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A simple and highly selective 'turn-on' type fluorescence chemodosimeter for Hg^{2+} based on 1-(2-phenyl-2H-[1,2,3]triazole-4-carbonyl)thiosemicarbazide

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ABSTRACT

1-(2-phenyl-2H-[1,2,3]triazole-4-carbonyl)-4-(4-methylphenyl)thiosemicarbazide (**M1**) has been synthesized and investigated as a fluorescence chemodosimeter for Hg^{2+} in dimethylsulfoxide. Highly selective 'turn-on' fluorescence alterations of **M1** were observed upon the addition of Hg^{2+}. Detection limit of Hg^{2+} by **M1** reaches $\sim 3.7 \times 10^{-8}$ mol/L (evaluated by 3σ criteria).The coexistent metal ions rendered no obvious interference toward the optical response of **M1** for Hg^{2+}.The mechanism of **M1** for the recognition of Hg^{2+} has been investigated by FT-IR, ^{1}H NMR and MS analyses.

1. Introduction

Over the past few years, molecular chemodosimeters for sensing metal cations have been extensively investigated due to their wide application in environmental science, medicine, chemistry, biotechnology, etc. [1–10]. Among these metal cations, Hg^{2+} is one of the most toxic ions [11], and can be accumulated over time in the bodies of human and animals, introducing serious damage to the brain, kidneys and endocrine system [12–14]. Exploring methods for the efficient detection of Hg^{2+} is attracting huge attention [15–18]. Thus, several traditional methods including atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry, and electrochemical workstation have been utilized to realize the detection of Hg^{2+} [19]. However, these traditional methods require expensive equipments and involve time-consuming and laborious procedures for sample-preparation [20]. Alternatively, analytical techniques based on fluorescence detection have drawn more and more attention due to the advantages of simple detection procedures, high sensitivity, and with no requirement of expensive equipments [21–23]. Two types of representative detection manners have been previously reported for the fluorescence detection of Hg^{2+}, referred as fluorescence 'turn-off' (fluorescence quenching) and 'turn-on' (fluorescence enhancing). Fluorescence 'turn-on' detection is much more preferable than the quenching mechanism due to the ease of detection (signals were strengthened during the detection process) and with less interference [24–28]. Preparation of fluorescence 'turn-on' type Hg^{2+} probes by simple synthetic route has drawn increasing interest in recent years [29–31].

Thanks to the specific interaction between Hg^{2+} and S atom, considerable efforts have been devoted to develop methods for Hg^{2+} probing by taking advantage of sulfur-containing derivatives [32–34]. These methods employ desulfurization or subsequent transformation reactions of thioamide [35], thiourea [36–40] and thione [41–44] containing optical-functionalized compounds. For example, Lin et al. designed colorimetric chemosensors for Hg^{2+} with high sensitivity in aqueous solutions [45]. Liu et al. reported a fluorescence chemodosimeter based on Hg(II)-promoted intramolecular cyclic guanylation [46]. Song et al. developed a fluorescent fluorogenic Hg^{2+}-selective chemodosimeter derived from 8-hydroxyquinoline [47].

In this context, we have designed a type of hydrazide-thiocarbonyl small molecular fluorescence chemodosimeter (**M1**). Optical response of **M1** toward various metal ions was investigated in this effort. With the addition of Hg^{2+}, thanks to the Hg^{2+}-induced desulfurization and the further intermolecular cyclization, the irreversible and unique fluorescence enhancement of **M1** was observed, indicating that **M1** hold the potential to act as Hg^{2+} fluorescence probe.

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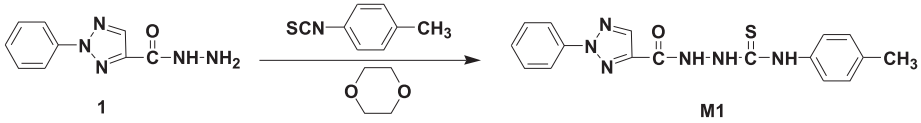
2. Experimental section

2.1. Measurements and characterization

^{1}H NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating at 400 MHz in deuterated DMSO solution with tetramethylsilane as the internal standard; IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets; UV–visible absorption spectra were recorded on a SHIMADZU RF-5301pc spectrophotometer UV-2450 UV–vis spectrophotometer. Fluorescence spectra were recorded on spectrophotometer.



Scheme 1. Synthesis and structures of **M1**.

