Spectrochimica Acta Part A 93 (2012) 245–249

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

A highly selective colorimetric sensor for Hg^{2+} based on nitrophenyl-aminothiourea

Juan Liu[a,b], Mei Yu[a], Xi-Cun Wang[a,*], Zhang Zhang[a]

[a] 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
[b] College of Chemical Engineering, Northwest University for Nationalities, Lanzhou, Gansu 730030, PR China

ARTICLE INFO

Article history:
Received 17 August 2011
Received in revised form 20 February 2012
Accepted 12 March 2012

Keywords:
Mercury cation
Colorimetric sensors
Thiourea
Single selectivity
Sensitivity

ABSTRACT

A simple and highly selective colorimetric sensor (L1) bearing thiosemicarbazide moiety as binding site and nitrophenyl moiety as signal group were synthesized. Sensor L1 showed great colorimetric single selectivity and high sensitivity for mercury cation in DMSO and DMSO/H_2O binary solutions. When Hg^{2+} was added to the DMSO solution of L1, dramatic color change from brown to colorless was observed. While the cations Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3+} could not cause any distinct interferer toward the recognition process for Hg^{2+}. The detection limit is allowable to 5.0×10^{-6} and 1.0×10^{-7} M level of Hg^{2+} according to visual color change and UV–vis change, respectively. The recognition mechanism of the sensor toward mercury cation was evaluated in DMSO solutions by UV–vis and ^1H NMR. The sensor selectively sense Hg^{2+} *via* the formation of a stable 1:1 complex through C=S and C=O group with Hg^{2+}. When these complex bonds formed, the sensor carried out an ICT transition induced color change.

1. Introduction

Development of chemosensors for mercury cation (Hg^{2+}) has received considerable attention because mercury has an extremely toxic impact on the environment and human health [1–4]. For example, mercury can lead to the dysfunction of the brain [3], kidney [5], and central nervous systems [6]. Therefore, the rational design and synthesis of efficient sensors to selectively recognize mercury cation is an important field of supramolecular chemistry [7–9]. Although previous work developed a wide variety of chemical [10–22] and physical [23,24] sensors for the detection of Hg^{2+}, so far, it is still a challenge to improvement of the detection selectivity in the context of interference from coexisting metal ions. Moreover, most of these methods require expensive equipment and involve time-consuming and laborious procedures that can be carried out only by trained professionals [23–25]. This will significantly restrict the practical applications of these Hg^{2+} sensors. For simplicity, convenience and low cost, the easily prepared Hg^{2+} colorimetric sensors [26,27] are highly demanding.

In view of these and as an attempt to obtain an efficient Hg^{2+} colorimetric sensor, we have designed and synthesized a Hg^{2+} sensor **L1** bearing thiosemicarbazide groups (Scheme 1). The strategies for design of the sensor are as follows. Firstly, we have introduced thiourea group as binding site. The C=S moiety on thiourea group possesses high affinity to Hg^{2+}. Secondly, in order to achieve "naked-eye" recognition, we introduced nitrophenyl groups as the signal group. Finally, the sensor was designed to be easy to synthesize. In order to figure out the signal group's contribution to the Hg^{2+} sensing abilities of the sensor **L1**, compound **L2** of analogue structure but without containing nitro-group were also synthesized. Interestingly, the sensor **L1** could "naked-eye" recognize Hg^{2+} with high selectivity and sensitivity, other cations such as Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3+} could not cause any interference.

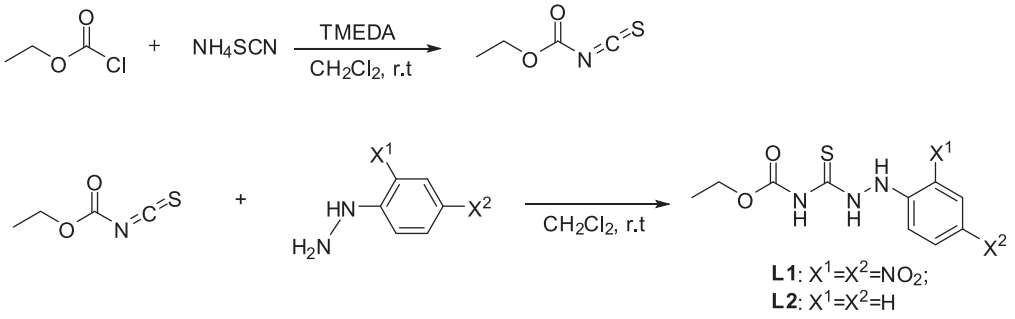
2. Experimental

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 resonances as internal standards). 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 FT-IR spectrophotometer.

