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Highly selective recognition of mercury ions through the "naked-eye"

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ABSTRACT

A new sensor 2-((E)-(3-(1H-imidazol-1-yl)propylimino)methyl)-5-(diethylamino)phenol (**1**) based on the combination of diethylaminosalicylaldehyde and imidazole groups was designed and synthesized as a Hg^{2+} selective colorimetric chemosensor. Upon treatment of **1** with mercury ions, sensor **1** showed a color-change from colorless to yellow in a mixture of H_2O/DMF (5:95), while many other ions such as Al^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Cr^{3+}, Ag^{+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mn^{2+} and Pb^{2+} had no influence. Notably, this chemosensor could distinguish clearly Hg^{2+} from Cu^{2+}, Ag^{+}, Fe^{2+} and Pb^{2+}. The underlying signaling mechanism is a ligand-to-metal charge-transfer (LMCT) process. Compound **1** showed the serial formation of the 1:1 and the 1:2 complexation between **1** and Hg^{2+}. This two-step binding mode was proposed based on the UV titration, ^{1}H NMR titration and ESI-mass studies.

Heavy and transition metal ions (HTM) such as Hg^{2+}, Cu^{2+}, Pb^{2+} and Cd^{2+} are well known for their high toxicity toward the environment and human health [1,2]. Among them, mercury is one of the most toxic metallic pollutants and can exist in ionic (Hg^{2+}), elemental (Hg^0) and organic forms (CH_3Hg^+) [3]. Methylmercury (CH_3Hg^+) enters the food chain and finally accumulates in the human body [4,5]. The so called "Minamata Disease" is a harsh consequence of methylmercury [6]. Mercury is the most lethal for living organisms because it can easily penetrate through the skin and respiratory cell membranes, leading to DNA damage, difficulty in thyroid and adrenal hormone system, mitosis impairment, and permanent damage to the central nervous system [7–12]. Considering these issues, the development of suitable methodologies for Hg^{2+} ion detection is important for environmental protection and human health.

Various techniques such as atomic absorption/emission spectroscopy [13,14], gas/liquid chromatography–inductively coupled plasma mass spectroscopy [15,16] and so on have been used to detect the Hg^{2+} ions. However, these methods usually have restrictions of sophisticated instruments, complicated procedures, expensive costs, or low sensitivity and selectivity. For these reasons, chromogenic chemosensors are especially attractive because they allow naked-eye detection of the color change without any use of spectroscopic instruments [17–22]. In addition, these colorimetric sensors ideally have the advantages of low cost, easy synthesis and storage, and more tolerance toward different experimental conditions [23,24]. Therefore, it is of considerable importance to develop probes with colorimetric sensing ability for detection of Hg^{2+}. However, some of the reported chemosensors have difficulty in distinguishing Hg^{2+} from Cu^{2+}, Ag^{+}, Fe^{2+} and Pb^{2+} due to their similar chemical behavior to Hg^{2+} [25–29]. Thus, many efforts have been made to develop the chemosensors for the selective and efficient detection that can distinguish Hg^{2+} from Cu^{2+}, Ag^{+}, Fe^{2+} and Pb^{2+}.

Recently, imidazole moiety was often chosen as a metal ion receptor [30,31], and diethylaminosalicyl-imine is a well-known chromophore and has been frequently used for the colorimetric chemosensor [32,33]. Therefore, we planned to incorporate the imidazole moiety into diethylaminosalicylaldehyde moiety to develop a novel chemosensor **1**, 2-((E)-(3-(1H-imidazol-1-yl)propylimino)methyl)-5-(diethylamino)phenol.

Herein, we report a new chemosensor **1** that can sense selectively Hg^{2+} in aqueous samples containing heavy and transition metal ions such as Cu^{2+}, Ag^{+}, Fe^{2+} and Pb^{2+} by means of a colorimetric monitoring.

