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Sulfonyl rhodamine hydrazide: A sensitive and selective chromogenic and fluorescent chemodosimeter for copper ion in aqueous media

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ABSTRACT

A novel, sulfonyl rhodamine hydrazide chemodosimeter displayed highly selective and sensitive recognition of Cu^{2+} in aqueous media, via colour change from colorless to pink. The colour change that occurred as a result of complexation with Cu^{2+} can be attributed to spirolactam ring-opening and hydrolysis of the hydrazide unit to afford C.I. Acid Red 52 (Rhodamine B) in the presence of Cu^{2+} . An analytical method was developed and successfully used for the determination of the copper content in a sample.

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1. Introduction

In recent years, the design and development of fluorescent probes for the detection of transition-metal ions have received considerable attention because fluorescent chemosensors have several advantages over other methods such as high sensitivity, selectivity, and real-time monitoring [1–3]. Considering the important roles of Cu²⁺ in biological and environment systems, a considerable effort has been put forth in the past few years to develop fluorescent probes for the detection of Cu^{2+} [4,5]. Whereas, most of the early reported fluorescent probes usually employ a fluorescence quenching mechanism upon binding with Cu²⁺ ion owing to the paramagnetic nature of Cu^{2+} [6,7]. However such a false positive signal may be induced by contaminants that are difficult to distinguish from the authentic analyte. These problems can be alleviated by a fluorescence enhancement mechanism that, instead, produces significant increases in fluorescence responses upon analyte recognition [8-19]. Recently, some examples of the fluorescent probes that display fluorescence enhancements by the addition of Cu²⁺ have been reported [20-34]. However, the fluorescence enhancement signal in most cases is still too weak, and it often suffers from a high

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background signal. In addition, some "turn-on" fluorescent probes can only be applied in non-aqueous solvents which limit their application in biological systems. Thus it is of significant importance to develop "turn-on" fluorescent probes that would allow accurate, sensitive, rapid recognition of Cu²⁺ in aqueous media.

C.I. Acid Red 52 enjoys extensive use as fluorescence label due to its excellent photophysical properties such as long absorption and emission wavelength, large absorption coefficient and high fluorescence quantum yield [35]. Rhodamine derivatives are nonfluorescent and colorless, but ring-opening of the corresponding spirolactam via coordination with metal ions or irreversible chemical reactions gives rise to a strong fluorescence emission and a pink color. Based on this mechanism, some rhodamine-based spirolactam derivatives have been designed as probes for the recognition of different metal ions [36].

The chemodosimeter system has attracted a tremendous amount of attention due to its ability to selectively perform a chemical reaction with a specific metal ion, which allows for selective and sensitive sensing [37]. Herein we describe our results concerning a chemodosimeter based on sulfonyl rhodamine hydrazide (**SRH**). The preliminary reaction relies upon a Cu²⁺-promoted hydrolysis reaction of **SRH** into C.I. Acid Red 52 in aqueous media [38], and **SRH** exhibited a pronounced chromogenic and fluorescent signaling behavior toward Cu²⁺ over other common interfering metal ions.

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Scheme 1. Synthesis of compound SRH.

2. Experimental

2.1. Apparatus and reagents

A Hitachi F-2500 spectrofluorimeter was used for fluorescence measurements. The absorption spectra were recorded with a Techcomp UV-8500 spectrophotometer (Shanghai, China). NMR spectra were measured on a Bruker DMX-500 spectrometer at 500 MHz in CD₃COCD₃. Elemental analyses were carried out with a Flash EA 1112 instrument. Electrospray ionization (ESI) mass spectra were measured with an LC-MS 2010A (Shimadzu) instrument. A Delta 320 pH-meter [Mettler-Toledo Instruments (Shanghai) Co., China] was used for pH measurements. All other chemicals used in experiments were of analytical grade. The solutions of metal ions were all prepared from their perchlorate salts. All solvents used in spectroscopic tests were of a spectrostropic grade. Distilled-deionized water was used throughout the experiment.

2.2. Synthetic procedure

A solution of C.I. Acid Red 52 (0.88 g, 2 mmol) in POCl₃ (15 mL) was heated under reflux for 4 h. The reaction mixture was then cooled and evaporated under vacuo to give the acid chloride which was dissolved in ClCH₂CH₂Cl (20 mL) together with *p*-toluene sulfohydrazide (0.37 g, 2 mmol) and triethylamine (2 mL). The mixture



Fig. 1. Absorption spectra of SRH (10 μ M) upon addition of respective metal ions (as perchlorate salt, 6 equiv.) in 50% (v/v) H₂O/CH₃CN buffered by 10 mM HEPES.



