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ORIGINAL PAPER

A new colorimetric and fluorescent chemosensor based on thiazolyl-hydrazone for sensitive detection of copper ions

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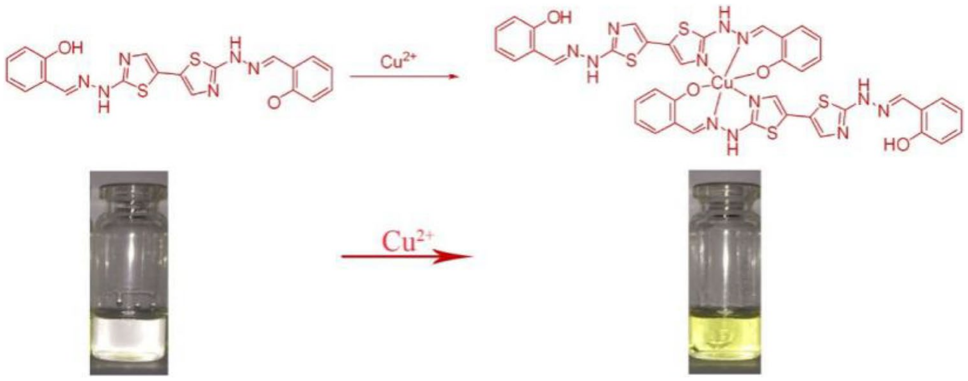
Abstract

A Cu^{2+}-specific chemosensor probe thiazolyl-hydrazone (BL) has been designed and prepared, which provide tridentate chelate NNO coordination mode for Cu^{2+} with binding stoichiometry of 1:1. The BL solution exhibits a rapid color change from colorless to yellow along with a new intense absorption band at 414 nm upon binding to Cu^{2+} cation, whereas other metal cations do not induce such a change. The analytical detection limit is 0.75 µM, and the naked eye detection limit is as low as 20 µM. Additionally, the emission signal of BL could be quenched by Cu^{2+} and Fe^{3+} with a detection limit of 7.2 µM and 4.3 µM, respectively.

Graphic abstract



Keywords Colorimetric probe · Copper(II) ions · Thiazolyl-hydrazone derivative

Introduction

Copper plays an important role in many physiological activities, and its concentration above or below the normal levels will cause an adverse effect on the organism [1–3]. Therefore, the design and synthesis of probes to detect copper ions is an important research topic [4–8]. It is well known that copper ions can be detected using several instrumental techniques, such as atomic absorption spectroscopy, physicochemical techniques, and electrochemistry. However, these methods rely on expensive instruments and need tedious sample preparation and operation scheme [9–11]. Recently, colorimetric methods for ion detections have

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received great attention due to their low cost and operational simplicity [12, 13]. To date, some Schiff base derivatives have shown highly sensitive detection of copper(II) ion with either a color change/absorption spectra change or fluorescent spectra change, due to their well-known coordinative capability [14–18]. From complexation point of view, phenol hydrazone derivatives could give similar geometric and cavity control compared with Schiff base. However, to the best of our knowledge, only a few chemosensors comprising phenol hydrazone units have been demonstrated to exhibit selective and sensitive for the detection of Cu^{2+} [19–21]. In this paper, we designed and synthesized phenol hydrazone derivative BL functionalized with thiazole, which provided a good possibility for chelation with transition metal ions [22, 23]. Specially, BL exhibits an exclusive sensing property toward the Cu^{2+} in the UV–Vis experiments as well as with a visual color change.

Experimental section

General

Unless otherwise indicated, all of the starting materials and regents were commercially available and utilized without further purification. Melting points were determined on an Electrothermal Programmable Melting Point Apparatus (XT4B). Infrared (IR) spectra were measured using a PerkinElmer with KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-600 spectrometer. Chemical shifts were expressed in ppm and coupling constants (J) in Hz. Mass spectrometric data were obtained by positive electron spray ionization (ESI–MS) technique on a Bruker Esquire 3000. Elemental analysis (EA) was carried out in a Flash EA 1112 elemental analyzer. Absorption and fluorescence spectra at room temperature were determined on TU-1901 spectrophotometer and Hitachi F-4600 fluorescence spectrometer, respectively. The solutions of metal ions in deionized water were prepared from their chloride salts.

