



A new fluorescent sensor bearing three dansyl fluorophores for highly sensitive and selective detection of mercury(II) ions

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ABSTRACT

A novel fluorometric sensor bearing three dansyl moieties based on tris[2-(2-aminoethylthio)ethyl]amine was prepared by a simple approach using a conventional two-step synthesis. The sensor exhibits highly Hg²⁺-selective ON–OFF fluorescence quenching behavior in aqueous acetonitrile solutions and is shown to discriminate various competing metal ions, particularly Cu²⁺, Ag⁺, and Pb²⁺ as well as Ca²⁺, Cd²⁺, Co²⁺, Fe³⁺, Mn²⁺, Na⁺, Ni²⁺, and Zn²⁺, with a detection limit of 1.15×10^{-7} M or 23 ppb.

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Mercury is one of the most highly toxic and widespread global pollutants which can contaminate the environment and biota with recognized accumulative and persistent characters.¹ Mercury can cause human health problems since it can easily pass through the skin and respiratory and cell membranes, leading to DNA damage, mitosis impairment, and permanent damage to the central nervous system.² In order to detect and monitor mercury concentrations in contaminated sources, fluorescence mercury sensors based on synthetic ligands have received much attention since they provide several advantages over other analytical methods in terms of high sensitivity, high selectivity, fast response times which can be used for real time monitoring, as well as non-destructive detection.

A number of fluorescence chemosensors for Hg²⁺ have been proposed and prepared based on synthetic or commercial ionophores, including cyclen,³ hydroxyquinoline,⁴ azine,⁵ cyclams,⁶ diazatetra-thia crown ethers,⁷ and calixarenes.⁸ However, many Hg²⁺-fluorescence chemosensors possess limitations for commercial and practical uses due to multi-step syntheses, high costs of starting materials or the requirements to operate in organic solvent systems.^{3,7,9} In addition, most of these studies have demonstrated that

nitrogen, oxygen and sulfur atoms present in the ionophores can promote the coordination of Hg²⁺.^{4b,5–7}

Although many fluorescent sensors have been designed for Hg²⁺-sensing, they often suffer from cross-sensitivity toward other ions, particularly potential competitors such as copper (Cu²⁺), silver (Ag⁺), and lead (Pb²⁺) due to their similar chemical behavior to Hg²⁺.^{4–8,10}

In this work, our inspiration was the design and synthesis of a new fluoroionophore with high sensitivity and selectivity for Hg²⁺ over a wide range of competing ions, but with a significantly reduced synthetic effort. Our designed compound, **4** was modified from the structure of tris(2-aminoethyl)amine (tren) by the addition of three sulfur atoms into the platform. Tren is an interesting motif for chelating metal ions and has been utilized for the detection of metal ions such as Cu²⁺, Ag²⁺, and Hg²⁺, due to its symmetrical tripodal structure containing several nitrogen donor atoms.^{8b,c,11} However, some of the reported tren-based Hg²⁺ sensors have serious drawbacks in terms of their utilization in organic solvent systems^{11d} and their lack of Hg²⁺-selectivity toward interfering ions,^{8b} or in the presence of competitive ions.^{8c}

Our molecular design was expected to serve as a Hg²⁺-sensitive and selective fluorescence chemosensor following these considerations: (1) Hg²⁺ can offer a strong and favorable electrostatic interaction with the sulfur atom which can increase the selectivity of the sensor system,^{7,10b,12} (2) the symmetrical tripodal structure of the tren-modified ligand offers good chelation ability for 'soft acid'

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metal ions and can provide a binding site suitable for Hg^{2+} complexation,^{8b,c,11d} and (3) the increase in the number of fluorophore moieties could improve the sensitivity of the sensor system. In this study, a dansyl fluorophore was chosen for the signalling portion of the sensor due to its strong fluorescence, relatively long emission wavelengths in the visible region and very large Stokes shift which can prevent self absorption.¹³

Herein, fluoroionophore **4** was prepared using a conventional two-step synthesis, according to the synthetic steps outlined in Scheme 1. Tris[2-(2-aminoethylthio)ethyl]amine (**3**) was obtained by alkylation of cysteamine hydrochloride (**1**) with tris(2-chloroethyl)amine hydrochloride (**2**).¹⁴ Compound **4** was prepared by substitution of **3** with dansyl chloride.¹⁵ Product **4** is a podant, acyclic host with pendant binding sites,¹⁶ containing three sulfur atoms and four nitrogen atoms which are covalently bound to three dansyl fluorophores.

In this study, the effects of water on the fluorescence emission behavior of **4** in the presence and absence of Hg^{2+} ions were systematically investigated in acetonitrile solutions in order to optimize the conditions for practical applications in environmental and biological samples. The effect of water content on the fluorescence behavior of **4** in acetonitrile solutions is shown in Figure 1.

The fluorescence emission of **4** was found to be strongly dependent on the amount of water in the acetonitrile solution. The results show that when the concentration of water was increased, the fluorescence emission intensity of **4** decreased progressively. It was found that, in the presence of 2.5 equiv of Hg^{2+} , the decrease in the response of **4** was greater in the low water concentration region than that in the high water concentration region. Based on this observation, we focused on the fluorescence behavior of **4** in response to various metal ions in 90:10 acetonitrile/water solution.