Fig. 2. Change in absorption spectra of **SRH** (10 μ M) in 50% (v/v) H₂O/CH₃CN buffered by 10 mM HEPES in the presence of different amount Cu²⁺. [Cu²⁺]: 0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20 μ M. Insert: absorbance at 557 nm as a function of Cu²⁺ concentration.

was stirred at room temperature for 12 h under N₂ and was then concentrated by evaporation. Water was added to the residue, and the aqueous phase extracted with ClCH₂CH₂Cl (3 \times 30 mL). The organic layer was washed with water, dried over Na₂SO₄, and concentrated by evaporation. The crude product was purified by silica gel column chromatography with EtOAc/Cyclohexane (1/3, v/v), affording SRH as a white solid 0.36 g, yield 60%. m.p.: 244–246 °C. ¹H NMR (CD₃COCD₃ 500 MHz, TMS): $\delta = 1.18$ (t, J = 7 Hz, 12H); 2.38 (s, 3H); 3.41 (q, J = 7 Hz, 8H); 6.19 (s, 2H); 6.35(m, 2H); 6.42 (s, 2H); 6.99 (d, *J* = 7.5 Hz, 1H); 7.13 (d, *J* = 8 Hz, 2H); 7.28 (d, J = 8.5 Hz, 2H); 7.53 (t, J = 7.5 Hz, 1H); 7.58 (t, J = 7.5 Hz, 1H); 7.82 (d, J = 7 Hz, 1H); 8.48 (s, 1H). ¹³C NMR (CD₃COCD₃, 250 MHz, TMS): δ 166.5, 153.4, 142.3, 138.4, 133.4, 128.7, 128.3, 126.8, 124.3, 122.6, 107.6, 105.1, 97.4, 43.9, 20.7, 12.0. ESI-MS 611.4 $[M + H]^+$; Anal. Cacld for C₃₅H₃₈N₄O₄S: C, 68.83; H, 6.27; N, 9.17; Found: C. 68.67: H. 5.98: N. 9.32.

2.3. General procedure for Cu^{2+} detection

A 1.0×10^{-3} M stock solution of compound SRH was prepared in CH_3CN. To 10 mL glass tubes containing 5 mL CH_3CN and different



Fig. 3. Fluorescence intensity of **SRH** (1 μ M) in 50% (v/v) H₂O/CH₃CN buffered by 10 mM HEPES upon the addition of 14 equiv. metal ions (Mⁿ⁺ denotes Na⁺, K⁺, Mg²⁺, Ca²⁺, Zn²⁺ and Ba²⁺). λ ex = 530 nm.



Fig. 4. Change in color of SRH (1 µM) in 50% (v/v) H₂O/CH₃CN buffered by 10 mM HEPES with different metal ions (14 µM). From left to right: Cu²⁺, Mg²⁺, Ce³⁺, Cd²⁺, Na⁺, Zn²⁺, K⁺, Pb²⁺, Hg²⁺, Ag⁺, Co²⁺, Ni²⁺, Ba²⁺ and Ca²⁺.

amounts of metal ions, appropriate volumes of this solution of **SRH** was added directly with a micropipette. The solutions were diluted with water to 10 mL, and then the absorption and fluorescence spectra were recorded immediately.

3. Results and discussion

3.1. Synthesis and structural characterization of SRH

As shown in Scheme 1, **SRH** was synthesized from rhodamine B by a two-step reaction, and its structure was confirmed by ¹H NMR, ¹³C NMR, MS and EA (Supporting Information, Fig. S1-2).

3.2. Uv-vis spectral responses of SRH

A solution of **SRH** in 50% (v/v) H₂O/CH₃CN buffered by 10 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) at pH 7.1 is colorless. As shown in Fig. 1, the absorption spectra of **SRH** exhibited only a very weak band over 500 nm region. The addition of Cu²⁺ into this solution immediately resulted in a significant enhancement of absorbance (about 600 fold) in the visible range of 500–600 nm and a new peak at 557 nm was observed. With increasing Cu²⁺ ion concentration, a shoulder peak could be observed (Fig. 2.). The absorbance of **SRH** at 557 nm was proportional to Cu²⁺ concentration over a range of 0–20 μ M. The color of the solution changed from colorless to pink-red upon titration with Cu²⁺ ions. Under identical condition, **SRH** exhibited no response to the addition of Mg²⁺, Ce³⁺, Cd²⁺, Na⁺, Zn²⁺, K⁺, Pb²⁺, Hg²⁺, Ag⁺, Co²⁺, Ni²⁺, Ba²⁺ and Ca²⁺.