* Corresponding author. Tel.: +86 931 7973193.
E-mail address: xicunwang@126.com (X.-C. Wang).

1386-1425/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2012.03.021



Scheme 1. Synthetic procedures for sensors **L1, L2**.

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 experiments

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 addition of perchlorate metal salts while keeping the ligand concentration constant in all experiments.

2.3. General procedure for ^{1}H NMR experiments

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

2.4. Synthesis and characterization of sensors L1, L2

The synthetic procedure is shown in Scheme 1, ethyl chloroformate (3 mmol), dry and powdered NH_4SCN (4 mmol) and 0.06 mL TMEDA (N, N, N′, N′-tetramethylethylenediamine, as catalyst) were added in dry dichloromethane (15 mL), the reaction mixture was stirred at room temperature for 2 h, then filtered out the inorganic salts, the filtrate is the solution of corresponding ethoxylcarbonyl isothiocyanate, which need not separate, added 2.8 mmol of (2,4-dinitrophenyl)hydrazine into the filtrate solution and stirred it in room temperature for 3 h, yield the precipitate of **L1**. After evaporated the solvent in vacuum, the precipitate was filtrated, washed with 75% ethanol three times, then recrystallized with ethanol to get yellow crystal of **L1**. The other compounds **L2** was prepared by the similar procedure.

L1: yield: 96.5%; m.p. 217–218 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.39 (s, 2H, NH), 10.49 (s, 1H, NH), 8.88 (s, 1H, ArH), 8.36–8.33 (m, 1H, ArH), 7.23–7.21 (m, 1H, ArH), 4.21 (q, J = 7.2, 2H, CH_2), 1.27 (t, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 181.02, 152.68, 147.41, 137.18, 129.89, 122.99, 116.09, 62.16, 14.18; IR (KBr, cm^{-1}) ν: 3444 (mb, N—H), 3309 (m, N—H), 3188 (s, N—H), 1736 (s, C=O), 1618 (s, C=C), 1596 (s, C=C), 1556 (s, C=C), 1510 (s, C=C), 1212 (s, C=S); Anal. Calcd. for $C_{10}H_{11}N_5O_6S$: C, 36.47; H, 3.37; N, 21.27; Found: C, 36.51; H, 3.65; N, 21.54.

L2: yield: 85.4%; m.p. 149–150 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.17 (s, 2H, NH), 10.42 (s, 1H, NH), 8.14–8.08 (m, 2H, ArH), 7.38–7.15 (m, 2H, ArH), 6.80–6.72 (m, 1H, ArH), 4.17 (q, J = 7.2, 2H, CH_2), 1.21 (t, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 180.23, 153.01, 147.55, 128.80, 127.90, 122.39, 119.50, 112.84, 61.93, 14.18; IR (KBr, cm^{-1}) ν: 3421 (mb, N—H), 3280 (s, N–H), 3168 (m, N–H), 1712 (s, C=O), 1602 (s, C=C), 1533 (s, C=C), 1492 (s, C=C), 1206 (s, C=S); Anal. Calcd. for $C_{10}H_{13}N_3O_2S$: C, 50.19; H, 5.48; N, 17.56; Found: C, 50.24; H, 5.25; N, 17.33.

