A new selective colorimetric and fluorescent sensor for Hg^{2+} and Cu^{2+} based on a thiourea featuring a pyrene unit

Wei-Chi Lin, Chen-Yu Wu, Zhao-Hong Liu, Chi-Yung Lin, Yao-Pin Yen*

Department of Applied Chemistry, Providence University, 200 Chungchi Road, Sha-Lu, Taichung Hsien 433, Taiwan

ABSTRACT

A new artificial receptor **1** was developed, and its chromogenic and fluorogenic behaviors toward various metal ions were investigated. Receptor **1** shows exclusively responses toward Hg^{2+} and Cu^{2+} ions. It selectively senses Hg^{2+} and Cu^{2+} ions through two different color changes in aqueous solution (DMSO/H$_2$O = 4/1) and also distinguishes them from other metal ions. In addition, receptor **1** also exhibits pronounced enhancements of the fluorescence, which can visually be discernible by an orchid fluorescence in the presence of Hg^{2+} ions and a strong blue fluorescence in the presence of Cu^{2+} ions.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The development of selective and sensitive chemosensors for the determination of transition and heavy metal ions has been received considerable attention because they play important roles in living systems and have an extremely toxic impact on the environment [1–5]. Among them, mercury is considered as one of the most dangerous metal ions for environment because it is widely distributed in air, water and soil. Mercury can accumulate in the human body and affects a wide variety of diseases even in a low concentration, such as prenatal brain damage, serious cognitive and motion disorders and Minamata disease [6–8]. On the other hand, copper is the third in abundance among the essential heavy metal ions in human body. The alterations of its cellular level are connected to serious neurodegenerative disease, such as Menkes and Wilson diseases [9–11]. Furthermore, copper ion is a significant environmental pollutant [12].

In recent years, many efforts have devoted to design various chemosensors specific for Hg^{2+} and Cu^{2+} detection [13–34]. One of the most attractive approaches focuses on the research of novel colorimetric and fluorescent Hg^{2+} and Cu^{2+} ion sensors, which allow naked eye's detection of the change of color and fluorescent emission upon Hg^{2+} and Cu^{2+} inducing reaction without any use of a spectroscopic instrument. However, most chemosensors developed so far have been known to be related to their fluorescence changes upon these metal ions [17,19,27,35–43]. As we know, chemosensors inducing both color changes and fluorescence changes are still rather rare [44–46].

Because Hg^{2+} and Cu^{2+} are both highly thiophilic metal ions, a suitable designed pyrene-substituted phenylthiourea might be a good candidate for the selective sensing of these two ions. In this context, the sensor proposed contains a pyrene unit and a 4-methylphenylthiourea moiety, in which the thiourea group is responsible for the Hg^{2+} and Cu^{2+} ions recognition leading to unique color and fluorescence changes. The pyrene subunit is versatile and frequently employed for the construction of important chemosensors having efficient fluorogenic behavior [47–49]. The 4-methylphenyl group herein is very useful because the color change is remarkably responsive to an electronic effect of substrate species in the event of the Hg^{2+} and Cu^{2+} ion-induced chemodosimetric desulfurization or complexation. In this paper, we report the synthesis of sensor **1** and its photochemical elucidation of its selective color and fluorescence changes toward Hg^{2+} and Cu^{2+} ions.

The receptor **1** was synthesized by the reaction of 4-methylphenyl isothiocyanate with 1-aminopyrene in high yield (Scheme 1). To make sure the mercury-induced desulfurization happened in this event, **2** (90% yield) was isolated from the reaction of **1** with 1 equivalent of Hg(NO$_3$)$_2$ in CHCl$_3$/CH$_3$CN at room temperature. Moreover, the authentic compound **2** was also prepared by the direct reaction of the corresponding 4-methylphenyl isocyanate with 1-aminopyrene in good yield. All of these compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR, and HRMS.

* Corresponding author. Tel.: +886 4 26328001x15218; fax: +886 4 26327554.
 E-mail address: ypyen@pu.edu.tw (Y.-P. Yen).
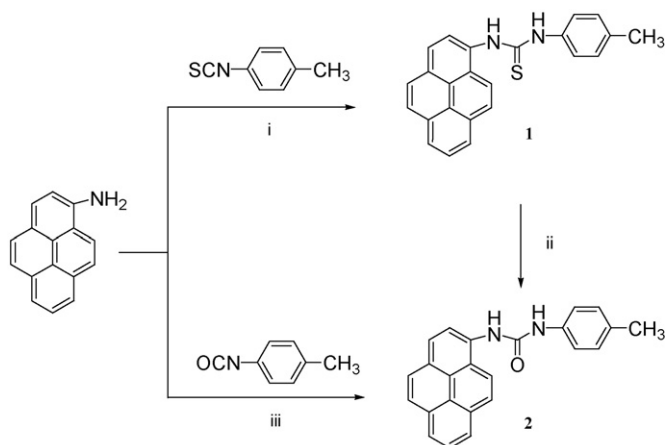
Scheme 1. Reagents and conditions: (i) CHCl₃/CH₃CN, reflux, 84 h; (ii) Hg(NO₃)₂, CHCl₃/CH₃CN, rt, 0.5 h and (iii) CHCl₃/CH₃CN, reflux, 84 h.

