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Colorimetric chemosensor and test kit for detection copper(II) cations in aqueous solution with specific selectivity and high sensitivity

Qi Lin [a,*], Pei Chen [a], Juan Liu [b], Yong-Peng Fu [a], You-Ming Zhang [a], Tai-Bao Wei [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 of Nationality, Lanzhou, Gansu 730030, PR China*

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ABSTRACT

The specific colorimetric detection of Cu^{2+} in the context of interference from coexisting metal ions in aqueous solution is a challenge. Therefore, a series of Cu^{2+} colorimetric chemosensors **CS1** ~ **CS3**, bearing acylthiosemicarbazide moiety as binding site and nitrophenyl moiety as signal group, were designed and synthesized. Among these sensors, **CS3** showed excellent colorimetric specific selectivity and high sensitivity for Cu^{2+} in DMSO/H_2O binary solutions. When Cu^{2+} was added to the solution of **CS3**, a dramatic color change from brown to green was observed, while the cations Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+} and Mg^{2+} did not interfere with the recognition process for Cu^{2+}. The detection limits were 5.0×10^{-6} and 1.0×10^{-7} M of Cu^{2+} using the visual color changes and UV–vis changes respectively. Test strips based on **CS3** were fabricated, which could act as a convenient and efficient Cu^{2+} test kit.

1. Introduction

Copper is an essential trace element, the third most abundant in humans, which is fundamental in many metabolic processes [1–5]. Excess copper, however, can cause various intoxications. For example, the increasing concentration of copper cations in body causes imbalance in cellular processes resulting in pathogenesis such as Wilson's disease [1,6,7], amyotrophic lateral sclerosis [8], Menkes syndrome [9,10], Alzheimer's disease [11] and Parkinson's disease [12]. According to the U.S. Environmental Protection Agency (EPA), the maximum acceptable level of Cu^{2+} in drinking water is $\sim 2 \times 10^{-5}$ M [13]. Therefore, the rational design and synthesis of efficient sensors to selectively recognize copper cations is an important topic in supramolecular chemistry [14–19]. Although previous work has involved the development of a wide variety of chemical [20–52] and physical [53–55] sensors for the detection of Cu^{2+}, 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 time-consuming and laborious procedures that can be carried out only by trained professionals, which significantly restricting the practical application of these Cu^{2+} sensors. For simplicity, convenience and low cost, easily-prepared Cu^{2+} colorimetric sensors [27–33] are needed. On the other hand, in biological and environmental systems, copper–sensor interactions commonly occur in aqueous solution [15,16,28,29,34–44], therefore, much attention has been paid to developing copper sensors that work in the aqueous phase [34–44].

In view of this requirement and as part of our research effort devoted to ion recognition [56–60], an attempt was made to obtain efficient colorimetric sensors which could sense Cu^{2+} with specific selectivity and high sensitivity in aqueous solutions. This paper details the design and synthesis of a series of Cu^{2+} colorimetric sensors **CS1** ~ **CS3** bearing acylthiosemicarbazide and nitrophenyl groups (Scheme 1). The strategies for the design of these sensors were as follows. Firstly, a acylthiosemicarbazide group was introduced as the binding site. The C=S and C=O moiety on the acylthiosemicarbazide group possesses a high affinity with Cu^{2+}. Secondly, in order to achieve "naked-eye" colorimetric recognition, we introduced nitrophenyl group 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 Cu^{2+}, compound **CS1** which without containing the nitro-group was also synthesized.

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* Corresponding authors.
E-mail addresses: linqi2004@126.com (Q. Lin), weitaibao@126.com (T.-B. Wei).

