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Original article

Quinoline-based colorimetric chemosensor for Cu²⁺: Cu²⁺-induced deprotonation leading to color change

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ABSTRACT

A quinoline-based colorimetric chemosensor (QDB) for Cu^{2+} was synthesized by coupling quinoline-2carbaldehyde with 4-(dimethylamino)benzohydrazide. Although most transition metal cations can cause redshifts in the UV-vis spectrum of QDB, the response of the chemosensor for Cu^{2+} can be easily distinguished because it exhibits the largest redshift together with a color change from colorless to red in response to Cu^{2+} . Other metal ions have no effect on the specific response of QDB to Cu^{2+} . The significant redshift and color change were attributed to Cu^{2+} -induced deprotonation of NH in the sensor. © 2013 En-Ju Wang, Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

1. Introduction

Copper is an essential trace element and plays important physiological roles in many biological systems. But at the same time, copper is a significant metal pollutant due to its widespread use. Both deficiency and excess of copper can lead to health problems. Therefore the development of colorimetric or fluorescent sensors for the selective and sensitive detection of Cu^{2+} in biological and environmental systems has attracted considerable attention [1–10].

Some metal ions can induce deprotonation of active NH, such as the NH groups conjugated to aromatic or carbonyl groups. This deprotonation process caused by complexation can be used for metal ions recognition and sensing. For the chemosensors based on intramolecular charge transfer, the deprotonations of coordination atoms in electron-donating groups can greatly enhance the electrondonating ability of electron donors and result in a redshift in emission and absorption spectra. Great achievement in the field of deprotonation-based chemosenors for metal ions has been made [6–12]. Guo reported two Zn^{2+} fluorescent sensors based on the metal ion-induced deprotonation of an imide group, which show red-shifts of both excitation and emission bands due to an extensive π -system resulted from deprotonation of imide groups [11]. Inspired by the idea, we synthesized a new chemosensor (QDB) by coupling quinoline-2-

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carbaldehyde with 4-(dimethylamino)benzohydrazide. QDB exhibits a color change response from colorless to red only toward Cu²⁺.

2. Experimental

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further purification. 4-(Dimethylamino)benzohydrazide was prepared according to the procedure reported in the literature [13]. The corresponding metal nitrates were used as the metal cation sources. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker-400 spectrometer with TMS as the internal standard. ESI-MS spectra were performed on a Bruker esquire HCT-Agilent 1200 spectrometer. UV–vis absorption spectra were recorded on TU-1901 spectrophotometer. X-ray diffraction data collection was performed on Gemini A Ultra diffractometer.

2.1. Synthesis of N'-(quinolin-2-ylmethylene)-4-(dimethylamino)benzohydrazide (QDB)

Quinoline-2-carbaldehyde (0.30 g, 1.91 mmol) and 4-(dimethylamino)benzohydrazide (0.35 g, 1.95 mmol) were stirred at 72 °C in methanol (30 mL) under nitrogen atmosphere until complete consumption of quinoline-2-carbaldehyde, monitored by TLC (about 10 h). The reaction mixture was cooled to room temperature to give a precipitate. The precipitate was collected by filtration and washed three times with cooled methanol to afford QDB as a pale yellow solid (0.38 g, 63%). ¹H NMR (DMSO-*d*₆): δ 11.92 (s, 1H), 8.60 (s, 1H), 8.42 (d, 1H, *J* = 8.8 Hz), 8.12 (d, 1H, *J* = 8.8 Hz), 8.05 (d,

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1H, *J* = 8.4 Hz), 8.02 (d, 1H, *J* = 8.4 Hz), 7.88 (d, 2H, *J* = 8.8 Hz), 7.7– 7.83 (m, 1H), 7.61–7.67 (m, 1H), 6.80 (d, 2H, *J* = 8.8 Hz), 3.03 (s, 6H). ¹³C NMR (DMSO-*d*₆): δ 163.2, 154.2, 152.7, 147.4, 146.2, 136.6, 130.0, 129.5, 128.8, 128.0, 127.8, 127.1, 119.1, 117.4, 110.8, 39.7; ESI-MS *m*/*z*: 319.4 [M+H]⁺, 341.4 [M+Na]⁺.

2.2. Preparation of QDB-Cu(II) complex

Needle-like crystals suitable for X-ray analysis were obtained by evaporating a solution of $QDB/Cu(NO_3)_2$ (1:1 molar ratio) in ethanol.

3. Results and discussion

Free QDB shows absorption maximum at 356 nm in ethanol. Upon the gradual addition of Cu^{2+} , the intensity of the absorption at 356 nm decreases and a new absorption band at 474 nm appears (Fig. 1), resulting in a color change from colorless to red. Other transition metal cations, such as Zn^{2+} , Co^{2+} and Ni^{2+} , also cause a decline of the absorbance at 356 nm and induce new absorption bands at longer wavelength than 356 nm. Nevertheless the induced new absorptions are lower in intensity and shorter at wavelength than that induced by Cu^{2+} (Fig. 2a), and Cu^{2+} is the only cation that causes an observable color change from colorless to red (Fig. 2b).

