



Single molecular probe for multiple analyte sensing: Efficient and selective detection of mercury and fluoride ions



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ARTICLE INFO

Article history:

Received 11 December 2014
Received in revised form 6 April 2015
Accepted 6 April 2015
Available online 20 April 2015

Keywords:

Dual sensor
Mercury sensor
Fluoride sensor
Oxime
Colorimetric

ABSTRACT

A molecular probe based on the newly exploited aldoxime chemistry was designed for the dual sensing of Hg^{2+} and F^- ions. Aldoxime-derived azobenzene-containing probe, (E)-4-((E)-(4-(bis(2-hydroxyethyl)amino)phenyl)diazenyl)benzaldehyde oxime (Azo-2), was synthesized and characterized. Azo-2 exhibited excellent sensitivity and selectivity toward mercury ions through a Hg^{2+} ion-catalyzed dehydration reaction at pH = 5 in a DMSO/ H_2O mixture (0.5/9.5, v/v). The probe exhibited a 70 nm red shift in its absorption maximum upon the addition of Hg^{2+} ions, which was accompanied by a change in the color of the solution from pale yellow to dark violet. Interestingly, Azo-2 also exhibited high sensitivity and selectivity toward F^- ions in a DMSO solution, which was achieved by the F^- ion-induced deprotonation of oxime-OH and the subsequent formation of an energetically favored HF_2^- species. A change in the color of the solution from pale yellow to dark red helped detect F^- ion visibly. The oxime-fluoride interaction and HF_2^- formation were confirmed by ^1H and ^{19}F nuclear magnetic resonance (NMR) spectroscopy. The oxime anion generated by F^- in a DMSO solution was reacted with water molecules to return to the original protonated oxime, proving that the entire process is reversible.

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1. Introduction

The development of molecular chemosensors/probes for the efficient and selective detection of physiologically and environmentally important toxic heavy metal ions and anions has attracted considerable attention over past few decades [1–7]. In particular, the recognition and sensing of extremely dangerous and toxic mercury and fluoride ions is an important focus in the field of chemo- and biosensors because of their critical role in biological and environmental systems [8–13]. The bioaccumulation of mercury ions throughout the food chain in the form of dangerous methylmercury species (CH_3HgX) by certain anaerobic bacteria affects the nervous system and leads to severe diseases [14–17]. This also causes a range of symptoms, such as prenatal brain damage, cognitive and motion disorders, vision and hearing loss, and Minamata disease [18–24]. Similarly, fluoride ions play a key role in a wide range of biological, medical and chemical processes, such as dental care, osteoporosis treatment and even in chemical warfare agents [25–29]. On the other hand, extreme levels of fluoride ions in drinking water can cause severe diseases including dental and skeletal fluorosis, osteosarcoma, and can also

lead to nephrotoxic changes and urolithiasis in humans [30–32]. Therefore, it is important to design new molecular probes for the rapid, efficient and selective sensing of mercury and fluoride ions. To date, there have been a large number of conventional chemosensors and chemodesimeters for the detection of mercury ions. These systems are based on specific chemical reactions, heavy atom effect driven fluorescence turn-off and metal coordination [10,11,33–43].

In addition, most popular design strategies employed for the detection of fluoride ions include fluoride-triggered specific chemical reaction and intermolecular hydrogen bonding between the receptor molecules and fluoride ions [9,13]. On the other hand, there is a huge demand for the development of advanced lab-on-molecule or molecular probes that can detect a range of analytes with a distinct output signal response [44,45]. The common approaches to the design of lab-on-molecule or molecular probes are based on the incorporation of more than one functionalities and the utilization of various output channels to detect one analyte per channel [4,46–49]. Innovative molecular designs, such as lab-on-molecules or single channel molecular probes using one binding site/reacting site for the dual detection of cations and anions are rarely reported.