Typical procedure for the synthesis of BL

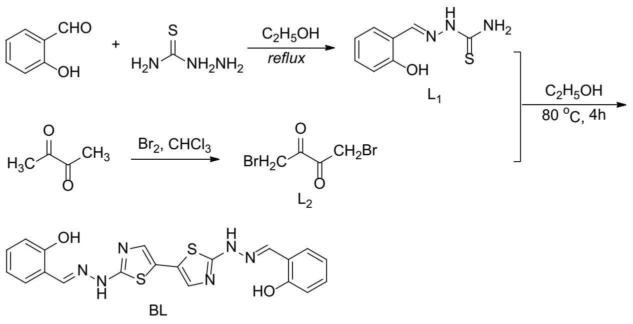
Thiazolyl-hydrazone (BL): 2-(2-hydroxybenzylidene) hydrazine-1-carbothioamide L_1 (780 mg, 4.0 mmol) and 1,4-dibromobutanedione L_2 (492 mg, 2.0 mol) were dissolved in 50 ml absolute ethanol. The reaction mixture was refluxed 4 h. After cooling to room temperature, the precipitate was filtered and recrystallized with DMF and ethanol to get brown compound BL. Yield: 924 mg (53%); calc. for $C_{20}H_{16}N_6O_2S_2$ $[M+H]^+$: 436.08; found: 436.3. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.20 (s, 2H), 10.15 (s, 2H), 8.34 (s, 2H), 7.64 (dd, $J=11.4$, 10.3 Hz, 2H), 7.29-7.18 (m, 2H), 7.01 (s, 2H), 6.96–6.84 (m, 4H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.5, 146.4, 140.7, 131.0, 127.1, 120.5, 120.0, 116.6, 104.8. Anal. Calcd for $C_{20}H_{16}N_6O_2S_2$: C, 55.15; H, 3.33; N, 19.37; S, 14.81. Found: C, 55.03; H, 3.69; N, 19.25; S, 14.69. IR (KBr, cm^{-1}): 3289, 3060, 1620, 1600, 1566, 1493, 1476, 1456, 1407, 1344, 1312, 1288, 1254, 1222, 1055, 756.

Results and discussion

Compounds L_1 and L_2 are synthesized according to the reported synthetic procedure, respectively [24, 25]. The compound BL is then obtained by the reaction of 1,4-dibromobutanedione and 2-hydroxybenzaldehyde in 82% yield (Scheme 1). The chemical structure of BL is confirmed by various characterizations (MS, ^{1}H, ^{13}C NMR, EA, and FT-IR).

The absorption spectrum of BL (50 μM) in DMSO exhibits a strong band with the maximum absorbance peak at about 358 nm due to intramolecular π–π* electronic transition, resulting in nearly colorless solution [26]. Upon an increase in the concentration of Cu^{2+} (0.2–2.2 equiv), the absorption intensity at 358 nm gradually decreased with a slightly hypsochromic shift. Notably, a new absorption peak at 414 nm is observed with a shoulder at 448 nm (Fig. 1a). The intensities of the absorption (414 nm) are linearly related to the copper ion concentration (Fig. 1b), suggesting that the detection limit of BL for Cu^{2+} is 0.75 μM, which is lower than those previously reported chemosensors based on phenol hydrazone derivatives [27, 28]. Moreover, as shown in Fig. 1c, the colorless solution of BL becomes yellow upon addition of Cu^{2+} and it is easy to detect by the naked eye at 0.4 equivalents (20 μM).

