Dyes and Pigments 96 (2013) 1-6

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

Colorimetric chemosensors designed to provide high sensitivity for Hg^{2+} in aqueous solutions

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ARTICLE INFO

Article history: Received 25 January 2012 Received in revised form 28 June 2012 Accepted 29 June 2012 Available online 25 July 2012

Keywords: Mercury cation Colorimetric sensor Specific selectivity High sensitivity Aqueous solutions Easy-to-make

1. Introduction

As mercury has an extremely toxic impact on the environment and human health [1–5], the development of chemosensors for the mercury cation (Hg^{2+}) has received considerable attention [6–10]. As is well known, mercury can lead to dysfunctions of the brain, kidney, stomach, and central nervous systems [1-5,11,12]. Therefore, the rational design and synthesis of efficient sensors to selectively recognize mercury cations is an important topic in supramolecular chemistry [6–10]. Although previous work has involved the development of a wide variety of chemical [13-43] and physical [44-48] sensors for the detection of Hg²⁺, so far, improving the detection selectivity in the context of interference from coexisting metal ions has been challenging. Moreover, most of these methods require expensive equipment and involve timeconsuming and laborious procedures that can be carried out only by trained professionals [44–48], which significantly restricting the practical application of these Hg^{2+} sensors. For simplicity, convenience and low cost, easily-prepared Hg^{2+} colorimetric sensors [15-23,30,38] are needed. On the other hand, in biological and environmental systems, mercury-sensor interactions commonly occur in aqueous solution [23-26], therefore, much

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ABSTRACT

The specific colorimetric detection of Hg²⁺ in the context of interference from coexisting metal ions in aqueous solutions is a challenge. Therefore, a series of easy-to-make Hg²⁺ colorimetric chemosensors **S1~S3**, bearing thiourea moiety as binding site and nitrophenyl moiety as signal group, were designed and synthesized. Among these sensors, **S3** showed excellent colorimetric specific selectivity and high sensitivity for Hg²⁺ in DMSO and DMSO/H₂O binary solutions. When Hg²⁺ was added to the solution of **S3**, a dramatic color change from brown to colorless was observed, while the cations Ca²⁺, Mg²⁺, Cd²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ag⁺ and Cr³⁺ did not interfere with the recognition process for Hg²⁺. The detection limits were 5.0×10^{-6} and 1.0×10^{-7} M of Hg²⁺ using the visual color changes and UV–vis changes respectively.

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attention has been paid to developing mercury sensors that work in the aqueous phase [17,23–26,32,34,49–52].

In view of this requirement and as part of our research effort devoted to ion recognition [53–60], an attempt was made to obtain efficient colorimetric sensors which could sense Hg^{2+} with specific selectivity and high sensitivity in aqueous solutions. This paper details the design and synthesis of a series of Hg^{2+} colorimetric sensors **S1~S3** bearing thiourea and nitrophenyl groups (Scheme 1). The strategies for the design of these sensors were as follows. Firstly, a thiourea group was introduced as the binding site. The C=S moiety on the thiourea group possesses a high affinity with Hg^{2+} . Secondly, in order to achieve "naked-eye" colorimetric recognition, we introduced nitrophenyl groups as the signal group. Finally, the sensor was designed to be easy to synthesize. In order to establish the signal group's contribution to the sensor's colorimetric sensing abilities for Hg^{2+} , compound **S1** which without containing the nitro-group was also synthesized.

2. Experimental section

2.1. Materials and physical methods

¹H NMR spectra were recorded with a Mercury-400BB spectrometer at 400 MHz ¹H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with the solvent



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Fig. 1. Color changes observed upon the addition of various cations (5 equiv.) to the solutions of sensor S3 (2×10^{-5} M) in DMSO solutions.

resonances as internal standards). High-resolution mass spectra were recorded on a Bruker APEXII Fourier transform ion cyclotron resonance (FTICR) MS instrument. Ultraviolet–visible (UV–vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer.

The inorganic salts $Ca(ClO_4)_2 \cdot 6H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$, $AgClO_4 \cdot H_2O$ and $Cr(ClO_4)_3 \cdot 6H_2O$ were purchased from Alfa Aesar Chemical Reagent Co. (Tianjin, China). All solvents and other reagents were of analytical grade.

2.2. General procedure for UV-vis spectroscopy

All the UV–vis experiments were carried out in DMSO solution on a Shimadzu UV-2550 spectrometer. Any changes in the UV–vis spectra of the synthesized compound were recorded on the addition of perchlorate metal salts while the ligand concentration was kept constant in all experiments.



