

A new fluorescent chemosensor for Hg²⁺ in aqueous solution

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ABSTRACT: We prepared an aminothiurea-derived Schiff base (DA) as a fluorescent chemosensor for Hg²⁺ ions. Addition of 1 equiv of Hg²⁺ ions to the aqueous solution of DA gave rise to an obvious fluorescence enhancement and the subsequent addition of more Hg²⁺ induced gradual fluorescence quenching. Other competing ions, including Pb²⁺, Cd²⁺, Cr³⁺, Zn²⁺, Fe²⁺, Co³⁺, Ni²⁺, Ca²⁺, Mg²⁺, K⁺ and Na⁺, did not induce any distinct fluorescence changes, indicating that DA can selectively detect Hg²⁺ ions in aqueous solution. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information can be found in the online version of this article.

Keywords: Schiff base; fluorescent chemosensor; Hg²⁺ determination; aqueous solution

Introduction

Heavy metals are of great concern not only among the scientific community, especially chemists, biologists and environmentalists, but also increasingly among the general population who are aware of some of the dangers associated with them. Among them, mercury is one of the most hazardous and ubiquitous pollutants released through natural events or human activities. (1–3). Some microorganisms produce methyl mercury, a potent neurotoxin, from other forms of mercury that poses serious health problems by damaging central nervous and endocrine systems, leading to many cognitive and motion disorders (4). This is due to its very high permeability through the skin, respiratory and gastrointestinal systems of the human body. The multiple pathways of spreading mercury through air, food, and water is a serious concern because it persists in the environment and subsequently bioaccumulates through the food chain (5,6). Concerns over toxic exposure to mercury provide motivation to explore new methods for monitoring Hg²⁺ ions from biological and environment samples. Several methods, including atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry, electrochemical sensing and the use of piezoelectric quartz crystals make it possible to detect low concentrations of Hg²⁺ ions (7–10). However, these methods require expensive equipment and involve time-consuming and laborious procedures that can only be carried out by trained professionals.

Alternatively, analytical techniques based on fluorescence detection are very popular because they are easy to perform and inexpensive and fluorescence measurements are usually very sensitive (parts per billion/trillion) (11–15). Furthermore, the photophysical properties of a fluorophore can be easily tuned using a range of techniques such as: charge-, electron-, energy-transfer, the influence of the heavy metal ions, as well as the destabilization of non-emissive n-π* excited states (11). Consequently, many studies involving on fluorescent chemosensors have been published (11–13,16–21). However, many of these

systems have shortcomings in practical use such as cross-sensitivity toward other metal ions, short emission wavelengths, narrow pH ranges and delayed response. Accordingly, developing new and practical sensing systems for Hg²⁺ ions remains a challenge. As a part of our continuing interest in the design of fluorescent chemosensors for HTM ions (11,12,22–24), we developed a dimethylaminocinnamaldehyde-aminothiurea derived Schiff base (DA) for the selective detection of Hg²⁺ ions in aqueous solution (Scheme 1).

Experimental

Apparatus

All UV–vis spectra and fluorescence spectra were recorded with an S-3100 spectrophotometer (Scinco Saoul, Korea) and a Hitachi F-4500 fluorescence spectrometer (Hitachi Hi-Tech, Tokyo, Japan), respectively. ¹H NMR spectra were recorded with a Bruker-400 instrument (Bruker BioSpin, Europe) at 400 MHz. Mass spectra were recorded with a Finnigan 4021C MS-spectrometer. X-ray analysis

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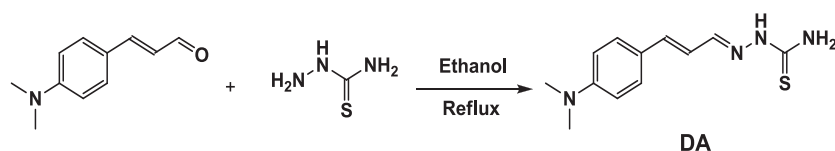
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Scheme 1. Synthesis of chemosensor DA.

was measured on a Rigaku R-Axis Rapid IP diffractometer (TST Trading Service Technology Co., Ltd., Ho Chi Minh City, Vietnam)