In recent years, aldoxime-based molecular probes have attracted considerable interest because of their easy synthesis and high reactivity toward various compounds under a wide

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range of distinct physical conditions. Most aldoxime-based probes are only known for the selective detection of hypochlorous acid/hypochlorite anions and chemical warfare agents [50–55]. Currently, there have been a few reports of aldoxime-based probes for the detection of mercury and fluoride ions individually or dually [56,57]. Therefore, the development of a one channel molecular probe for the selective detection of mercury and fluoride ions using aldoxime as a reaction site is an attractive and challenging approach.

This paper reports the synthesis of an aldoxime-derived azobenzene-containing single molecular probe, Azo-2, for use as one channel probe for the rapid and selective detection of Hg^{2+} and F^- ions. The high sensitivity and selectivity of Azo-2 for Hg^{2+} ions was achieved by the Hg^{2+} ion-catalyzed dehydration reaction of oxime, resulting in the formation of a strong electron-withdrawing nitrile group. Similarly, the high basic nature of F^- ions was used to detect F^- ions in DMSO by the deprotonation of oxime-OH to form an energetically favored HF_2^- ion.

2. Experimental

2.1. Materials and instrumental methods

N-(2-Hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid (HEPES), nitrobenzaldehyde, N-phenyldiethanolamine, tin chloride (SnCl_2), sodium nitrite, hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$), as well as all metal salts and tetrabutylammonium salts were purchased from Aldrich with the highest purity available and used as received. 4-Aminobenzaldehyde was synthesized using a previous literature procedure [58]. The ^1H , ^{13}C , ^{19}F nuclear magnetic resonance (NMR) spectra of the compounds were collected in CDCl_3 and D_2O on a Bruker Avance 300 and 500 MHz NMR spectrometer. The ultraviolet-visible (UV-vis) absorption spectral and sensing studies were carried out using a Varian Cary 100 UV-vis spectrophotometer.

2.2. Synthesis of (E)-4-((4-(bis(2-hydroxyethyl)amino)phenyl) diazenyl)benzaldehyde Azo-1

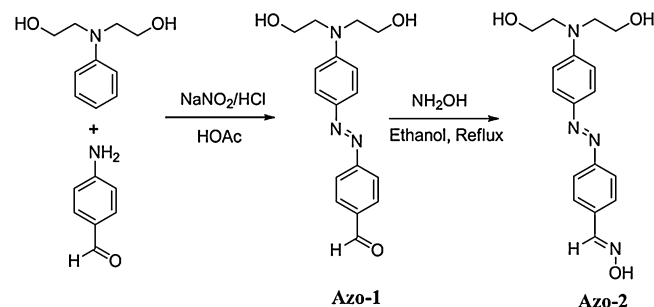
N-Phenyldiethanolamine and 4-aminobenzaldehyde were subjected to a diazotization reaction using a previously reported procedure [58]. ^1H NMR (300 MHz, δ in ppm): 10.09 (1H, s, CHO), 8.03–7.91 (6H, m, Ar-H), 6.83–6.80 (2H, d, Ar-H), 3.98 (2H, t, $\text{CH}_2\text{-OH}$), 3.77 (2H, t, N- CH_2).

2.3. Synthesis of (E)-4-((E)-4-(bis(2-hydroxyethyl)amino) phenyl) diazenyl)benzaldehyde oxime Azo-2

Azo-1 (1 mmol) and hydroxylamine hydrochloride (2.5 mmol) were heated under reflux in dry ethanol at 60°C for 12 h. The solvent was removed under vacuum condition to obtain the orange red solid product. The final product was further purified by column chromatography. ^1H NMR (300 MHz, δ in ppm): 11.41 (1H, s, N-OH), 8.20–6.84 (8H, m, Ar-H), 4.86 (1H, s, Ar-CH=N), 3.61–3.41 (8H, m, aliphatic H).