3. Results and discussion

The colorimetric sensing abilities were primarily investigated by adding various cations Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Ag^+ and Cr^{3+} to the DMSO solutions of sensor **L1** (Figs. 1 and 2). When adding 5 equiv. of Ca^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Cr^{3+} to the solutions of sensor **L1** (2.0×10^{-5} M), respectively, no significant color or spectrum changes were observed. While, when adding 5 equiv. of Hg^{2+} to the solution of **L1** (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 Cu^{2+}, the DMSO solution of **L1** showed color changes from brown to green, in the corresponding UV–vis spectrum, the absorption at 470 nm was shifted to 447 nm and a weak broad absorption peak appeared at 640 nm. Meanwhile, the addition of Ag^+ and Fe^{3+} also lead to slight color and UV–vis spectrum changes. Even though sensors **L1** showed colorimetric response toward Cu^{2+}, Ag^+ and Fe^{3+} in DMSO solutions, owing to only Hg^{2+} could bleaches the solution, the sensor **L1** exhibited single selectivity for Hg^{2+}.

The same tests were applied to **L2** with various cations. No obvious color changes were observed when any of the cations were added to the solutions of **L2** in same conditions. These results elucidated that nitrophenyl moiety acted as a signal group and played a crucial role in the process of colorimetric recognition.

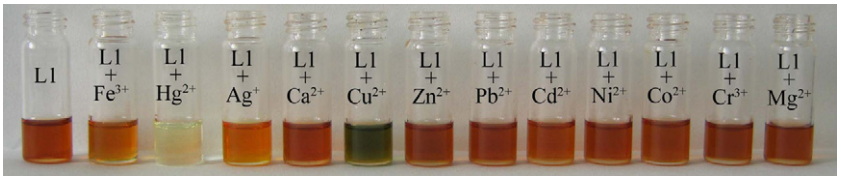


Fig. 1. Color changes observed upon the addition of various cations (5 equiv) to the solutions of sensor **L1** (2×10^{-5} M) in DMSO solutions. (For interpretation of references to color in this figure legend, the reader is referred to the web version of this article.)

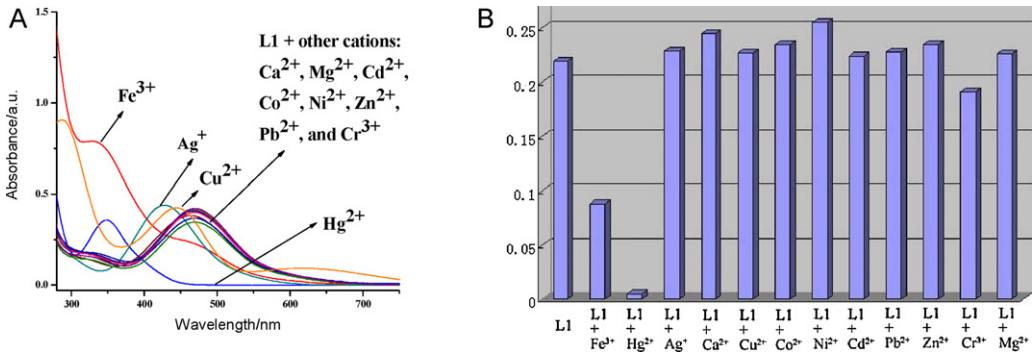


Fig. 2. (a) UV–vis absorption spectrum and (b) UV–vis absorption at 470 nm of **L1** (2.0×10^{-5} M) in the presence of 5 equiv of various cations in DMSO solution at room temperature.

In biological and environmental systems, cation-sensor interactions commonly occur in aqueous solution, therefore, much attention has been paid to developing cation sensors that work in the aqueous phase. For these reasons, we investigated the cation recognition abilities of sensor **L1** in DMSO/H_2O binary solutions using UV–vis spectroscopy. We carried out the similar experiments in 9:1 DMSO/H_2O HEPES (10 mM) buffered solution at pH 7.40 for sensors **L1** (2.0×10^{-5} M). When adding 5 equiv. of Hg^{2+} to the 9:1 DMSO/H_2O HEPES buffered solution of **L1**, the sensor responded with dramatic color changes from brown to colorless, meanwhile, in the corresponding UV–vis spectrum, the absorption at 470 nm disappeared (Fig. 3). While other cations could not cause such distinct color and spectrum changes, therefore, sensor **L1** could colorimetric recognition Hg^{2+} in DMSO/H_2O binary solutions with special selectivity.