Obviously, the above observations result from the complexation between BL and Cu^{2+}. Meanwhile, when the Cu^{2+} concentration is higher than 2.0 equiv, the absorption spectrum shows little changes, suggesting that the complexation between Cu^{2+} and BL reaches equilibrium. To understand the structure of the BL–Cu^{2+} complexes,



Scheme 1 Synthetic route to compound BL

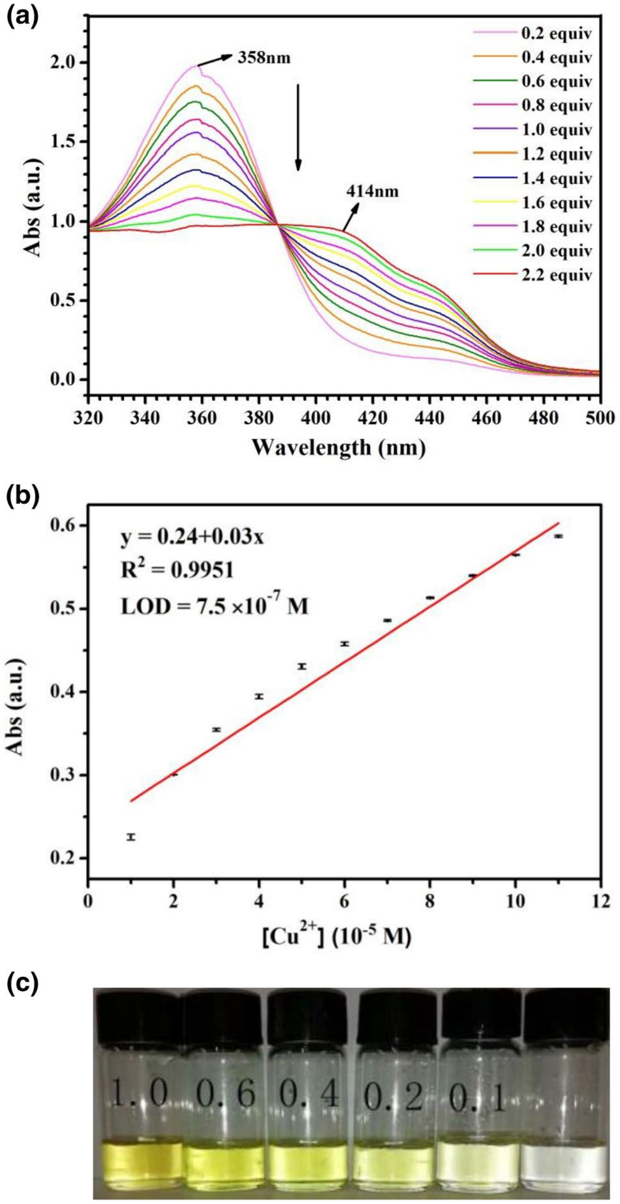


Fig. 1 **a** Absorption spectra of BL recorded in DMSO (5.0×10^{-5} M) after the addition of 0.2 to 2.2 equiv. Cu^{2+}. **b** Plot for calculation of the detection limit of BL (50 μM) with Cu^{2+} in DMSO. **c** Visual color changes upon addition of 0.1 to 1.0 equiv. Cu^{2+} in the receptor solution