2.4. Sensing studies

A 3.5 mM stock solution of Azo-2 was prepared in a DMSO solution. Solutions (100 mM) of the metal ions Cu^{2+} , Pb^{2+} , Na^+ , Ag^+ , K^+ , Co^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} were prepared by dissolving the corresponding salt in water. For the anion studies, stock solutions of corresponding tetrabutylammonium salts (100 mM) of anions F^- , Cl^- , Br^- , I^- , CN^- , ClO_4^- , HSO_4^- , SCN^- , and SCN_3^- in DMSO were prepared. A 10 μL aliquot of each cation and anion from the stock solutions was added into a 0.435 mL sample solution of Azo-2



Scheme 1. Synthesis of aldoxime functionalized azobenzene-containing molecular probe (Azo-2) for the dual sensing of Hg^{2+} and F^- ions.

using a microsyringe, placed in a cuvette and monitored by UV-Vis absorption spectroscopy.

3. Results and discussion

3.1. Synthesis and characterization of Azo-2

An aldoxime-functionalized azo-based colorimetric probe was synthesized, as shown in Scheme 1. (E)-4-((4-(bis(2-hydroxyethyl)amino)phenyl) diazenyl)benzaldehyde (Azo-1) was synthesized by a diazotization reaction between 4-aminobenzaldehyde and N-phenyldiethanolamine at 0°C . The aldehyde group of Azo-1 was converted to an aldoxime by reacting with hydroxylamine in ethanol at 60°C , resulting in (E)-4-((E)-4-(bis(2-hydroxyethyl)amino)phenyl) diazenyl)benzaldehyde oxime (Azo-2). The resulting Azo-2 was characterized by ^1H NMR spectroscopy (Fig. 1). The successful synthesis of Azo-2 was confirmed by the disappearance of the $-\text{CHO}$ proton (peak a) of Azo-1 at 10.09 ppm and the appearance of $-\text{CH}=\text{N}-\text{OH}$ and $-\text{CH}=\text{N}-\text{OH}$ protons (peak g and h) of Azo-2 at 11.41 and 4.86 ppm, respectively.

3.2. Selective colorimetric sensing of Hg^{2+} ions

The sensing ability of Azo-2 toward Hg^{2+} ions was evaluated by UV-vis absorption spectroscopy in a DMSO/HEPES buffer (0.5:9.5, v/v) solution. First, pH-dependent sensing studies were carried out to examine the suitable pH ranges for Hg^{2+} ion detection. No detection of Hg^{2+} ions was achieved when the pH of the solution was 7.0 and 9.0 (Fig. S1). Azo-2 showed the optimal responses at pH = 5.0 with an enhanced red shift in the UV-vis absorption spectra (Fig. 2a). Upon the gradual addition of Hg^{2+} ions, absorption maximum was red-shifted from 465 nm to 535 nm with an isobestic point at 490 nm. As a consequence, the pale yellow solution of Azo-2 turned to dark violet, which can be observed easily by the naked eye (Fig. 2a, photograph). The immediate response took place in 1 s. To obtain greater insight into the sensing behaviors, the titration reaction curve was plotted with A_{535}/A_{465} (where A_{535}/A_{465} is the ratio of the absorbance at 465 nm to that at 535 nm) against the amount of Hg^{2+} ions added to the solution (Fig. 2b). The absorbance at 535 nm increased drastically with the gradual addition of Hg^{2+} ions until saturation, suggesting the formation of strong electron-withdrawing groups after the addition of Hg^{2+} ions. Based on earlier reports, it is reasonable to expect that an oxime group of Azo-2 underwent Hg^{2+} ion-catalyzed dehydration reaction [56]. The lowest detection limit of Azo-2 toward Hg^{2+} ions was found to be 4 mM. To trace this hypothesis, the ^1H NMR spectroscopy of Azo-2 was performed before and after the addition of Hg^{2+} ions. After the addition of Hg^{2+} ions, the $-\text{CH}=\text{N}-\text{OH}$ and $-\text{CH}=\text{N}-\text{OH}$ protons (peaks g and h) of Azo-2 at 11.41 and

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