To gain an insight into the stoichiometry of the sensor **L1**-Hg^{2+} complex, the method of continuous variations (Job's plot) was used (Fig. 4a). As expected, when the molar fraction of sensor **L1** was 0.50, the absorbance value approached a maximum, which demonstrated the formation of a 1:1 complex between sensor **L1** and Hg^{2+}.

The further binding properties of sensor **3** toward Hg^{2+} were studied by UV–vis titration experiments (Fig. 4b). It turned out that in DMSO solution of **L1**, with increasing of Hg^{2+}, the absorbance at 470 nm decreases while a new band appears at 401 nm. Such a blue shift led to the solution color changing from brown to colorless. Two clear isosbestic points are observed at 435 and 363 nm, which indicates the formation of **L1**-Hg^{2+} complex. By nonlinear least-squares fitting [28] at λ_{max} = 469 nm, the association constants Ka of the sensor **L1** toward Hg^{2+} was obtained as 6.04×10^4 M^{-1}.

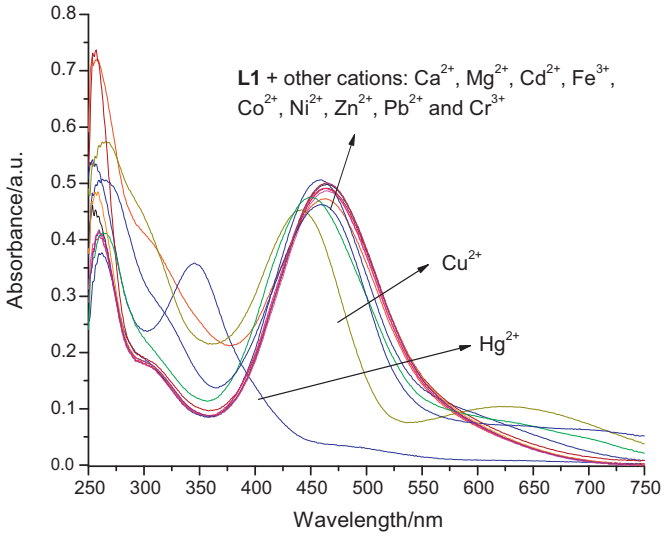


Fig. 3. UV–vis absorption spectrum of **L1** (2.0×10^{-5} M) in the presence of 5 equiv of various cations in 9:1 DMSO/H_2O HEPES (10 mM) buffered solution at pH 7.40, room temperature.

To further elucidate the binding mode of sensor **L1** with Hg^{2+}, ^1H NMR-titration spectra were measured, which illustrated the characteristic structural changes occurring upon interaction with Hg^{2+} in DMSO-d_6 solution. As shown in Fig. 5, there are two intramolecular hydrogen bonds in the molecular of **L1**, the one is N—H^b. . .O=C, the other is N—H^a. . .O=N. The formation of these hydrogen bonds

