

Both “Naked-Eye” and Fluorescent Sensor for Hg²⁺ Based upon 8-Hydroxyquinoline

Yang Yu · Wei Dou · Xiong Hu · Xiaoliang Tang · Xiaoyan Zhou · Weisheng Liu

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Abstract A chemosensor, 2,2'-(1,4-phenylenedivinylene)-bis-8-acetoxyquinoline (**1**), its fluorescent sensing behavior toward representative alkali ions (Na⁺, K⁺), alkaline earth ions (Mg²⁺, Ca²⁺), and transition-metal ions (Ni²⁺, Cu²⁺, Zn²⁺, Hg²⁺, Pb²⁺, Cd²⁺) was intensively investigated. The compound (**1**) exhibited pronounced Hg²⁺ selective on–off-type fluoroionophoric properties among the representative ions in DMF/ethanol (1:9, v/v) solution. Moreover, the highly Hg²⁺-selective fluorescence quenching property in conjunction with a visible colorimetric change from colorless to light yellow can be observed, leading to potential fabrication of both “naked-eye” and fluorescent detection of Hg²⁺.

Keywords Fluorescent sensor · Hg²⁺ selective · Naked-eye detection

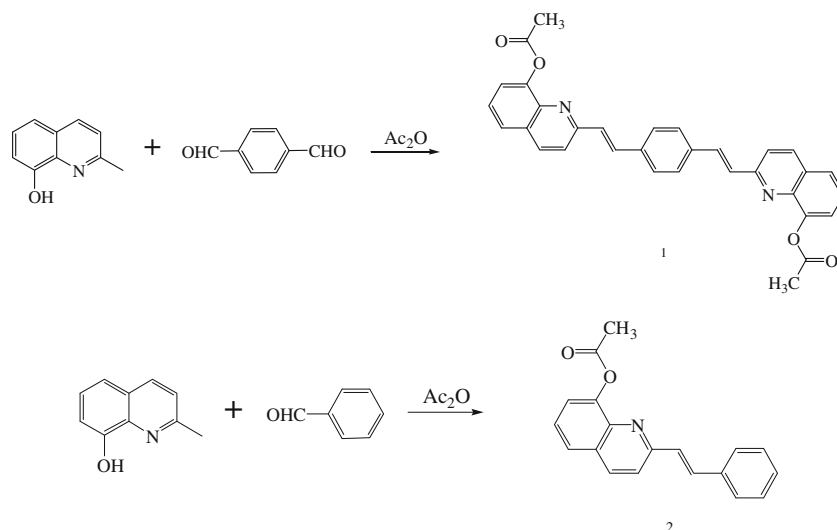
Introduction

In recent years, there has been an upsurge of interest in the development of fluorescent sensors for the

detection of heavy metal ions that are of concerning in toxicology and environmental science [1–5]. Such sensors based on ion-induced changes in fluorescence appear to be particularly attractive due to their simplicity, high sensitivity, high selectivity and instantaneous response [6]. Therefore, numerous studies focus on the design, synthesis of fluorescent chemosensors and the analysis of transition- or heavy-metal ions such as Hg²⁺, Cu²⁺, Pb²⁺ and so on [7–13]. Among them, mercury is notorious as an environmental toxin which causes severe neurotoxic, genotoxic, and immunotoxic effects and thus poses severe risk for human beings and other organisms [14, 15]. Mercury contamination of ecosystems occurs through a variety of natural and anthropogenic sources, including oceanic and volcanic emissions, solid waste incineration, and the combustion of fossil fuels [16, 17]. Many current techniques for mercury screenings such as atomic absorption/emission spectroscopy, and selective cold vapor atomic fluorescence spectrometry require expensive and sophisticated instrumentation and complicated sample preparation processes [17]. Fluorescence detection with Hg²⁺-responsive chemosensors offers a promising approach for simple and rapid tracking of mercury ions in biological, toxicological, and environmental samples [18–20]. Many efforts have been made to develop the chemosensors for the selective and efficient detection of mercury ions [7, 8, 21–23].