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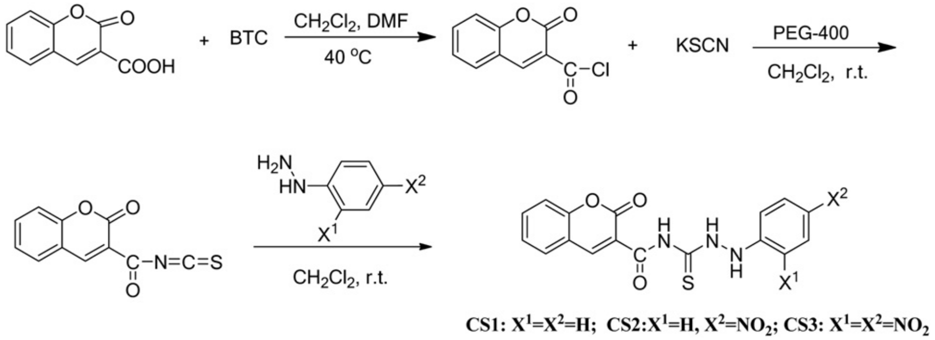

Scheme 1. Synthetic procedures for sensors **CS1** ~ **CS3**.

2. Experimental section

2.1. Materials and physical methods

^{1}H NMR spectra were recorded with a Mercury-400BB spectrometer at 400 MHz. ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with the solvent resonances as internal standards). 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.

2.3. General procedure for ^{1}H NMR

For ^{1}H 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 *CS1* ~ *CS3*

Coumarin-3-carboxylic acid (3 mmol) and bis(trichlormethyl) carbonate (BTC, 1.5 mmol) were added into dry dichloromethane (15 mL). Then the reaction mixture was stirred at 40 °C for 3 h under reflux. In this process, the coumarin-3-carboxylic acid has been converted to the coumarin-3-carbonyl chloride, which did not need separating. Then, dry and powdered KSCN (4 mmol) and PEG-400 (0.1 mL, as phase transfer catalyst) were added to the reaction solution and stirred it at room temperature for 2 h, and the inorganic salts were filtered out. The filtrate was a solution of the corresponding coumarin-3-carbonyl isothiocyanate, which did not need separating also. Then 2.8 mmol of phenylhydrazine was added to the filtrate solution and stirred at room temperature for 3 h, yielding the precipitate of **CS1**. 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 **CS1**. The other compounds **CS2** and **CS3** were prepared by similar procedures.

CS1: yield: 81%; m.p. 256–259 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.36 (s, 1H, NH), 8.64 (s, 2H, NH, ArH), 8.37 (s, 1H, ArH), 7.83–7.30 (m, 9H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 162.40, 158.89, 153.95, 147.57, 143.10, 134.50, 133.20, 130.21, 129.35, 128.94, 125.21, 124.96, 124.32, 118.84, 118.01, 116.37, 116.25; IR (KBr, cm^{-1}) v: 3215 (N–H), 1717, 1668 (C=O), 1152 (C=S); Anal. Calcd. for $C_{17}H_{13}N_3O_3S$: C, 60.17; H, 3.86; N, 12.38; Found: C, 60.15; H, 3.84; N, 12.41.

CS2: yield: 85%; m.p. 265–268 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.41 (s, 1H, NH), 9.34 (s, 1H, NH), 8.82 (s, 2H, NH, ArH), 8.12–8.09 (d, J = 12, 1H, ArH), 8.00–7.97 (d, J = 12, 1H, ArH), 7.81–7.76 (m, 1H, ArH), 7.56–7.44 (m, 2H, ArH), 6.92–6.88 (m, 2H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 162.06, 159.32, 154.41, 153.98, 147.46, 138.44, 134.35, 130.25, 125.87, 125.26, 119.44, 118.27, 116.30, 111.01; IR (KBr, cm^{-1}) v: 3227 (N–H), 1719, 1681 (C=O), 1154 (C=S); Anal. Calcd. for $C_{17}H_{12}N_4O_5S$: C, 53.12; H, 3.15; N, 14.58; Found: C, 53.09; H, 3.17; N, 14.56.

