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ARTICLE TYPE

A Facile Naphthalene-Based Fluorescent Chemodosimeter for Mercury Ions in Aqueous Solution

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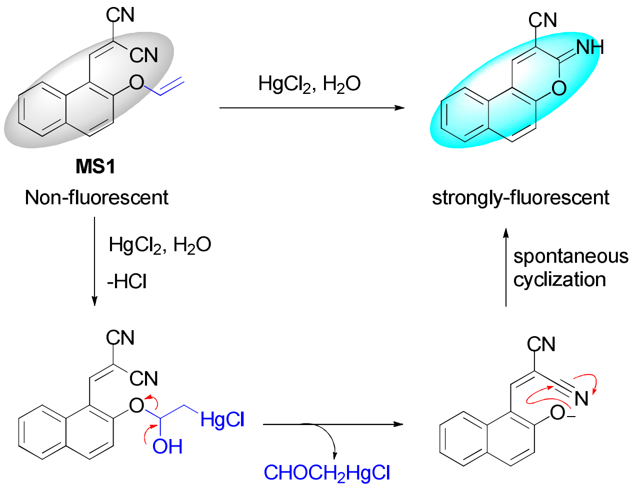
A facile naphthalene-based fluorescence "turn-on" chemodosimeter, 2-((2-(vinyloxy)naphthalen-1-yl)methylene) malononitrile (MS1), for rapid, selective and sensitive detection of Hg^{2+} by mercury-promoted hydrolysis of vinylether group has been reported. The probe displayed a fast response time, and sensitive fluorescence response (100-fold fluorescence enhancement) to the detection of Hg^{2+} in aqueous solution.

Mercury, which is widely distributed in the environment such as the air, soil, and water due to its use in batteries, dental amalgam, electrical apparatus, and industrial chemicals, is one of the most ubiquitous and poisonous heavy metals.[1] Mercury ions are not biodegradable, and hence can concentrate through the food chain in the tissues of fish and marine mammals. Excess mercury accumulation may induce strong damage to the central nervous system, various cognitive and motor disorders, and Minamata disease.[2] Due to the toxicity of Hg^{2+}, the determination of mercury in biological and environmental samples is crucial both to the monitoring of environmental pollution and to the diagnosis of clinical disorders.

In the past several years, considerable efforts have been made to develop fluorescent chemosensors for Hg^{2+} based on the coordination of Hg^{2+} to heteroatom-based ligands, Hg^{2+} catalyzed desulfurization, and Hg^{2+} promoted hydrolysis of the vinyl ether group and β-alkynyl ether group.[3] However, most of them still have limitations such as interference from other coexisting metal ions, poor water-solubility, and laborious synthesis processes expensive chemicals.[4] Therefore, for practical applications, it is still desirable to develop simple Hg^{2+} sensors with good water solubility and high selectivity and sensitivity.

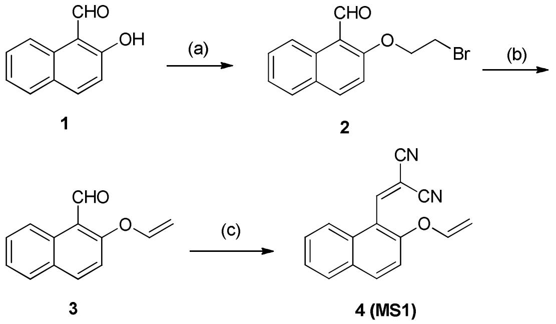
Compared with the typically-developed chemosensors,[5] fluorescent chemodosimeters, based-on highly specific chemical reactions between the dosimeters and the analytes, have received much research attention due to their relatively higher selectivity.[6] Recently, Peng, Talukdar, Wu, and Ahn's groups have reported fluorescent chemodosimeters based on "deprotection-cyclization strategy" for the detection of fluoride ions,[6] while the development of chemodosimeters for the specific determination of Hg^{2+} is drawing increasing research efforts. However, among the few available Hg^{2+} chemodosimeters reported,[3] most employ the pH-sensitive fluorescein or 7-amino coumarin as the fluorophore and their pH-dependence may pose detection errors to the results. It is therefore strongly desirable to develop simple yet specific fluorescent chemodosimeters for Hg^{2+} that is immune to pH turbulence.