Design of chemosensors by incorporation of fluorophores can be based on either fluorescent ON–OFF [24–30] or OFF–ON [31–33] phenomenon. Many of

Y. Yu · W. Dou · X. Hu · X. Tang · X. Zhou · W. Liu (✉)
Key Laboratory of Nonferrous Metals Chemistry and Resources
Utilization of Gansu Province and State Key Laboratory
of Applied Organic Chemistry, College of Chemistry
and Chemical Engineering, Lanzhou University,
Lanzhou 730000, China
e-mail: liuws@lzu.edu.cn

Scheme 1 Synthesis of fluorescent sensor (1) and (2)

the reported fluorescent sensors for Hg^{2+} that operate through fluorescence quenching are often hampered by interference from chemically related cations like Cu^{2+} which also causes nonspecific fluorescent quenching [34]. Therefore, there is a great need for such chemosensors, which have high sensitivity and selectivity for detecting and monitoring Hg^{2+} by employing a simple response.

A few works demonstrated ideal selectivity and sensitivity for Hg^{2+} . For example, several Hg^{2+} sensors that exhibit fluorescence turn-on have been revealed which include a biaryl pyridine species linked to an argogel resin [35] and xanthene-based MF1 [20]. Other reported Hg^{2+} detection strategies relying on fluorescence output involve nanoparticles [36], polymers [37], and biomolecules [38, 39]. Many colorimetric Hg^{2+} indicators have also been documented [40, 41]. Nevertheless, the syntheses of these fluorophores are found to be relatively complicated or low-yielding. So, the development of easy-access and new kinds of Hg^{2+} fluorescent sensors is still quite important. The 8-Hydroxyquinolin platform has been receiving much attention in the design of efficient fluorophores because of the appreciable change in fluorescence upon metal binding [42]. 8-Hydroxyquinolin has been used to construct many unique ionophoric systems for the recognition of important metal ions, such as Zn^{2+} , Al^{3+} , Fe^{3+} , and Hg^{2+} , as well as effective light-emitting devices [43] due to its unique molecular structure and properties, for instance, an extra binding site or signaling unit can be introduced at some well-defined periphery on the appending alkyl group [42].

Herein, we describe a simple fluorescent Hg^{2+} sensor, 2,2'-(1,4-phenylenedivinylene)bis-8-acetoxyquinoline (**1**) based on the 8-Hydroxyquinolin platform. The sensor, as depicted in Scheme 1, is selective for Hg^{2+} over some representative metal and transition-metal ions, and exhibits fluorescence quenching immediately following Hg^{2+} coordination in DMF/ethanol solution. More importantly, the highly Hg^{2+} -selective fluorescence quenching property in conjunction with a visible colorimetric change from colorless to light yellow can be observed, leading to potential fabrication of both “naked-eye” and fluorescent detection of Hg^{2+} .

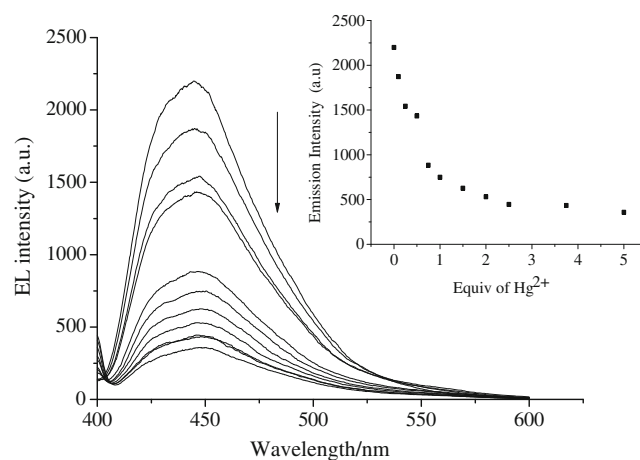
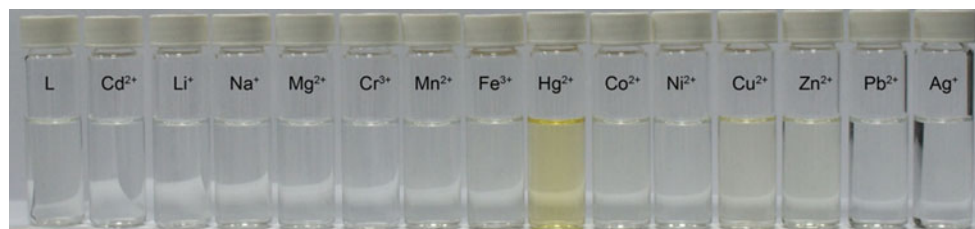