CS3: yield: 80%; m.p. 273–276 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.79 (s, 1H, NH), 10.33(s, 1H, NH), 8.91 (s, 2H, NH, ArH), 8.36–8.32 (d, J = 16, 1H, ArH), 8.05–8.03 (d, J = 8, 1H, ArH), 7.83–7.79 (m, 1H, ArH), 7.58–7.35 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 161.64, 159.34, 154.07, 148.24, 148.11, 137.04, 134.64, 130.43, 130.00, 125.34, 123.09, 118.69, 118.21, 116.32, 115.89; IR (KBr, cm^{-1}) v: 3235 (N–H), 1708, 1617 (C=O), 1159 (C=S); Anal. Calcd. for $C_{17}H_{11}N_5O_7S$: C, 47.55; H, 2.58; N, 16.31; Found: C, 47.58; H, 2.56; N, 16.33.

3. Results and discussion

In order to investigate the Cu^{2+} recognition abilities of the sensors **CS1** ~ **3** in aqueous solution, we carried out a series of Host–Guest recognition experiments in DMSO/H_2O (9:1/v:v) HEPES buffered solution at pH 7.0. 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/H_2O (9:1/v:v, pH 7.0) solutions of sensor **CS3**. When 5 equivalent (equiv.) of Cu^{2+} was added to the solution of **CS3**

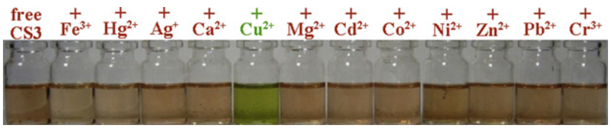

Fig. 1. Color changes observed upon the addition of various cations (5 equiv.) to the solutions of sensor **CS3** (2×10^{-5} M) in DMSO/H_2O (9:1, v:v; HEPES buffered, pH 7.0) solutions. Left to right: free **CS3**, Fe^{3+}, Hg^{2+}, Ag^+ Ca^{2+}, Cu^{2+}, Mg^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Cr^{3+}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

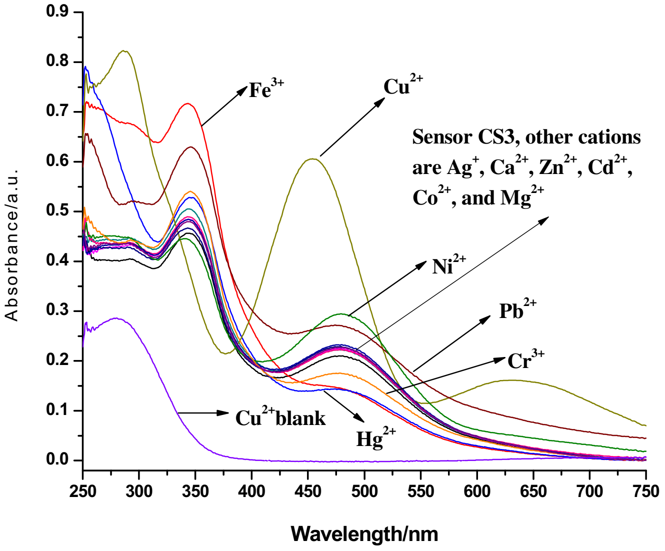

Fig. 2. UV–vis absorption spectra of **CS3** in the presence of 5 equiv. of various cations in DMSO/H_2O (9:1, v:v; HEPES buffered, pH 7.0) solution at room temperature.

(2.0×10^{-5} M), the sensor responded with dramatic color changes from brown to green (Fig. 1). In the corresponding UV–vis spectrum (Fig. 2), the absorption peak at 475 nm took place a 25 nm blue shift to 450 nm. Meanwhile, a new peak appeared at 650 nm, which attributed to the color change from brown to green. However, when adding 5 equiv. of other cations Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3+} into the DMSO/H_2O (9:1/v:v, pH 7.0) solution of sensor **CS3** respectively, no significant color changes were observed. Meanwhile, in the corresponding UV–vis spectra (Fig. 2), only a slight absorption changes were induced by adding Fe^{3+}, Ni^{2+}, Hg^{2+}, Pb^{2+}, and Cr^{3+}. Other cations couldn't induce any UV–vis changes. Therefore, in DMSO/H_2O solution, **CS3** showed specific colorimetric selectivity to Cu^{2+}.