2. Experimental

2.1. Chemicals

All reagents used were of at least analytical grade. All metal ions, in the form of nitrate salts (NO_3^- does not complex with receptor **1**; see Fig. S1 in Supporting Information), were purchased from Sigma or Aldrich chemical company and were stored in desiccators under vacuum containing self-indicating silica. Solvents were purified prior to use and were stored under nitrogen. Dimethyl sulfoxide was dried with calcium hydride and distilled in reduced pressure.

2.2. Instrumentation

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. UV–vis spectra were measured on a Cary 300 spectrophotometer. Fluorescence spectra were performed on HITACHI F-4500 fluorescence spectrophotometer.

2.3. Synthesis and characterization of compounds **1–2**

1-(4-Methylphenyl)-3-(pyren-1-yl)thiourea (**1**): Under nitrogen, to a stirred solution of 1-aminopyrene (0.22 g, 1.0 mmol) in CHCl₃/CH₃CN (3/1, v/v, 20 mL), 4-methylphenyl isothiocyanate (0.14 g, 1.0 mmol) in CHCl₃ (10 mL) was slowly added at room temperature. The resulting mixture was stirred and heated to reflux for 84 h. The solution was cooled and filtered. The residue was purified

by recrystallization from ethanol to give **1** (0.31 g, 82% yield) as a pale dark olivegreen solid. Mp: 196.1–197.0 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.16 (s, 1H), 9.76 (s, 1H), 8.32–8.22 (m, 5H), 8.20–8.18 (m, 2H), 8.10–8.06 (m, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): 181.8, 137.4, 134.3, 133.6, 131.1, 131.0, 130.8, 126.2, 125.8, 125.6, 125.4, 125.0, 124.9, 124.4, 124.3, 123.2, 21.0 ppm. FAB MS m/z = 366.1193 [M]⁺, calc. for $C_{24}H_{18}N_2S$ = 366.1192.

1-(4-Methylphenyl)-3-(pyren-1-yl)urea (**2**): The preparation of **2** followed the above-mentioned procedure using 1-aminopyrene and 4-methylphenyl isocyanate in the same molar ratio. Yield: 0.29 g (65%). Mp: 278–279 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.16 (s, 1H), 9.05 (s, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.36 (d, J = 9.2 Hz, 1H), 8.29–8.15 (m, 4H), 8.13–8.00 (m, 3H), 7.45 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): 153.5, 137.6, 133.6, 131.6, 131.3, 131.1, 139.8, 127.8, 127.4, 126.9, 126.8, 126.1, 125.8, 125.4, 125.0, 124.9, 124.7, 121.5, 121.4, 120.3, 118.8, 20.80 ppm. FAB MS m/z = 350.1393 [M]⁺, calc. for $C_{24}H_{18}N_2O$ = 350.1396.

2.4. Isolation and characterization of compound **2**

Isolation of 1-(4-methylphenyl)-3-(pyren-1-yl)urea (**2**): To a solution of **1** (0.05 g, 0.1 mmol) in CHCl₃/CH₃CN (3/1, v/v, 20 mL), Hg(NO₃)₂·H₂O (0.10 g, 0.3 mmol) in CHCl₃ (10 mL) was slowly added. The resulting mixture was stirred at room temperature for 30 min and then washed with saturated Na₂S solution and water, dried over MgSO₄ and evaporated in vacuo. The residue was purified by column chromatography on SiO₂ using CHCl₃/CH₃CN/hexane = 2/1/1 as the eluent to give **2** (0.04 g, 81%) as a yellow solid. The spectral data are consistent with the above data.

