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Short Communication

Simple and sensitive colorimetric sensors for the selective detection of Cu^{2+} in aqueous buffer

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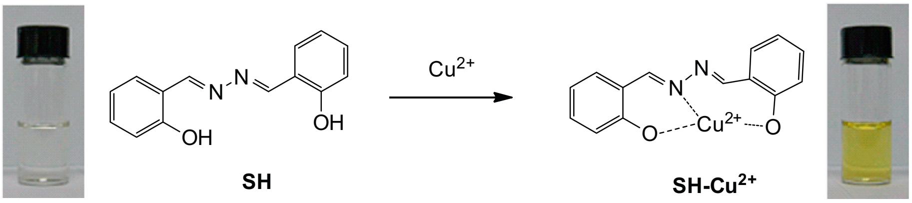
HIGHLIGHTS

- An easy-to-make Cu^{2+} colorimetric sensor **SH** was designed and synthesized.
- **SH** displayed colorimetric specific selectivity for Cu^{2+} in aqueous solution.
- The simple approach is useful for routine analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Simple chromogenic sensor for the selective detection of Cu^{2+} was described. With the addition of Cu^{2+}, a bathochromic shift about 82 nm was observed in the UV–VIS spectra, with the color change from colorless to bright yellow. This suggested that the coordination between receptor and Cu^{2+} was formed, and the strong push–pull system occurred. The followed IR spectra indicated that Cu^{2+} coordinated to the two phenolic oxygen atoms and one of two azomethines in the receptor.

Introduction

Recognition and sensing of heavy and transition metal (HTM) ions attracted much attention in the supramolecular chemistry [1–5] due to their significant importance in the chemistry, biology and environment science. Among these species, Cu^{2+}, as the third in abundance in the human body, plays a crucial role in the fundamental physiological processes in organism [6]. However, the superfluous Cu^{2+} in the body resulted in serous neurodegenerative diseases [6]. Furthermore, Cu^{2+} is a significant environmental pollutant due to its widespread use. Thus, the detection and monitoring of Cu^{2+}, with high sensitivity, high detection limit and quick response, are in great demand [7]. Within these detection approaches for Cu^{2+}, those related with the colorimetric response attracted much attention [4,8,9] because of their simple use and without sophisticated equipments than closely related approaches involving fluorescence and electrochemical response, as well as the intrinsic paramagnetic nature of Cu^{2+} turning off the fluorescence response of most of fluorescent sensors [10–12] and rendering low signal outputs less advantageous for practical analysis. Colorimetric sensors would have direct application in the development of the disposable dip-stick rapid assays or optodes based on the absorption changes. With the simplicity, convenience and low cost in mind, the efficient Cu^{2+} colorimetric sensors are necessary. Moreover, the interaction between the sensors and Cu^{2+} commonly occur in aqueous solution in the practical application. Therefore, the design and synthesis of cupric sensors operating in the system containing water are desirable.

According to these requirements, various chemosensors with soft heteroatoms (e.g. nitrogen and sulfur) for chelate of metal cations [13–15], have been used for the selective detection of Cu^{2+}. In

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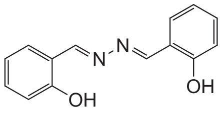
these chemosensors, receptor containing the Schiff base structure was prevalent [14–16], because (a) it is easily prepared in high yield by simple starting materials, (b) Schiff base can adjust the coordination cavity to accommodate metal ions by configuration change. Furthermore, Schiff bases and their metal complexes are used as models for biological system for their antimicrobial and anticancer activities [17,18]. Therefore, the biomimetic of the interaction between Schiff base and metal is significant [17]. On the other hand, up to now, only few investigations involved the phenol groups as a key component to obtain the Cu^{2+} binding [14,15,19], although the phenol commonly plays an important role in the cation binding in the biological system. Another issue relating to the cupric recognition came from the serious interference by other metal ions (e.g. Ag^{+}, Hg^{2+}) [20–23]. Based on the above-mentioned background and as part of our research effort devoted to ion recognition, herein we reported the cupric sensing and binding properties of **SH** based on 2-hydroxyl Schiff base as the binding site by UV–VIS in dilute solution. Results showed that **SH** was preferential selective colorimetric cation sensors for Cu^{2+}.



SH

Experimental

Reagents

All reagents for synthesis were of analytic grade without further purification. In the titration experiments, Cu^{2+}, Pb^{2+}, Ag^{+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Cr^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Na^{+}, K^{+}, and Li^{+} were added in the form of nitrate.