Fig. 1 Fluorescence response of (**1**) in DMF/ethanol solution (1:9, v/v) in the presence of increasing concentration of $[\text{Hg}^{2+}]$ (0, 0.10, 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, 2.5, 3.75 and 5.0×10^{-5} M). $[\mathbf{1}] = 1.0 \times 10^{-5}$ M. Inset shows variation of fluorescence intensity against equivalents of Hg^{2+} (job's plot)

Fig. 2 Photograph of compound (1) with the addition of different metal ions



Data Treatment and Discussion

First, we attempted to determine the selective fluoronophoric properties of 2,2'-(1,4-phenylenedivinylene)bis-8-acetoxyquinoline (1) toward representative alkali (Na^+ , K^+), alkaline earth (Mg^{2+} , Ca^{2+}), and transition-metal ions (Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} , Cd^{2+}). After systematic insight into selective signaling toward a specific target metal ion, we found that DMF/ethanol mixing solution was relatively well optimized sensing media. Therefore, all the fluorescence measurements were carried out in a DMF/ethanol solution (1:9, v/v), where the most pronounced selectivity toward Hg^{2+} ions was realized.

Compound (1) exhibited a characteristic fluorescence emission band at 445 nm. However, upon the addition of Hg^{2+} ion, the remarkable fluorescence quenching was observed instantaneously with an increase of the concentration of Hg^{2+} in DMF/ethanol (1:9, v/v), which was shown in Fig. 1. The maximum quenching of fluorescence was reached when the Hg^{2+} concentration

was up to 5 equiv (1 equiv is 1.0×10^{-5} M), (see the insert of Fig. 1). We need to note that when the concentration of compound (1) was 1.0×10^{-6} mol/L, the quenching was also observed when Hg^{2+} was added into the (1) solution of DMF/ethanol, but due to the lower concentration of compound (1), fluorescence intensity is not enough strong, therefore we chose the concentration of (1) at 1.0×10^{-5} mol/L through this study. The result suggests that the detection limit of compound (1) is about 1.0×10^{-6} mol/L. Moreover, the Hg^{2+} sensing and the concomitant absorption changes were clearly visible to the naked eye, as can be seen in the photograph (Fig. 2) where the colorless solution of (1) became light yellow when the concentration of Hg^{2+} ions reached up to 1.0×10^{-5} M. It was also clear from Fig. 2 that the addition of other metal ions (1.0×10^{-5} M) studied to the DMF/ethanol (1:9, v/v) solution of (1), however did not change the solution color clearly. These interesting phenomena proved that compound (1) can serve as a “naked eye” chemosensor specific for Hg^{2+} .

Fig. 3 Fluorescence responses of (1) at 445 nm in the presence of different metal ions: Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cr^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Ag^+ and Al^{3+} (as their ClO_4^- salts) in DMF/ethanol (1:9, v/v). $[\mathbf{1}] = 1.0 \times 10^{-5}$ M, $[\text{M}^{n+}] = 5.0 \times 10^{-5}$ M