3. Results and discussion

3.1. UV–vis titration studies

The absorption spectrum of **1** shows the typical pyrene absorption bands in the region of 235–350 nm which was responsible for its pale yellow color. Upon addition of increasing amounts of Hg²⁺ ions to a solution of **1** (3.0×10^{-5} M) in the mixed solvent (DMSO/H₂O = 4/1, v/v, buffered with HEPES, pH 7.8), the absorption peaks initially at 278 and 334 nm were gradually decreased while two new peaks at 284 and 361 nm were evolved with two isosbestic points at 281 and 336 nm, respectively (Fig. 1a). The color of the solution changed from pale yellow to brown color (Fig. 3b). On the other hand, upon treatment with Cu²⁺ ions, the absorption peaks at 278, 334 and a shoulder peak at 388 nm were gradually
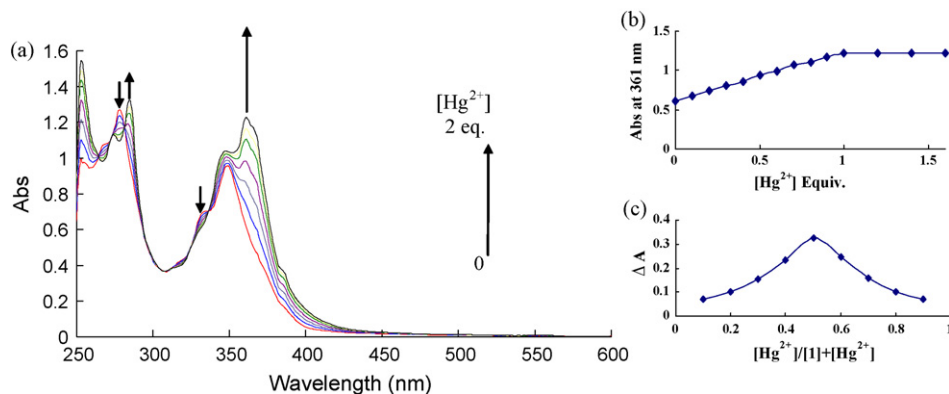
Fig. 1. Family of spectra taken in the course of the titration of **1** (3.0×10^{-5} M, DMSO/H₂O = 4/1, v/v, buffered with HEPES, pH 7.8) with a standard solution of Hg²⁺ at 25 °C. Titration profiles (insert) indicate the formation of a 1:1 complex.
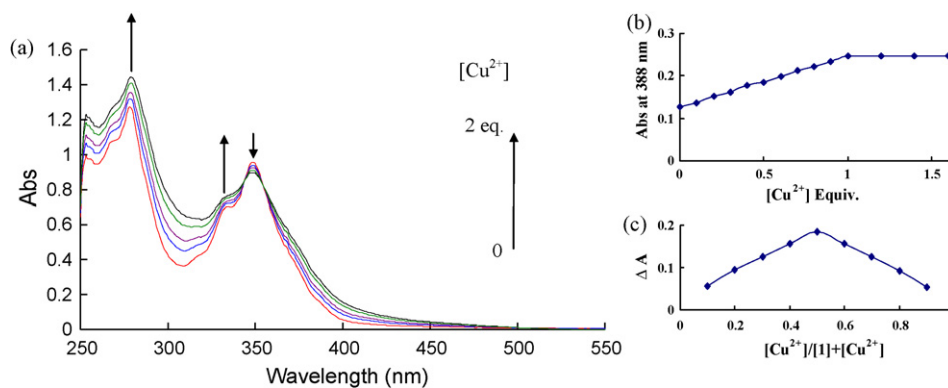
Fig. 2. (a) Family of spectra taken in the course of the titration of **1** (3.0×10^{-5} M, DMSO/H$_2$O = 4/1, v/v, buffered with HEPES, pH 7.8) with a standard solution of Cu^{2+} at 25 °C. Titration profiles (insert) indicate the formation of a 1:1 complex.

increased while the peak at 348 nm was gradually decreased with two isosbestic points at 344 and 354 nm (Fig. 2a). The color of the solution changed from pale yellow to green yellow (Fig. 3b). Both signals were complete within 1 min (see Figs. S2 and S3 in Supporting Information). By plotting the changes in **1** in the absorbance intensity at 361 nm as a function of Hg^{2+} concentration or at 388 nm as a function of Cu^{2+} concentration, sigmoidal curves were obtained and are shown in the inset of Figs. 1b and 2b, respectively. To corroborate 1:1 ratio between **1** and Hg^{2+} or Cu^{2+} ions, Job's plots analyses were also executed and both confirmed the 1:1 stoichiometry (Figs. 1c and 2c).

3.2. Interference from other metal ions

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 **1** in aqueous solutions caused by miscellaneous metal ions including Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} were recorded in Fig. 3a. It is noticeable that the miscellaneous competitive metal ions did not lead to any significant spectral change, in the presence of miscellaneous competitive metal ions, the Hg^{2+} and Cu^{2+} ions still resulted in the similar absorption changes (see Figs. S4a and S4b in Supporting Information). These results implied

that the selectivity of **1** toward Hg^{2+} and Cu^{2+} was remarkable and made **1** as a selective chromogenic sensor for Hg^{2+} and Cu^{2+} ions.