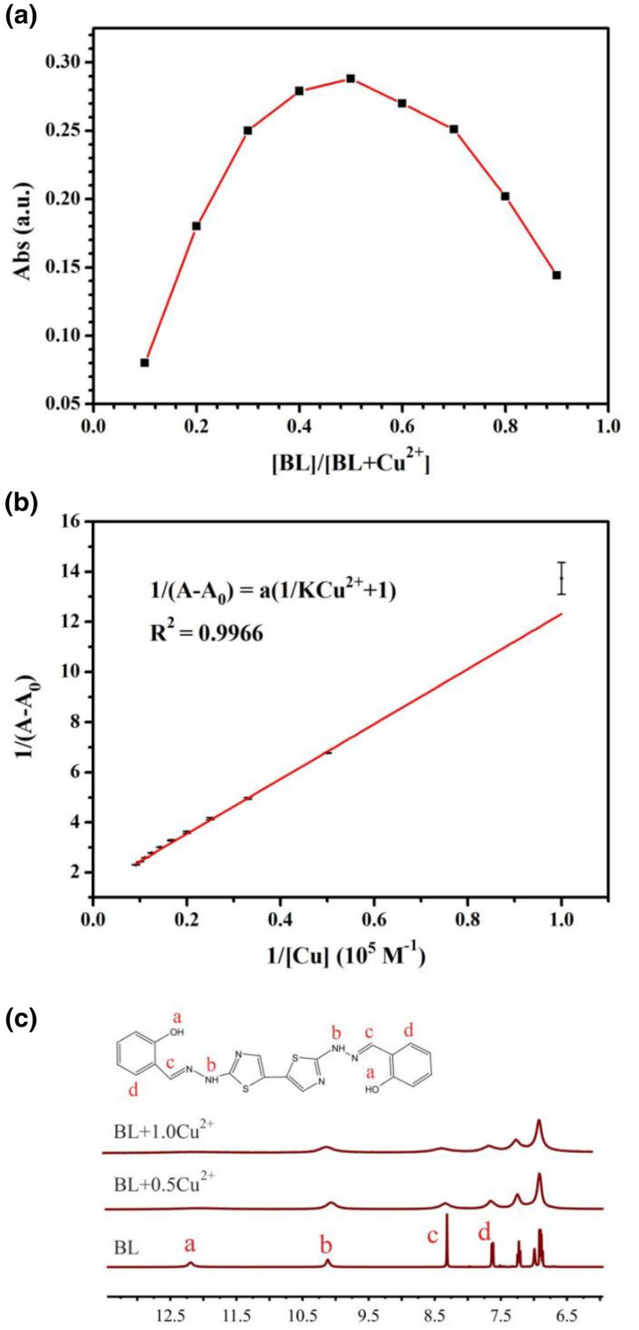


Fig. 2 **a** Job plot of the Cu^{2+}–BL complex in DMSO. The total concentration of BL and Cu^{2+} was 50.0 μM. The monitored wave length was 482 nm. **b** Benesi–Hildebrand plot of BL with Cu^{2+}. **c** ^{1}H NMR changes of BL in the presence of Cu^{2+} ions (0–1.0 eq) recorded in DMSO d_6 at 298 K

the composition of BL–Cu^{2+} complex is studied by the Job's plots using the changes in absorption intensity at 414 nm as a function of mole fraction of BL (Fig. 2a). The maximum intensity is reached when the molar fraction of BL is 0.5, which indicated the complex formed by BL and Cu^{2+} is 1:1. The binding constant of BL–Cu^{2+} complex is calculated by utilizing Benesi–Hildebrand (B-H) equation [29]. From the B-H plot (Fig. 2b), a well linear relationship is obtained from the measured absorption intensity [$1/(A-A_0)$] as a function of $1/[Cu^{2+}]$ at 414 nm. The binding constant value of BL–Cu^{2+} complex is then obtained from the slope and intercept ($K=4.481\times10^3\,M^{-1}$, $R^2=0.9966$) [30]. Furthermore, the proton signal (H_a) at 12.15 ppm almost completely disappears upon the addition of Cu^{2+} (1.0 equiv), which not only indicates the formation of complexes with 1:1 stoichiometry but also indicates Cu^{2+} binds to deprotonated phenol group (Fig. 2c).

Selectivity is an important characteristic for an ion-selective chemosensor. The absorption spectral changes of BL in the presence of some common ions (10 equiv) including Zn^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Ag^{+}, Na^{+}, and K^{+} are investigated. As shown in Fig. 3a, b, the absorption spectra and the color of solution have no significant change except of Cu^{2+} ions. Encouraged