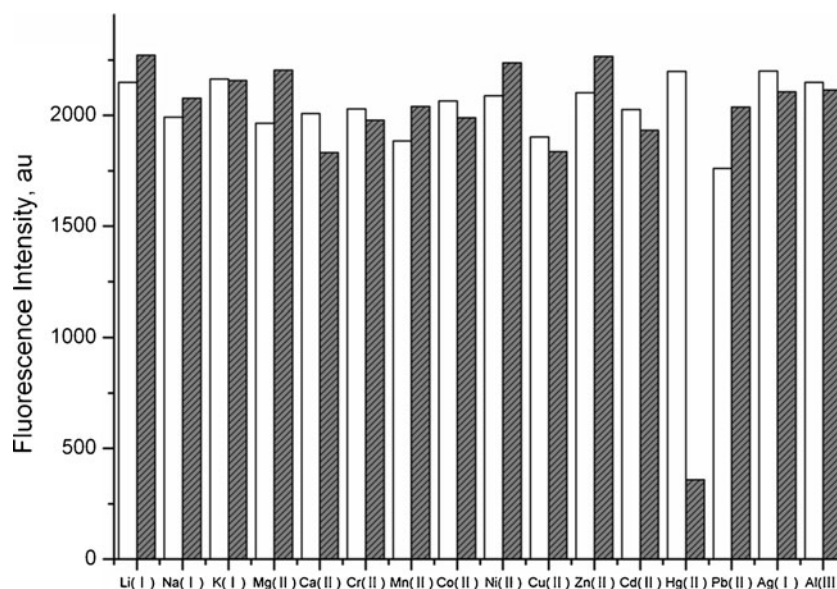
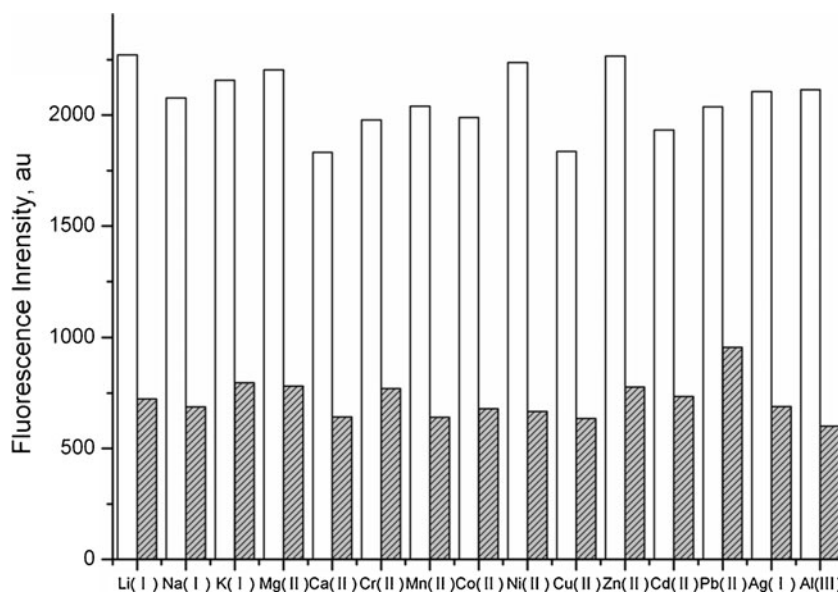


Fig. 4 Fluorescence responses of (**1**) at 445 nm upon the addition of 5 equiv of Hg^{2+} in the presence of 50 equiv of background metal ions (5.0×10^{-4} M). $[\mathbf{1}] = 1.0 \times 10^{-5}$ M



In addition, the fluorescence response of (**1**) to other metal ions was also investigated (see Fig. 3). Although the fluorescence of (**1**) at 445 nm was obviously quenched by adding Hg^{2+} , no significant spectral changes took place in the presence of 5 equiv each of alkali ions (Na^+ , K^+), alkaline earth ions (Mg^{2+} , Ca^{2+}), and transition-metal ions (Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+}). Of practical significance was that even 50 equiv (5.0×10^{-4} M) each of these metal ions did not interfere in the sensing of Hg^{2+} , as shown in Fig. 4. Figure 5 showed the photograph of compound (**1**) in DMF/ethanol (1:9, v/v) solution taken under the fluorescence light. It was obvious that the appearance of both alkali ions (Na^+ , K^+), alkaline earth ions (Mg^{2+} , Ca^{2+}), and transition-metal ions (Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+}) did not quench the fluorescence of (**1**), except Hg^{2+} ion. Moreover, Fig. 5 also showed that the presence of other

metal ions did not interfere the quenching of the ligand (**1**) due to Hg^{2+} . These results suggested that the compound (**1**) had a high selectivity toward Hg^{2+} among various metal ions.

