



N-(3-Imidazolyl)propyl dansylamide as a selective Hg²⁺ sensor in aqueous media through electron transfer



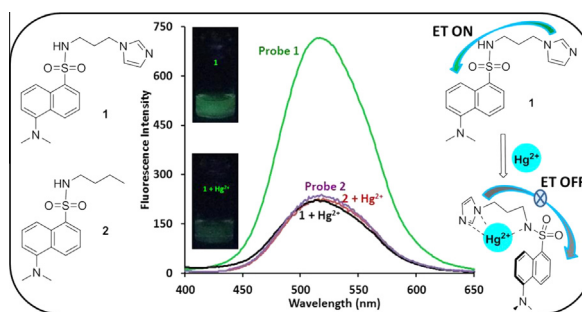
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HIGHLIGHTS

- A highly Hg²⁺ selective chemosensor **1** was synthesized and investigated.
- N-(3-Imidazolyl)propyl dansylamide acting as a selective Hg²⁺ sensor in aqueous media.
- The sensor showed high selectivity for Hg²⁺ even in the presence of other interfering metals (Ag⁺, Cu²⁺, Zn²⁺).
- The detecting mechanism of Hg²⁺ was based on the electron transfer (ET).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 January 2015

Received in revised form 26 February 2015

Accepted 21 March 2015

Available online 28 March 2015

Keywords:

Fluorogenic probe

Dansylamide

Hg²⁺ ion sensor

Quenching

ET

ABSTRACT

N-Imidazolylpropyl dansylamide **1** was synthesized for the sensing of metal ions and found to be selective and sensitive toward Hg²⁺ ions in a PBS–EtOH (1:4, pH = 7.4) solution. The sensing ability of probe **1** was examined by UV–Vis, fluorescence, and ¹H NMR spectroscopy. The sensing of Hg²⁺ exhibited a quenching of emission band at $\lambda_{max} = 515$ nm of probe **1**, which was associated with quenching of green fluorescence emission under 365 nm illumination. Probe **1** showed a good association constant with Hg²⁺ ($K_a = 6.48 \times 10^4 \text{ M}^{-1}$) with a stoichiometry of 1:1 in PBS–EtOH (1:4, pH = 7.4) having the lowest detection limit of 1 μM for Hg²⁺; on the other hand, probe **2**, which has no imidazole moiety, was not able to detect any metal ion. In the case of probe **1**, electrons on the imidazole nitrogen are available for electron transfer (ET), which was responsible for its green emission band that was quenched on addition of Hg²⁺; this clearly indicates that these electrons were used for the formation of a coordinate bond with Hg²⁺ and that ET was switched off.

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Introduction

Metal ions play an essential role in about one third of the known enzymes; in particular, they can modify the electron flow in a substrate or enzyme, thus effectively controlling an enzyme-catalyzed reaction [1–5]. Without the appropriate metal ion, a biochemical reaction catalyzed by a particular metalloenzyme may proceed, if at all, very slowly. Some of the metal ions, such as mercury and lead,

are very toxic to organisms, including human [6–8]. The high affinity of mercury and its derivatives for thiol groups in proteins and enzymes causes dysfunction of cells, leading to health problems. Moreover, it can accumulate in plants, thereby reducing the rate of photosynthesis and transpiration, and in the human body, resulting in a variety of damaging health effects such as prenatal-brain damage, cognitive disorders, and immune system dysfunction, even at relatively low concentrations. Methyl-mercurial species are readily absorbed by the human gastrointestinal (GI) tract; they can cross the blood–brain barrier and target the central nervous system [9–15]. A noteworthy epidemic occurred in Iraq following

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the use of methyl mercury-tainted seed grain for bread. The United States Environmental Protection Agency (EPA) has mandated an upper limit of 2 ppb (10 nM) for Hg^{2+} in drinking water [16]. The health concerns over exposure to mercury have motivated the exploration of selective and efficient methods for the monitoring of mercury in biological and environmental samples. Fluorescent molecules appended with different types of architectures, such as thioether containing crown ethers/acetals [17–19], thioureas [20–23], podands [24–27], amines/amides [28–33], spirolactones [34–35], and heterocycle-based moieties [36–40], are used for Hg^{2+} sensing. Most of these are chemodosimeters, i.e., irreversibly selective Hg^{2+} sensors. Others are chemosensors, i.e., they can reversibly detect Hg^{2+} , albeit non-selectively, showing some interference from either $\text{Cu}^{2+}/\text{Ag}^{+}$ [41–45]. In continuation of our research efforts on metal ion sensing [46–52], in this study we focus on Hg^{2+} sensing in aqueous media.

Dansyl, which is a good fluorescent tag used extensively in research, has a variety of binding sites for metal ion sensing [53–57]. Thus, we synthesized a dansyl-appended amide of 3-aminopropylimidazole/*n*-butylamine, i.e., probes **1** and **2**, respectively, for metal ion sensing in aqueous media. These probes were easily synthesized in a single step by the reaction of dansyl chloride with the corresponding amine, e.g., 3-aminopropylimidazole/*n*-butylamine in good yield.

