



A “turn-on” fluorescent chemosensor for the detection of Hg(II) in buffer-free aqueous solution with excellent selectivity

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ABSTRACT

The development of chemosensors for detecting Hg(II) has long been a great concern due to its high toxicity and widespread distribution in the environment. In this work, a new fluorescent chemosensor of 2,3-diphenylpyrido [2,3-b]pyrazine (**1**) was facilely synthesized, which exhibited “turn-on” fluorescent response to Hg(II) with excellent selectivity and anti-interference capability. Mechanism study showed that a complex was formed by Hg(II) and **1** with a metal-to-ligand ratio of 1:1 and the formation of the complex was reversible. More importantly, the sensing process can be performed in pure water environment and barely affected by pH, which enables the detection of Hg(II) using **1** perform in aqueous solution without any buffer system or organic solvent.

1. Introduction

As one of the most toxic metal ions for human health, mercury ion (Hg(II)) is widespread in air, water, and soil [1–4]. Thus, much effort has been devoted to develop selective and sensitive methods for the detection of Hg(II) in environmental samples [5–12]. Among different methods, fluorescent chemosensor has been proven to be an effective method to detect Hg(II) due to its advantages such as high sensitivity, non-destructive emission signals, capability of rapid detection and low cost [13–17]. The reported fluorescent chemosensors for detecting Hg(II) can be divided into two categories according to different response mechanisms. One category is developed based on Hg(II)-induced chemical reactions, which exhibits excellent selectivity for Hg(II) [18–25]. However, most of these reactions are irreversible and the sensing processes usually take a long time because of the limited rates of the reactions [19–21,24–26]. The other category is developed based on the formation of complexes between the chemosensors and Hg(II). These chemosensors usually exhibit reversible and fast response to Hg(II) with high signal-magnification [27–45]. Nevertheless, the formation of complexes can be interfered by other metal ions, resulting in relatively poor selectivity [28,33,37,46–51]. Meanwhile, because of the competition between acid/base and the chemosensors in the formation of complexes with Hg(II), most of the reported fluorescent chemosensors can only be used in specific solution environment such as a certain pH and a certain amount of organic solvent, which inevitably limit their application in real samples [18,19,24,30,31,36,37,40,43–48,51–55].

Therefore, it is still a great challenge to develop a highly selective and high signal-magnification fluorescent chemosensor to detect Hg(II) with reversible and fast response in buffer-free aqueous solution.

In this work, a new fluorescent chemosensor of 2,3-diphenylpyrido [2,3-b]pyrazine (**1**) was reported for the detection of Hg(II) in buffer-free aqueous solution. As shown in Schemes 1, **1** can be facilely synthesized by one step reaction with a yield of 65%. **1** exhibits an 18-fold “turn-on” fluorescent response to Hg(II) with excellent selectivity and anti-interference capability. Mechanism study showed that a complex was formed between Hg(II) and **1** by 1:1 metal-to-ligand ratio and the formation of the complex is reversible. A linear range of 0–75.0 $\mu\text{mol L}^{-1}$ and a detection limit of 1.06 $\mu\text{mol L}^{-1}$ are achieved, respectively. More importantly, the sensing process can be performed in pure water environment and barely affected by pH, which enables the detection of Hg(II) using **1** perform in aqueous solution without any buffer system or organic solvent.

2. Experimental

2.1. Reagents

Unless otherwise expressly noted, all materials used in this work were commercially available without any further purification. Benzil, o-phenylenediamine and 2,3-diaminopyridine were purchased from J&K Chemical Co., Beijing, China. All the other materials were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China. The

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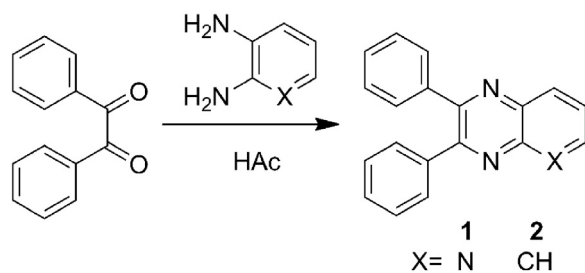
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Scheme 1. Synthesis of 1 and 2.

