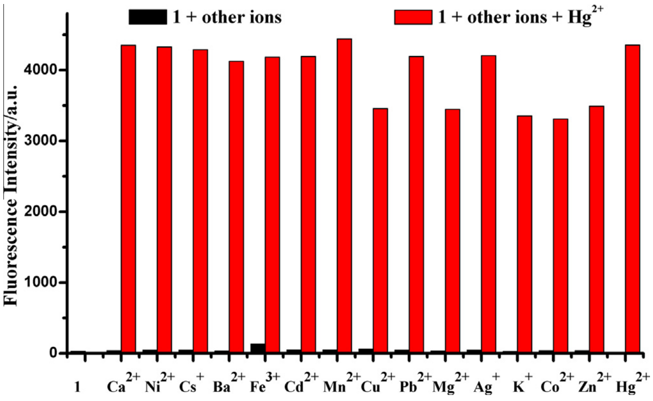


Figure 5. Results of the competition experiments of probe **1** (1×10^{-6} M) between Hg^{2+} (1×10^{-5} M) and selected metal ions (1×10^{-4} M) in CH_3CN–HEPES (0.02 M, pH = 7.0) (7/3, v/v) at 298 K; λ_{ex} = 364 nm and the emission intensity was measured at 445 nm.

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