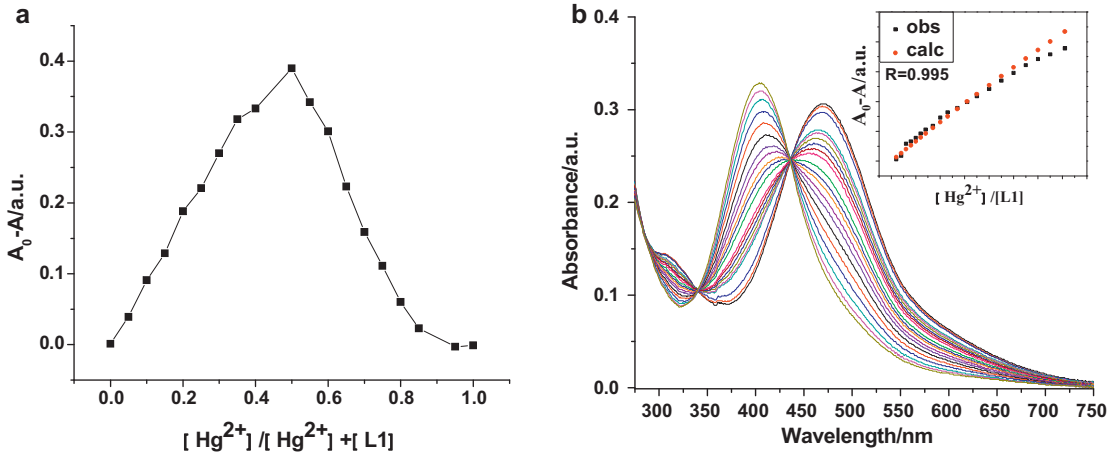


Fig. 4. (a) Job's plot of **L1** and Hg^{2+}, which indicated the stoichiometry of **L1**-Hg^{2+} complex is 1:1. (b) UV–vis spectral titration of sensor **L1** with Hg^{2+} in DMSO solution. The non-linear fitting curve of change in absorbance of **L1** with respect to amounts of Hg^{2+} was shown in the inset.

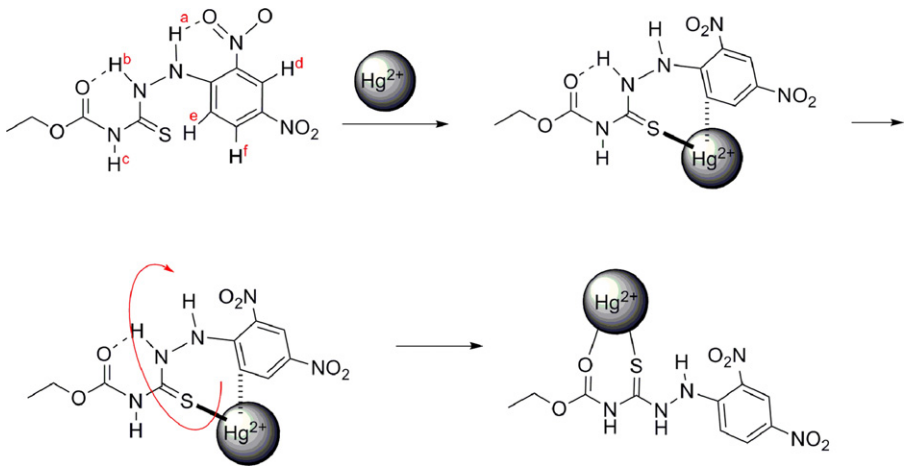


Fig. 5. The proposed reaction mechanism of the sensor **L1** with Hg^{2+}.

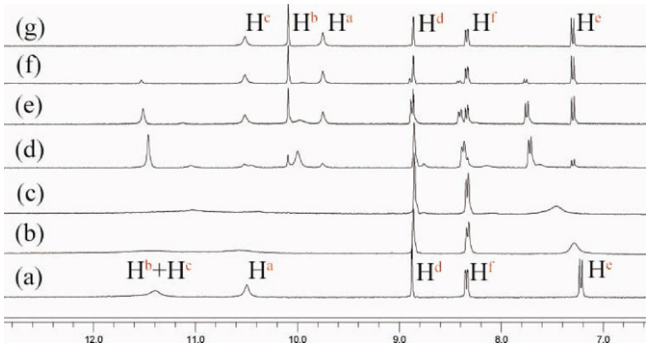


Fig. 6. Partial ^{1}H NMR spectra of sensor **L1** (2.5 mM) in DMSO-d_6 upon the addition of Hg^{2+}. (a) Free **L1**, after adding (b) 0.1, (c) 0.2, (d) 0.5, (e) 0.7, (f) 0.9 and (g) 1 equiv of Hg^{2+}.