3.3. Fluorescent studies

To further explore the utility of **1** as an ion-selective fluorescence sensor for Hg^{2+} and Cu^{2+} ions, the fluorogenic behavior of **1** was investigated under the same conditions. Upon addition of the Hg^{2+} ions, two new emission peaks at 401 and 424 nm were gradually evolved (Fig. 4). Similarly, upon addition of Cu^{2+} ion, the emission peaks at 396 and 439 nm were also gradually increased (Fig. 5). The fluorescence enhancement induced either by the addition of Hg^{2+} or Cu^{2+} ion was observed and both signals were complete within 1 min (see Figs. S5 and S6 in Supporting Information). Upon interaction with various metal ions (Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}), only Hg^{2+} and Cu^{2+} ions can induce a sizable enhancement in fluorescence intensities (55-fold and 45-fold, respectively). The fluorescence changes were observed from weak blue to orchid for the determination of Hg^{2+} or from weak blue to strong blue for the determination of Cu^{2+} ions (Fig. 6b). Other metal ions revealed almost insignificant responses. Moreover, in the presence of miscellaneous competitive metal ions, the Hg^{2+} and Cu^{2+} ions still resulted in the similar fluorescence changes (Fig. 6a). The increases of absorbance and fluorescence
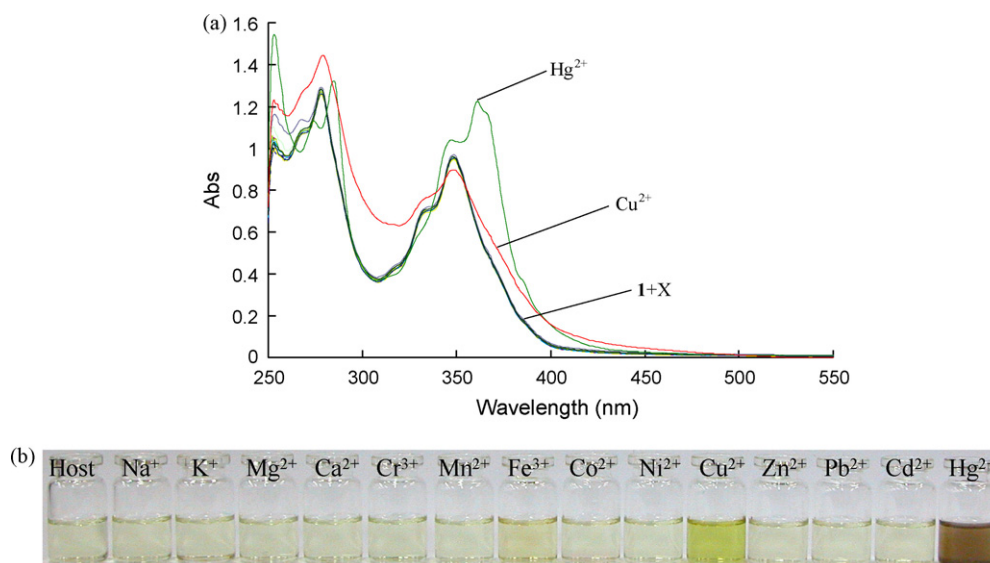
Fig. 3. (a) UV–vis spectra of **1** (3.0×10^{-5} M) in the presence of 2 equivalents of different metal ions. (b) Color changes of **1** (5.0×10^{-4} M) upon addition of different metal ions in aqueous solution (DMSO/H$_2$O = 4/1, v/v, buffered with HEPES, pH 7.8).
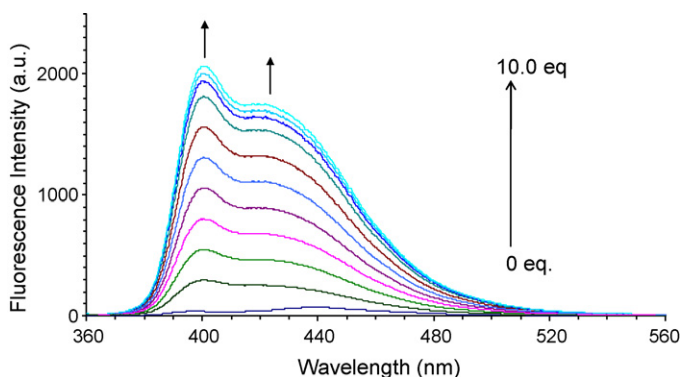
Fig. 4. Fluorescent emission spectra of **1** (5.0×10^{-7} M) in the presence of different equivalents of Hg^{2+} in aqueous solution (DMSO/H_2O = 4/1, v/v, buffered with HEPES, pH 7.8). Excitation wavelength and emission were 348 and 401 nm, respectively.

Fig. 5. Fluorescent emission spectra of **1** (5.0×10^{-7} M) in the presence of different equivalents of Cu^{2+} in aqueous solution (DMSO/H_2O = 4/1, v/v, buffered with HEPES, pH 7.8). Excitation wavelength and emission were 348 and 439 nm, respectively.

intensities resulting from the addition of Hg^{2+} and Cu^{2+} ions were not influenced by the subsequent addition of miscellaneous metal ions. These results indicated that the selectivity of **1** toward Hg^{2+} and Cu^{2+} ions over other competitive metal ions in the aqueous medium was remarkably high. The fluorescence features of **1** for Hg^{2+} and Cu^{2+} ions are summarized in Table 1 [50].

Table 1
Summarized fluorescence properties of **1** for Hg^{2+} and Cu^{2+} ions, such as excitation wavelength (λ_{ex}), extinction coefficient (ε), excitation energy (ΔE), emission wavelength (λ_{em}), and quantum yields (Φ_f).

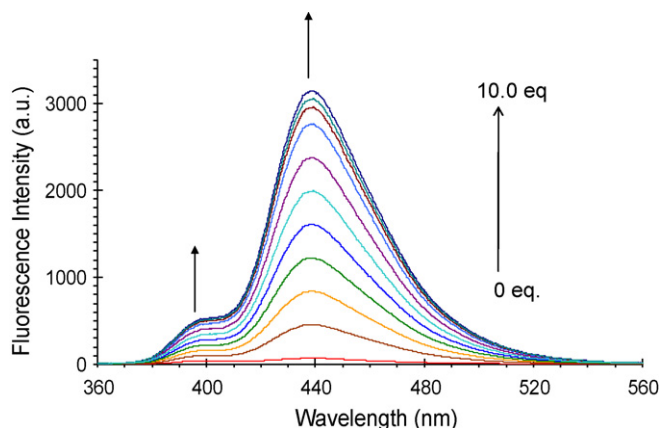| Parametes	**1**	**1** Hg^{2+}	**1** Cu^{2+}
λ_{ex} (nm) (log ε)	348[a] (4.11)	348[a] (4.18)	348[a] (4.23)
λ_{em} (nm)	437	401, 424	396, 439
Φ_f	0.016	0.261	0.284

