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A new rhodamine-based colorimetric chemosensor for naked-eye detection of Cu^{2+} in aqueous solution

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Abstract

A new colormetric probe **1** based on rhodamine B lactam was developed for naked-eye detection of Cu^{2+} . The optical feature of **1** for Cu^{2+} was investigated by UV-vis absorption spectroscopy. Upon the addition of Cu^{2+} , the **1** displayed a distinct color change from colorless to pink, which can be directly detected by the naked eye. The stoichiometry of **1** to Cu^{2+} complex was found to be 1:1 and the naked-eye detection limit was determined as low as 2 μ M. The results suggest that the probe **1** may provide a conveniently method for visual detection of Cu^{2+} with high sensitivity.

Key words

Rhodamine B, Colormetric probe, Cu²⁺, Spirolactam

1. Introdution

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The development of chemosensors for the detection of metal ions has received considerable attention because of their important roles in medicine, living systems and the environment.^{1,2} Among the methods available for chemosensors, a colorimetric technique appeared to be the most attractive, which could be widely used owing to the low cost and lack of equipment required, and a color change that can easily be observed by the naked eyes, even at very low analyte concentration. On the other hand, Cu^{2+} is not only a significant metallic pollutant, but also an essential element for living organisms.³⁻⁶ So far, many progress has been achieved in the creation of a chemosensor for Cu^{2+} ,⁷⁻¹⁸ however there is still room to develop easy-to-make, simple-to-use and observable colorimetric sensors for Cu^{2+} in aqueous solution. Work related to this area is of great challenge and increasing interest.

Rhodamine is an ideal platforms for development of colormetric and fluorescent probe owing to its excellent photophysical properties.^{19,20} Specifically, it is based on spirolactam (colorless and nonfluorescent) to ring-opened amide (color and fluorescent) process utilized for the detection of metal ions.²¹⁻³¹ Based on this mechanism, our ambition was to design and synthesize a new colormetric probe for detection of Cu²⁺ in aqueous media. Herein, we introduce a novel and simple method to prepare rhodamine B-based chemosensor by two steps reaction. The sensor **1** showed "off–on" type chromogenic behavior toward Cu²⁺ over other interfering metal ions.

2. Experimental

2.1. Reagents

All the reagents were purchased from commercial suppliers and used without further purification. The salts used in stock solutions of metal ions were $CoCl_2 \cdot 6H_2O$, ZnCl₂, MnCl₂ · 4H₂O, KCl, NaCl, CuCl₂ · 2H₂O, NiCl₂ · 6H₂O, CdCl₂ · 2H₂O, HgCl₂, FeCl₃ · 6H₂O, MgCl₂ · 6H₂O, CrCl₃ · 6H₂O, Pb(NO₃)₂.

2.2. Apparatus

NMR spectra were measured on a Varian Mercury 300 spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C relative to tetramethylsilane as internal standard. MS spectra were obtained on a Finnigan Trace MS spectrometer. Elemental analyses were performed with a Vario EL-III instrument (Germany). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption reported in cm⁻¹. Absorption spectra were determined on UV-2501 PC spectrophotometer.

2.3. Synthesis of rhodamine derivate (1)

The synthetic route of the compound **1** is shown in Scheme 1. Rhodamine B hydrazide (2)³² was synthesized according to the previously reported procedure. To a 100mL flask, rhodamine B hydrazide(**2**) (0.91 g, 2.0 mmol) was dissolved in 50 mL ethanol. After the addition of acetylacetone (1 mL, excess), the stirred mixture was heated to reflux for 24 h. The residue was recrystallized from ethanol and afforded compound **1** as a white solid, yield: 85% (Scheme 1). The colorless crystals were obtained by slow evaporation of a solution of **1** in CHCl₃-CH₃OH (20:1, v/v) mixture at room temperature. M.p.184–185°C, IR(ν_{max} , KBr, cm⁻¹): 3446, 2972, 2364, 1714, 1620, 1576, 1513, 1429, 1352, 1272, 1221, 1115, 1084, 968, 865, 818, 756; ¹H NMR (300 MHz, CDCl₃): δ 11.12(s, 1H), 7.18-7.98 (m, 4H), 6.29-6.49(m,6H), 4.96(s,1H),

