



# A highly selective and sensitive fluorescent chemosensor for mercury ions based on the mechanism of supramolecular self-assembly



Wen-juan Qu, Guo-ying Gao, Bing-bing Shi, Tai-bao Wei, You-ming Zhang\*, Qi Lin, Hong Yao

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, PR China

## ARTICLE INFO

### Article history:

Received 14 March 2014

Received in revised form 12 July 2014

Accepted 23 July 2014

Available online 1 August 2014

### Keywords:

Mercury ion

Fluorescent sensor

Supramolecular self-assembly

Semicarbazone

Aqueous solution

Recyclable

## ABSTRACT

In this work, a highly sensitive and selective mercury fluorescent sensor (E)-1-((5-(4-nitrophenyl)furan-2-yl)methylene) semicarbazone (BI) based on the 5-(4-nitrophenyl)-2-furan and semicarbazide groups was designed, prepared and utilized to monitor mercury ions in aqueous solution. Upon addition of mercury to BI in DMSO/H<sub>2</sub>O (8:2, v/v) HEPES buffer (pH = 7.2) solution, an observable decrease of fluorescent to dim red change occurs that can be monitored by using fluorescence spectroscopy at room temperature. Concomitantly, a remarkably reducing in the emission maximum of BI takes place from 580 (a.u.) to 300 (a.u.). The observations indicate that association of the chemosensor with mercury ions leads to the supramolecular self-assembly breaking and the cooperation reaction occurrence, intra molecular charge density decreased in the chemosensor, the phenomenon likely responsible for the large decrease observed in emission spectra. And the detection limit of BI for the determination of mercury was estimated to be  $2.084 \times 10^{-9}$  M. Notably, this sensor serves as a recyclable component in sensing materials. The experiment proved that this sensor can be repeated use above 10 times. Therefore, the chemosensor has good application prospect for recognizing and detecting Hg<sup>2+</sup> in the environment.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Transition metal ions are particularly attractive, because these ions play important roles in living systems and have an extremely impact on the environment. Among transition-metal ions, mercury is considered as one of the most dangerous cations for the environment. Moreover, mercury has the persistent character in the environment and living organisms [1,2]. As a consequence of this pollution, mercury can accumulate in the human body, its high affinity for thiol groups in proteins and enzymes lead to the dysfunction of cells and consequently causing health problems, such as prenatal brain damage, serious cognitive and minamata disease [3–5]. As a result, there has been considerable interest in the development of effective tools for detecting Hg<sup>2+</sup> ions in the environment. As fluorescence measurement provides a powerful way for detecting metal ions because of its low detection limit and simple instrumentation, considerable efforts have been devoted to design fluorescent chemical sensors for detecting Hg<sup>2+</sup> [6–10]. Many Hg<sup>2+</sup> sensors based on pyrene, naphthalimide, bispyrenyl,

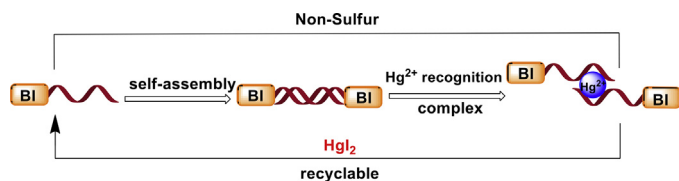
terphenyl, naphthylthiourea, dansyl have been reported [11]. However, most of these sensors are contain a sulfur moiety and the sensing process involves an irreversible coordination of mercury ion to the S atom. The mechanism for traditional sensors includes an affinity irreversible organic reaction driven by the extremely strong Hg–S affinity. (1) ring opening of spirocyclic systems (rhodamine, fluorescein, etc.), (2) intramolecular cyclic guanylation of thiourea derivatives, and (3) conversion of thio-carbonyl compounds into their carbonyl analogues or a sequential desulfurization–lactonization reaction [12–14].

Correspondingly, most of the traditional chemosensors, which contain a sulfur moiety and the sensing process involves an irreversible coordination of Hg<sup>2+</sup> to the S atom were unrecyclable. So the recyclable sensors for Hg<sup>2+</sup> are badly needed [15].

In current study, we have designed and synthesized a non-sulfur new fluorescent chemosensor which based on the mechanism of supramolecular self-assembly. (Scheme 1) [16]. The observations indicate that association of the probe with mercury ions leads to the supramolecular self-assembly breaking and the cooperation reaction occurrence, intra molecular charge density decreased in the probe, the phenomenon likely responsible for the large decrease observed in emission spectra. In addition, the 5-(4-nitrophenyl)-2-furan group act as fluorophores, while the presence

\* Corresponding author. Tel.: +86 9317973191.

E-mail address: [zhangwnu@126.com](mailto:zhangwnu@126.com) (Y.-m. Zhang).



**Scheme 1.** Tactics for the sensing of  $\text{Hg}^{2+}$ .

of semicarbazone in the same sensor molecule as the functional groups. A remarkable luminescence property is found and attribute to the hydrogen bond between semicarbazone group of Schiff base and the molecules form as a supramolecular system by means of self-assemble which enhance the rigidity of the molecules [17,18]. When  $\text{Hg}^{2+}$  is added, the fluorescence quenches rapidly ascribing the sensor and  $\text{Hg}^{2+}$  form as a complex broking the supramolecular system. Sensor BI showed fluorescent selectivity for mercury ion in DMSO/ $\text{H}_2\text{O}$  (8:2, v/v) HEPES buffer (pH = 7.2) solution over other common physiologically important metal. Moreover, probe BI displays a very fast response (<30 s) to mercury at room temperature, and the fluorescence intensity decreased by more than 300 a.u. with the addition of mercury can be observed by naked eyes. Furthermore, the test strips based on BI were fabricated, which could act as a convenient and efficient mercury ion test kits. To the best of our knowledge, this is a novel approach for selective recognition of mercury ions.