Synthesis

To a stirred ethanol solution of 1.22 g salicylaldehyde at room temperature, 0.25 ml of hydrazine hydrate (99%) was added. The mixture was stirred continually for 16 h. The yellow precipitated product was rapidly filtered, washed several times with cold ethanol to afford pure **SH**. Yield: 89%. m.p. 219.5-220.6 °C. EI-MS: *m/z* 241.3 (M + H^{+}), ^{1}H NMR (DMSO-d_6): δ 11.122 (s, 2H, Ar—OH), 9.001 (s, 2H, CH═N), 7.673-7.701 (m, 2H, Ar—CH), 7.374-7.416 (m, 2H, Ar—CH), 6.946-6.985 (m, 2H, Ar—CH).

General approaches for UV–VIS spectroscopy

Serial working solutions were prepared by adding the incremental multiples of metal ions in the HEPES buffer (10 mM, pH = 7.0) to the DMSO solution of the **SH** (2.5×10^{-5} M), and finally diluted with HEPES buffer to make the volume ratio of DMSO to HEPES buffer constant (4:1), and were stored at room temperature for 0.5 h before used in the experiment. UV–VIS absorption spectra were measured on Shimadzu UV-2450PC in the range of 250–600 nm with a slit width of 1.0 nm.

Results and discussion

The optical properties of **SH** were investigated by mixing it with metal ions (Cu^{2+}, Pb^{2+}, Ag^{+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Cr^{3+}, Ba^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+} and Li^{+}). The spectroscopic studies were performed in DMSO/HEPES buffer (v/v, 4:1, pH = 7.0). As shown in Fig. 1, in the absence of metal ions, the UV–VIS spectra of **SH** exhibited two maximum absorption band at 360 nm and 300 nm, which can be assigned to π–π* and n–π* [24] (namely, the intramolecular charge transfer from C═N and OH to the phenyl group). In the presence of 2.0 equiv. of Cu^{2+}, the absorption band at 360 nm disappeared, at the same time, the new bathochromic shift band at 442 nm occurred with the concomitant color change from colorless to yellow. This new band was attributed to the metal-induced intramolecular charge transfer [25] from the 'push' **SH** to the 'pull' Cu^{2+} [26]. A similar but less remarkable spectral change was observed upon addition of Ni^{2+}, however, this perturbation did not afford naked-eye detection. On the other hand, the other metal ions (even at higher concentration) resulted in negligible changes in the UV–VIS spectra under the same conditions. The significant cation-induced spectroscopic differences between Cu^{2+} and other metal ions were ascribed to the high thermodynamic affinity of Cu^{2+} for typical N- and O-donor ligand and fast metal-to-ligand binding kinetics [27,28].

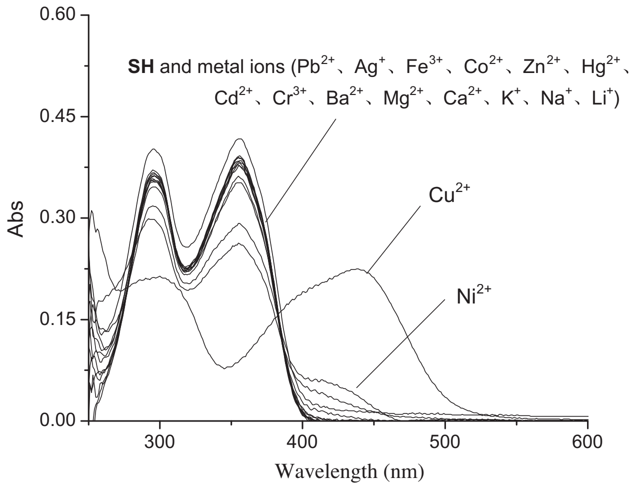


Fig. 1. Absorption spectra of **SH** (1×10^{-5} M) recorded in DMSO/HEPES buffer (10 mM, pH = 7.0, v/v, 4:1) after the addition of 2 equiv. of Cu^{2+} and 10 equiv of other metal ions.

In order to explore the effect of other metal ions on the binding of Cu^{2+} with **SH**, the competitive experiments were carried out by addition of Cu^{2+} to the solution of **SH** containing other metal ions. As shown in Fig. 2, the visible absorbance of **SH**–Cu^{2+} complex at 442 nm and the corresponding color changes were largely uninfluenced by other metal ions (Pb^{2+}, Ag^{+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Cr^{3+}, Ba^{2+}, Mg^{2+}, Ca^{2+}, Li^{+}, Na^{+} and K^{+}) even at higher concentration. These results indicated that the simple **SH** was preferential