The UV–vis absorption spectrum of (**1**), recorded in DMF/ethanol (1:9, v/v) solution, exhibited a strong band at 380 nm (Fig. 6). A weak band at 308 nm was also observed, which was assigned to the π - π^* transitions of the 8-quinolinoloxo groups.²⁰ Upon progressive addition of Hg^{2+} ions to a solution of (**1**) in DMF/ethanol (1:9, v/v), The absorbance of ligand at 380 nm gradually decreased in intensity with the concomitant decrease of band at 308 nm, whereas a new band at 445 nm appeared and its absorbance gradually increased with the addition of Hg^{2+} (Fig. 6). The quenching mechanism could be explained as being caused by the charge transition from the large conjugative

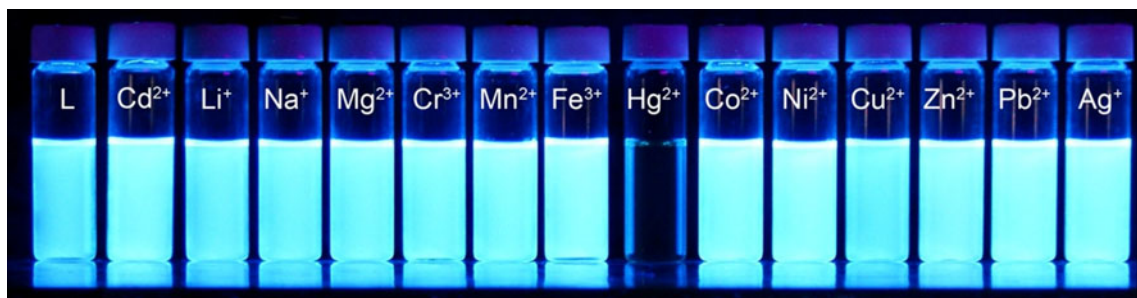


Fig. 5 Photograph of compound (**1**) in DMF/ethanol (1:9, v/v) solution in the presence of various metal ions under the fluorescence light. $[\mathbf{1}] = 1.0 \times 10^{-5}$ M, $[\text{M}^{n+}] = 5.0 \times 10^{-4}$ M

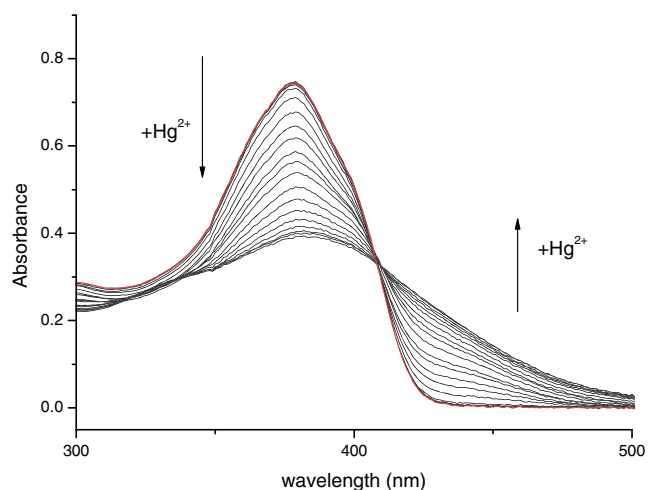
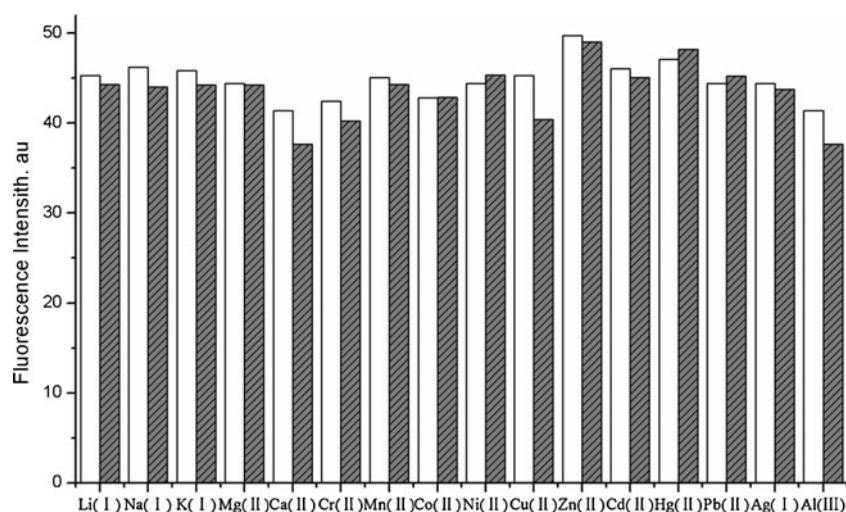