Scheme 1 Hydrolysis of **MS1** by mercury ions.

It is known that Hg^{2+} catalyzes hydrolysis of vinylether to form the corresponding hydroxyl group.[7] We proposed that the Hg^{2+} ion promoted hydrolysis of the vinyl enol ether group in **MS1** would generate the hydroxy intermediate, which will readily spontaneous cyclize to form a highly fluorescent chemodosimeter (Scheme 1).

Our research group is actively engaged in the development of novel selective and sensitive fluorescent probes for heavy



Scheme 2 Synthesis of **MS1**: (a) 1, 2-dibromoethane/K_2CO_3, acetone, reflux, 3 h, 62%; (b) *t*-BuOK/DMSO, rt, 12 h, 46%; (c) $CH_2(CN)_2$/ piperidine, enthanol, rt, 1h, 48%.

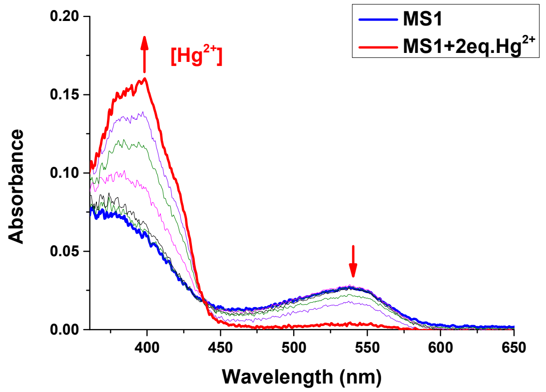


Fig. 1 Absorption spectra of **MS1** (20 μM) in PBS buffer solution (10 mM, pH 7.4, containing 1% CH_3CN) in the presence of different concentrations of Hg^{2+} (0-2.0 equiv.).

metal ions.[8] Herein, we report the synthesis and properties of a deprotection-cyclization reaction based fluorescent chemodosimeter (**MS1**) that shows high selectivity and sensitivity for Hg^{2+}.

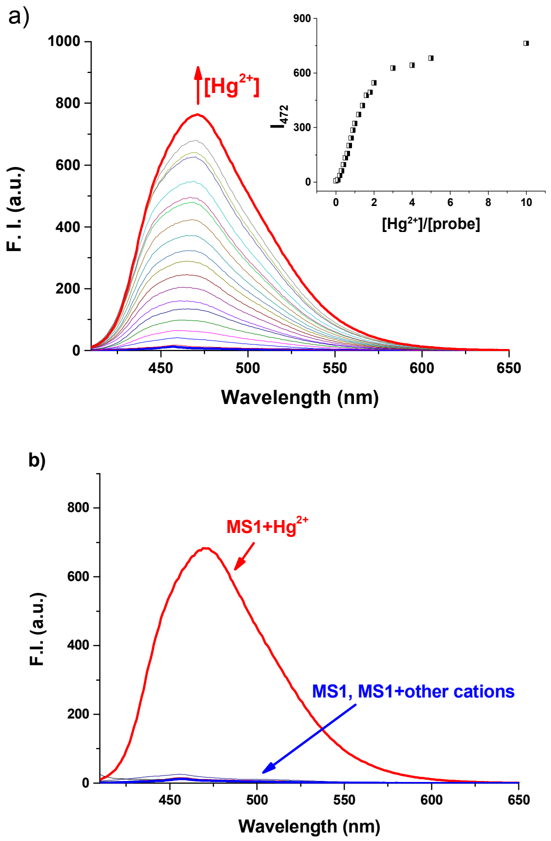


Fig. 2 (a) Fluorescence spectra of **MS1** (10 μM) in PBS buffer solution (pH 7.4, containing 1% CH_3CN) in the presence of different concentrations of Hg^{2+} (0-50 μM) (λ_{ex} = 395 nm). Inset: fluorescence intensity changes as a function of Hg^{2+} concentration. (b) Emission spectra of **MS1** (10 μM) in PBS buffer solution (pH 7.4, containing 1% CH_3CN) in the presence of various metal ions (λ_{ex} = 395 nm, 5.0 eq. of Hg^{2+}, and 10.0 eq. of Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Sn^{4+}, Ag^+, Ca^{2+}, and Zn^{2+}, respectively).