In order to exclude the possibility of these results being due to Cu^{2+} self absorption, a blank test were carried out *via* adding the same amount of Cu^{2+} to blank DMSO/H_2O solution (without containing **CS3**), as a result, no color change was observed. In corresponding UV–vis spectra, there is no absorption peak appeared at

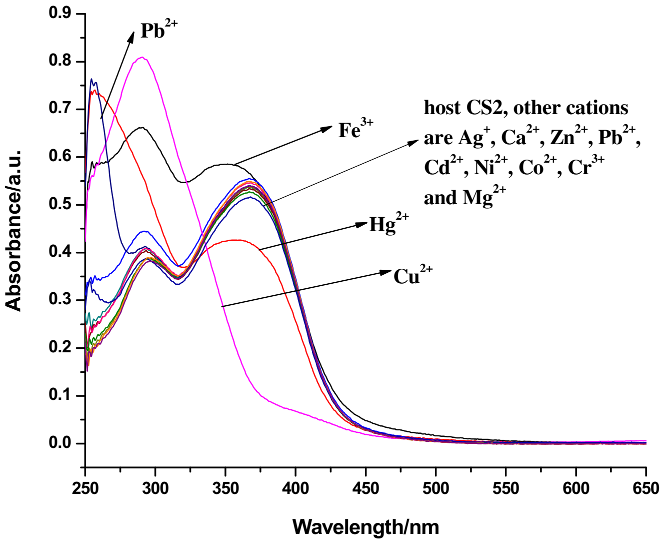

Fig. 3. UV–vis absorption spectra of **CS2** in the presence of 5 equiv. of various cations in DMSO/H_2O (9:1, v:v; HEPES buffered, pH 7.0) solution at room temperature.

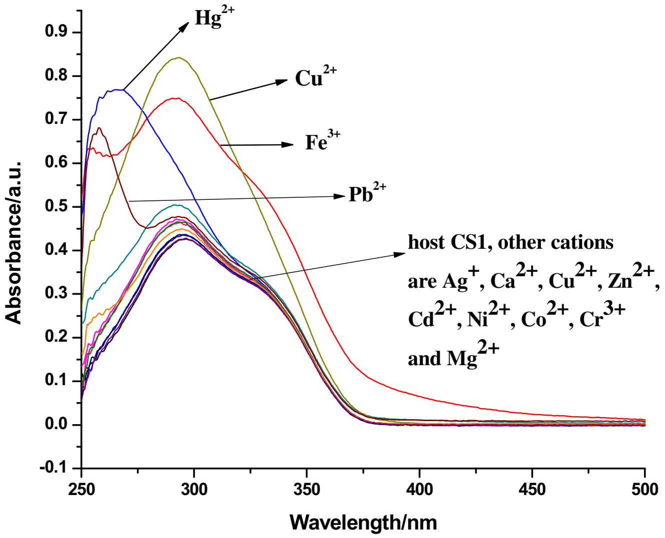

Fig. 4. UV–vis absorption spectra of **CS1** in the presence of 5 equiv. of various cations in DMSO/H_2O (9:1, v:v; HEPES buffered, pH 7.0) solution at room temperature.