leads to the ^{1}H NMR chemical shifts of N—H^a and N—H^b appeared at low-field. Owing the N—H^b. . .O=C is a very stronger intramolecular hydrogen bond, [29–34] as shown in Fig. 6, the ^{1}H NMR chemical shifts of N—H^b appeared at the lowest field of the molecular of **L1** at δ 11.39 ppm, which overlap the proton signal of N—H^c. While the ^{1}H NMR chemical shifts of N—H^a appeared at δ 10.49 ppm. After the addition of 0.2 equiv. of Hg^{2+}, a transition-state was formed between **L1** and Hg^{2+}(Fig. 5), which induced the ^{1}H NMR chemical shifts of the N—H^a, N—H^b and N—H^c appeared 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. 6). With the continuous addition of Hg^{2+}, as shown in Fig. 5, the molecule structure carried out an intramolecular rotation, which induced the rupture of N—H^b. . .O. . .C and N—H^a. . .O=N, simultaneously, the interactions between the Hg^{2+}. . .H^e—C and Hg^{2+}. . .H^f—C were interrupted also. As a result, the stable Hg^{2+}-**L1** 1: 1 complex formed by the coordinate of Hg^{2+} with S=C and O=C groups on **L1**, however, the rupture of the hydrogen bonds lead to the signals of N—H^b and N—H^a moved up field (Fig. 6d–f), on the other hand, owing to the interactions between the Hg^{2+}. . .H^e—C and Hg^{2+}. . .H^f—C were interrupted, the signals of C—H^e and C—H^f backed to the original location (Fig. 6d–f). Along with these processes, the intramolecular charge-transfer (ICT) transition was interrupted, which induced a blue-shift in UV–vis spectrum and depigmentation of **L1**. Namely, before all the 1 equiv. of Hg^{2+} was added, the transition-state and the stable Hg^{2+}-**L1** complex coexisted in the solution, therefore, every proton signals of N—H^a, N—H^b, N—H^c, C—H^e and C—H^f displayed two signals, for the transition-state and the stable Hg^{2+}-**L1** complex state, respectively (Fig. 6d–**f**). After 1 equiv. of Hg^{2+} had been added, the transition-state completely changed into stable Hg^{2+}-**L1** 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 10.23 ppm respectively and the proton signals of C—H^e and C—H^f backed to the original position (Fig. 6g). In summary, according to the ^{1}H NMR-titration experiments, the Hg^{2+} and **L1** formed a stable 1: 1 complex by the coordinate of Hg^{2+} with S=C and O=C groups on **L1**.

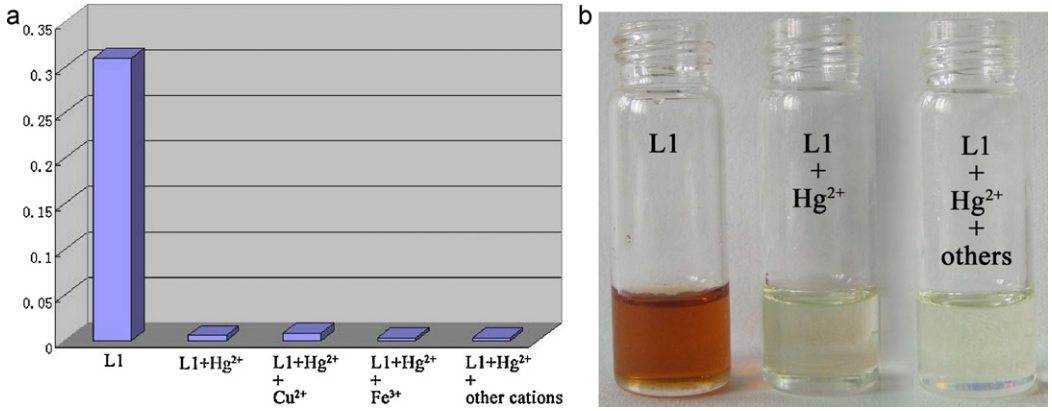


Fig. 7. UV–vis absorbance (a) and photographs (b) of sensor **L1** (2.0×10^{-5} M) in DMSO solutions in the presence of Hg^{2+} (5 equiv) and miscellaneous cations including Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3} (5equiv, respectively, at 470 nm).