Reagents

4-*N,N'*-Dimethylaminocinnamaldehyde and aminothiurea were purchased from Aldrich (Sigma-Aldrich Pte. Ltd. VN R.O., Ho Chi Minh City, Vietnam) and used without further purification. Pb(ClO₄)₂, Cd(ClO₄)₂, HgCl₂, CrCl₃, Zn(ClO₄)₂, FeCl₂, CoCl₃, NiCl₂, Ca(ClO₄)₂, Mg(ClO₄)₂, KCl and NaCl were purchased from Aldrich and used as received. Ethanol for spectral detection was HPLC reagent without fluorescent impurity and H₂O was deionized water. All solvents were analytical grade reagents.

Synthesis of dimethylaminocinnamaldehyde-aminothiurea (DA)

4-*N,N'*-Dimethylamino-cinnamaldehyde (175 mg, 1.0 mmol) and aminothiurea (100 mg, 1.1 mmol) were combined in absolute ethanol (40 mL). The reaction solution was refluxed for 6 h under a N₂ atmosphere and stirred for another 2 h at room temperature until a solid precipitated. The solid was filtrated, washed with ethanol three times and the crude product was purified by recrystallization from absolute ethanol to give 207 mg of dimethylaminocinnamaldehyde-aminothiurea (DA) in 83.0% yield as follows: ¹H NMR (DMSO-d₆); δ 11.23 (s, 1H); 8.03 (s, 1H); 7.86 (d, 1H); 7.47 (s, 1H); 7.38 (d, 2H); 6.70 (d, 1H); 6.63 (d, 2H); 6.59 (s, 1H); 2.96 (s, 6H); FAB-MS (M + H⁺); m/z = 250.1.

General procedure

A 1.0 × 10⁻³ M stock solution of DA was prepared in EtOH and diluted to 1.0 × 10⁻⁵ M in 1:9 EtOH/H₂O solution (v/v). The metal ion stock solutions were dissolved in deionized water to a concentration of 1.0 × 10⁻³ M for the spectral analysis. Each time, a 2-mL solution of DA was added to a quartz cell of 1 cm optical path length and different stock solutions of metal ions were gradually added into the quartz cell using a micropipette. The volume of ionic stock solution added was < 100 μL to prevent any changes in the total volume of the testing solution. Excitation wavelength was at 390 nm and the temperature was ~ 25 °C.

Results and discussion

Dimethylaminocinnamaldehyde with a donor-acceptor structure was selected as a fluorophore and the aminothiurea unit was used as a strong binding receptor for HTM ions. The aminothiurea unit could also increase the water compatibility and biocompatibility (25). As expected, DA gave rise to a strong green emission at 510 nm in aqueous solution with a quantum yield of 0.25 and exhibited good stability under a wide pH range from 5 to 9, covering physiological conditions. The emission could be increased by ~ 30% by adding 1.0 equiv of Hg²⁺ in aqueous solution and gradually quenched by subsequent addition of more

Hg²⁺ ions. However, other competing ions did not lead to any obvious quenching, indicating that DA can be used as a fluorescent chemosensor for selective detection of Hg²⁺ in aqueous solution.

Crystals of DA suitable for X-ray diffraction analysis were grown by the vapour diffusion of *n*-hexane into an ethanol of DA for 2 days (Fig. 1). Crystal data and details of the data collection are provided in Table S1 (Supporting Information). Diffraction data for ligand DA were collected on a Bruker SMART D8 goniometer (Bruker AXS, Beijing Office, Beijing, China) with an APEX CCD detector (Bruker AXS) using MoKα radiation λ = 0.71073 Å (graphite monochromator). The structures were solved by direct methods (SHELXTL) and refined on F² by full matrix least-squares techniques. (26) Hydrogen atoms were included by using a riding model. The selected bond length and angle are shown in Table S2 (Supporting Information). The crystal analysis clearly confirmed the molecular structure of DA (CCDC number: 857562).

