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Highly selective colorimetric schiff base chemosensor for detection of Cu^{2+}

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A highly selective colorimetric chemosensor for Cu^{2+} has been designed using a novel Schiff base based on 2-hydroxy-1-naphthaldehyde. On addition of Cu^{2+}, the color of Schiff base solution changes from yellow to colorless, which can be viewed with the naked eye. The proposed chemosensor is sensitive to Cu^{2+} with the detection limit of 1.3×10^{-7} mol L^{-1}. The mechanism of the colorimetric chemosensor for the detection of Cu^{2+} has been investigated in detail through UV-vis, Job plot, ^{1}H NMR and FT-IR data. The results show that a stoichiometric complex (1:1) is formed between Schiff base and Cu^{2+}, based on the molecular proton transfer process. The selectively of the chemosensor for detection of Cu^{2+} over common cations has been investigated by UV-vis spectroscopy. The test strip for Cu^{2+} prepared according to the principle of colorimetric chemosensor illustrates the advantages of this method in terms of convenience and effectiveness.

Keywords: Analytical chemistry, Colorimetric recognition, Selectivity, Copper, Schiff Base

Copper ion (Cu^{2+}) is the third most abundant essential metal element in human body, after zinc and iron. It also plays a pivotal role in the field of environmental and chemical systems[1, 2]. Cu^{2+} can act as a catalytic cofactor for metalloenzyme, such as superoxide dismutase, cytochrome oxidase and tyrosinase in fundamental physiological processes[3]. However, an excess amount of Cu^{2+} *in vivo* may express toxicity in liver cells, and even induce some diseases like Wilson's disease, Parkinson's, Alzheimer and liver damage[4-6]. Besides, with its widespread usage, it contributes significantly to metal pollution. Various analytical methods including absorption spectrometry (AAS), electrochemistry (EC), inductively coupled plasma atomic emission spectrometry (ICP-AES) and fluorescence spectrometry have been adopted for determination of Cu^{2+}. Nevertheless, these methods are expensive and require sophisticated instruments and time-consuming sample preparation[7-11]. Hence, colorimetric methods have attracted great attention due to the direct determination by color change, which can be easily observed via naked eyes[12].

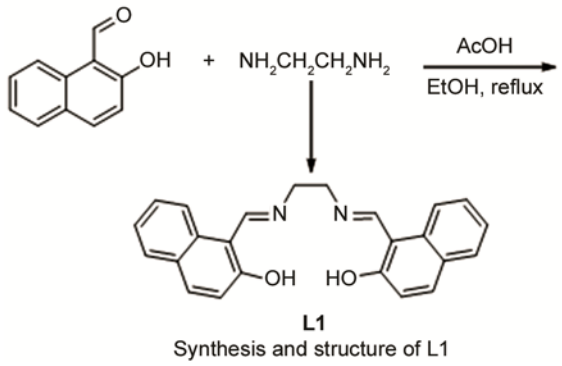
Recently, many copper-selective chemosensors have been constructed on the basis of ion-induced fluorescence or spectral changes[13-15]. Schiff base possess excellent coordination ability and biological/ pharmacological activity, which can be applied to design chemosensors for Cu^{2+} detection[16-18]. However, due to drawbacks of Schiff base sensors such as complicated preparation procedures, poor selectivity and anti-interference ability, it has been rarely used for the specific determination of Cu^{2+}.

Herein, a novel Cu^{2+} selective colorimetric chemosensor (L1) based on the simple preparation of Schiff base is proposed. Firstly, the *ortho*-hydroxy-imino segment was formed by 2-hydroxy-1-naphthaldehyde and ethylenediamine as the typical intramolecular proton transfer functional group. Secondly, in order to achieve 'naked-eye' colorimetric recognition, the naphthalene nucleus was used as the signal group. The chemosensor was applied to specifically determine Cu^{2+} cation by the formation of ion-binding cavity between –OH and Schiff base. This method involves easy synthesis, mild reaction conditions and high yield.