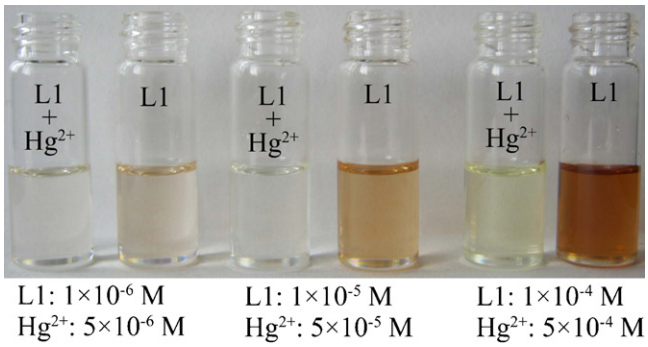


Fig. 8. Color changes observed upon the addition of 5 equiv. of Hg^{2+} to the solutions of sensor **L1** (from right to left 1×10^{-4} M, 1×10^{-5} M, 1×10^{-6} M) in DMSO solutions. (For interpretation of references to color in this figure legend, the reader is referred to the web version of this article.)

An important feature of the sensor is its high selectivity toward analyte over other competitive species. Variations of UV–vis spectral and visual color changes of sensor **L1** in DMSO solutions caused by miscellaneous metal ions including Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3+} are recorded in Fig. 7. It is noticeable that the miscellaneous competitive metal ions did not lead to any significant spectral change: in the presence of these metal ions, the Hg^{2+} still resulted in the similar absorption changes (see Fig. 7). These results implied that the selectivity of sensor **L1** toward Hg^{2+} was remarkable and sensor **L1** can be used as a potential chemosensor for Hg^{2+} ions.

The colorimetric and UV–vis limits of sensor **L1** for Hg^{2+} cation was also tested and presented in Fig. 8. The detection limit within visual color changes is allowable to 5.0×10^{-6} M level of Hg^{2+} cation in 1.0×10^{-6} M solution of sensor **L1**. While the detection limit of the UV–vis changes calculated on the basis of $3\,s_B/S$ [35] is 1.0×10^{-7} M for Hg^{2+} cation, pointing to the high detection sensitivity.

4. Conclusion

In conclusion, we designed and synthesized an easy-to-make Hg^{2+} sensor **L1** which bearing thiosemicarbazide moiety as recognition site and nitrophenyl moiety as signal group. Sensor **L1** showed colorimetric single selectivity for Hg^{2+} in DMSO and DMSO/H_2O binary solutions. Comparison with sensor **L2** indicates that the nitrophenyl moiety acted as a signal group and played a crucial role in the process of colorimetric recognition. The researches of recognition mechanism indicated that the sensor **L1** recognize Hg^{2+} by form a stable 1:1 **L1**-Hg^{2+} complex. The coexisting of other cations could not interfere the Hg^{2+} recognition process, moreover, the detection limit of the sensor **L1** toward Hg^{2+} is 1.0×10^{-7} M, which indicated that the sensor **L1** could potentially be useful as a probe for monitoring Hg^{2+} levels in physiological and environmental systems.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (Nos. 20902073 and 21062017), the Natural Science Foundation of Gansu Province (No. 096RJZA116), and the Fundamental Research Funds for the Central Universities" (No. zyz2011062).