The selectivity of QDB for Cu^{2+} was examined upon treatment with binary mixtures of Cu^{2+} with various metal cations in ethanol. The intensity of the Cu^{2+} -induced absorption at 474 nm is hardly affected by any other metal cations (Fig. 3). The sensor displays an extremely high selectivity for Cu^{2+} than other metal ions. That was attributed to the far higher binding affinity of QDB to Cu^{2+} than that to other metal cations.

In aqueous ethanol, QDB exhibits similar absorption spectral behavior as that in ethanol, which is significant for detection of Cu^{2+} , because metal ion-containing samples usually are aqueous. The UV/vis responses of QDB to various metal cations and the selective responses of QDB to Cu^{2+} in 50% aqueous ethanol are shown in Fig. 4a and b. The Ni²⁺-induced change in the UV/vis spectrum of QDB is very similar to that of Cu^{2+} -induced, which perhaps interferes with distinguishing between Cu^{2+} and Ni²⁺. But fortunately, Ni²⁺ leads to a color change from colorless to yellow, while Cu^{2+} induces a change from colorless to red. In the presence



Fig. 1. UV/vis spectra of QDB $(5.0\times10^{-5}\mbox{ mol}/L)$ upon the titration of Cu^{2+} (0–1.6 equiv.) in ethanol. Inset: Absorbance at 474 nm as a function of Cu^{2+} concentrations.



Fig. 2. (a) UV/vis responses of QDB (5.0×10^{-5} mol/L) to various metal ions in ethanol. (b) The color changes of QDB (5.0×10^{-5} mol/L) upon addition of various metal ions in ethanol. (Amount of the metal ions: 10 equiv. for Na⁺, K⁺, Ca²⁺, Mg²⁺ and 1.0 equiv. for other metal ions).

of mixed Cu²⁺ and Ni²⁺, the UV/vis spectrum QBD shows absorption maximum at 451 nm (454 nm for Cu²⁺, 440 nm for Ni²⁺) and the color change from colorless to red occurs (Fig. 4c). We can deduce that Cu²⁺ is more competitive in complexation with QDB than Ni²⁺. Therefore QDB can selectively recognize and signal Cu²⁺ and other metal cations have no effect on the specific response of QDB to Cu²⁺ in 50% aqueous ethanol.

With the stepwise addition of Cu^{2+} (0–1.6 equiv.) to QDB, the absorbance increases approximately linearly. When the molar ratio of Cu^{2+} to QDB was over 1, the absorption intensity remained unchanged (Fig. 1 inset). This implies the formation of a 1:1 complex between QDB and Cu^{2+} . ESI-MS spectra of QDB in the presence of Cu^{2+} exhibits a peak at m/z 380.3, which is assigned to [Cu(QDB)-1]⁺ (calcd. 380.1). This confirms the 1:1 stoichiometry



Fig. 3. Absorbance of QDB in the presence of various cations (10 equiv. for Na⁺, K⁺, Ca²⁺, Mg²⁺ and 1.0 equiv. for other metal ions) at 474 nm (black bars) and the selective responses of QDB to Cu²⁺ (1.0 equiv.) in the presence of other cations ((10 equiv. for Na⁺, K⁺, Ca²⁺, Mg²⁺ and 1.0 equiv. for other metal ions) at 474 nm (gray bars) in ethanol.

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Fig. 4. (a) UV/vis responses of QDB (5.0×10^{-5} mol/L) to various metal cations (10 equiv. for Na⁺, K⁺, Ca²⁺, Mg²⁺ and 1.0 equiv. for other metal ions) in aqueous ethanol (50%, v/v). (b) Absorption responses of QDB in the presence of various metal cations (10 equiv. for Na⁺, K⁺, Ca²⁺, Mg²⁺ and 1.0 equiv. for other metal ions) (black bars) and in the presence of the mixtures of Cu²⁺ (1.0 equiv.) and various metal cations (10 equiv. for Na⁺, K⁺, Ca²⁺, Mg²⁺ and 1.0 equiv. for other metal ions) (gray bars) in aqueous ethanol (50% v/v). (c) The color changes of QDB (2.0×10^{-5} mol/L) in the presence of Cu²⁺ (1.0 equiv.), Ni²⁺ (1.0 equiv.) or their mixture (1.0 equiv. for each ion).