Experimental

Fresh doubly distilled water was used throughout the experiments. All reagents and solvents (analytical grade) were commercially available and were used without further purification. ^{1}H-NMR spectra was recorded on a Mercury-400MHz instrument. Chemical shifts are reported in ppm downfield from tetramethylsiane (TMS). The UV-vis spectra were obtained using a UV-2550 spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus and are uncorrected. Infrared spectra were recorded on a Digilab FTS-3000 FT-IR spectrophotometer.

The chemosensor (L1) was prepared as follows: 2-Hydroxy-1-naphthaldehyde (napht, 2.2 mmol) and ethylenediamine solution (2.0 mmol) were taken in a flask under stirring. Then, 20 mL of ethanol and acetic acid were added to the mixed solution. After heating under reflux on an oil bath at 80 °C for 8 h, the obtained bright yellow product was centrifuged and washed by ethanol at least three times. The schematic diagram for preparation of the chemosensor L1 is showed in Scheme 1.



Scheme 1

Chemosensor L1: bright yellow powder, yield: 85%, m. pt.>300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ:14.23 (s, 2H, OH), 9.15 (s, 2H, CH), 8.04-8.06 (d, 2H, J=8 ArH), 7.72-7.74 (d, 2H, J=8 ArH), 7.63-7.65 (d, 2H, J=8 ArH), 7.40-7.43 (t, 2H, J=12 ArH), 7.19-7.23 (d, 2H, J=16 ArH), 6.76-6.79 (d, 2H, J=12 ArH), 4.04 (s, 4H, CH_2); IR (KBr, cm^{-1}): 3425 (OH), 3098 (N=CH), 3025 (ArH), 2934, 2862 (CH_2), 1613 (C=N), 1547, 1489, 1447 (C=C), 1208 (C-N). Anal. (%): calcd (found) for $C_{22}H_{20}N_2O_2$: C 71.69 (71.71), H 5.47 (5.43), N 7.63 (7.61). ESI-MS Calcd for $C_{22}H_{20}N_2O_2$: 369.3 $[M+H]^+$ (369.2).

Results and discussion

The recognition ability of Cu^{2+} was investigated by recording the changes in absorption spectrum of the complexation reaction. As shown in Fig. 1, the compound L1 in DMSO displays yellow colour and strong absorption peak at 402 nm and 426 nm. When Cu^{2+}(10 equivalents) was added to the L1 solution, the sensor responded with a dramatic color change from yellow to colorless with the absorption peak showing a blue shift to 375 nm and 400 nm.

The binding properties of chemosensor L1 with Cu^{2+} were further studied by UV-vis titration experiments (Fig. 2a). The absorption peak at 426 nm gradually decreased with the increasing amount of Cu^{2+} when the compound L1 (dissolved in DMSO solution) was added. Three isosbestic points were clearly observed at 330 nm, 360 nm and 390 nm, indicating the formation of L1-Cu^{2+} complex. No further decrease in absorption at 426 nm was observed when the amount of Cu^{2+} exceeded 1 equivalent, illustrating the formation of 1:1 complex between the compound L1 and Cu^{2+} (inset, Fig. 2a). The method of continuous variation (Job's method) was also adopted to explore the stoichiometry of the L1-Cu^{2+} complex, and the results were identical, with

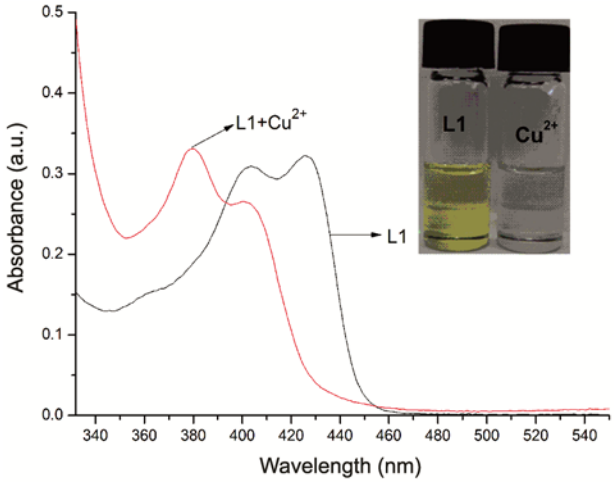


Fig. 1 — Absorption of L1 in DMSO (20 μM) upon addition of 10 equiv. of Cu^{2+}. [Inset: Color change of L1 upon addition of Cu^{2+}].