Fig. 2. UV–Vis absorption spectra of **S3** in the presence of 5 equiv. of various cations in DMSO solution at room temperature.

2.3. General procedure for ¹H NMR

For ¹H NMR titrations, two stock solutions were prepared in DMSO- d_6 : one of them contained the host only and the second one contained an appropriate concentration of guest. Aliquots of the two solutions were mixed directly in NMR tubes.

2.4. Synthesis and characterization of sensors S1~S3

Benzoyl chloride (3 mmol), dry and powdered KSCN (4 mmol) and PEG-400 (0.1 mL, as phase transfer catalyst) were added to dry dichloromethane (15 mL). Then the reaction mixture was stirred at room temperature for 2 h, and the inorganic salts were filtered out. The filtrate was a solution of the corresponding benzoyl isothiocyanate, which did not need separating. Then 2.8 mmol of phenylhydrazine was added to the filtrate solution and stirred at room temperature for 3 h, yielding the precipitate of **S1**. After evaporating the solvent in a vacuum, the precipitate was filtered, washed with 75% ethanol three times, and recrystallized with ethanol to get white crystal of **S1**. The other compounds **S2** and **S3** were prepared by similar procedures.

S1: yield: 80.5%; m.p. 138–140 °C; ¹H-NMR (DMSO- d_6 , 400 MHz) δ 12.61 (s, 2H, NH), 11.59 (s, 1H, NH), 7.99–7.97 (m, 2H, ArH), 7.71–7.65 (m, 2H, ArH), 7.57–7.53 (m, 2H, ArH), 7.45–7.41 (m, 2H, ArH), 7.30–7.26 (m, 2H, ArH); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 179.18, 168.37, 138.02, 133.20, 132.18, 128.75, 128.69, 128.53, 126.42, 124.37; IR (KBr, cm⁻¹) v: 3444 (mb, N–H), 3310 (m, N–H), 3235 (m, N–H), 1678 (s, C=O), 1601 (s, C=C), 1525 (s, C=C), 1474 (s, C=C), 1276 (s, C=S); Anal. calcd. for C₁₄H₁₃N₃OS: C, 61.97; H, 4.83; N, 15.49; Found: C, 61.85; H, 4.74; N, 15.58.

S2: yield: 95.7%; m.p. 199–201 °C; ¹H-NMR (DMSO- d_6 , 400 MHz) δ 12.02 (s, 2H, NH), 9.77 (s, 1H, NH), 8.15–8.12 (m, 1H, ArH), 7.95–7.92 (m, 2H, ArH), 7.72–7.69 (m, 2H, ArH), 8.15–8.12 (m, 2H, ArH), 6.98–6.94 (m, 2H, ArH); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 182.07, 167.02, 159.06, 138.56, 133.11, 132.07, 128.94, 126.42, 125.86, 111.14; IR (KBr, cm⁻¹) v: 3441 (mb, N–H), 3259 (m, N–H), 3065 (m, N–H), 1648 (s, C=O), 1609 (s, C=C), 1571 (s, C=C), 1470 (s, C=C), 1292 (s, C=S); ESI-HRMS calcd. for [M + H] ⁺: *m/z* 316.0630, Found: 317.0710; Anal. calcd. for C₁₄H₁₂N₄O₃S: C, 53.16; H, 3.82; N, 17.71; Found: C, 53.37; H, 3.65; N, 17.59.

S3: yield: 85.4%; m.p. 216–219 °C; ¹H-NMR (DMSO-*d*₆, 400 MHz) δ 11.77 (s, 2H, NH), 10.65 (s, 1H, NH), 8.90 (s, 1H, ArH), 8.37 (d, 1H, J = 7.2, ArH), 8.00 (d, 2H, J = 8.0, ArH), 7.67 (t, 1H, J = 7.2, ArH), 7.55 (t,



Fig. 3. UV–vis absorption of sensor (a) S2, (b) S1 $(2.0 \times 10^{-5} \text{ M})$ in the presence of 5 equiv. of various cations in DMSO solution at room temperature.

2H, J = 7.6, ArH), 7.33 (d, 1H, J = 9.6, ArH); ¹³C NMR (DMSO- d_6 , 100 MHz) δ 181.35, 167.07, 162.32, 147.00, 137.25, 133.18, 132.01, 129.99, 128.78, 128.50, 123.07, 116.17; IR (KBr, cm⁻¹) v: 3367 (m, N–H), 3265 (m, N–H), 3143 (m, N–H), 1682 (s, C=O), 1618 (s, C=C), 1596 (s, C=C), 1490 (s, C=C), 1275 (s, C=S); ESI-HRMS calcd. for [M + H]⁺: m/z 362.0481, Found: 362.0554; Anal. calcd. for C₁₄H₁₁N₅O₅S: C, 46.54; H, 3.07; N, 19.38; Found: C, 46.83; H, 3.28; N, 19.27.