Fig. 5. Coordination mode of QDB with Cu^{2+} . The non-coordinated H_2O and $(NO_3)^-$ are omitted for clarity. Selected bond distances (Å): Cu-N(1) 2.079, Cu-N(2) 1.920, Cu-O(1) 1.981, Cu-O(2) 1.932, C(11)-O(1) 1.284, C(11)-N(3) 1.341.

between QDB and Cu²⁺, and furthermore, it is evidence for the deprotonation of NH upon coordination to Cu²⁺. In the crystal of the QDB-Cu(II) complex (Fig. 5), The bond distance of 1.284 Å for C(11)–O(1) is greater than the bond distance range of C=O (1.19–1.23 Å), but it approximates the distance of conjugated C-O (1.30 Å). The bond distance of C(11)–N(3)(1.341 Å) lies in the bond distance range of C=N (1.34–1.38 Å), That suggests a conversion from amide group to imidic acid together with the deprotonation of N(3)–H upon binding Cu²⁺. The deprotonation leads to an extended conjugated system in QDB and favors charge transfer process from 4-(dimethylamino)benzamido group to quinoline group, which accounts for the large redshift in absorption spectrum and the color change.

4. Conclusion

In summary, we have developed a quinine-based colorimetric chemosensor for Cu^{2+} detection. The sensor displays an apparent response to Cu^{2+} by a significantly red-shifted absorption band and a color change from colorless to red. Other metal ions have no effect on its specific response to Cu^{2+} . The 1:1 binding mode was proposed based on UV-vis titrations, ESI-MS and X-ray analysis. When binding with Cu^{2+} , the deprotonation process of NH in the sensor would occur, which causes the large redshift and the color change.

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References

- Y. Jeong, J. Yoon, Recent progress on fluorescent chemosensors for metal ions, Inorg. Chim. Acta 381 (2012) 2–14.
- [2] X. Chen, J. Wang, J. Cui, Z. Xu, X. Peng, A ratiometric and exclusively selective Cu^{II} fluorescent probe based on internal charge transfer (ICT), Tetrahedron 67 (2011) 4869–4873.
- [3] Z. Xu, Y. Xiao, X. Qian, J. Cui, D. Cui, Ratiometric and selective fluorescent sensor for Cu^{II} based on internal charge transfer (ICT), Org. Lett. 7 (2005) 889–892.
- [4] Y. Shiraishi, K. Tanaka, T. Hirai, Colorimetric sensing of Cu(II) in aqueous media with a spiropyran derivative via a oxidative dehydrogenation mechanism, ACS Appl. Mater. Interfaces 5 (2013) 3456–3463.
- [5] C.D. Sun, J.M. Chen, H.M. Ma, et al., A new Cu²⁺-induced color reaction of a rhodamine derivative N-(3-carboxy)acryloyl rhodamine B hydrazide, Sci. China Chem. 54 (2011) 1101–1108.
- [6] J.H. Huang, Y.F. Xu, X.H. Qian, A colorimetric sensor for Cu²⁺ in aqueous solution based on metal ion-induced deprotonation: deprotonation/protonation mediated by Cu²⁺-ligand interactions, Dalton Trans. (2009) 1761–1766.
- [7] S.P. Wu, R.Y. Huang, K.J. Du, Colorimetric sensing of Cu(II) by 2-methyl-3-[(pyridin-2-ylmethyl)-amino]-1,4-naphthoquinone: Cu(II) induced deprotonation of NH responsible for color changes, Dalton Trans. (2009) 4735–4740.
- [8] Z.C. Xu, X.H. Qian, J.N. Cui, Colorimetric and ratiometric fluorescent chemosensor with a large red-shift in emission: Cu(II)-only sensing by deprotonation of secondary amines as receptor conjugated to naphthalimide fluorophore, Org. Lett. 7 (2005) 3029–3032.
- [9] J. Jiang, H. Jiang, X. Tang, et al., An efficient sensor for Zn²⁺ and Cu²⁺ based on different binding modes, Dalton Trans. 40 (2011) 6367–6370.
- [10] Z. Xu, J. Pan, D. X. Spring, J. Cui, J. Yoon, Ratiometric fluorescent and colorimetric sensors for Cu²⁺ based on 4,5-disubstituted-1,8-naphthalimide and sensing cyanide via Cu²⁺ displacement approach, Tetrahedron 66 (2010) 1678–1683.
- [11] D.Y. Wu, L.X. Xie, C.L. Zhang, et al., Quinoline-based molecular clips for selective fluorescent detection of Zn²⁺, Dalton Trans. (2006) 3528–3533.
- [12] N. Zhang, Y. Su, M. Yu, A novel cell-impermeable fluorescent zinc sensor containing poly(ethylene glycol) chain, Chin. Chem. Lett. 22 (2011) 863–866.
- [13] H. Mu, R. Gong, L. Ren, et al., An intramolecular charge transfer fluorescent probe: Synthesis and selective fluorescent sensing of Ag⁺, Spectrochim. Acta A 70 (2008) 923–928.

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Cu

Ni²⁺