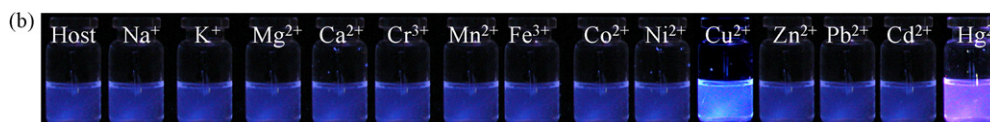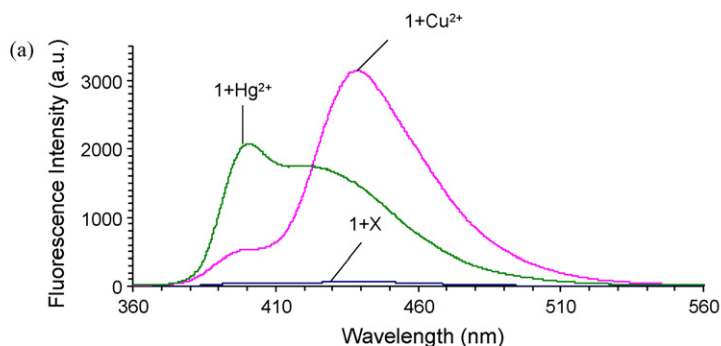[a] The excitation energy $\Delta E = hc/\lambda = 82.18$ kcal/mol.

3.4. NMR studies

The distinct color change and large fluorescence enhancement of **1** was caused by the Hg^{2+}-induced transformation of the thiourea function into an urea group as depicted in Scheme 1. The hydrolytic conversion of thioureas into ureas catalyzed by certain metal ions has been known to be very efficient [51]. In the present case, the conversion was effective, occurring exclusively with Hg^{2+} ions in aqueous DMSO solution. This behavior is quite reminiscent of Czarnik's Hg^{2+}-selective chemodosimeter that is based on the thioamide derivative of anthracene [26]. Further evidence for the above process came from the independent synthesis of **2** from the direct reaction of **1** and Hg(NO$_3$)$_2$ or alternatively from the 1-aminopyrene direct reaction with 4-methylphenyl isocyanate (Scheme 1). On comparing the ^{13}C NMR data of **1** and **2**, we found that the resonance evident at 182 ppm for **1** was replaced by a signal at 153 ppm for **2**, indicating that a C=O group was presented in **2** and the C=S group of **1** vanished during the desulfurization process from **1** to **2** (Fig. 7).

On the contrary, upon addition of different concentrations of Cu^{2+} ions to the solution of the receptor **1**, the chemical shift of **1** at 182 ppm (C=S) was not replaced by a signal at 153 ppm (C=O) in the ^{13}C NMR spectra of **1** with Cu^{2+} ions (see Fig. S7 in Supporting Information). This result indicated that the receptor **1** did not undergo the Cu^{2+}-induced desulfurization process to form **2**. To further clarify the coordination behavior, ^{1}H NMR spectra were acquired (Fig. 8). Protons on the thiourea moiety (H_1 and H_2) of **1** shifted downfield ($\Delta\delta = 0.10$ and 0.08 ppm, respectively) and the peaks were broadened upon addition of Cu^{2+}. This was due to the decrease in electron density of the thiourea moiety, which indicated that Cu^{2+} coordinated to the sulfur atom of the thiourea group of **1**. Protons on the benzene moiety (H_3 and H_4) displayed upfield shifts ($\Delta\delta = 0.08$ and 0.02 ppm, respectively), which indicated that the benzene moiety was involved in Cu^{2+} coordination. The coordination of **1** with Cu^{2+} ions could be proposed as shown in the optimized geometry of the receptor **1**–Cu^{2+} interaction (Fig. 9b).

Fig. 6. (a) Fluorescence spectra of **1** in the presence of Hg^{2+} and Cu^{2+} ions and miscellaneous metal ions (X) including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+}. (b) Color changes of **1** (5.0×10^{-7} M) upon addition of NO_3^- salts of X, Hg^{2+} and Cu^{2+} in aqueous solution (DMSO/H_2O = 4/1, v/v, buffered with HEPES, pH 7.8).