3. Results and discussion

The colorimetric sensing abilities were primarily investigated by adding various cations (Ca²⁺, Mg²⁺, Cd²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Hg²⁺, Zn²⁺, Pb²⁺, Ag⁺ and Cr³⁺) to the DMSO solutions of sensor **S3**. When 5 equivalent (equiv.) of Hg²⁺ was added to the solution of **S3** (2.0×10^{-5} M), the sensor responded with dramatic color changes from brown to colorless (Fig. 1). In the corresponding UV–vis spectrum, the absorption at 470 nm disappeared (Fig. 2). When adding 5 equiv. of Cu²⁺, the DMSO solution of **S3** showed color changes from brown to green. Meanwhile, the addition of Ag⁺ and Fe³⁺ also lead to slight color and UV–vis spectrum changes. Whereas when adding the cations Ca²⁺, Mg²⁺, Cd²⁺, Co²⁺, Ni²⁺, Zn²⁺, Pb²⁺, or Cr³⁺ into the DMSO solutions of sensor **S3**, no significant color or spectra changes were observed. Even though sensor **S3** showed colorimetric response toward Cu²⁺, Ag⁺ and Fe³⁺ in DMSO solutions, owing to only Hg²⁺ could bleaches the solution,



Fig. 4. UV–Vis absorption spectra of $S3~(2.0\times10^{-5}~M)$ in the presence of 5 equiv. of various cations in (9:1/v:v) DMSO/H_2O HEPES buffered solution at pH 7.40, room temperature.

therefore, in DMSO solution, ${\bf S3}$ showed specific colorimetric selectivity to ${\rm Hg}^{2+}.$

The same tests were applied to **S2** and **S1**. In this case, when various cations were added to the DMSO solutions of **S2** respectively, it was not only Hg^{2+} that induced a large blue shift from 495 nm to 372 nm (corresponding to a distinct color change from brown to colorless), but Fe^{3+} and Cr^{3+} caused similar spectra and color changes also (Fig. 3(a)). So sensor **S2** produced a colorimetric response to Hg^{2+} , Fe^{3+} and Cr^{3+} in DMSO solutions, however, owing to the color and UV–vis spectra changes were very similar, sensor **S2** could not selectively recognize Hg^{2+} , Fe^{3+} and Cr^{3+} . In addition, when various cations were added to the DMSO solutions of **S1** respectively, no obvious color or spectra changes were observed (Fig. 3(b)). Which indicated that **S1** couldn't colorimetric sense any cations under these conditions.

In order to investigate the mercury recognition abilities of **S3** in aqueous solution, we carried out the similar experiments in DMSO/ H_2O (9:1/v:v) HEPES buffered solution at pH 7.40. When adding 5 equiv. of Hg^{2+} to the DMSO/ H_2O HEPES buffered solution of **S3** (2.0×10^{-5} M), the sensor responded with dramatic color changes from brown to colorless, meanwhile, in the corresponding UV–vis spectra, the absorption at 470 nm disappeared (Fig. 4). While other cations couldn't cause such distinct color and spectra changes, therefore, the sensor **S3** could colorimetric recognition Hg^{2+} in DMSO/ H_2O binary solutions with specific selectivity.

Simultaneously, the same tests were applied to **S2** and **S1** also. As shown in Fig. S-1 in Supplementary data, the compound **S2** could response a lot of cations such as Hg^{2+} , Cu^{2+} , Cc^{2+} , Cr^{3+} and Fe^{3+} in DMSO/H₂O (9:1/v:v) HEPES buffered solution, however, **S2** could not selectively recognize these cations. Similarly, **S1** couldn't colorimetric response any cations in DMSO/H₂O binary solutions as well (Fig. S-2 in Supplementary data).

Therefore, according to these results we can find that, on the one hand, the nitrophenyl moiety acted as a signal group and played a crucial role in the process of colorimetric recognition. Because the **S1** doesn't employ nitrophenyl as signal group, it could not colorimetric sense any cations. On the other hand, **S2** and **S3** employ 4-nitrophenyl and 2,4-dinitrophenyl as signal groups respectively, they all possess colorimetric response abilities for above mentioned cations. However, due to the steric effects of *ortho*-nitro group on **S3**, other cations except Hg²⁺ couldn't coordinate with **S3**, thus the sensor **S3** showed specific selectivity toward Hg²⁺. Owing to the compound **S2** does not contain *ortho*-nitro group, there are no steric effects, many cations could coordinate with **S2**, hence the **S2** could not show selectivity toward those cations.