the formation of L1-Cu^{2+} complex (1:1). The binding constant K_a of the L1-Cu^{2+} complex was determined via Benesie-Hildebrand method to simulate the UV-vis adsorption. Figure 2b revealed the linear relationship between absorbance and Cu^{2+} concentration in the range of 10 μM–120 μM, with a regression equation of y = –0.195x+0.372 (R^2=0.999) and detection limit of 1.3×10^{-7} M (S_B/S = 3), respectively. The association constant K_a of the chemosensor L1 towards Cu^{2+} was calculated as 6.35×10^6 M^{-1}, suggesting that the compound L1 could be used as a sensitive chemosensor for Cu^{2+} detection.

The reaction mechanism for complexation of the compound L1 with Cu^{2+} was investigated by FT-IR. The FT-IR spectrum of compound L1 displayed well-defined characteristic peaks at 1613 cm^{-1} and 1547 cm^{-1}, ascribed to the stretching vibration of C=N and C=C. However, after the addition of Cu^{2+}, the absorption peaks of C=N disappeared, and two new peaks appeared at 1643 cm^{-1} and 3218 cm^{-1}, due to the stretching vibration of C=O and N-H, respectively. Simultaneously, the stretching vibration absorption peaks of C=C showed a red shift to 1574 cm^{-1}, indicating that the compound L1 has been complexed with Cu^{2+}.

This was also supported by the ^{1}H NMR titration. As revealed in Fig. 4, the compound L1 showed two single peaks at 14.23 and 9.15 ppm in DMSO solution, corresponding to the protons of OH and CH=N, respectively. The proton of the phenolic OH at 14.23 ppm disappeared after adding Cu^{2+} to the L1 solution and a new single peak gradually appeared at 10.65 ppm. Meanwhile, the protons of CH=N at 9.15 ppm

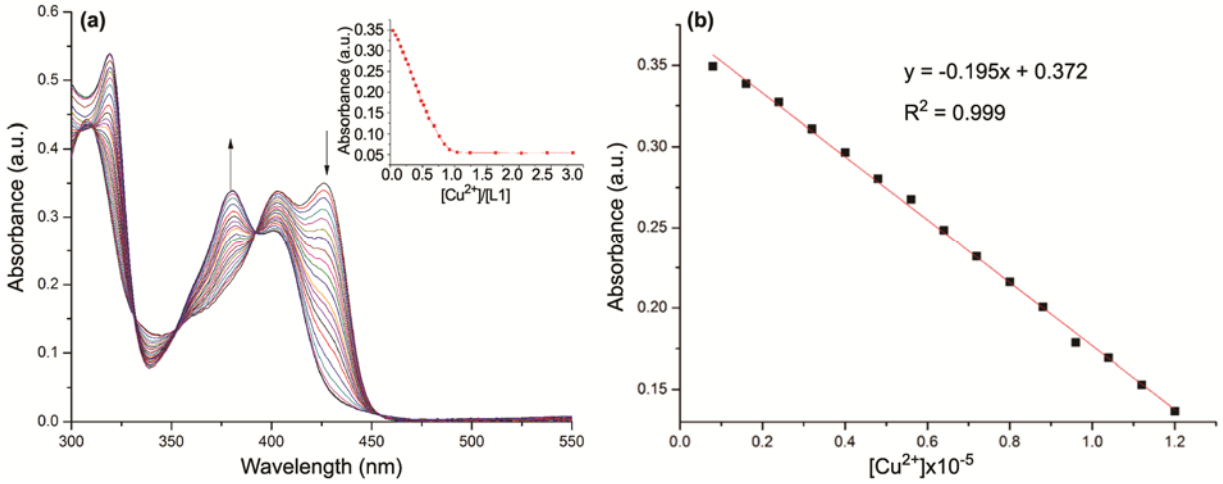


Fig. 2 — (a) Titration curves of L1 in DMSO (20 μM) upon addition of Cu^{2+}. [Inset: Changes of absorbance at 426 nm]. (b) Benesi-Hilderbrand plot of L1 with Cu^{2+} at 426 nm.