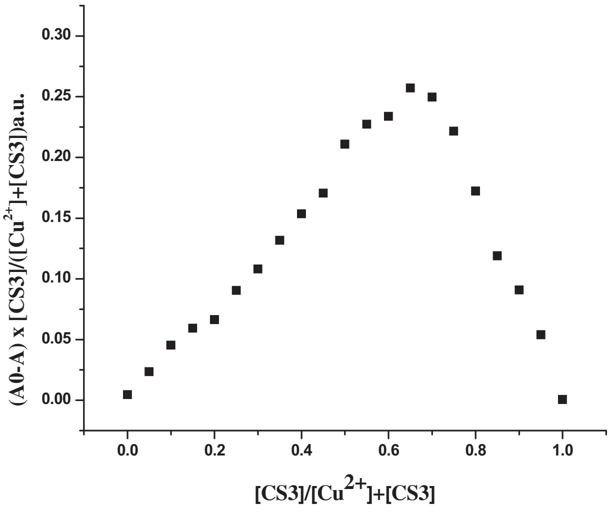

Fig. 5. (a) A Job plot of **CS3** and Cu^{2+}, which indicated that the stoichiometry of **CS3**-Cu^{2+} complex was 2:1.

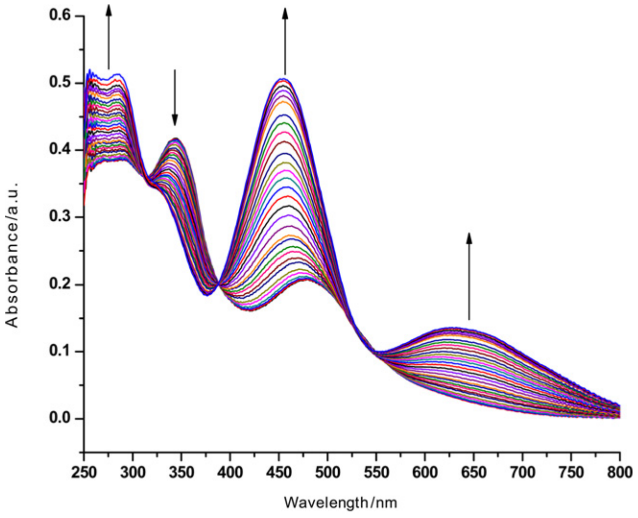

Fig. 6. UV–vis spectral titration of sensor **CS3** with Cu^{2+} in DMSO solution.

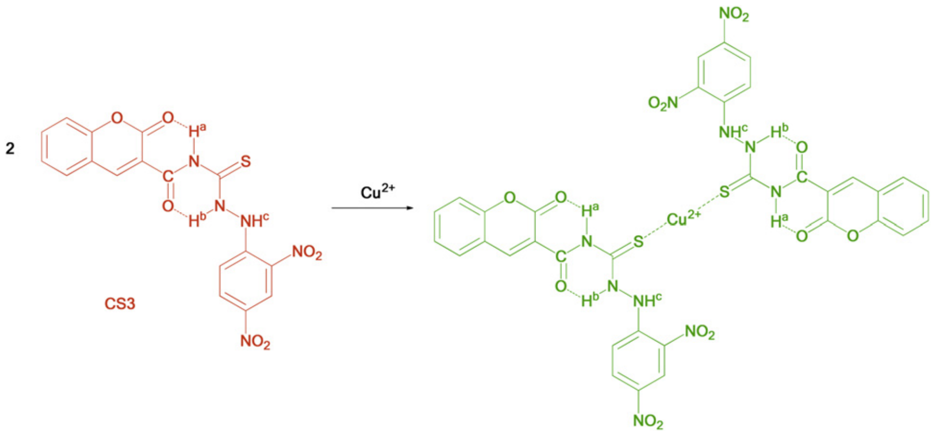

Fig. 7. The proposed reaction mechanism of the sensor **CS3** with Cu^{2+}.

the visible region (Fig. 2). Which confirmed that **CS3** could colorimetrically detect Cu^{2+} in DMSO/H_2O binary solution.