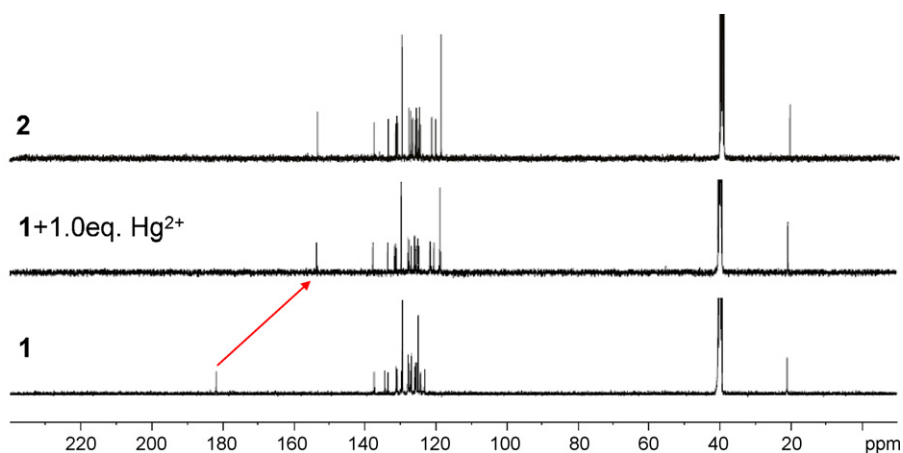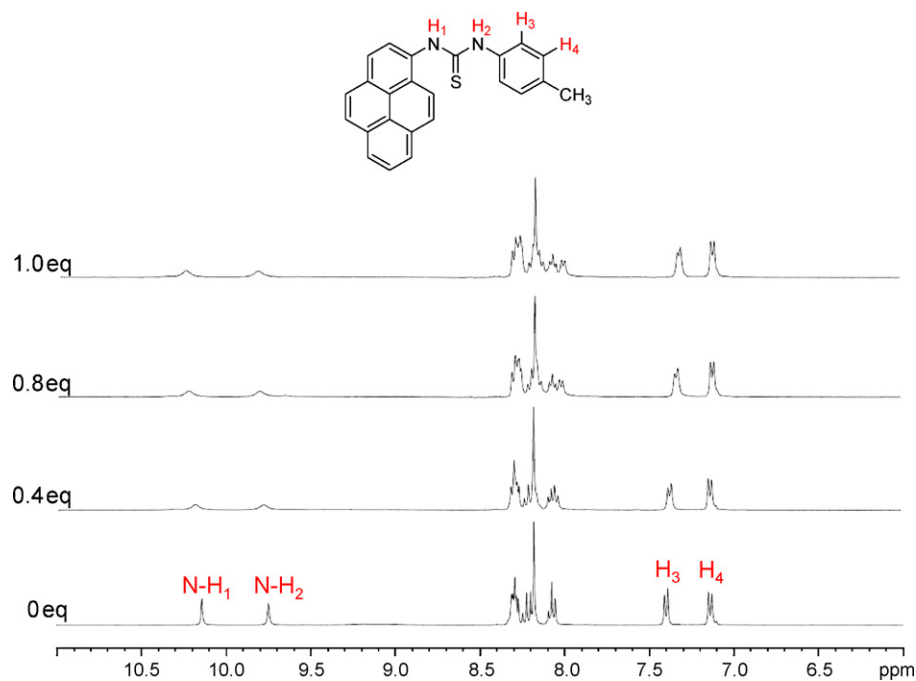**Fig. 7.** ^{13}C NMR spectra of **1**, **1** with 1 equivalent of Hg^{2+} ion and **2** (DMSO-d_6, 100 MHz).

Fig. 8. ^{1}H NMR spectra of **1** with different concentrations of Cu^{2+} ions.

The alternative evidence of the binding complex of the receptor **1** with Cu^{2+} was also supported by the electrospray ionization ESI–MS spectrum of the Cu^{2+} titration solution of **1**. The peak at m/z 525.9 was assigned to the [Cu(**1**)+NO$_3$]$^+$·2H$_2$O species (Fig. S8). Our repeated efforts to obtain the crystal structure to elucidate the coordination behavior between **1** and Cu^{2+} were not successful. The binding strength for the **1**–Cu^{2+} complex is expressed by the binding constant which is calculated as 1.09×10^4 [52,53].

3.5. Colorimetric and fluorescent detection limits

Colorimetric and fluorescent detection limits of **1** for Hg^{2+} and Cu^{2+} ions were also tested and presented in Figs. 10 and 11,
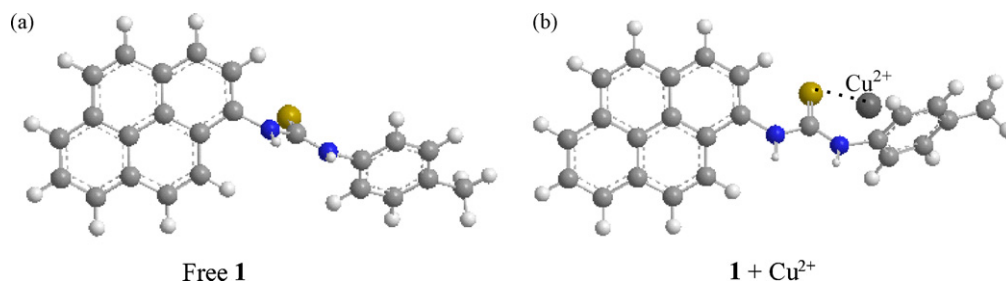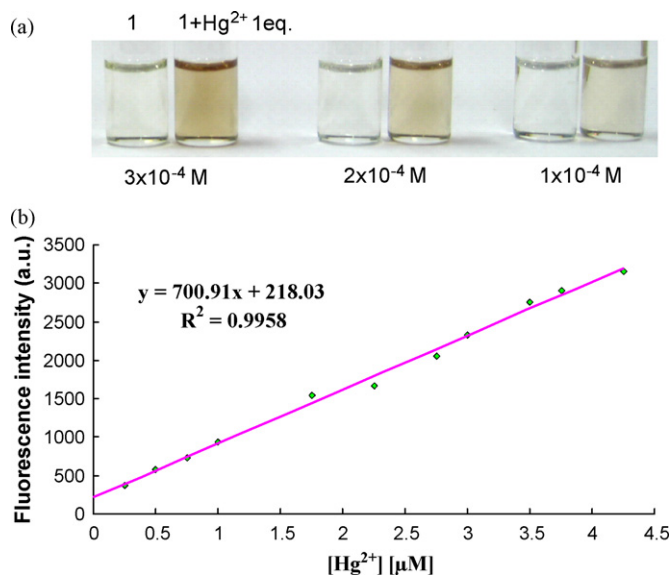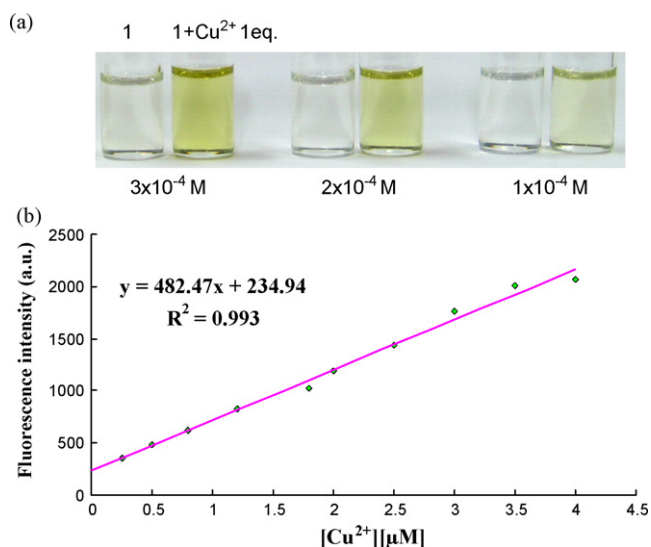