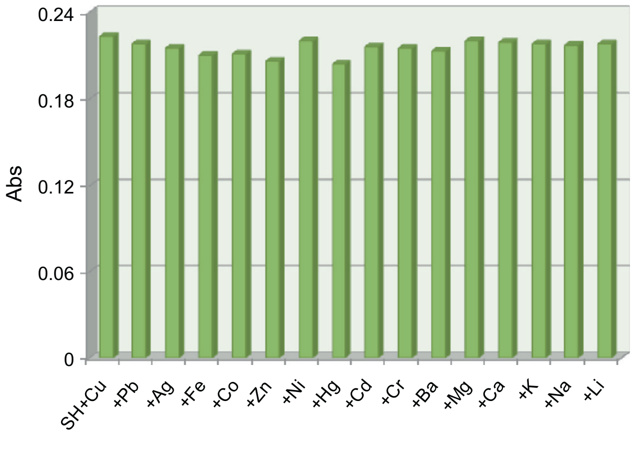


Fig. 2. Optical absorbance of **SH** (1×10^{-5}M) in DMSO/HEPES buffer (v/v, 4:1, pH = 7.0) in presence of 2 equiv. of Cu^{2+} and other metal ions (Pb^{2+}, Ag^{+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Cr^{3+}, Ba^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+} and Li^{+}). Detection wavelength: 442 nm.

selective colorimetric sensors for Cu^{2+} compared with other metal ions at the same conditions. This also represented a significant improvement in the sense of Cu^{2+} for **SH** compared to the other reported sensors, which was generally interfered by other metal ions (*e.g.* Ag^{+}, Hg^{2+}) [20–23]. Moreover, this suggested the stronger binding capacity of **SH** toward Cu^{2+}.

The significant optical response of probe **SH** exhibited a ratiometric response to Cu^{2+}. The ratio of the long-wavelength at 442 nm to the short-wavelength at 360 nm increased with the increasing Cu^{2+} concentration. These changes allowed the Cu^{2+} concentration to be determined ratiometrically. Other tested metal ions did not greatly alter the ratiometric value relative to **SH** itself (Supplementary data, Fig. S1). This indicated that the co-existence of other metal ions had a negligible interfering effect on the reliable detection of Cu^{2+}. Furthermore, the Cu^{2+}-induced absorption ratio A_{442}/A_{360} displayed good linearity, which can be expressed as $A_{442}/A_{360} = 18.87\ [\mathrm{Cu}^{2+}] - 0.104$ ($R = 0.996$) in the Cu^{2+} concentration range of 10.0–80.0 μM (Fig. 3). This indicated that the probe **SH** could be used for the practical quantitative detection. The limit of detection (LOD) was determined to be 6.5×10^{-6} M. Then the proposed Cu^{2+}-selective approach was used for the determination of Cu^{2+} in the real-life samples according to the literature [29]. The interfering species, such as Cd^{2+}–Ni^{2+}, Ca^{2+}–Mg^{2+}, Co^{2+}–Zn^{2+}, Ag^{+}–Hg^{2+} and various anions (AcO^{-}, NO_3^- and Cl^{-}), were added to a standard solution containing Cu^{2+} (40 μM), with the succedent addition of **SH** (2.5×10^{-5} M). Subsequently, the samples were quantitatively measured by UV–VIS analysis at 442 nm and 360 nm, respectively. The quantification data of Cu^{2+} was fitted in the calibration (Fig. 3). This suggested that the sensors could be applied to detect Cu^{2+} real sample.

The absorption peak at 442 nm and 360 nm for **SH**–Cu^{2+} is closely related to the degree of deprotonation of the phenolic subunit, which is dependent on the pH of the medium. So, the effect of pH on the **SH**–Cu^{2+} was investigated. Result indicated that **SH**–Cu^{2+} showed an optimum absorption at pH = 7.0 (Supplementary data, Fig. S2). Therefore, pH = 7.0 was selected for recognition. Furthermore, addition of EDTA·Na$_2$ to the solution of **SH**–Cu^{2+} resulted in a reverse color change from bright yellow to colorless. This suggested that Cu^{2+}-induced color change is reversible.

The binding properties of **SH** with Cu^{2+} were studied in detail by UV–VIS titration experiment. As shown in Fig. 4, with the gradual increase amount of Cu^{2+}, the absorption band at 360 nm decreased slowly and the new red-shifted maximum absorption band at 442 nm formed and developed. As a result, the color of the solution changed from colorless to bright yellow. These indicated that push–pull **SH** displayed strong intramolecular charge transfer [26]. Simultaneously, the well-defined isosbestic point at 385 nm occurred, which indicated that **SH** forms a 1:1 molecular complex with Cu^{2+} in DMSO/H$_2$O. This was also confirmed by Job plot analysis (Fig. 4). The binding constant of complex **SH**–Cu^{2+} was estimated at Ka = 1.3 × 106 mol^{-1} dm^{3} ($R = 0.97$) by the satisfactory non-linear least-square analysis [30,31] of the absorbance changes at the new band maximum (Supplementary data, Fig. S3).