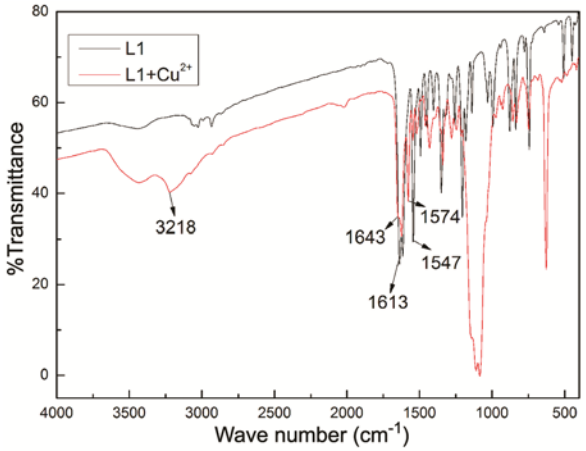


Fig. 3 — FT-IR spectra of L1 and L1-Cu^{2+}.

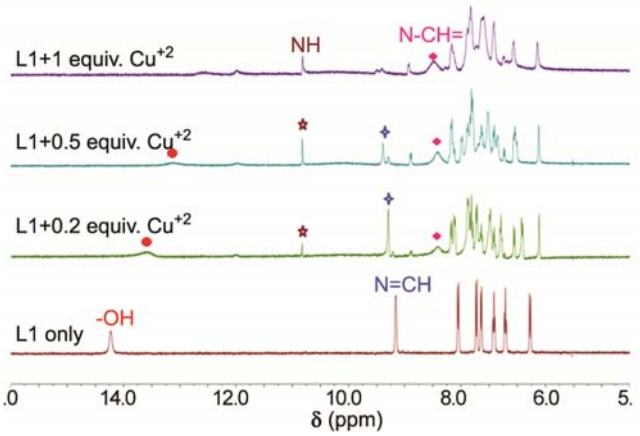
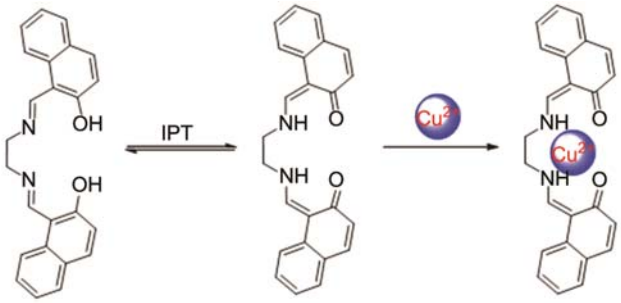


Fig. 4 — Partial ^1H NMR spectra of L1 (2.0 mM, DMSO-d_6) in the presence of varying amounts of Cu^{2+}.

disappeared gradually with the increasing amount of Cu^{2+}, and a new peak of N-CH= appeared at 8.4 ppm in the high field, indicating that the compound L1 has been coordinated with Cu^{2+} by intramolecular proton transfer.

It can be partially proved that the reaction between the compound L1 and Cu^{2+} had taken place by two steps: Scheme 2 shows that, the intramolecular proton transfer takes place on the compound L1 with addition of Cu^{2+} leading to keto-enol tautomerization. The Cu^{2+} conjugates with N and O atom on the keto form of compound L1 to generate a small conjugated length, which contributes to blue shift and the fading of color.

Selectivity is an important feature of the chemsensor L1 towards Cu^{2+} detection. The variations of UV-vis spectral and visual color changes of the sensor L1 were recorded in DMSO solution (20 μM) after adding 10 equiv of other metal ions, viz., Fe^{3+}, Hg^{2+}, Ag^{+}, Zn^{2+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Cr^{3+}, Mg^{2+}. It was noticed that the interfering metal ions did not cause any significant changes to absorbance; significant change was presented only by Cu^{2+} (Fig. 5a), which showed a dramatic color change from yellow to colorless (Fig. 5b). Moreover, when