DA showed a characteristic absorption wavelength at 380 nm. When 5 equiv of various competing metal ions such as Hg²⁺, Pb²⁺, Cd²⁺, Cr³⁺, Zn²⁺, Fe²⁺, Co³⁺, Ni²⁺, Ca²⁺ and Na⁺ were added to the aqueous solution of DA, no distinct changes in its absorption spectra were observed. However, in the same experimental conditions, their fluorescence spectra showed different changes upon addition of these cations. As shown in Fig. 2, DA exhibited an extensive

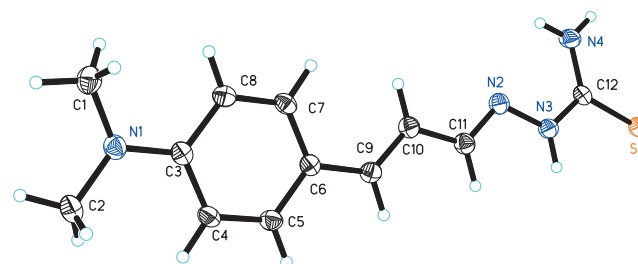


Figure 1. ORTEP diagrams of chemosensor DA with displacement atomic ellipsoids drawn at 30% probability level.

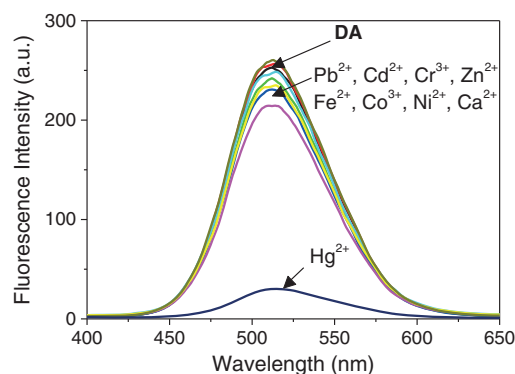


Figure 2. Changes of fluorescence spectra of DA (10 μM) in EtOH/H₂O solution (1/9, v/v) at pH 7 upon addition of different metal ions including Hg²⁺, Pb²⁺, Cd²⁺, Cr³⁺, Zn²⁺, Fe²⁺, Co³⁺, Ni²⁺, Ca²⁺, and Na⁺ ions (50 μM each) with an excitation wavelength at 390 nm.

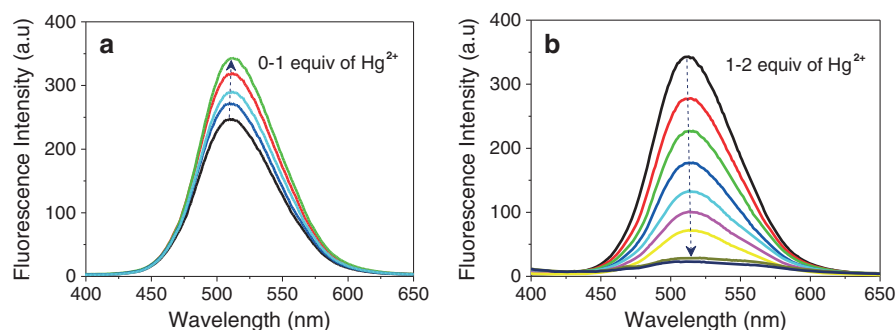
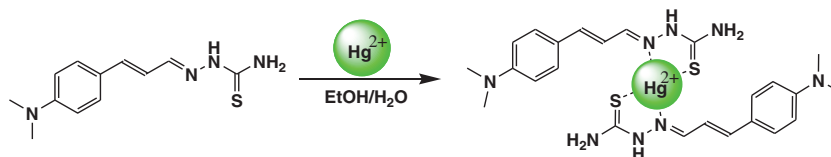


Figure 3. Fluorescent titration spectra of DA (10 μM) in EtOH/H₂O (1/9, v/v) at pH 7 (a) upon addition of 0–1 equiv of Hg²⁺ ions and (b) upon subsequent addition of 1–2 equiv of Hg²⁺ ions with an excitation wavelength at 390 nm.



Scheme 2. The proposed interaction mechanism between DA and Hg²⁺.