The same tests were applied to **CS2** and **CS1**. In this case, when various cations were added to the DMSO/H_2O (9:1/v:v, pH 7.0) solutions of **CS2** or **CS1** respectively, no obvious color changes were observed. In corresponding UV–vis spectra of **CS2** or **CS1** (Figs. 3 and 4), although Cu^{2+}, Hg^{2+}, Pb^{2+} and Fe^{3+} induced the absorption peaks at ultraviolet region took place slight shifts, however, at the visible region of these spectra, there is no absorption peak appeared. Which indicated that **CS2** or **CS1** couldn't colorimetric sense any cations under these conditions.

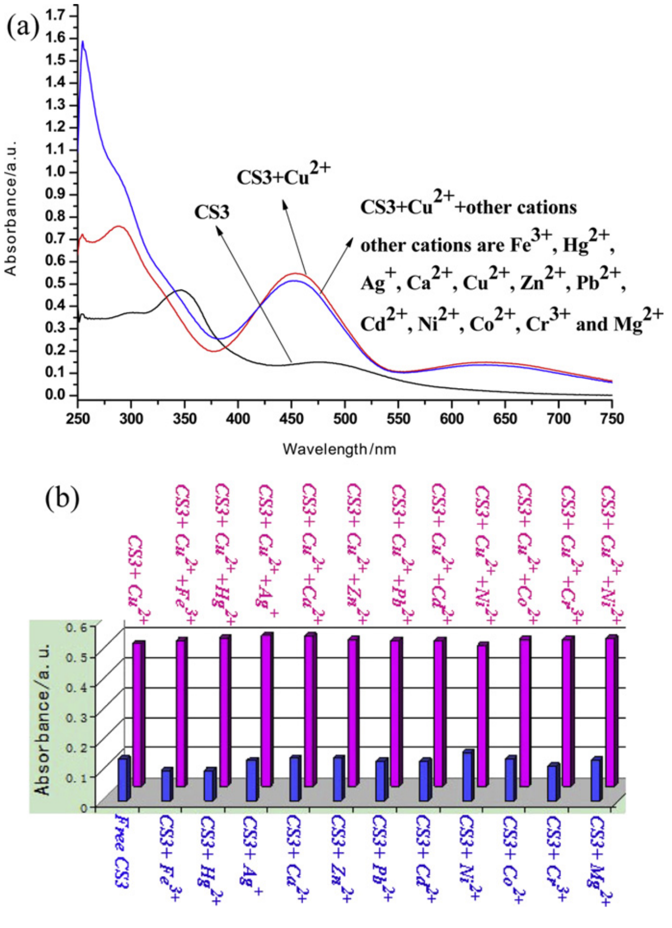

Fig. 8. (a) UV–vis absorption spectra sensor **CS3** (2.0×10^{-5} M) in DMSO/H_2O solutions in the presence of Cu^{2+} (5 equiv.) and the miscellaneous cations Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3+} (5 equiv., respectively). (b) UV–vis absorption at 475 nm of sensor **CS3** (2.0×10^{-5} M) in DMSO solutions in the presence of Cu^{2+} (5 equiv.) and the miscellaneous cations Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3+} (5 equiv., respectively).

Therefore, according to these results we can find that the nitrophenyl moiety acted as a signal group and played a crucial role in the process of colorimetric recognition. The sensor **CS3** employ 2,4-dinitrophenyl as signal groups, which possess colorimetric response abilities for Cu^{2+} cations. Because the **CS1** doesn't employ nitrophenyl as signal group, it could not colorimetric sense any cations. Although **CS2** employ a nitrophenyl as single group, owing to **CS2** only has one nitrophenyl group, the chromogenic capability of **CS2** is too weak to colorimetric recognize any cations also.

As **CS3** showed specific selectivity for Cu^{2+}, a series of experiments was carried out to investigate the Cu^{2+} recognition capability and mechanism of **CS3**. To gain an insight into the stoichiometry of the **CS3**-Cu^{2+} complex, the method of continuous variations (Job's method) was used (Fig. 5). When the molar fraction of sensor **CS3** was 0.67, the absorbance value approached a maximum, which demonstrated the formation of a 2:1 complex between the sensor **CS3** and Cu^{2+} [61].