As **S3** showed specific selectivity for Hg^{2+} , a series of experiments was carried out to investigate the Hg^{2+} recognition capability and mechanism of **S3**. To gain an insight into the stoichiometry of the **S3**- Hg^{2+} complex, the method of continuous



Fig. 5. (a) A Job plot of S3 and Hg²⁺, which indicated that the stoichiometry of S3-Hg²⁺ complex was 1:1. (b) UV–vis spectral titration of sensor S3 with Hg²⁺ in DMSO solution. The non-linear fitting curve of the change in absorbance of S3 with respect to the amounts of Hg²⁺ is shown in the inset.



Fig. 6. The proposed reaction mechanism of the sensor S3 with Hg²⁺.

variations (Job's method) was used (Fig. 5a). As expected, when the molar fraction of sensor **S3** was 0.50, the absorbance value approached a maximum, which demonstrated the formation of a 1:1 complex between the sensor **S3** and Hg^{2+} .

The binding properties of sensor **S3** with Hg^{2+} were further studied by UV–vis titration experiments (Fig. 5b). It turned out that in DMSO solution of **S3**, with an increasing amount of Hg^{2+} , the absorbance at 470 nm decreased while a new band appeared at 398 nm. Such a blue



Fig. 7. Partial ¹H NMR of sensor **S3** (2.5 mM) in DMSO- d_6 upon the addition of Hg²⁺: (a) **S3** alone, then after adding (b) 0.1, (c) 0.2, (d) 0.5, (e) 0.7, (f) 0.9 and (g) 1 equiv. of Hg²⁺.

shift led to the solution color changing from brown to colorless. Two clear isosbestic points were observed at 434 and 337 nm, which indicated the formation of an **S3**-Hg²⁺ complex. By nonlinear least-squares fitting [61] at $\lambda_{max} = 469$ nm, the association constant Ka of the sensor **S3** toward Hg²⁺ was obtained as 6.04×10^4 M⁻¹.

To further elucidate the binding mode of the sensor S3 with Hg²⁺, ¹H NMR-titration were carried out by gradually adding Hg²⁺ into DMSO- d_6 solution of **S3**. As shown in Fig. 6, before the addition of Hg^{2+} , there were two intramolecular hydrogen bonds in the molecular structure of **S3**: one was $N-H^b...O=C$, and the other was $N-H^{c}...O=N$. The formation of these hydrogen bonds led to the ¹H NMR chemical shifts of $N-H^b$ and $N-H^c$ appearing at low-field. Owing to the fact that N-H^b...O=C is a very strong intramolecular hydrogen bond, as shown in Fig. 7, the ¹H NMR chemical shift of N-H^b appeared at the lowest field of the molecular **S3** at δ 11.77 ppm, which overlapped the proton signal of N–H^a. The ¹H NMR chemical shift of N–H^c appeared at δ 10.65 ppm. After the addition of 0.2 equivalent of Hg²⁺, an intergradation was formed between **S3** and Hg^{2+} (Fig. 6), which caused the ¹H NMR chemical shifts of the N–H^a, N–H^b and N–H^c to appear as two very broad peaks. For the same reason, the proton signals of N-H^e and N-H^f shifted downfield and broadened (Fig. 7). With the continuous addition of Hg²⁺, as shown in Fig. 6 the molecular structure underwent an intramolecular rotation, which induced the breaking of N–H^b...O=C and N–H^c...O=N; simultaneously, the interactions between the Hg²⁺...H^e–C and Hg²⁺...H^f–C were interrupted also.



Fig. 8. (a) UV–Vis absorption spectra, (b) photographs and UV–Vis absorption at 470 nm of sensor S3 (2.0×10^{-5} M) in DMSO solutions in the presence of Hg²⁺ (5 equiv.) and the miscellaneous cations Ca²⁺, Mg²⁺, Cd²⁺, Fa³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ag⁺ and Cr³⁺ (5 equiv., respectively).



Fig. 9. Color changes observed upon the addition of 5 equiv. of Hg^{2+} to the solutions of sensor **S3** (from right to left, 1×10^{-4} M, 1×10^{-5} M, 1×10^{-6} M) in DMSO solutions.