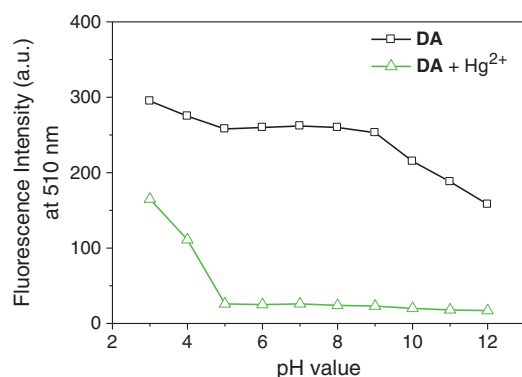


Figure 4. Fluorescence intensity (510 nm) of DA (10 μM) in the absence and presence of 5 equiv of Hg²⁺ ions in EtOH/H₂O solution (1/9, v/v) with different pH conditions.

emission centered at 510 nm and its fluorescence quantum yield was about 0.25 in EtOH/H₂O solution (1/9, v/v). We clearly observed fluorescence quenching (~95%) at 510 nm in the presence of 5 equiv of Hg²⁺ ions. This quenching phenomenon could be due to the electron transfer of DA into the paramagnetic heavy metal ion, which is widely used for fluorescence quenching of HTM ions. (27,28) In contrast, other metal ions including Pb²⁺, Cd²⁺, Cr³⁺, Zn²⁺, Fe²⁺, Co³⁺, Ni²⁺, Ca²⁺ and Na⁺ did not lead to any distinct changes in fluorescence. As a result, DA as a fluorescent chemosensor could selectively detect Hg²⁺ ions in aqueous solution.

Fluorescence titration spectra were performed to further investigate the interactions of DA with Hg²⁺ ions (Fig. 3). As shown in Fig. 3(a), the fluorescence intensity of DA was increased ~30% upon addition of 1.0 equiv of Hg²⁺ ions, probably due to the increased ICT effect when Hg²⁺ was bound with the aminothiourea of DA. Subsequent addition of Hg²⁺ ions (1–2 equiv) to the solution of DA did not result in obviously fluorescence quenching due to the well known heavy metal ion effect

(Fig. 3b). Accordingly, chemosensor DA could be potentially used to determine Hg²⁺ in a simple and efficient way.

To further understand the binding mechanism, MALDI-TOF mass spectrum of DA in the presence of Hg²⁺ was performed in EtOH/H₂O (9/1, v/v) solution. In the presence of Hg²⁺, a peak at m/z 696.783 corresponding to the adduct (2 DA + Hg)⁺ was observed, indicating the formation of a 2:1 complex between chemosensor DA and Hg²⁺. Since one metal cation can bind with two chemosensor molecules, it is proposed that Hg²⁺ could locate at the center of the pseudocavity of two DA molecules and coordinated with two nitrogen atoms of imines and two sulfur atoms of aminothiourea. The possible interaction mechanism between DA and Hg²⁺ is shown in Scheme 2.

For practical application, the proper pH environment of DA for the selective sensing of Hg²⁺ was also evaluated. Fig. 4 shows the fluorescence changes of the free DA (black) and DA + Hg²⁺ (green) at different pH conditions. It is obvious that the optimum pH range using DA to determine Hg²⁺ ions was 5~9 because in this region, DA without Hg²⁺ showed a platform in its fluorescence intensity at 510 nm whereas DA with Hg²⁺ induced the largest fluorescence quenching. In addition, the sensing process was very fast and the complexation interaction of DA with metal cations was completed within 30 seconds, indicating that chemosensor DA also shows a high sensitivity to Hg²⁺ in aqueous solution.

Conclusions

In conclusion, we have developed a new aminothiourea-derived Schiff base (DA) as a fluorescent chemosensor that showed good selectivity toward Hg²⁺ over other competing ions in aqueous solution. The pH range of DA for detection of Hg²⁺ was 5~9 and the sensing process was highly sensitive, which makes it promising as a practical method for determining Hg²⁺ ions.

Supporting information

Supporting information can be found in the online version of this article.

Acknowledgements

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