The binding properties of sensor **CS3** with Cu^{2+} were further studied by UV–vis titration experiments (Fig. 6). It turned out that in DMSO solution of **CS3**, with an increasing amount of Cu^{2+}, the absorption peak at 480 nm gradually shifted to 454 nm. Meanwhile, at 650 nm, a new peak gradually appeared. Three clear isosbestic points were observed at 311, 387 and 530 nm, which indicated the formation of an **CS3**-Cu^{2+} complex. The binding constant K_s of the metal complex was determined by Equation (1) [61], assuming that the concentration of free metal is about equal to its total concentration ($[M] \approx [M]_t$), where A_0, A_e, and A_m are the corrected UV–Vis absorbances of the complex at initial, interval, and the final states at which the complex was fully formed upon addition of metal ion,

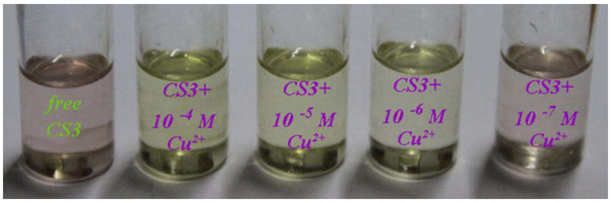

Fig. 9. Color changes observed upon the addition of varying quantities of Cu^{2+} (from left to right: free **CS3**, 1×10^{-4} M, 1×10^{-5} M, 1×10^{-6} M, 1×10^{-7} M) to the solutions of sensor **CS3** (1×10^{-5} M; DMSO/H_2O, 9:1, v:v; HEPES buffered, pH 7.0). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 10. Photographs of the **CS3** based test strips colorimetric detect Cu^{2+}. (a) Left to right: free test strip, test strip + DMSO, test strip + DMSO solution of Cu^{2+}. (b) After addition the DMSO solutions of various metal cations respectively and dried them under room temperature. Left to right: free, Cu^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Cr^{3+}.

respectively. The binding constant K_s was determined from the plot of the linear regression of $\ln[(A_0 - A_e)/(A_e - A_m)]$ versus $\ln[M]$ in Equation (1), to obtain the intercept as $\ln K_s$ and the slope as n. The association constant K_s of the chemosensors **CS3** toward Cu^{2+} was calculated as 1.5×10^4 M^{-1}.

$$\ln[(A_0 - A_e)/(A_e - A_m)] = \ln K_s + n\ln[M] \tag{1}$$

The recognition mechanism of the sensor **CS3** with Cu^{2+} were investigated by IR spectra and ^1H NMR titration methods. In the IR spectra (Fig. S-1 in Supplementary data) of **CS3**, the stretching vibration absorption peaks of coumarin C=O, acyl C=O and thiosemicarbazide C=S appeared at 1709, 1616 and 1184 cm^{-1} respectively. However, when **CS3** coordinated with Cu^{2+}, the stretching vibration absorption peaks of thiosemicarbazide C=S shifted to 1143 cm^{-1}, while, other absorption peaks such as the stretching vibration absorption peaks of N–H, coumarin C=O and acyl C=O didn't take place any shift, which indicated that **CS3** complexed with Cu^{2+} *via* Cu^{2+}-S coordination bond as shown in Fig. 7.