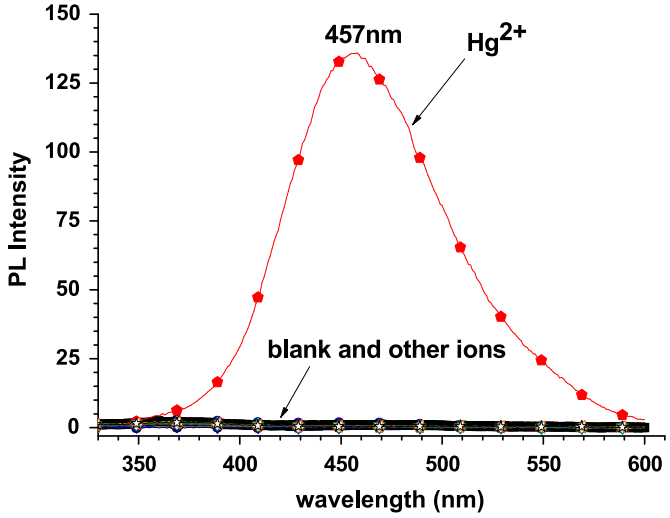


Fig. 1. Fluorescence spectra of **M1** ($\sim 1.0\times10^{-5}$ M) in DMSO with the addition of Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+} and Hg^{2+} (17 equiv., excitation wavelength was controlled at 275 nm).

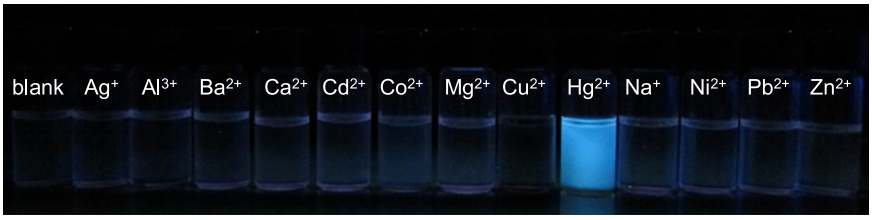


Fig. 2. Visual photographs of **M1** ($\sim 1.0\times10^{-5}$ M) in DMSO with the presence of 17 equiv. of different cations (excited by 365 nm, provided by a portable UV lamp).

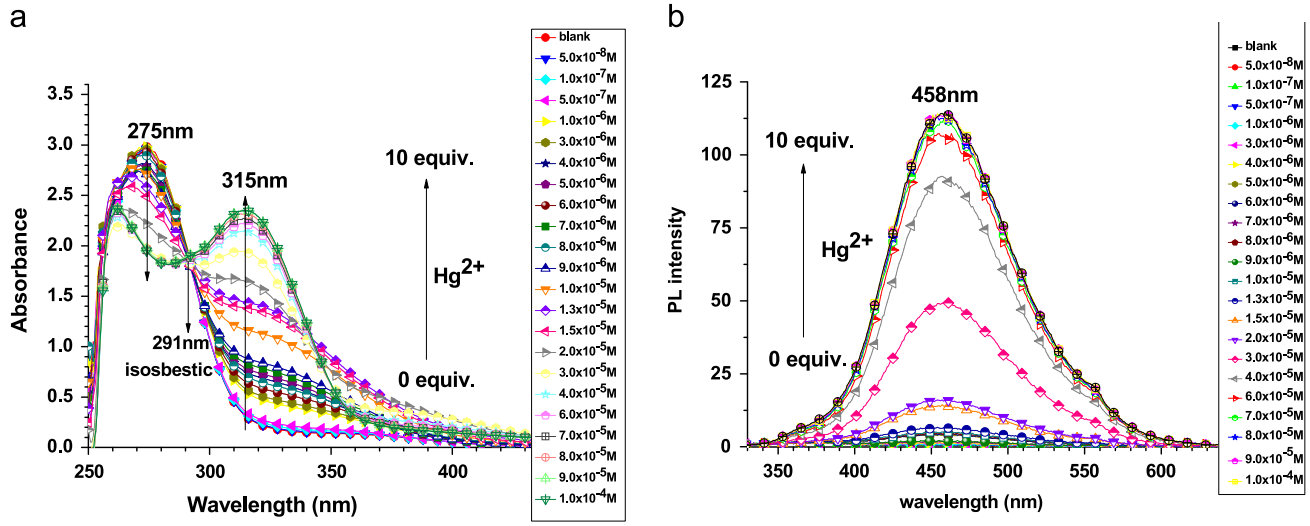


Fig. 3. (a) Absorption spectra of **M1** ($\sim 1.0\times10^{-5}$ M) in DMSO in the presence of increasing concentration of Hg^{2+}(0–10 equiv.). (b) Fluorescence emission spectra (excitation at 275 nm) of **M1**($\sim 1.0\times10^{-5}$ M) in DMSO in the presence of various concentrations of Hg^{2+} (0–10 equiv.). Inset: the fluorescent at 457 nm of **M1** ($\sim 1.0\times10^{-5}$ M) as a function of Hg^{2+} concentrations (0–10 equiv.).