Results and discussion

Probe **1** was easily synthesized by the reaction of dansyl chloride with 1(3-aminopropyl)-imidazole in dichloromethane in good yield (Scheme 1). The ^1H NMR spectrum of probe **1** in DMSO-d_6 showed three CH_2 propyl-chain groups: two as multiplet at δ 1.67–1.74, 2.69–2.74, and one as a triplet at δ 3.86 for SO_2NHCH_2 ; one singlet at δ 2.82 for six protons of $-\text{N}(\text{CH}_3)_2$; and three imidazole protons as singlet at δ 6.88, 6.97, and 7.53 for the H-b, -c, and, -a protons, respectively. In the ^{13}C NMR spectrum of probe **1**, imidazole C-2 appears at δ 151.83. The high-resolution

mass spectrum (HRMS) of probe **1** clearly showed a molecular ion peak for $[\text{M}+\text{H}]^+$ at $m/z = 359.1543$ (see ESI). Similarly, probe **2** was synthesized in a single step from dansyl chloride and characterized by ^1H and ^{13}C NMR as well as HRMS.

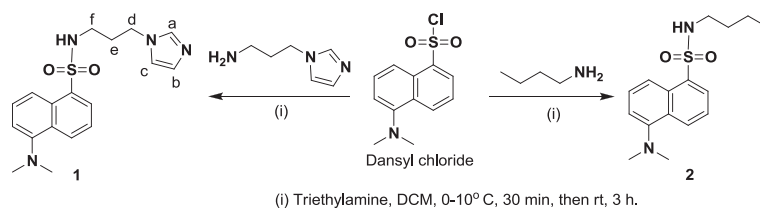
The UV–Vis absorption spectrum of probe **1** (20 μM , PBS–EtOH (1:4), pH = 7.4) exhibited absorption maxima at $\lambda_{\text{max}} = 338$ nm. Upon addition of different metal ions, such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , Ga^{3+} , In^{3+} , and Hg^{2+} , only Hg^{2+} showed a significant red shift ($\lambda_{\text{max}} = 370$ nm); the other metal ions did not show any significant changes in the UV–Vis spectra of probe **1** (Fig. S1 1).

Excitation of probe **1** (3 μM , PBS–EtOH (1:4), pH = 7.4) at 338 nm (λ_{max} in the UV–Vis spectra of probe **1**) resulted in fluorescence emission maxima at 515 nm with high quantum yield ($\Phi = 0.31$). Upon addition of different metal ions, such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , Ga^{3+} , In^{3+} , and Hg^{2+} , only Hg^{2+} caused quenching of the green emission band at $\lambda_{\text{max}} = 515$ nm; other metal ions did not show any significant changes in the fluorescence emission band of probe **1** (Figs. 1 and S1 2).

Upon gradual aliquot additions of $\text{Hg}(\text{ClO}_4)_2$ to probe **1** (3 μM , PBS–EtOH (1:4), pH = 7.4), the emission intensity at 515 nm slowly decreased until saturation. The fitting of these fluorescence titration data shows the formation of a 1:1 complex with a good association constant ($K_a = 6.48 \times 10^4 \text{ M}^{-1}$) (Fig. 2). Probe **1** can detect Hg^{2+} in the range of 1–11 μM : that was determined from the linear relationship between fluorescence emission intensity at $\lambda_{\text{max}} = 515$ nm i.e., I_{515} vs $[\text{Hg}^{2+}]$ having $R = 0.9969$ on titration of probe **1** with Hg^{2+} (Fig. S1 3). The formation of the 1:1 complex of probe **1** with Hg^{2+} ion was also observed from Job's plot (Fig. 3).

In order to check their interference, 10 equiv of other metal ions were added to the solution of **1** + $[\text{Hg}^{2+}]$ (1:1)-complex; it was found that probe **1** could detect Hg^{2+} ions even in the presence of other metal ions (Fig. 4).

In the case of probe **2** (3 μM , PBS–EtOH (1:4), pH = 7.4), excitation at 338 nm (λ_{max} in the UV–Vis spectra of probe **2**) resulted in



Scheme 1. Synthesis of probes **1** and **2**.

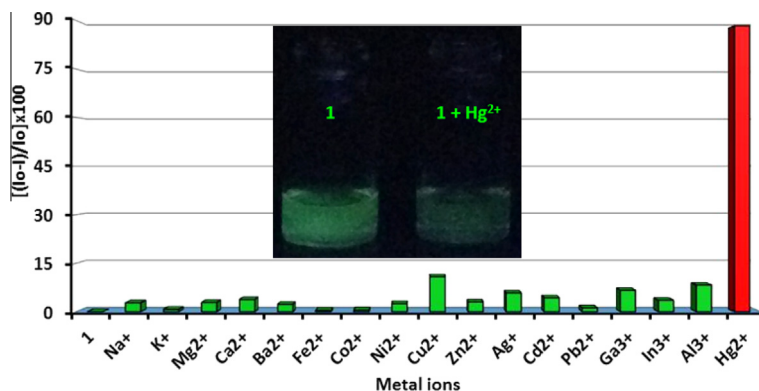


Fig. 1. Fluorescence relative intensity of probe **1** (3 μM , PBS–EtOH (1:4), pH = 7.4) on addition of 10 equiv of different metal ions ($\lambda_{\text{ex}} = 338$ nm, $\lambda_{\text{em}} = 515$ nm); also in the figure, visual fluorescence color change of probe **1** (3 μM) with Hg^{2+} (10 equiv) under illumination at 365 nm is shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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