References

[1] A. Curley, V.A. Sedlak, E.F. Girling, R.E. Hawk, W.F. Barthel, P.E. Pierce, W.H. Likosky, Science 2 (1971) 65–67.
[2] H.H. Harris, I.J. Pickering, G.N. George, Science 301 (2003), 1203-1203.
[3] P.B. Tchounwou, W.K. Ayensu, N. Ninashvili, D. Sutton, Environ. Toxicol. 18 (2003) 149–175.
[4] L. Campbell, D.G. Dixon, R.E. Hecky, J. Toxicol, Environ. Health Part B 6 (2003) 325–356.
[5] R.K. Zalups, Pharmacol. Rev. 52 (2000) 113–143.
[6] L.E. Strong, J. Chem. Educ. 49 (1972) 28–29.
[7] G. Aragay, J. Pons, A. Merkoçi, Chem. Rev. 111 (2011) 3433–3458.
[8] E.M. Nolan, S.J. Lippard, Chem. Rev. 108 (2008) 3443–3480.
[9] D.T. Quang, J.S. Kim, Chem. Rev. 110 (2010) 6280–6301.
[10] E. Coronado, J.R. Galán-Mascarós, C. Martí-Gastaldo, E. Palomares, J.R. Durrant, R. Vilar, M. Gratzel, M.K. Nazeeruddin, J. Am. Chem. Soc. 127 (2005) 12351–12356.
[11] S.-K. Ko, Y.-K. Yang, J. Tae, I. Shin, J. Am. Chem. Soc. 128 (2006) 14150–14155.
[12] F. Song, S. Watanabe, P.E. Floreancig, K. Koide, J. Am. Chem. Soc. 130 (2008) 16460–16461.
[13] S. Ando, K. Koide, J. Am. Chem. Soc. 133 (2011) 2556–2566.
[14] M. Santra, B. Roy, K.H. Ahn, Org. Lett. 13 (2011) 3422–3425.
[15] Y. Yan, Y. Hu, G. Zhao, X. Kou, Dyes Pigments 79 (2008) 210–215.
[16] C. Chen, R.Y. Wang, L.Q. Guo, N.Y. Fu, H.J. Dong, Y.F. Yuan, Org. Lett. 13 (2011) 1162–1165.
[17] G.V. Ramesh, T.P. Radhakrishnan, ACS Appl. Mater. Interfaces 3 (2011) 988–994.
[18] M. Suresh, A.K. Mandal, S. Saha, E. Suresh, A. Mandoli, R.D. Liddo, P.P. Parnigotto, A. Das, Org. Lett. 12 (2010) 5406–5409.
[19] P. Mahato, A. Ghosh, S. Saha, S. Mishra, S.K. Mishra, A. Das, Inorg. Chem. 49 (2010) 11485–11492.
[20] M. Suresh, S. Mishra, S.K. Mishra, E. Suresh, A.K. Mandal, A. Shrivastav, A. Das, Org. Lett. 11 (2009) 2719–2956.
[21] A. Ghosh, B. Ganguly, A. Das, Inorg. Chem. 46 (2007) 9912–9918.
[22] S. Saha, P. Mahato, U.G. Reddy, E. Suresh, A. Chakrabarty, M. Baidya, S.K. Ghosh, A. Das, Inorg. Chem. 51 (2012) 336–345.
[23] L.-Y. Lin, L.-F. Chang, S.-J. Jiang, J. Agric. Food Chem. 56 (2008) 6868–6872.
[24] S.P. Dolan, D.A. Nortrup, P.M. Bolger, S.G. Capar, J. Agric. Food Chem. 51 (2003) 1307–1312.
[25] I.S. Osborne, Science 19 (2004) 1733.
[26] L. Tang, F. Li, M. Liu, R. Nandhakumar, Spectrochim. Acta A 78 (2011) 1168–1172.
[27] M. Kadarkaraisamy, S. Thammavongkeo, P.N. Basa, G. Caple, A.G. Sykes, Org. Lett. 13 (2011) 2364–2367.
[28] B. Valeur, J. Pouget, J. Bouson, M. Kaschke, N.P. Ernsting, J. Phys. Chem. 96 (1992) 6545–6549.
[29] Q. Lin, T.-B. Wei, Y.-M. Zhang, Phosphorus Sulfur and Silicon and the Related Elements 182 (2007) 863–871.
[30] D.A. Jose, D.K. Kumar, P. Kar, S. Verma, A. Ghosh, B. Ganguly, H.N. Ghosh, A. Das, Tetrahedron 63 (2007) 12007–12014.
[31] D.A. Jose, D.K. Kumar, B. Ganguly, A. Das, Org. Lett. 6 (2004) 3445–3448.
[32] M. Suresh, S.K. Mishra, S. Mishra, A. Das, Chem. Commun. 18 (2009) 2496–2498.
[33] M. Suresh, A. Ghosh, A. Das, Chem. Commun. 33 (2008) 3906–3908.
[34] A. Ghosh, D.A. Jose, A. Das, B. Ganguly, J. Mol. Model. 16 (2010) 1441–1448.
[35] Analytical Methods Committee, Recommendations for the definition, estimation and use of the detection limit, Analyst 112 (1987) 199–204.