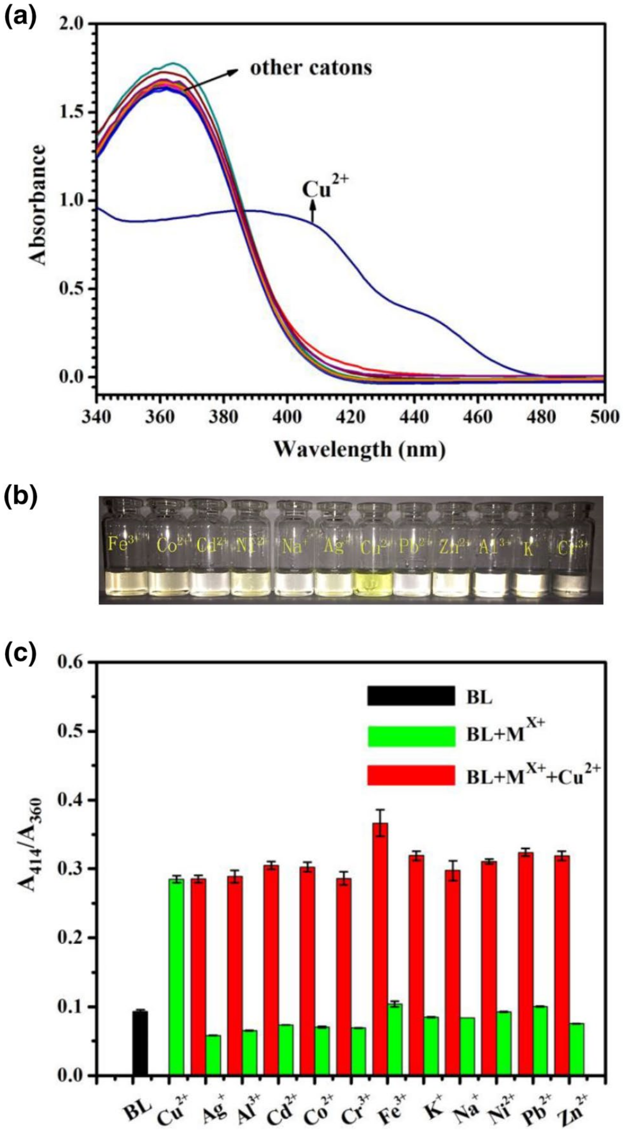


Fig. 3 **a** Absorbance spectra change of the sensor BL (50 µM) upon the addition of various metal ions in DMSO. **b** Color change of BL in the presence of different metal cations. **c** The absorbance of BL toward Cu^{2+} ions and relevant metal ions in DMSO. The green bars in each group represent the absorbance of BL in the presence of various metal ions (10 equiv). The red bars in each group represent the change in absorbance that occurs upon subsequent addition of Cu^{2+} ions (10 equiv)