Fig. 6 UV-vis spectra of (**1**) in DMF/ethanol (1:9, v/v) in the presence of increasing concentration of Hg^{2+} (0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 eq.). $[\mathbf{1}] = 1.0 \times 10^{-5}$ M

ligand to the Hg^{2+} (LMCT). As shown in Fig. 6, the absorption band showed a red shift and overlapped with emission band in the region of 400–500 nm, which reflects that the electron was dispersed due to the presence of Hg^{2+} . To confirm our conclusion, the compound (**2**), a relatively smaller conjugative ligand but with a similar molecular structure was prepared. Compared with (**1**), the smaller conjugative compound (**2**) has not shown obvious response to most metal ions including Hg^{2+} (Fig. 7). In addition, Job's plot in the insert of Fig. 1 shows that the fluorescence intensity reached platform when the concentration of compound

Fig. 7 Fluorescence responses of (**2**) at 405 nm in the presence of different metal ions: Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cr^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Ag^+ and Al^{3+} (as their ClO_4^- salts) in DMF/ethanol (1:9, v/v). $[\mathbf{2}] = 1.0 \times 10^{-5}$ M, $[\text{M}^{n+}] = 5.0 \times 10^{-4}$ M



(**1**) is 1 equiv of Hg^{2+} (1.0×10^{-5} M), suggesting that a 1:1 binding of ligand to Hg^{2+} .

Moreover, we also found that these metal ions did not interfere in the sensing of Hg^{2+} , and the results of the competition experiments are shown in Fig. 4. It is worthy noting that **1** still shows highly selective fluorescence quenching toward Hg^{2+} over other metal ions, probably because of very selective and strong binding of the former with **1**. The quenching mechanism can be explained as being caused by the electron transfer from the quinoline nitrogen to the Hg^{2+} .

Conclusion

In conclusion, a 8-Hydroxyquinolin derivative, 2,2'-(1,4-phenylenedivinylene)-bis-8-acetoxyquinoline (**1**), has been facilely synthesized which exhibited a high affinity toward Hg^{2+} over alkali metal ions (Na^+ , K^+), alkaline earth metal ions (Mg^{2+} , Ca^{2+}), and transition-metal ions (Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+}). The highly selective fluorescence quenching behavior of the fluorescent sensor **1** toward Hg^{2+} , its sensing ability in DMF/ethanol (1:9, v/v) solution systems suggested that it can be used as an ON-OFF fluorescent sensor toward Hg^{2+} ion. The fluorescent sensor **1** exhibited no affinity to other metal ions, thereby reducing the possibility of interference by these metal ions. A visible colorimetric change from colorless to light yellow can be observed only in the presence of Hg^{2+} ion, revealing the potential fabrication of both “naked-eye” and fluorescent detection of Hg^{2+} .

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