To elucidate the quantitative binding affinity of **4**, fluorescence titrations of **4** with Hg^{2+} were performed. The absorption and emission spectra of **4** illustrated a very large Stokes shift, approximately 180 nm (Supplementary data, Fig. S1). Figure 2 shows the fluorescence spectra obtained for **4** in 90:10 acetonitrile/water in the presence and absence of Hg^{2+} ions. The fluorescence behavior of **4** clearly demonstrated the ON–OFF switching mechanism which occurred in response to Hg^{2+} ion complexation. In the absence of Hg^{2+} ions, the fluorescence response was at a maximum and fluorescence ‘turn-off’ took place as the Hg^{2+} concentration increased. More than

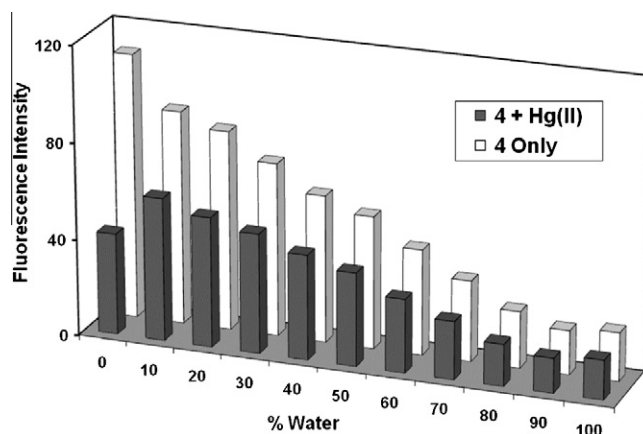


Figure 1. Fluorescence intensity changes (516 nm) of **4** (9.2×10^{-8} M) as a function of water content in aqueous acetonitrile solution in the absence and presence of Hg^{2+} (2.5 equiv), λ_{ex} 336 nm.

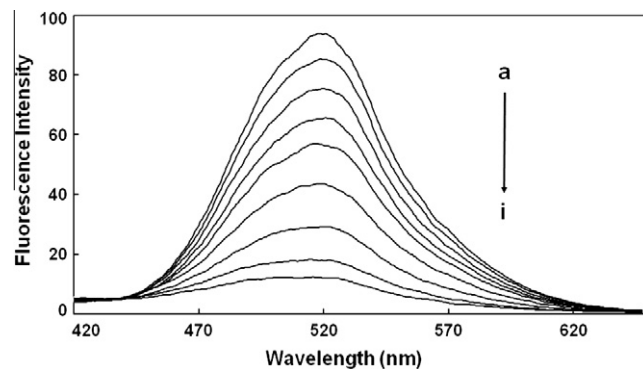
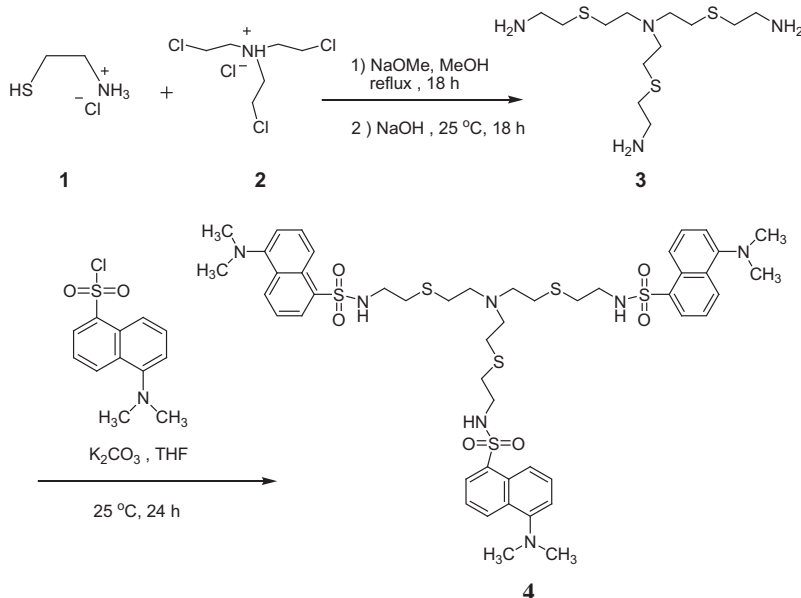


Figure 2. Fluorescence emission spectra (λ_{ex} 336 nm) of **4** (0.12 μM) in 90:10 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ as a function of $[\text{Hg}^{2+}]$. (a) 0 μM , (b) 0.13 μM , (c) 0.17 μM , (d) 0.20 μM , (e) 0.23 μM , (f) 0.30 μM , (g) 0.47 μM , (h) 3.33 μM , (i) 4.16 μM .

85% of the initial fluorescence intensity of **4** was quenched by adding mercury acetate (more than 35 times higher than the



Scheme 1. Preparation of **4**.

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