Mercapto thiadiazole-based sensors with high selectivity and sensitivity for Hg^{2+} in aqueous solution

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Two simple mercapto thiadiazole-based sensors have been synthesised by a convenient method and exhibit excellent sensitivity and selectivity for Hg^{2+} in DMSO/H_2O (1:1, v/v) aqueous solution. The sensors react with Hg^{2+} to form stable complexes and the association constants, Ka, are 4.4×10^4 M^{-1} and 1.0×10^3 M^{-1}, respectively. Furthermore, the detection limit of one sensor towards Hg^{2+} is 8.0×10^{-7} M.

Keywords: mercury ion sensors, mercapto thiadiazole, cation recognition

The development of selective chemosensors for the detection of mercury ion is of particular interest, because mercury is considered one of the most toxic and dangerous heavy metal elements.[1–4] The design and synthesis of efficient sensors to selectively recognise Hg^{2+} is a fundamental goal for organic and analytical chemists.[5,6] Much effort has gone into the development of sensing devices for Hg^{2+}, involving chromogenic[7,8] and fluorescent chemosensors[9,10], and sensors based on electrochemical devices.[11] However, several significant challenges remain in these systems for practical application, such as cross-sensitivities toward other metal ions, low water solubility, and especially complicated and expensive synthesis. In view of this, and as a part of our research interest in molecular recognition,[12–14] we have attempted to obtain some easy-to-synthesise, highly selective and sensitive Hg^{2+} sensors. Our strategy for the design of Hg^{2+} sensors has been as follows. First, in order to obtain an optimum response towards Hg^{2+}, we have introduced S–H and thiadiazole groups into the same sensor molecule to strengthen the Hg^{2+} coordination capacity.[15] Second, the receptors were designed to be easily synthesised. The results showed that compounds **1** and **2** (see Scheme 1) displayed a highly selective and sensitive response toward Hg^{2+} in neutral aqueous solution.

Results and discussion

Compounds **1** and **2** were synthesised according to literature methods.[16] Compound **1** was prepared by mixing thiosemicarbazide (6.37 g, 0.06 mol) and CS_2 (7.61 g, 0.10 mol) in DMF solution under reflux conditions for 6 h. Then compound **1** (0.67 g, 0.005 mol) and *p*-nitrobenzaldehyde (0.76 g, 0.005 mol) were mixed in absolute ethanol, the solution was refluxed with stirring for 2–3 h, then cooled to room temperature and the solvent was removed by evaporation. Finally, the crude product was purified by recrystallisation from ethanol to give compound **2**.

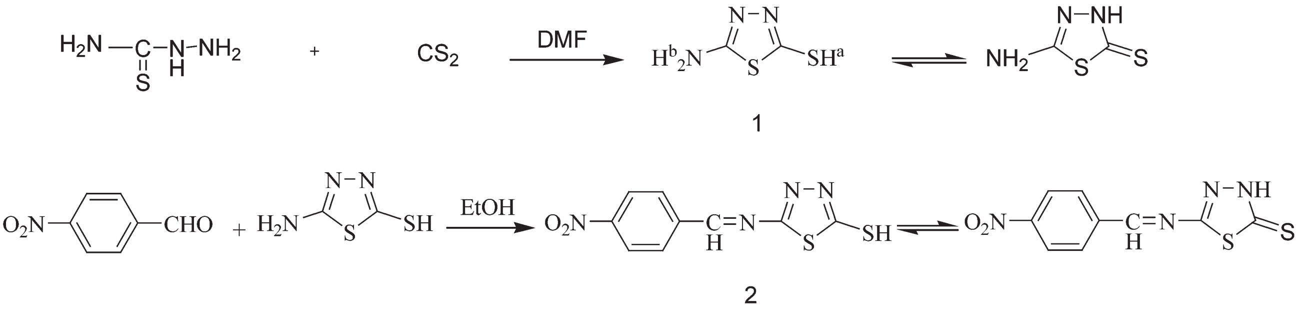
1: Yield: 89%, m.p. 235–236 °C (lit. 234–235 °C), ^{1}H NMR (DMSO-d_6, 400MHz) δ 13.21 (s, 1H, S–H), 7.13 (s, 2H, N–H), IR (KBr, cm^{-1}) *ν*: 3334 (N–H), 2925 (S–H), 1059 (C–N);

2: Yield: 60%, m.p. 219–221 °C (lit. 219–221 °C), ^{1}H NMR (DMSO-d_6, 400MHz) δ 8.81 (s, 1H, CH=N), 7.64 (S, 1H, N–H), 7.99–8.51 (m, 4H, PhH), IR (KBr, cm^{-1}) *ν*: 1561 (C=N), 3400–3250 (N–H).