3.34 (q,8H), 1.93(s,3H), 1.54 (s,3H),1.16(t,12H, J=6.9 Hz); ¹³CNMR (75 MHz, CDCl₃): δ 195.6, 165.5, 163.0, 153.6, 150.2, 148.6, 132.8, 129.2, 128.1, 128.0, 123.9, 122.9, 107.4, 103.8, 97.5, 96.6, 66.2, 43.9, 28.5, 17.6, 12.1. ESI-mass: m/z 539.37 ([M+H]⁺). Elemental analysis: C₃₃H₃₈N₄O₃, Calcd: C, 73.58; H, 7.11; N, 10.40. Found: C, 73.42; H, 7.03; N, 10.29. Crystal data for C₃₃H₃₈N₄O₃: crystal size: 0.20×0.08× 0.05 mm, monoclinic, space group P2₁/c, *a* = 17.4047(17) Å, *b* = 15.0879(19) Å, *c* = 11.5212(11)Å, *V* = 1367.1(2) Å³, *Z* = 4, *T* = 293(2) K, $\theta_{\text{max}} = 50.04^{\circ}$, Dc = 1.214 g cm⁻³, 14012 reflections measured, 5309 unique (*R*_{int} = 0.0767). Final R indices [*I*>2 σ (*I*)]: *R*1 = 0.0697, *wR*2 = 0.1277 and GOF =1.025.

(Scheme 1)

2.4. X-ray crystallography of compound 1

Suitable single crystals of **1** for X-ray structural analysis were obtained by slow evaporation of a solution of **1** in CHCl₃-CH₃OH (20:1, v/v) mixture at room temperature. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 296(2) K. The structures were solved by direct methods with SHELXS-97 program and refinements on F^2 were performed with SHELXL-97 program by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All H atoms were initially located in a difference Fourier map. All H atoms were placed in geometrically idealized positions and constrained to ride on their

parent atoms, with C–H = 0.93Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

2.5. Analytical procedure

The stock solutions of $1(1.0\times10^{-5} \text{ M})$ were prepared by dissolving 1 in EtOH/ water (9:1, v/v) containing HEPES buffer(10 mM, pH =7.0). The cationic stocks were all in H₂O with a concentration of 3.0×10^{-3} M for UV–vis absorption spectra analysis. For metal ion absorption titration experiments, each time 3 mL solution of 1 filled in a quartz cell of 1 cm optical path length, and we increased concentrations of metal ions by stepwise addition of different equivalents using a micro-syringe. After each addition of Cu²⁺ ion, the solution was stirred for 5 min. The volume of cationic stock solution added was less than 100 µL with the purpose of keeping the total volume of testing solution without obvious change.

3. Results and discussion

3.1. Synthesis and structural characteristics of 1

The compound **1** was obtained by the reaction of rhodamine B hydrazide (**6**) with excess acetylacetone in EtOH under reflux. The yield of **1** was 85%. The structures of **1** were identified by using ¹H NMR, ¹³C NMR, ESI-MS (Fig. S1-3), and further comfirmed by X-ray diffraction analysis. The molecular view of **1** is shown in Fig. 1. The crystal structure of **1** clearly reveals the unique spirolactam ring formation, the ketone carbonyl oxygen (O2) and nitrogen atom (N4) form the intramolecular hydrogen bond. Notably, a hexatomic ring (C9-C11-C12-N4-H-O2) is formed with the aid of the hydrogen binding.

(Fig. 1)

3.2. Spectral characteristics

To examine the binding properties of **1** with metal ions, the UV/vis titration absorption spectra of **1**(10 μ M) in EtOH/water (9:1, v/v) containing HEPES buffer(10mM, pH =7.0) was first explored in the presence of 2 equivalent of different metal ions and the results were depicted in Fig. 2. A solution of **1** in EtOH/ water (9:1, v/v) containing HEPES buffer (10mM, pH = 7.0) is colorless. The sensor **1** exhibited very weak absorption in the visible range. Upon binding of metal ions (K⁺, Na⁺, Ni²⁺, Mg²⁺, Mn²⁺, Cr³⁺, Pb²⁺, Zn²⁺, Cd²⁺, Cu²⁺, Co²⁺, Fe³⁺ and Hg²⁺)(as their chloride salts), it was found that only the Cu²⁺ ion causes the absorption peak intensity obvious change at 552 nm. At the same time, the solution changed from colorless to pink which could easily be detected by the naked-eye. Other metal ions did not cause this colour change under the same conditions (Fig. 3). Accordingly, **1** was sensitive to Cu²⁺ ions in the visible light region.