As a result, the stable Hg^{2+} -**S3** 1: 1 complex was formed via the coordination of Hg^{2+} with S=C and O=C groups on S3. The breaking of the hydrogen bonds led to an obvious up field shift of N-H^b and $N-H^{c}$ (Fig. 7d-f). On the other hand, owing to the interactions between the $Hg^{2+}...H^{e}-C$ and $Hg^{2+}...H^{f}-C$ were broken, the signals of N-H^e and N-H^f returned to their original positions (Fig. 7d–f). Namely, before all the 1 equiv. of Hg^{2+} was added, the intergradations and the stable Hg²⁺-S3 complex coexisted in the solution. Therefore, every proton signal of N-H^a, N-H^b, N-H^c, $C-H^e$ and $C-H^f$ displayed two signals, for the intergradations state and the stable Hg^{2+} -**S3** complex state respectively (Fig. 7d-f). After 1 equiv. of Hg^{2+} had been added, the intergradations completely changed into stable Hg²⁺-S3 complex. Accordingly, in the whole titration process, the signals of N-H^c, N-H^b and N-H^a shifted to δ 11.22, 10.49 and 10.24 ppm, respectively, and the proton signals of C–H^e and C–H^f were back to their original positions (Fig. 7g). In summary, according to the ¹H NMR-titration experiments, the Hg^{2+} ions and **S3** formed a stable 1: 1 complex by the coordination of Hg^{2+} with S=C and O=C groups on **S3**.

The recognition mechanism of the sensor **S3** with Hg²⁺ were investigated by IR spectra (Fig. S-3 in Supplementary data) also. In the IR spectra of **S3**, the stretching vibration absorption peaks of C=O and C=S appeared at 1682 and 1275 cm⁻¹ respectively. However, when **S3** coordinated with Hg²⁺ (1:1, solid complex, KBr), an electron transfer effect occurred from C=S and C=O to Hg²⁺, which induced the stretching vibration absorption peaks of C=O and C=S shifted to 1643 and 1262 cm⁻¹ accordingly. At the same time, owing to the influence of above mentioned electron transfer effect and the rupture of intramolecular hydrogen bonds N–H^b...O=C and N–H^c...O=N, stretching vibration absorption peaks of N–H^b and N–H^c shifted from 3265 and 3143 to 3225 and 3100 cm⁻¹ respectively. Which confirmed that **S3** coordinated with Hg²⁺ by C=O and C=S groups as shown in Fig. 6.

An important feature of the sensor is its high selectivity toward the analyte over other competitive species. The variations of UV–vis spectral and visual color changes of sensor **S3** in DMSO solutions caused by the metal ions Ca^{2+} , Mg^{2+} , Cd^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ag^+ and Cr^{3+} were recorded in Fig. 8. It is noticeable that the miscellaneous competitive metal ions did not lead to any significant interference. In the presence of these ions, the Hg²⁺ still produced similar color (Fig. 8(b)) and absorption changes (Fig. 8(a): the absorption at 470 nm disappeared). These results shown that the selectivity of sensor **S3** toward Hg²⁺ was not affected by the presence of other cations and suggested that it could be used as a colorimetric chemosensor for Hg²⁺.

The colorimetric and UV–vis limits of sensor **S3** for Hg²⁺ cation were also tested and are presented in Fig. 9. The detection limit using visual color changes was a concentration of 5.0×10^{-6} M of Hg²⁺ cation in 1.0×10^{-6} M solution of sensor **S3**, while the detection limit of the UV–vis changes calculated on the basis of $3s_B/S$ [62] is 1.0×10^{-7} M for Hg²⁺ cation, which pointing to the high detection sensitivity.

4. Conclusion

An easy-to-make Hg²⁺ colorimetric sensor **S3**, bearing thiourea moiety as the binding site and nitrophenyl moiety as the signal group, was designed and synthesized. This sensor showed specific selectivity for Hg²⁺ in DMSO and DMSO/H₂O binary solutions. Comparison with sensor **S1** indicated that the nitrophenyl moiety acted as a signal group and played a crucial role in the process of colorimetric recognition. Investigation of the recognition mechanism indicated that the sensor **S3** recognized Hg²⁺ by forming a stable 1:1 **S3**-Hg²⁺ complex. The coexistence of other cations did not interfere with the Hg²⁺ recognition process. Moreover, the detection limit of the sensor **S3** may be useful as a colorimetric sensor for monitoring Hg²⁺ levels in physiological and environmental systems.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (NSFC) (Nos. 21064006 and 21161018), the Natural Science Foundation of Gansu Province (1010RJZA018) and the Program for Changjian Scholars and innovative Research Team in University of Ministry of Education of China (IRT1177).

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.dyepig.2012.06.023.

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