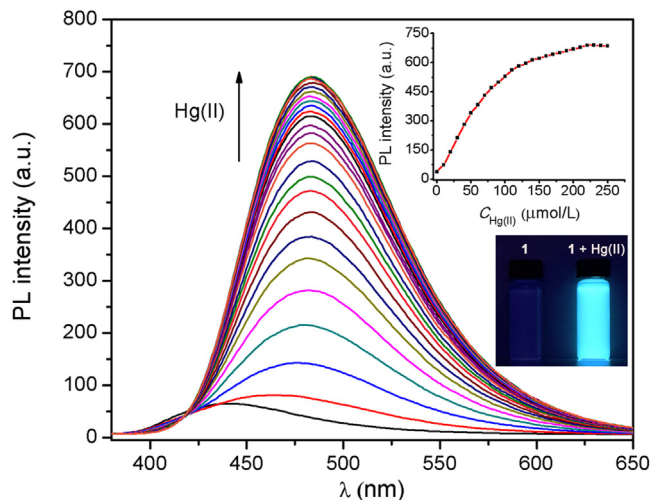


Fig. 1. Fluorescence spectra of $20 \mu\text{mol L}^{-1}$ **1** in aqueous solution upon the addition of Hg(II). Inset: The fluorescence intensity at 485 nm as a function of Hg(II) concentration. The photographs are **1** in the absence and presence of 10 equiv. Hg(II) in a glass cuvette under irradiation by 365 nm UV light. The excitation was performed at 360 nm.

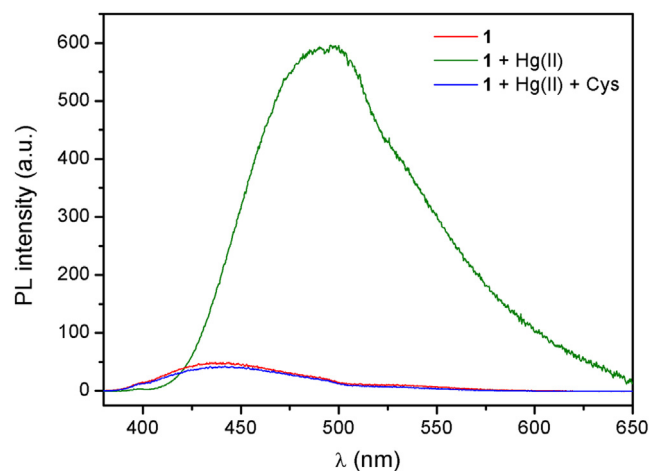


Fig. 2. Fluorescence spectra of $20 \mu\text{mol L}^{-1}$ **1** in aqueous solution in the absence and presence of 10 equiv. Hg(II) and 50 equiv. Cys. The excitation was performed at 360 nm.

solutions of all metal ions were prepared from their nitrate salts or perchlorate salts of analytical grade. Doubly distilled deionized water was used throughout the experiment.

2.2. Apparatus

UV–vis absorption spectra in solutions were obtained on a JASCO V-750 spectrophotometer with 1 cm quartz cell. Fluorescence spectra

