Sensors and Actuators B xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

New pyrrole-based single-molecule multianalyte sensor for Cu^{2+}, Zn^{2+}, and Hg^{2+} and its AIE activity

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ARTICLE INFO

Article history:
Received 17 April 2017
Received in revised form
18 September 2017
Accepted 20 September 2017
Available online xxx

Keywords:
Colorimetric
Fluorescent
Multi-chemosensor
Hydrazone
Pyrrole

ABSTRACT

An aggregation-induced emission (AIE) active bis-hydrazone in the aqueous medium is designed and prepared, which can be used as a multi-probe that selectively detects Cu2+, Zn2+, and Hg2+ by monitoring the changes in absorption and fluorescence spectral patterns. Results show that Zn2+ and Hg2+ can enhance the fluorescence in EtOH solution. The addition of Cu2+ strongly improves absorption in the visible range. In contrast to the fluorescence of 1 + Zn2+, the fluorescence of 1 + Hg2+ can be maintained in the presence of water. The crystal structure of the Hg(II) complex based on 1 is further determined through X-ray crystallographic analysis. To test the practical use of the probe, the determination of Hg2+ in real water samples was also evaluated.

1. Introduction

Selective and sensitive sensors for metal ions have been widely developed [1,2]. Colorimetric and fluorescent methods based on molecular chemosensors have also emerged as important tools used to recognize metal ions because of their operational simplicity and low detection limits [3–6]. As a new chemosensor design concept, single sensors for multiple analytes have been proposed. Detection methods for numerous metal ions with different responses are more efficient and less expensive than one-to-one analysis methods [7].

Cu^{2+} and Zn^{2+} play important roles in biological systems of plants, humans, and living cells. However, high concentrations of these ions can cause disorders associated with neurodegenerative diseases [8]. Excessive Cu^{2+}/Zn^{2+}concentrations are also harmful to the environment [9]. Unlike Cu^{2+}/Zn^{2+}, Hg^{2+} is considered a highly toxic metal. Hg^{2+} present in soil or effluent water is assimilated by lower forms of aquatic organisms; consequently, these organisms can convert this ion to methylmercury, which is a potent neurotoxin affecting humans [3]. Therefore, new approaches that are highly sensitive and specific to Cu^{2+}, Zn^{2+}, and Hg^{2+} should be developed.

Numerous one-to-one Schiff base sensors for Cu^{2+} [10–12], Zn^{2+} [13–19], and Hg^{2+} [20,21] should be investigated because of their simplicity, sensitivity, easy synthesis, and low cost. Although many dual-function fluorescent chemosensors have been designed to detect two of these metal ions [7–9,22–25], molecular chemosensors based on a Schiff base scaffold have yet to be widely used to determine Cu^{2+}, Zn^{2+}, and Hg^{2+} simultaneously and selectively. In this study, bis-hydrazone **1** (Scheme 1) containing pyrrole units was fabricated and utilized as a fluorescent off-on probe for Zn^{2+} and Hg^{2+} and colorimetric probe for Cu^{2+}. The fluorescent sensor was also applied to monitor Hg^{2+} in real water samples.

2. Results and Discussions

2.1. Synthesis and characterization

Probe **1** (Fig. 1a) was easily prepared by one-step condensation of ethyl 5-formyl-2,4-dimethyl-1H-pyrrole-3-carboxylate and hydrazinium hydroxide with high yield. The complex **1**-Hg (Fig. 1b) was generated by reaction of **1** with equimolar of $HgCl_2$ in EtOH/DMF solution at room temperature. The chemical struc-

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https://doi.org/10.1016/j.snb.2017.09.133
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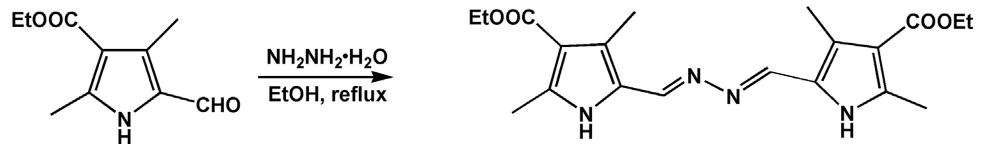
Please cite this article in press as: Y. Wang, et al., New pyrrole-based single-molecule multianalyte sensor for Cu^{2+}, Zn^{2+}, and Hg^{2+} and its AIE activity, Sens. Actuators B: Chem. (2017), https://doi.org/10.1016/j.snb.2017.09.133



Scheme 1. Synthesis route of the probe **1**.