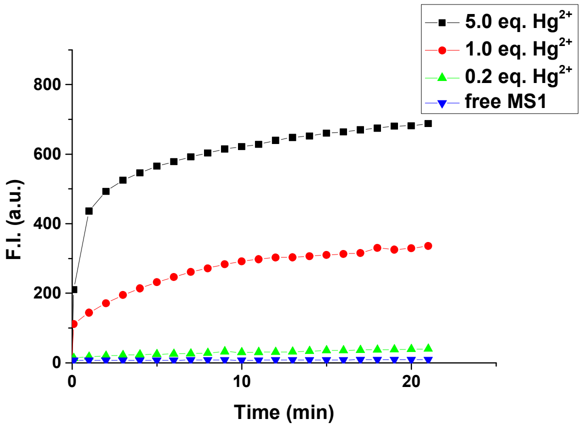


Fig. 3 Time-dependent fluorescence intensity changes of **MS1** (10 μM) upon addition of various concentration of Hg^{2+} (0, 0.2, 1.0, 5.0 equiv. each) in PBS buffer solution (pH 7.4, containing 1% CH_3CN) (λ_{ex} = 395 nm).

As shown in Scheme 2, **MS1** can be readily prepared in three convenient steps under facile conditions with high yield starting with commercially available 2-hydroxy-1-naphthaldehyde. The product (**MS1**) was well characterized by ^1H, ^{13}C NMR, and HR-MS (ESI†).

We firstly assessed the UV-vis spectroscopic properties of **MS1** in PBS buffer solution (10 mM, pH = 7.4, containing 1% CH_3CN). **MS1** (20 μM) displayed a moderate UV-vis absorption around 538 nm. Upon addition of Hg^{2+} (0-2 equiv.), the absorption band at 538 nm decreased and a new band at 399 nm appeared instantly with an isosbestic point at 439 nm, which is owing to the loss of vinyl enol ether group and the formation of cyclic compound (Fig. 1).

As expected, **MS1** alone is almost non-fluorescent (λ_{ex} = 395 nm, Φ = 0.002, Table S1, ESI†) in neutral aqueous solution (10 mM PBS buffer, pH 7.4, containing 1% CH_3CN), while the addition of increasing concentrations of Hg^{2+} gradually enhanced the fluorescent signal and *ca*. 100-fold increasing was observed when 5.0 equiv. of Hg^{2+} was added (Fig. 2a, Table S1, ESI†), which was attributed to the cleavage of vinyl enol group by mercury ion promoted hydrolysis reaction and the formation of a highly fluorescent cyclic compound (Scheme 1). Moreover, a blue-green fluorescent compound **5** have been isolated from **MS1**-Hg^{2+} system (ESI†), which was agreed well with the proposed mercury induced deprotection-cyclization mechanism.

Subsequently, the time-dependence of **MS1** fluorescence was also evaluated in the presence of different concentration of Hg^{2+}. The result shows that the fluorescence of all tested solutions remarkably increased to their maximum value within the 10 minutes. No changes in fluorescense were detected in the absence of Hg^{2+} (Fig. 3).