To further investigate the sensing properties of compound **1**, UV/Vis titration of compound **1** with Cu^{2+} was performed. With the addition of increasing amounts of Cu^{2+} to a solution of **1** (10 μ M) in EtOH/water (9:1, v/v) containing HEPES buffer (10mM, pH =7.0), the maximum absorbance at 552 nm increased dramatically with each addition of Cu^{2+} (Fig. 4), which can be attributed to the delocalized xanthene

moiety of the ring-open amide form of 1.

(Fig. 4)

To investigate the binding stoichiometry between **1** and the Cu^{2+} ion, the Job's plot experiment³³ was carried out by keeping the total concentration of **1** and Cu^{2+} ions at 10µM and changing the molar ration of $Cu^{2+}([Cu^{2+}]/[1+Cu^{2+}])$ from 0 to 1. As shown in Fig.5, the result shows that a maximum at a molar fraction of 0.5, indicating the formation of 1:1complex of **1** and Cu^{2+} . The 1:1 complexation is also supported from ESI-MS spectra analyses (Fig. S4), which show a prominent peak at 600.18 (calculated value, 600.22) due to $[1+Cu^{2+}-H)]^+$. The stability constants *K*a of 1:1 **1**-Cu²⁺ complexe was determined by the Benesi–Hilderbrand equation:^{34,12}

$$1/\Delta A = 1/\Delta A_{\text{sat}} + 1/(\Delta A_{\text{sat}} K_{\text{a}}[\text{Cu}^{2+}])$$
(1)

where ΔA is the absorbance difference at 552 nm and ΔA_{sat} is the maximum absorbance difference at 552 nm. The association constant *K*a was evaluated graphically by plotting1/ ΔA against 1/[Cu²⁺]. Typical plots (1/ Δ absorbance *vs.* 1/[Cu²⁺] are shown in Fig.6. Data were linearly fitted according to eqn **1** and the *K*a value was obtained from the slope and intercept of the line. The *K*a value of 1-Cu²⁺complexe was 6.06× 10⁴ M⁻¹. The analytical detection limit of Cu²⁺ by the naked eye³⁵ is as low as 2.0 μ M (Fig. S5), lower than the limit of copper in drinking water (~20 μ M). These results suggest that compound **1** has a high selectivity to Cu²⁺, and could be exploited as a colorimetric sensor for Cu²⁺.

(Fig. 5)

(Fig. 6)

To test the practical applicability of our visual chemosensor for Cu^{2+} , the competition experiments of Cu^{2+} mixed with other metal ions were also carried out from UV-vis absorption spectra and the results were shown in Fig. 7. When $1(10 \ \mu M)$ was treated with 2 equiv of Cu^{2+} in the presence of the same concentration of other metal ions, the Cu^{2+} -induced UV/vis response of 1 was almost unaffected by the presence of the other metal ions.

(Fig. 7)

Additionally, the effects of anionic counterions on the sensing behavior of compound **1** to Cu^{2+} were also investigated. The separate concomitant additions of different copper salts, such as $Cu(AcO)_2$, $CuCl_2$, $Cu(NO_3)_2$, and $CuSO_4$ to the compound **1**, gave rise to the same absorption profiles (Fig. 8) and visible colour changes in their response to Cu^{2+} (Fig. S6) indicating a negligible effect of the counter anions on the recognition ability and photophysical properties of compound **1**.

(Fig. 8)

Furthermore, the EDTA-adding experiment was conducted to analyze the chemical reversibility behavior of the binding of **1** and Cu^{2+} (Fig. 9). When excess

EDTA was added into the mixture solution of 1 and Cu^{2+} , the absorbance intensity at 552 nm decreased immediately. Thus, the sensing process was considered to be reversible rather than an ion-catalyzed reaction.

(Fig. 9)

An NMR study for complexation was not available due to the paramagnetic property of Cu^{2+} .^[36] Instead, IR of **1** and **1**- Cu^{2+} complex was measured to study the binding mechanism (Fig. 10). The IR spectra was primarily characterized by band in the double-bond region. Two bands, 1714cm⁻¹ and 1620 cm⁻¹, were associated with the ketone carbonyl and amide carbonyl absorption in chemosensor **1**, respectively. upon addition of Cu^{2+} , two carbonyl groups IR peak at 1714 cm⁻¹ and 1620 cm⁻¹ dispeared, a new IR peak appeared at 1591 cm⁻¹. This suggests that the ketone and amide carbonyl O of **1** is actually involved in the coordination with Cu^{2+} .