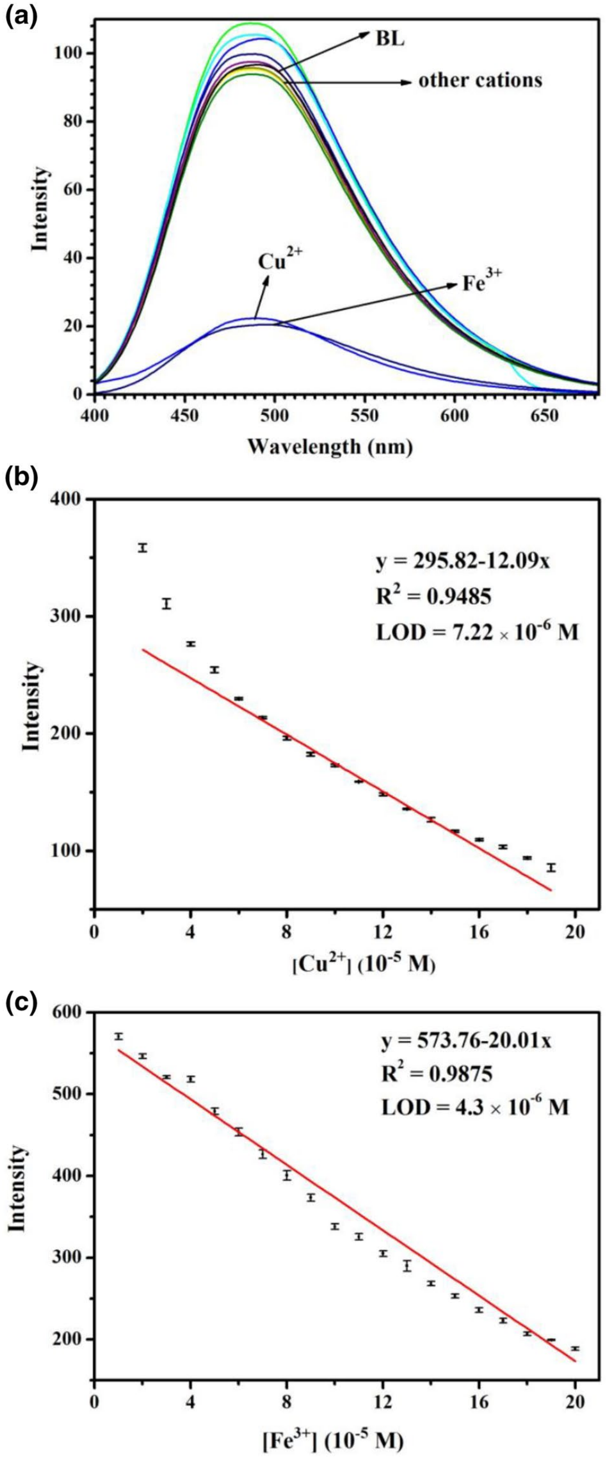


Fig. 4 **a** Emission spectra change of BL (in DMSO) upon addition of different metal cations (10 equiv). **b** Curve of fluorescence intensity at 482 nm of BL (50 µM) versus increasing concentrations of Cu^{2+}. **c** A plot of fluorescence intensity versus concentrations of Fe^{3+} for BL. Excitation wavelength was 358 nm

from the high selectivity, the sensing capabilities are next investigated under competition environment. The subsequent addition of 2.0 equiv. Cu^{2+} to the mixed solution of BL and other metal ion (10 equiv) results in an absorption spectral change (red bar) similar with that of BL and Cu^{2+} (green bar) (Fig. 3c). These results indicate that the detection of Cu^{2+} based on BL is hardly interfered by the coexistent common metal ions, and thus BL could be used as a potential chemosensor for Cu^{2+} with a high selectivity.

As BL could exhibit intense fluorescence with peak at around 482 nm, cations-induced changes in the emission intensity of BL are also carried out. Upon the addition of Cu^{2+} and Fe^{3+} (3 equiv), the BL solution shows a significant fluorescence quenching (Fig. 4a), which is probably due to the deactivation of emission from excited state of BL caused by the paramagnetic nature of Cu^{2+} and Fe^{3+} ions [31]. However, under similar experimental conditions, the other common cations (such as K^+, Na^+, Cd^{2+}, Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, and Cr^{3+}) show either little increase or neglect change in the emission intensity. Additionally, the static and dynamic model for BL fluorescence quenching is studied by addition of small aliquots of Cu^{2+}/Fe^{3+} (Fig. S1). The uniform quenching of fluorescence intensity shows good linearity in the range 0–200 μM with a lower detection limit of 7.2 μM for Cu^{2+} and 4.3 μM for Fe^{3+}, suggesting that BL is a potential fluorescent sensor for copper ions and ferric irons (Fig. 4b, c). Additionally, as shown in Fig. S2, the subsequent addition of Cu^{2+}/Fe^{3+} (3 equiv) to the solution of BL and other common cations (10 equiv) elicits a protuberant fluorescence quenching (blue bar), suggesting that the common metal cations do not show significant interference on the Cu^{2+}/Fe^{3+} assay.

Conclusions

In conclusion, a new colorimetric and fluorescent sensor BL, bearing a thiazolyl-hydrazone unit as a metal binding pocket, has been successfully prepared. The key finding with the BL is that a new absorption peak at ca. 414 nm appears upon titration with Cu^{2+} ions followed by a solution color change from colorless to yellow, which is not affected by the other common metal ions. The selectively detection limits are 0.75 μM by UV–Vis spectrometer and 20 μM by the naked eye, respectively, suggesting that BL can be useful in the detection of trace quantities of Cu^{2+} ions. Additionally, this new chemosensor further displays turn-off fluorescence responses toward Cu^{2+} and Fe^{3+} ions with detection limits of 7.2 μM and 4.3 μM, respectively. Therefore, this study provides a sensitive and selective sensor for the detection of Cu^{2+} ion.

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Supplementary material Containing fluorescence titration and selectivity of BL with Cu^{2+} and Fe^{3+} in DMSO.

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