Further, the fluorescence titration of **MS1** with various metal ions was conducted to examine the selectivity (Fig.2b). Much to our delight, the turn-on response of **MS1** is highly specific for Hg^{2+} and no obvious change of fluorescent emission was observed when it is treated with Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Sn^{4+}, Ag^+, Ca^{2+}, and Zn^{2+}. It should be mentioned that **MS1** still responds to Hg^{2+} sensitively even in the presence of other relevant

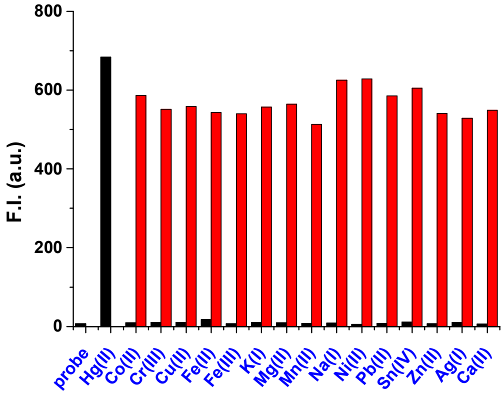


Fig. 4 Fluorescence responses of **MS1** to various metal ions. Black bars represent the addition of 5.0 equiv. of Hg^{2+} and 10.0 equiv. of the other appropriate metal ion to a 10 μM solution of **MS1**. Red bars represent the addition of 5.0 equiv. of Hg^{2+} to the solutions containing **MS1** (10 μM) and the appropriated metals (10.0 equiv.).

competing ions (Fig. 4). Therefore, these results suggest that **MS1** displays high selectivity toward Hg^{2+} in neutral aqueous solution.

Moreover, the Hg^{2+}-sensing ability of **MS1** at a wide range of pH values was investigated. As depicted in Fig. 5, **MS1** alone is inert to pH in the range of 4.0-11.0. But in the presence of Hg^{2+}, **MS1** have no fluorescence response in the highly basic environment (pH ≥ 9) due to the reaction rate of mercury ion-promoted hydrolysis of vinyl enol ether becomes slow at high pH value.[6] However, satisfactory Hg^{2+}-sensing abilities were exhibited in the range of pH from 4.0 to 8.0, indicating that **MS1** could be used in neutral natural systems, or a mildly acidic or basic environment.

For practical purposes, the detection limit of **MS1** for the analysis of Hg^{2+} was also an important parameter. The fluorescence titration curve revealed that the fluorescence intensity of **MS1** at 470 nm increased linearly with the amount of Hg^{2+} in the range of 0-5.0 μM (R^2 = 0.994) (Fig. S1, ESI†). Thus, the detection limit of **MS1** for Hg^{2+} was calculated to be 4.31×10^{-8} M (Hg content = 8.8 ppb), which reveals the high sensitivity for the analysis of the mercury ions.

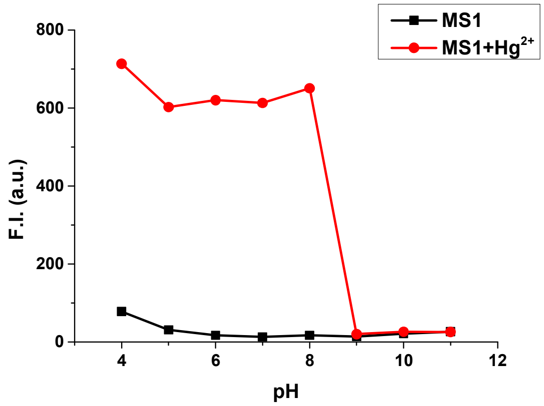


Fig. 5 Effect of the pH on the fluorescence emission of **MS1** (10 μM) alone and **MS1** (10 μM) reacted with Hg^{2+} (3.0 equiv.).

In conclusion, we have successfully developed a simple naphthalene-based fluorescense probe for Hg^{2+} based on mercury triggered cleavage reaction under mild conditions. The probe has the unique advantage of easy-preparation, good water solubility, and excellent selectivity and sensitivity response towards Hg^{2+} in aqueous solution. We anticipate that the experimental results of this study will inspire the future design of metal-ion sensors in water for a variety of chemical and biological applications.

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† Electronic Supplementary Information (ESI) available: Experimental details, synthetic details of MS1, additional spectroscopic data, and copies of NMR spectra. See DOI: 10.1039/b000000x/

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