(Fig. 10)

According to the above experiments, a proposed binding mechanism of Cu^{2+} with 1 was shown in Scheme 2. The oxygen on the enolic hydroxyl group, oxygen on the amide carbonyl group, as well as nitrogen on the hydrazone moiety can cooperatively participate in the binding with Cu^{2+} . The clorimetric change from colorless to pink can be attributed to the spirolactam ring-opening, which was induced by the complexation of Cu^{2+} . Moreover, this process is reversible, which has been proved by

the test using $EDTA/Cu^{2+}$.

4. Conclusion

In summary, a novel and simple structure rhodamine-base colorimetric chemosensor 1 was developed for the detection of Cu^{2+} in neutral ethanol aqueous solution. The recognition of Cu^{2+} gave rise to color changes from colorless to pink that was clearly visible to the naked eye. The response of the sensor to Cu^{2+} is unaffected by the presence of other commonmetal ions. Its selectivity is excellent, and the naked eyes detection of Cu^{2+} at 2 μ M level is possible. Such Cu^{2+} selective colorimetric chemosensor could meet the sensitive and selective requirements for biomedical and environmental application and be of great importance for real-time and instrument free detection.

Supplementary material

The crystallographic data (excluding structure factors) of **1** have been deposited with the Cambridge Crystallographic Center as supplementary publication no. 1406446. Copy of this information may be obtained free of charge viawww: http://www.ccdc.cam.ac.uk or from The Director, CCDC, 12 Union Road, Cambridge CB221EZ, UK (fax: t44 1223/336 033; email: deposite@ccdc.cam.ac.uk). Structural factors are available on request from the authors.

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Fig. 1



18

Pb2+ Zn2

Fig. 5

Fig. 7

Captions:

Schem 1. Synthesis of rhodamine derivate 1

Fig. 1. Crystal structure of the compound 1 (30% probability level for the thermal ellipsoids).

Fig. 2. UV–vis spectral changes of compound 1 (10 μ M) in EtOH/water(9:1, v/v) containing HEPES buffer(10mM, pH =7.0) upon additions of various metal ions (20 μ M).

Fig. 3. Visual color change of **1** (10 μ M) in EtOH/water (9:1, v/v) containing HEPES buffer (10mM, pH=7.0) upon addition of 2.0 eqiv of various metal ions as their chloride salts.

Fig. 4. UV–vis absorption spectra of $1(10 \ \mu\text{M})$ in EtOH/water (9:1, v/v) containing HEPES buffer (10mM, pH = 7.0) upon the addition of Cu²⁺ (0–20 μ M).

Fig. 5. Job' plot of 1 and Cu^{2+} . The total concentration of 1 and Cu^{2+} was kept at a fixed 10 μ M. The absorbance is monitored at 552 nm.

Fig. 6. Benesi–Hildebrand plot of chemosensor 1 with Cu^{2+} .

Fig. 6. Competitive experiments in the $1 + Cu^{2+}$ system with interfering metal ions. [1] = 10 μ M, [Cu²⁺] = 20 μ M, and [Mⁿ⁺] = 20 μ M.

Fig. 8. Absorption spectra of **1** (10 μ M) in EtOH/water(9:1, v/v) containing HEPES buffer(10 mM, pH =7.0) in the presence of different copper salts (20 μ M).

Fig. 9. Absorption response in EtOH/water(9:1, v/v) containing HEPES buffer (10mM, pH =7.0). a: Only **1** (10 μ M); b: **1**(10 μ M) with Cu²⁺ (20 μ M); c: **1** (10 μ M)

with Cu^{2+} (20 μ M) and then addition of EDTA (30 μ M); d: **1** (10 μ M) with Cu^{2+} (20 μ M) and EDTA (30 μ M) then addition of Cu^{2+} (35 μ M).

Fig. 10. Infrared spectra (KBr) of free 1 (a) and $1-Cu^{2+}$ complex (b) at room temperature.

Scheme 2. Proposed binding mechanism for 1 with Cu^{2+} .

Highlights

- The rhodamine-based sensor is simple to synthesize. Its structure was confirmed by single crystal X-ray diffraction.
- This sensor can be used to determine Cu²⁺ ion with high selectivity and sensitivity. The recognition of Cu²⁺ gave rise to color changes from colorless to pink that was clearly visible to the naked eye.

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