The chemosensor **1** was synthesized by the condensation reaction of 4-diethylaminosalicylaldehyde with 1-(3-aminopropyl)imidazole in ethanol at room temperature (Scheme 1), and characterized by ^{1}H and ^{13}C NMR, ESI-mass spectrometry and elemental analysis.

The absorption response of **1** toward the nitrate or perchlorate salts of Al^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Cr^{3+}, Hg^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mn^{2+} and Pb^{2+} was carried out in a mixture of water and dimethylformamide (DMF) (5:95, v/v) (Fig. 1(a)). Upon the addition of 16 equiv of each metal ion to **1**, only Hg^{2+} induced a noticeable spectral change while other metal ions showed either no or some

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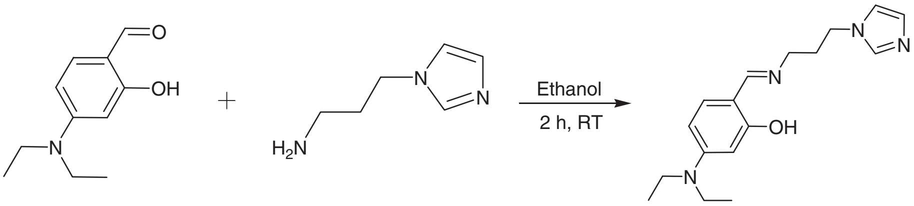

Scheme 1. Synthesis of **1**.

change in the absorption spectra relative to the free receptor **1**. For example, Al^{3+}, Cu^{2+} and Zn^{2+} showed to some extent changes of the absorption spectra in comparison with **1**. However, only Hg^{2+} produced an instant color change from colorless to yellow (Fig. 1(b)).

To explore the interaction between **1** and Hg^{2+}, UV–vis absorption spectral variation of **1** was investigated during titration with different concentrations of Hg^{2+} (Fig. 2). Once one looks into Fig. 2(a), there is the two-step change of the absorption bands. The first change is that a gradual decrease in the absorption at 345 nm was observed and a peak at 385 nm increased with the isosbestic points at 298 and 357 nm (Fig. 2(b)), implying that only one product was generated from **1** upon binding to Hg^{2+}. In the second change, a distinctly different spectral pattern was observed with an increase in absorption intensity at 448 nm (Fig. 2(c)). This change was associated with a new isosbestic point at 317 nm.

ESI-mass spectrometry analysis hinted the binding ratio of **1** and Hg^{2+} (Fig. 3). When Hg^{2+} ions were introduced to a **1** solution, a peak of 1:1 compound appeared at m/z 563.9, which was assigned to single-charged complex $[\mathbf{1} + Hg^{2+} + NO_3^-]^+$ (calcd. 564.15). In addition, a 1:2 compound appeared at m/z 409.7, which was assigned to double-charged complex $[\mathbf{1} + 2Hg^{2+} + 3H_2O + NO_3^-]^{2+}$ (calcd. 409.58). Binding constants for the 1:1 ($\mathbf{1}$–Hg^{2+}) and 1:2 ($\mathbf{1}$–$2Hg^{2+}$) complex formations ($K_1 = 3.13\ (\pm 0.03) \times 10^2\ M^{-1}$ and $K_2 = 2.33\ (\pm 0.02) \times 10^2\ M^{-1}$) were evaluated from the plots of the changes in absorbance at 385 and 448 nm, respectively (Fig. S1).