The results of ^1H NMR titration experiments also support this presumption. As shown in Fig. 7, before addition of Cu^{2+}, there were two intramolecular hydrogen bonds in the molecular structure of **CS3**: one was $N-H^a\ldots O=C$, and the other was $N-H^b\ldots O=C$. Owing to the fact that $N-H^a\ldots O=C$ and $N-H^b\ldots O=C$ are very strong intramolecular hydrogen bonds, as shown in Fig. S-2 in Supplementary data, the ^1H NMR chemical shift of $N-H^a$ and $N-H^b$ appeared at the low field of the molecular **CS3** at δ 10.79 and 10.33 ppm respectively. The $N-H^c$ appeared at 8.91 ppm. After the addition of 0.2–2.5 equivalent of Cu^{2+} into the DMSO-d_6 solution of **CS3** gradually, the corresponding ^1H NMR spectra didn't take place any changes. Which indicated that due to the shackle of strong hydrogen bonds $N-H^a\ldots O=C$ and $N-H^b\ldots O=C$, the coumarin C=O and acyl C=O didn't coordinate with Cu^{2+}. Therefore, the **CS3** coordinated with Cu^{2+} only though C=S and form a **CS3**-Cu^{2+} complex.

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 **CS3** in DMSO/H_2O binary solutions caused by the metal ions Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Hg^{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 Cu^{2+} still produced similar color and absorption changes (Fig. 8). These results shown that the selectivity of sensor **CS3** toward Cu^{2+} was not affected by the presence of other cations and suggested that it could be used as a colorimetric chemosensor for Cu^{2+}.

The colorimetric and UV–vis limits of sensor **CS3** for Cu^{2+} cation were also tested. As presented in Fig. 9, the detection limit using visual color changes is a concentration of 1.0×10^{-6} M of Cu^{2+} cation in 1.0×10^{-5} M solution of sensor **CS3**. While, as shown in Fig. 6, with the gradual addition of Cu^{2+}, a sharp increase in the absorbance at 480 nm and an obvious decrease in the absorbance at 344 nm are observed. Simultaneously, the ratio of A480/A344 increase with the increasing in Cu^{2+} concentrations, which allowing the Cu^{2+} concentration to be determined ratiometrically. The detection limit of the UV–vis changes calculated on the basis of $3s_B/S$ [62] is 1.0×10^{-7} M for Cu^{2+} cation, which pointing to the high detection sensitivity.

To investigate the practical application of chemosensor **CS3**, test strips were prepared by immersing filter papers into a DMSO solution of **CS3** (0.1 M) and then drying in air. The test strips containing **CS3** were utilized to sense different cations. As shown in Fig. 10, when different cation solutions were added on the test kits respectively, the obvious color change was observed only with Cu^{2+} solution. Therefore, the test strips could directly detect Cu^{2+} in DMSO or DMSO/H_2O binary solutions. In addition, the test strips could detect Cu^{2+} in pure water also, before adding the pure water solution of Cu^{2+} to the test strip, one drop of DMSO has been added to the test strip and the test strip was moistened by DMSO. Then the pure water solution of Cu^{2+} was added to the DMSO moistened test strip, the test strip carried out similar color changes just like the DMSO/H_2O solution of Cu^{2+} added to the dry test strip. Therefore, the DMSO moistened test strip could conveniently detect the Cu^{2+} in pure water.

4. Conclusion

An easy-to-make Cu^{2+} colorimetric sensor **CS3**, bearing thiourea moiety as the binding site and nitrophenyl moiety as the signal group, was designed and synthesized. This sensor showed specific selectivity for Cu^{2+} in DMSO/H_2O binary solutions. Comparison with sensor **CS1** 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 **CS3** recognized Cu^{2+} by forming a stable 2:1 **CS3**-Cu^{2+} complex. The coexistence of other cations did not interfere with the Cu^{2+} recognition process. Moreover, the detection limit of the sensor **CS3** toward Cu^{2+} was 1.0×10^{-7} M, which indicated that the sensor **CS3** may be useful as a colorimetric sensor for monitoring Cu^{2+} levels in physiological and environmental systems. In addition, test strips based on **CS3** were fabricated, which also exhibits a good selectivity to Cu^{2+} as in solution. We believe the test strips could act as a convenient and efficient Cu^{2+} test kit.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.01.024.

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