Fig. 9. Optimized geometries from *ab initio* HF/6-31G(D) calculation.

Fig. 10. (a) Photograph of **1** in aqueous solution (DMSO/H$_2$O = 4/1, v/v, buffered with HEPES, pH 7.8) in the presence of the Hg^{2+} ion. (b) Fluorescence intensity of **1** *vs* Hg^{2+} concentrations. [**1**] = 5.0 × 10^{-7} M.

Fig. 11. (a) Photograph of **1** in aqueous solution (DMSO/H$_2$O = 4/1, v/v, buffered with HEPES, pH 7.8) in the presence of the Cu^{2+} ion. (b) Fluorescence intensity of **1** *vs* Cu^{2+} concentrations. [**1**] = 5.0 × 10^{-7} M.

respectively. The detection limit within visual color changes is allowable to 1.0 × 10^{-4} M level of Hg^{2+} or Cu^{2+} ions in 1.0 × 10^{-4} M solution of **1**, as presented in Figs. 10a and 11a, respectively. While the detection limits of the fluorescence changes calculated on the basis of 3σ/K [36,54] are 0.09 and 0.10 ppm for Hg^{2+} and Cu^{2+} ions respectively, pointing to the high detection sensitivity (Figs. 10b and 11b).

4. Conclusions

In conclusion, a new artificial receptor **1** was developed, and it shows exclusively responses toward Hg^{2+} and Cu^{2+} ions. It can selectively sense Hg^{2+} and Cu^{2+} ions through two different color changes in aqueous solution (DMSO/H$_2$O = 4/1, v/v, buffered with HEPES, pH 7.8) and also distinguish them from other metal ions. The receptor **1** also exhibits pronounced enhancements of the fluores-

cence, which can visually be discernible by an orchid fluorescence in the presence of Hg^{2+} ion and a strong blue fluorescence in the presence of Cu^{2+} ion. Thus, the colorimentric and fluorescent receptor **1** can be used to determine Hg^{2+} and Cu^{2+} ions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.02.012.