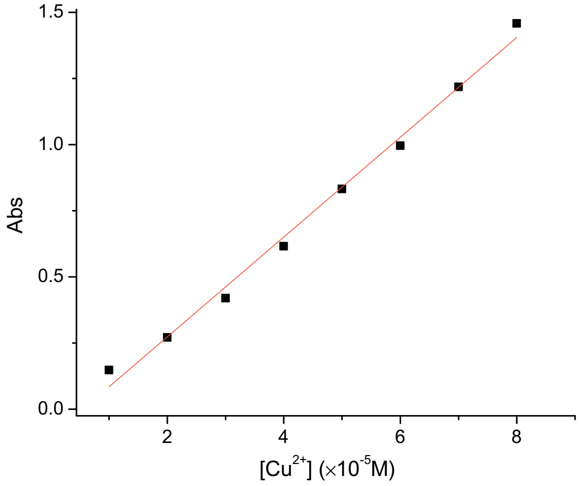


Fig. 3. Linear response of the absorbance ratio A_{442}/A_{360} as a function of Cu^{2+} concentration.

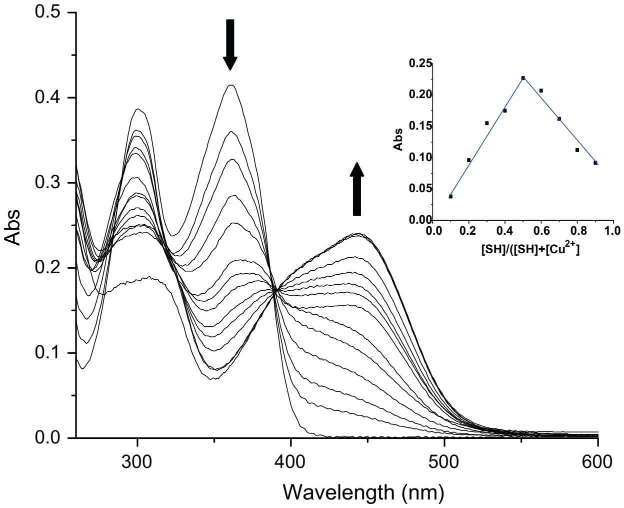
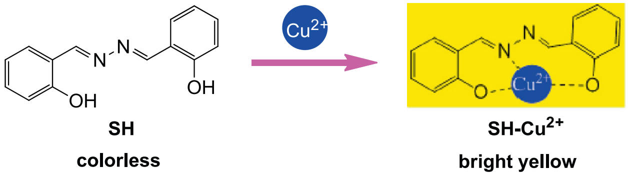


Fig. 4. UV–VIS titration of **SH** (1×10^{-5}M) with Cu^{2+} (0–1.5 equiv.) in DMSO/HEPES buffer (pH = 7.0, v/v, 4:1). Insert displays the Job plot of absorbance of SH at 442 nm the complex formed by SH and Cu^{2+} at an invariant total concentration of 20 μM.



Scheme 1. A proposed response mechanism of **SH**–Cu^{2+}.

To further explore the binding mode of **SH** and Cu^{2+}, the important IR spectra were performed which illustrated the characteristic structure changes during the interaction of **SH** with Cu^{2+}. The band at 2624 cm^{-1}, which was assigned to the OH···N=C intramolecular hydrogen bond of **SH** [32], disappeared upon the coordination of Cu^{2+}. This suggested that Cu^{2+} coordinated to the two deprotonated phenolate groups in **SH**. Moreover, the C=N stretching vibration 1628 cm^{-1} of **SH** appeared in the **SH**:Cu^{2+} complex, and the new lower frequency at 1620 cm^{-1} emerged which was ascribed to the coordination of C=N and Cu^{2+} [32]. These results clearly indicated that one of two azomethines in the ligand **SH** coordinated to the Cu^{2+}, as illustrated in Scheme 1. The occurrence of complexation of two deprotonated phenolate groups and the single C=N to Cu^{2+} allowed the charge transfer from ligand to metal, which resulted in the new absorption band at 442 nm and the obvious color change from colorless to bright yellow. Furthermore, the coordination also indicated that the planar **SH** distorted, and one of the aromatic rings rotated perpendicular to another around C=N facilitating the binding of Cu^{2+}.

Conclusion

The simple probe **SH** displayed colorimetric and ratiometric response with a large red-shift of UV–VIS absorption that was applied to the detection of cupric cation with high selectivity and low LOD among HTM ions. The dramatic color change from colorless to bright yellow was ascribed to the intramolecular charge transfer from the phenolic oxygen atoms and nitrogen atom of **SH**–Cu^{2+}.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.09.104.

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