The sensing abilities both **1** and **2** toward various metal cations, such as Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+} and Cu^{2+}, were primarily investigated by UV-Vis spectroscopy. Upon adding 2 equiv. of Hg^{2+} to DMSO solutions of sensor **1**, the absorption at 322 nm in the corresponding UV-Vis spectrum decreased sharply, accompanied by a blue shift of 42 nm. To validate the selectivity of **1**, the same tests were applied to other cations; no obvious changes were observed (Fig. 1). The binding of sensor **2** with metal cations in DMSO was also studied and a similar result was observed.

The selective response of **1** was investigated by adding various cations to its H_2O/DMSO (1:1, v/v) solution. Upon addition of 2 equiv. of Hg^{2+}, sensor **1** showed obvious changes in its UV-Vis spectrum (Fig. 2, in Electronic Supplementary Information, ESI). Other cations did not cause such a change. With the aim of excluding the possibility of these results being due to pH changes, we carried out the same experiments in DMSO/H_2O (9.5:0.5, v/v), HEPES (10 mM) buffered solutions at pH 7.20 for sensor **1**. A similar spectroscopic variation of the absorption band was found as above for aqueous solutions. Note also that the pH of the solution did not change during these experiments, clearly excluding any pH effects.

To explore further the utility of sensor **1** as an ion-selective chemosensor for Hg^{2+}, competitive experiments were carried out in the presence of 2.0 equiv. of Hg^{2+} and 2.0 equiv. of various metal ions in a HEPES-buffered solution of sensor **1**. The optical absorbance of sensor **1** with Hg^{2+} at 283 nm (Fig. 3 in ESI) was not influenced by the subsequent addition



Scheme 1 The synthesis of sensors **1** and **2**.

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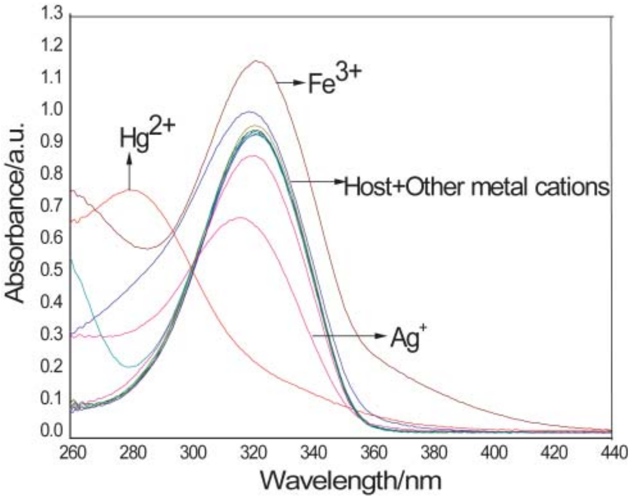

Fig. 1 UV-Vis absorption of sensor **1** (c = 4.0 × 10^{-5} mol L^{-1}) with various cations in DMSO at room temperature.

of miscellaneous cations, such as Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}, and Ca^{2+}, except for Fe^{3+} and Cu^{2+}. Owing to the competitive coordination of Fe^{3+} and Cu^{2+}, the optical absorbance of sensor **1** increased about 20% and 22% upon addition of Fe^{3+} and Cu^{2+}. Thus the sensitivity and selectivity of sensor **1** to Hg^{2+} exceed the other metallic cations.

The binding properties of sensors **1** and **2** toward Hg^{2+} were studied by UV-Vis titration experiments. It turned out that in DMSO solutions, following the increase of concentration of Hg^{2+}, an isosbestic point is clearly observed at 300 nm (Fig. 4), indicating the sensors **1** and **2** reacted with Hg^{2+} and formed stable complexes.[17] The association constants *K*a of sensors **1** and **2** toward Hg^{2+} were obtained as 4.4×10^{4} M^{-1} (R = 0.998) and 1.0×10^{3} M^{-1} (R = 0.997), respectively. Taken together, compared with the sensor **1**, the recognition abilities of sensor **2** toward Hg^{2+} are relatively weak. These results illustrated that **1** was the Hg^{2+}-specific chemosensor. Furthermore, with the probe concentrations employed in our studies, sensor **1** toward Hg^{2+} could be detected at least down to 8.0×10^{-7} M.

To further elucidate the binding mode, ^{1}H NMR-titration experiments of sensor **1** were conducted in DMSO-d_6 (Fig. 5). Before the addition of Hg^{2+}, the ^{1}H NMR chemical shifts of the S–H^a and N–H^b protons on sensor **1** were at δ 13.20 and 7.13 ppm, respectively. After the addition of 0.2 equiv. of Hg^{2+}, the signal peak shifted to δ 13.21 and 7.21 ppm for the S–H^a and N–H^b protons, respectively. With the addition of 0.5 equiv. of Hg^{2+}, the peak of the S–H^a proton was disappeared completely, and the resonance for N–H^b was shifted to δ 7.47 ppm. The above results suggested a possible interaction mode between sensor **1** and Hg^{2+}, in which Hg^{2+} was coordinated with the S of the mercapto group and the N of the thiadiazole.