## 2. Experimental

### 2.1. Materials and physical methods

Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification.  $^1\text{H}$  NMR spectra were recorded with a Mercury-400BB spectrometer at 400 MHz.  $^1\text{H}$  chemical shifts are reported in ppm downfield

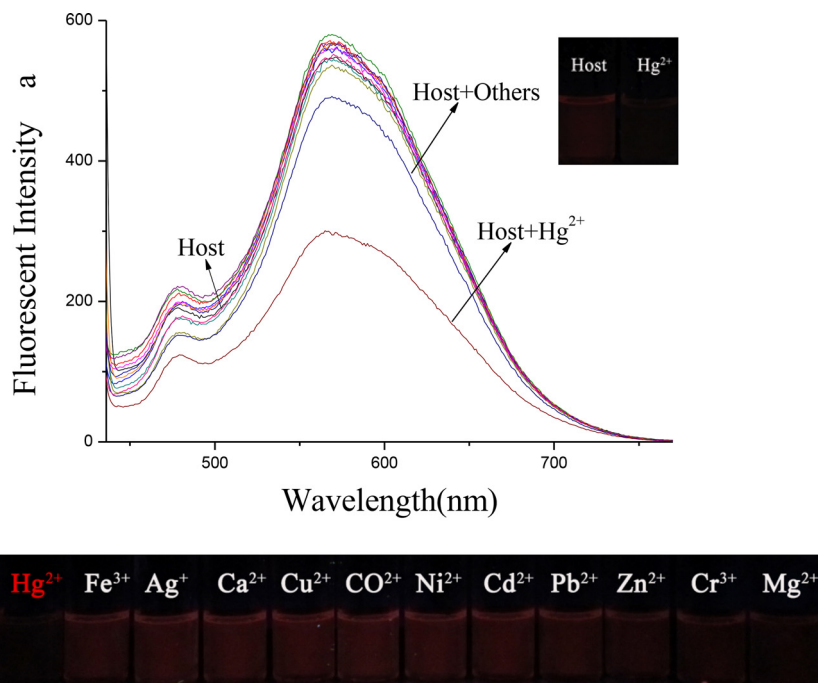
from tetramethylsilane (TMS,  $\delta$  scale) with the solvent resonances as internal standards. Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. XRD patterns were recorded at a scanning rate of  $5^\circ/\text{min}$  in the  $2\theta$  range of  $2\text{--}50^\circ$  with  $\text{Cu K}\alpha$  radiation.

### 2.2. Synthesis of sensor molecule BI

Compound BI can be readily prepared by a simple and low-cost Schiff base reaction of 5-(4-nitrophenyl)-2-furan formaldehyde and semicarbazide (Scheme 2). 5-(4-Nitrophenyl)-2-furan formaldehyde (0.418 g, 2 mmol), semicarbazide (0.1875 g, 2.5 mmol) and catalytic amount of acetic acid (AcOH) were combined in hot absolute ethanol (30 mL). The solution was stirred under reflux for 4 h. After cooling to room temperature, the yellow precipitate was filtered, washed three times with hot absolute ethanol, then recrystallized with EtOH to give a yellow powder product BI (1.472 mmol) in 73.6% yield (m.p.  $229^\circ\text{C}$ ),  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  10.46 (s 1H, N=CH), 8.29–7.02 (m 6H, ArH), 7.81 (m 1H, N–H), 6.51 (m 2H, H–N–H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ /ppm 156.27, 151.57, 151.29, 146.00, 135.37, 128.81, 124.32, 124.29, 113.36, 112.28. IR (KBr)  $\nu$ : 1606 (CH=N), 1527 (C=C), 3081 (ArH), 3583, 3525 (H–N–H)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_4$ : C, 52.55; H, 3.65; N, 20.44; O, 23.36. Found C, 52.47; H, 3.68; N, 20.45; O, 23.40. ESI-MS calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_4^+$  297.0, found 297.0.

### 2.3. General procedure for UV-vis experiments

All the UV-vis experiments were carried out in DMSO/ $\text{H}_2\text{O}$  (8:2, v/v) HEPES buffer (pH = 7.2) solution on a Shimadzu UV-2550



**Fig. 1.** (a) Fluorescence spectra upon excitation at 417 nm in DMSO/ $\text{H}_2\text{O}$  (8:2, v/v) HEPES buffer (pH = 7.2) solution of BI (20  $\mu\text{M}$ ) before and after addition of  $\text{Hg}^{2+}$  (20 equiv.). Inset: photographs showing the change in the fluorescence of BI after addition of  $\text{Hg}^{2+}$  (20 equiv.) in DMSO/ $\text{H}_2\text{O}$  (8:2, v/v) HEPES buffer (pH = 7.2) solution ( $\lambda_{\text{em}} = 568$  nm;  $\lambda_{\text{ex}} = 417$  nm). (b) Visual fluorescence emissions of probe BI (20  $\mu\text{M}$ ) after the addition of  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Mg}^{2+}$  (20 equiv.) in DMSO/ $\text{H}_2\text{O}$  (8:2, v/v) HEPES buffer (pH = 7.2) solution on excitation at 417 nm using UV-lamp at room temperature.

Download English Version:

<https://daneshyari.com/en/article/741990>

Download Persian Version:

<https://daneshyari.com/article/741990>

[Daneshyari.com](https://daneshyari.com)