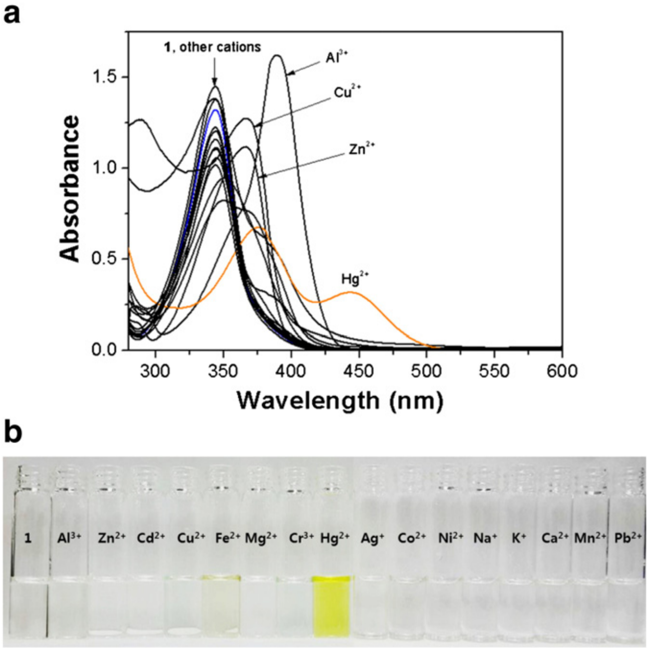

Fig. 1. (a) Absorption spectra changes of **1** (40 μM) in the presence of 16 equiv of different metal ions in a mixture of water and DMF (5:95, v/v). (b) The color changes of **1** (40 μM) upon addition of various metal ions (16 equiv).

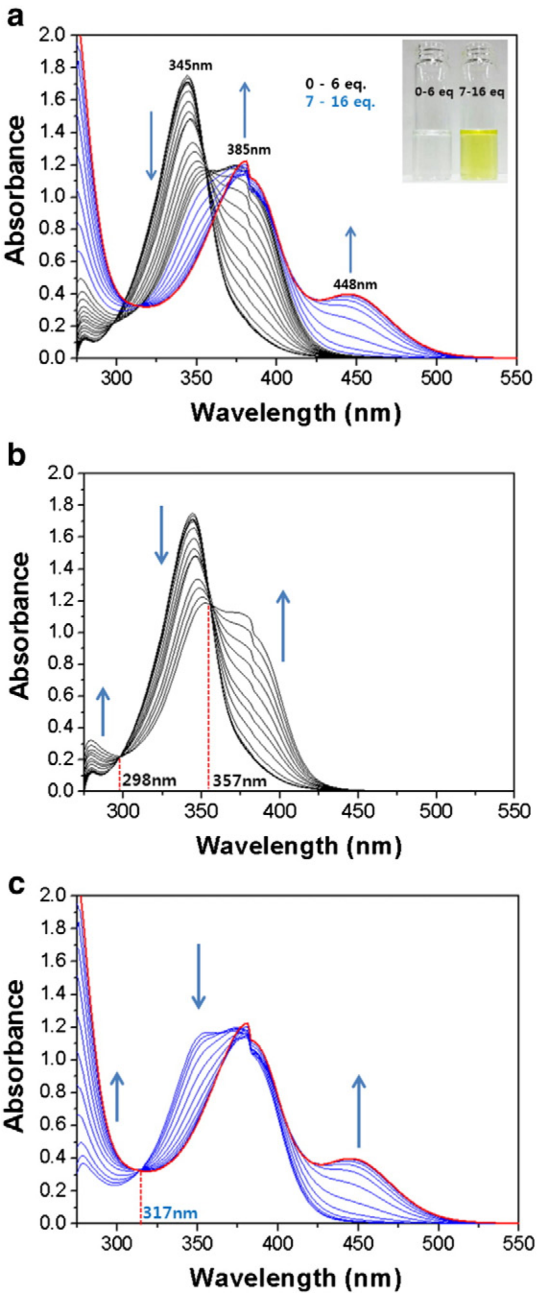

Fig. 2. (a) Absorption spectra changes of **1** (40 μM) in the presence of different concentrations of Hg^{2+} ions in a mixture of water and DMF (5:95, v/v). (b) Absorption spectra changes of **1** in the presence of 0–6.0 equiv of Hg^{2+}. (c) Absorption spectra changes of **1** in the presence of 7.0–16.0 equiv of Hg^{2+}.