Scheme 2

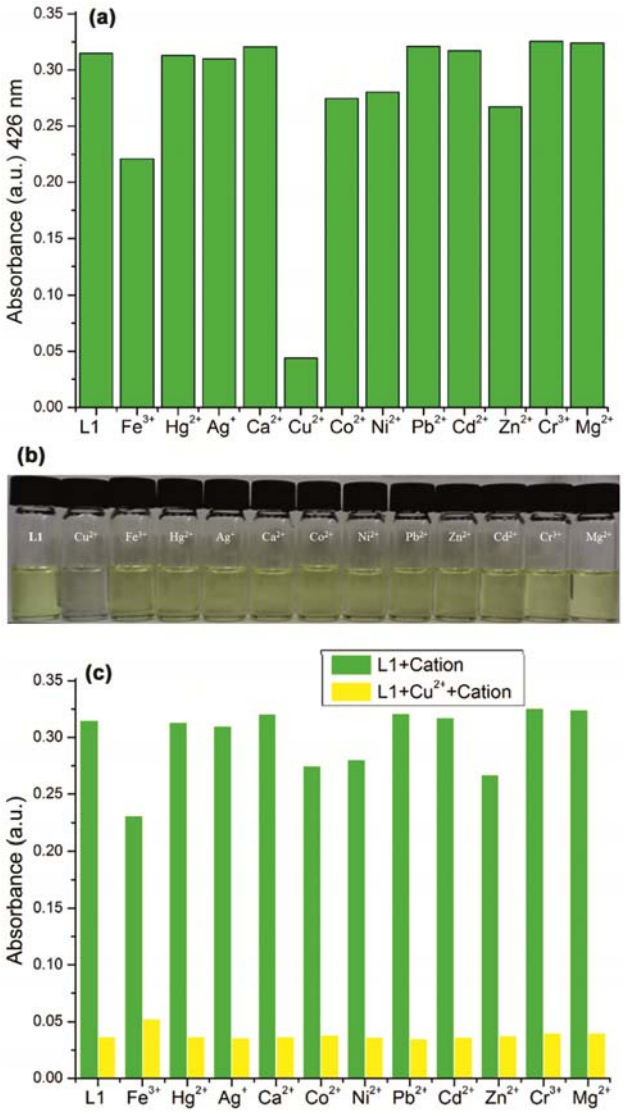


Fig. 5 — (a) Absorption of L1 in DMSO (20 μM) upon addition of 10 equiv. of various perchlorate metal salts at 426 nm. (b) Color change for L1 in DMSO (20 μM) upon addition of 10 equiv. of various perchlorate metal salts. (c) Absorption of L1 in DMSO (20 μM) in the presence of Cu^{2+} (10 equiv.) and various cations including Fe^{3+}, Hg^{2+}, Ag^{+}, Zn^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Cr^{3+}, Mg^{2+} (at 426 nm).

10 equiv of Cu^{2+} was added to the above solution containing other competitive metal ions, the color became colorless and the absorption peak at 426 nm corresponding to Cu^{2+} disappeared. Figure 5c shows that the selectivity of the sensor L1 towards Cu^{2+} was not affected by the presence of other cations, demonstrating that it could be selected favorably as a colorimetric chemosensor for Cu^{2+} determination. The Schiff base chemosensor exhibited only very weak fluorescence, and hence this aspect was not investigated further.

Fig. 6 — Test strips of L1 and L1+Cu^{2+}.

For the purpose of proving its practical application, test strips were prepared by immersing filter papers into a dilute hydrochloric acid solution and then washing to neutral by distilled water and drying in vacuum. The obtained filter papers were immersed into the sensor L1 solution (0.01 mol L^{-1}) and after drying in vacuum, these were utilized to sense Cu^{2+}. As shown in Fig. 6, the test strips containing L1 displayed yellow colour, while the color changed to colorless with addition of Cu^{2+}. This shows that the test strips can be used for real-time detection of Cu^{2+}.

In conclusion, this work presents a facile, low-cost and efficient Schiff base as a highly selective chemosensor of Cu^{2+}. The Cu^{2+} could be recognized by the sensor L1 by forming a stable 1:1 L1-Cu^{2+}. complex, at a low detection limit of 2×10^{-7} mol L^{-1} The sensor possesses high specific selectivity for Cu^{2+} in DMSO solution and the coexistence of other cations did not affect the Cu^{2+} recognition process. Results demonstrate that the sensor L1 may be used as a colorimetric sensor for monitoring Cu^{2+} as test strips in convenient and efficient Cu^{2+} test kit.

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