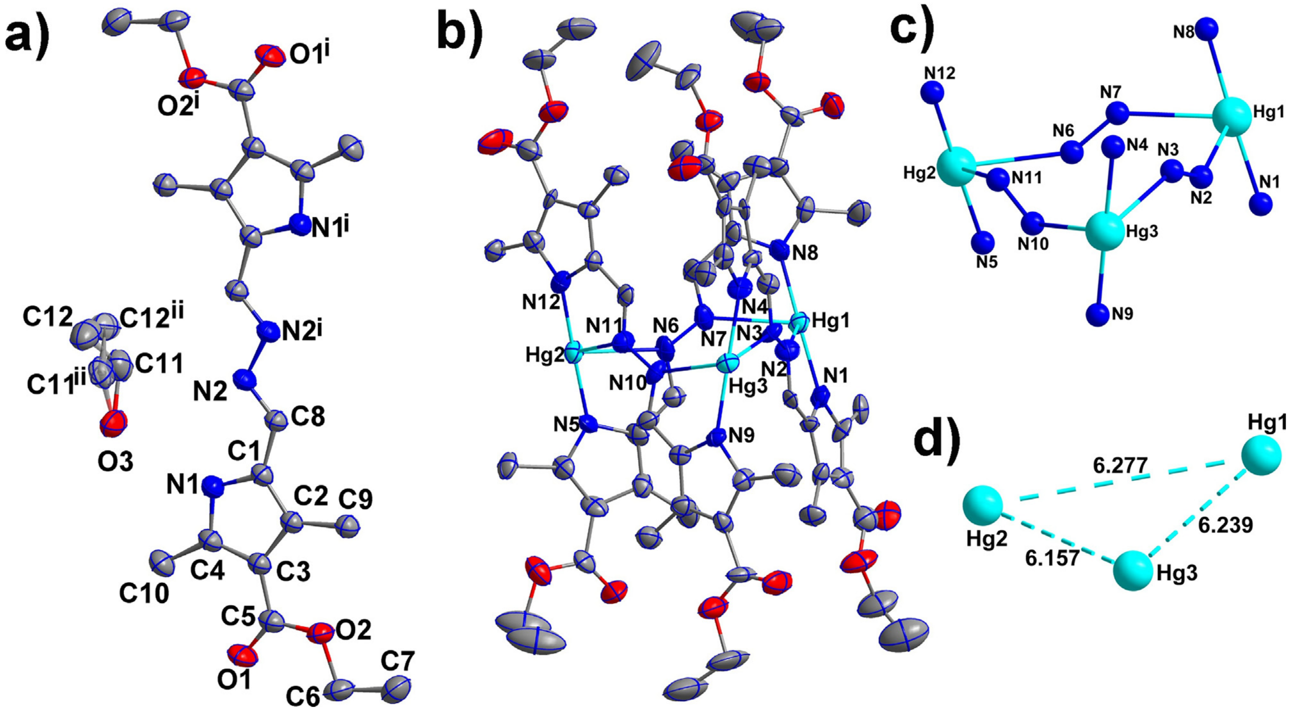


Fig. 1. Crystal structures of **1**·2EtOH (a) and complex **1**-Hg (b); coordination envionment of Hg^{2+} ions (c) and Hg-Hg distances (d) in complex **1**-Hg.

tures were fully characterized by ^1H NMR, MS and X-ray diffraction analysis, as shown in experimental part in S1, ESI.

2.2. Aggregation-induced emission (AIE)of 1

It has been demonstrated that AIE active molecules have potential uses in a wide range of applications such as photo memory, fluorescence sensors, and solid-state optical functional materials/devices [26]. Among them, several bis-hydrazones have been reported due to their AIE activities [27,28]. Therefore, the AIE property of **1** (5 μM) is investigated in water/DMF (from 0 to 100%, v/v) solution. As presented in Fig. 2, **1** is non-emissive when dissolved in a good solvent DMF, while the emission is turned on when the water volume fraction reaches to 90% (λ_{ex} = 360 nm). The emission intensity at 514 nm for **1** increased 120-fold in 100% water, suggesting that **1** is an AIE active compound in the aqueous medium. From the SEM morphology in Fig. 3, it can be seen clearly that **1** forms needle-like particles regularly and the width is estimated to be about 200–500 nm. This AIE effect could normally be explained by the blocking of the nonradiative intramolecular rotation decay of excited molecules through formation of J- or H-aggregates [27].

2.3. UV–vis spectroscopic analyses of 1 with metal ions in EtOH solution

Probe **1** in EtOH solution was allowed to interact with 1 eq. of various metal ions, such as Ag^+, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+},K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+},and Zn^{2+}, through UV–vis absorption spectroscopic analysis. In Fig. 4, the UV–vis spectrum of probe **1** exhibited one band centered at 370 nm, which could be assigned to the n–π∗ transition of imine units [18]. After the metal ions were added, a broad band for Cu^{2+} appeared at 510 nm, and this band corresponded to an orange appearance (Fig. 4, inset). However, the other tested metal ions exhibited no evident absorbance band in the visible range. To estimate the selectivity of **1** for Cu^{2+}, we conducted a competitive experiment in the presence of other metal ions under the same conditions (Fig. S1, ESI). Notably, the comparison of the results obtained in the presence or absence of other metal ions showed that the competitive metal ions did not induce significant changes in the absorbance of the **1** + Cu^{2+} system. This experiment established that the presence of other metal ions did not interfere with the detection of Cu^{2+}. As expected, **1** is a "naked-eye" colorimetric probe selective for Cu^{2+}.

A titration experiment was conducted with the gradual addition of Cu^{2+} (0–8 eq.) to gain insights into the sensing properties of **1** (5 μM) as a receptor. In Fig. 5, a new band centered at 510 nm with a shoulder at approximately 540 nm was observed in the progressive addition of Cu^{2+}; this band could be attributed to the charge transfer in the **1**-Cu^{2+} complex [8,22]. The absorption band centered at 370 nm gradually decreased as Cu^{2+} concentration increased. The appearance of two isosbestic points at 325 and 406 nm indicated that the coordination reaction is clean and straightforward, that is, no side reaction that may perturb isosbestic point occurs [18]. In addition, the probe showed a good linear relationship between the absorbance at 510 nm and the concentration of Cu^{2+} (0–5 μM) (Fig. 5, inset). This result suggested that sensor **1** is potentially applied to analyze Cu^{2+} quantitatively. The detection limit of **1** for Cu^{2+} was 38.2 nM, as calculated using the

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