In conclusion, chemosensors **1** and **2** were synthesized and showed high selectivity and sensitivities to Hg^{2+} in aqueous solution. There were three good features for these sensors. First, these sensors were very simple and easy to synthesise and showed remarkably high sensitivity and selectivity

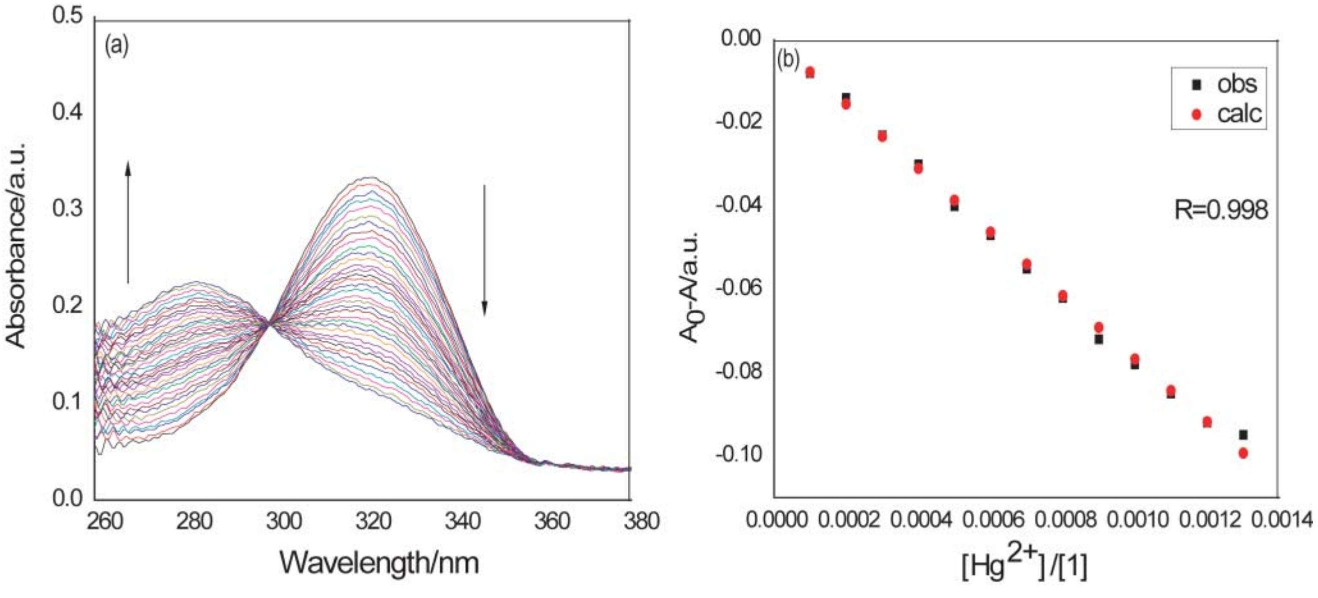

Fig. 4 (a) UV-Vis titration of sensor **1** (c = 2.0 × 10^{-5} mol L^{-1}) with Hg^{2+} (0-0.3equiv.) in DMSO solution. (b) The nonlinear fitting curve of change in absorbance of **1** at 322 nm with respect to amounts of Hg^{2+} in DMSO.

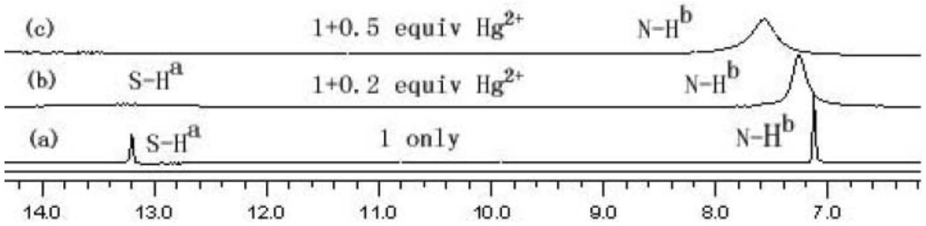

Fig. 5 Hg^{2+} ^{1}H NMR titration of sensor **1** (10.0 mM) in DMSO-d_6: (a) **1** only, (b) **1**+0.2 equiv. of Hg^{2+}, and (c) **1**+0.5 equiv. of Hg^{2+}.

toward Hg^{2+}. Second, Hg^{2+} could be detected at least down to 8.0×10^{-7} M. Third, these sensors could sense Hg^{2+} in aqueous solutions, which made it possible to determine Hg^{2+} for practical analysis.

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Electronic Supplementary Information

Figures 2 and 3 have been deposited in the ESI available through stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data.

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