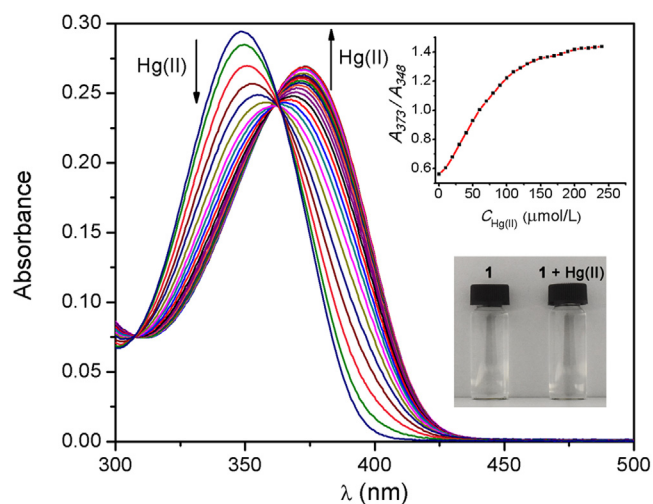


Fig. 3. Absorption spectra of $20 \mu\text{mol L}^{-1}$ **1** in aqueous solution upon the addition of Hg(II). Inset: The absorbance ratio (A_{373}/A_{348}) as a function of Hg(II) concentration. The photographs are **1** in the absence and presence of 10 equiv. Hg(II) in a glass cuvette under irradiation by sunlight.

were obtained on a JASCO FP-8300 fluorescence spectrometer with 1 cm quartz cell. All pH measurements were made with a METTLER TOLEDO FE20/EL20 pH meter. ^1H and ^{13}C NMR spectra were recorded on a Bruker 600 Avance NMR spectrometer operated at 600 MHz. Electrospray ionization mass spectrometry (ESI-MS) were obtained on Agilent Technologies 6420 triple quadrupole LC/MS spectrometer (Fig. S5) and GCT premier CAB048 mass spectrometer (Fig. S6–S7). Single-crystal X-ray diffraction intensity data were recorded using a Rigaku Saturn 724 CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The photos were taken by a Nikon D5500 camera. All the measurement experiments were performed at room temperature.

2.3. Synthesis

Compounds **1** and **2** were successfully synthesized by a simply one-step synthesis according to the synthetic step outlined in Scheme 1. The structures of compounds **1** and **2** were confirmed by NMR, HRMS and single-crystal X-ray diffraction. Single crystals of **1** and **2** suitable for single crystal X-ray diffraction analysis were obtained from a mixture of methanol-dichloromethane by slow solvent evaporation at room temperature. The single crystal structures of compounds **1** and **2** were depicted in Fig. S1 and the parameters associated with crystal data were shown in Table S1.

2, 3 – diphenylpyrido[2, 3 – b] pyrazine (1)

Benzil (0.42 g, 2 mmol) and 2,3-diaminopyridine (0.22 g, 2 mmol) were dissolved in 3 mL glacial acetic acid in a 5 mL flask. The mixture was heated to 110°C and stirred for 3 h. Claybank precipitation was obtained after cooling to room temperature. Then the precipitation was filtered and washed by 10 mL glacial acetic acid for three times. The crude product was purified by recrystallization in glacial acetic acid to get **1** (0.36 g, yield 65%) as claybank solid. ^1H NMR (DMSO- d_6) δ (ppm): 9.20(dd, 1 H, $J = 4.2, 1.8$ Hz), 8.62(dd, 1 H, $J = 8.4, 1.8$ Hz), 7.92(dd, 1 H $J = 7.8, 3.6$ Hz), 7.52(m, 4 H), 7.43(m, 2 H), 7.39(dd, 4 H, $J = 13.8, 6.6$ Hz). ^{13}C NMR (DMSO- d_6) δ (ppm): 156.20, 154.95, 154.59, 149.61, 138.77, 138.36, 136.17, 130.28, 130.22, 129.68, 129.55, 128.58, 126.41. ESI-MS spectrometry: m/z calcd for $[\text{M} + \text{H}]^+$: 284.12; found: 284.11.

2, 3 – diphenyl – 1, 4 – quinoxaline (2)

Benzil (0.42 g, 2 mmol) and 1,2-diaminobenzene (0.22 g, 2 mmol) were dissolved in 3 mL glacial acetic acid in a 5 mL flask. The mixture was heated to 110°C and stirred for 3 h. White precipitation was

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