References

[1] A.W. Czarnik, Fluorescent Chemosensors for Ion and Molecule Recognition, American Chemical Society, Washington, DC, 1993.
[2] A.P. de Silva, D.B. Fox, A.J.M. Huxley, T.S. Moody, Coord. Chem. Rev. 205 (2000) 41.
[3] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515.
[4] J.P. Desvergne, A.W. Czarnik, Chemosensors of Ion and Molecule Recognition, Kluwer, Dordrecht, 1997.
[5] P.B. Tchounwou, W.K. Ayensu, N. Ninashvili, D. Sutton, Environ. Toxicol. 18 (2003) 149.
[6] P. Grandjean, P. Weihe, R.F. White, F. Debes, Environ. Res. 77 (1998) 165.
[7] T. Takeuchi, N. Morikawa, H. Matsumoto, Y. Shiraishi, Acta Neuropathol. 2 (1962) 40.
[8] M. Harada, Crit. Rev. Toxicol. 25 (1995) 1.
[9] D.J. Waggoner, T.B. Bartnikas, J.D. Gitlin, Neurobiol. Dis. 6 (1999) 221.
[10] C. Vulpe, B. Levinson, S. Whitney, S. Packman, J. Gitschier, Nat. Genet. 3 (1993) 7.
[11] P.C. Bull, G.R. Thomas, J.M. Rommens, J.R. Forbes, D.W. Cox, Nat. Genet. 5 (1993) 327.
[12] R. Kramer, Angew. Chem. Int. Ed. 37 (1998) 772.
[13] A. Coskun, M.D. Yilmaz, E.U. Akkaya, Org. Lett. 9 (2007) 607.
[14] M.H. Lee, J.S. Wu, J.W. Lee, J.H. Jung, J.S. Kim, Org. Lett. 9 (2007) 2501.
[15] J. Wang, X. Qian, Org. Lett. 8 (2006) 3721.
[16] S. Yoon, A.E. Albers, A. Wong, C.J. Chang, J. Am. Chem. Soc. 127 (2005) 16030.
[17] X. Guo, X. Qian, L. Jia, J. Am. Chem. Soc. 126 (2004) 2272.
[18] K.C. Song, J.S. Kim, S.M. Park, K.-C. Chung, S. Ahn, S.-K. Chang, Org. Lett. 8 (2006) 3413.
[19] E.M. Nolan, S.J. Lippard, J. Am. Chem. Soc. 125 (2003) 14270.
[20] X. Zhu, S. Fu, W. Wong, J. Guo, W. Wong, Angew. Chem. Int. Ed. 45 (2006) 3150.
[21] E.M. Nolan, S.J. Lippard, Chem. Rev. 108 (2008) 3443.
[22] J.C. Manimala, E.V. Anslyn, Eur. J. Org. Chem. 23 (2002) 3909.
[23] K.S. Kim, L. Qian, Tetrahedron Lett. 34 (1993) 7677.
[24] R.A. Batey, D.A. Powell, Org. Lett. 2 (2000) 3237.
[25] D. Boeglin, S. Cantel, A. Heitz, J. Martinez, J.A. Fehrentz, Org. Lett. 5 (2003) 4465.
[26] M.-Y. Chae, A.W. Czarnik, J. Am. Chem. Soc. 144 (1992) 9704.
[27] G. Hennrich, W. Walther, U. Resch-Genger, H. Sonnenschein, Inorg. Chem. 40 (2001) 641.
[28] B. Liu, H. Tian, Chem. Commun. (2005) 3156.
[29] Y.-K. Yang, K.-J. Yook, J. Tae, J. Am. Chem. Soc. 127 (2005) 16760.
[30] S.-K. Ko, Y.-K. Yang, J. Tae, I. Shin, J. Am. Chem. Soc. 128 (2006) 14150.
[31] J.-S. Wu, I.-C. Hwang, K.S. Kim, J.S. Kim, Org. Lett. 9 (2007) 907.
[32] J. Ros-Lis, M.D. Marcos, R. Martinez-manez, J. Soto, Angew. Chem. Int. Ed. 44 (2005) 4405.
[33] R. Martinez-manez, F. Sancenon, Chem. Rev. 103 (2003) 4419.
[34] M.H. Lee, B.-K. Cho, J. Yoon, J.S. Kim, Org. Lett. 9 (2007) 4515.
[35] A.B. Descalzo, R. Martinez-manez, R. Radeglia, K. Rurack, J. Soto, J. Am. Chem. Soc. 125 (2003) 3418.
[36] A. Ono, H. Togashi, Angew. Chem. Int. Ed. 43 (2004) 4300, Detection limit is defined by 3σ/K. Here σ and K refer to standard deviation of the blank solutions and the slope of linear regression curve observed in Figures 10b and 11b, respectively.
[37] G. Hennrich, H. Sonnenschein, U. Resch-Genger, J. Am. Chem. Soc. 121 (1999) 5073.
[38] G. Zhang, D. Zhang, S. Yin, X. Yang, Z. Shuai, D. Zhu, Chem. Commun. (2005) 2161.
[39] P. Ghosh, P.K. Bharadwaj, J. Am. Chem. Soc. 118 (1996) 1553.
[40] B. Ramachandram, A. Samanta, Chem. Commun. (1997) 1037.
[41] K. Rurack, M. Kollmannsberger, U. Resch-Genger, J. Daub, J. Am. Chem. Soc. 122 (2000) 968.
[42] J.-S. Yang, C.-S. Lin, C.-Y. Hwang, Org. Lett. 3 (2001) 889.
[43] Q. Wu, E.V. Anslyn, J. Am. Chem. Soc. 126 (2004) 14682.

[44] R. Martinez, F. Zapata, A. Caballero, A. Espinosa, A. Tarraga, P. Molina, Org. Lett. 8 (2006) 3235.

[45] A. Caballero, R. Martinez, V. Lioveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina, J. Veciana, J. Am. Chem. Soc. 127 (2005) 15666.

[46] R. Martinez, A. Espinosa, A. Tarraga, P. Molina, Org. Lett. 7 (2005) 5869.

[47] F.M. Winnik, Chem. Rev. 93 (1993) 587.

[48] J.S. Kim, K.H. Noh, S.H. Lee, S.K. Kim, J. Yoon, J. Org. Chem. 68 (2003) 597.

[49] H. Yuasa, N. Miyagawa, T. Izumi, M. Nakatani, M. Izumi, H. Hashimoto, Org. Lett. 6 (2004) 1489.

[50] W.R. Dawson, M.W. Windsor, J. Phys. Chem. 72 (1968) 3251, The fluorescence quantum yields were measured with respect to anthracene as standard ($\Phi = 0.27 \pm 0.03$).

[51] A. Corsaro, V. Pistara, Tetrahedron 54 (1998) 15027.

[52] H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.

[53] K.A. Connors, Binding Constants: The measurement of Molecular Complex Stability, John Wiley and Sons, New York, 1987, pp. 141–188.

[54] J. Liu, Y. Lu, Angew. Chem. Int. Ed. 46 (2007) 7587.