Fig. 5. Fluorescence ($\lambda ex = 530$ nm) titration spectra of **SRH** (1 μ M) with Cu²⁺ (1–14 μ M) in 50% (v/v) H₂O/CH₃CN buffered by 10 mM HEPES. Insert: The plot of fluorescence intensity change of **SRH** (1 μ M) against varied concentration of Cu²⁺.

3.3. Fluorescence spectral responses of SRH

Fig. 3 shows the fluorescence spectra ($\lambda ex = 530$ nm) of **SRH** (1 µM) measured in 50% (v/v) H₂O/CH₃CN buffered by 10 mM HEPES at pH 7.1 with the addition of respective metal cations (14 equiv.). SRH showed only a very weak fluorescence in the absence of metal ions. The addition of Cu²⁺ resulted in a remarkably enhanced fluorescence intensity (about 1000-fold). Also, change of the color from colorless to red could be visually observed after addition of Cu^{2+} in 1 μ M concentration of **SRH** (Fig. 4.), indicating that **SRH** can serve as a visual probe for Cu^{2+} . Under the same condition, additions of other metal ions including Mg^{2+} , Ce^{3+} , Cd^{2+} , Na^+ , Zn^{2+} , K^+ , Hg^{2+} , Ag^+ , Co^{2+} , Ni^{2+} , Pb^{2+} , Ba^{2+} and Ca^{2+} induced no obvious fluorescence enhancements and color changes. These observations indicated that **SRH** could selectively recognize Cu^{2+} in 50% (v/v) H₂O/CH₃CN. To further investigate the interaction of Cu²⁺ and SRH, a fluorescence titration experiment was carried out. As shown in Fig. 5, a linear increase of fluorescence intensity could be observed with increasing Cu²⁺ concentration over the range of 1-14 µM. Binding analysis using the method of continuous variations (Job's plot) established a 1:1 stoichiometry for the **SRH**-Cu²⁺ complex (Supporting Information, Fig. S3).

To explore the practical applicability of this new chemodosimeter system, the detection limit toward Cu^{2+} was evaluated. From the fluorescence titration profile as shown in Fig. 6, a detection limit for Cu^{2+} was obtained as 10 nM based on the signal-tonoise ratio of three, which is sufficiently low for the detection of Cu^{2+} ions present in many chemical and biological systems.

The influence of solution pH toward the fluorescence of probe **SRH** itself is shown in Fig. 7. No obvious characteristic color and fluorescence of rhodamine could be observed when the pH ranged between 6.0 and 9.0, suggesting that **SRH** was insensitive to pH in



Fig. 6. An assay for Cu²⁺, 10–50 nm. SRH (0.1 $\mu M)$ in 50% (v/v) H_2O/CH_3CN buffered by 10 mM HEPES; $\lambda ex=530$ nm.



Fig. 7. Variation of fluorescence intensity ($\lambda ex = 530 \text{ nm}$) of SRH (1 μ M) in 50% (v/v) H₂O/CH₃CN as a function of pH.

this range. The influence of solution pH on the fluorescence enhancement of **SRH** upon addition of Cu^{2+} is shown in Fig. 8. A best response toward Cu^{2+} ion could be achieved within the pH range of about 7–8. This result indicates that **SRH** can be used as a good fluorescent probe for Cu^{2+} determination in nearly neutral conditions typical of many biological system.

3.4. The proposed reaction mechanism

In order to explore the reaction mechanism of **SRH** and Cu^{2+} , the reaction products of **SRH** and Cu^{2+} were investigated by ESI mass spectral analyses (Supporting Information, Fig. S4). The main ion peak was detected at m/z 443.3, which was characterized to be rhodamine B, indicating the generation of rhodamine B as a final product. In addition, three minor ion peaks were detected at m/z



Fig. 8. Variation of fluorescence intensity($\lambda ex = 530$ nm) of SRH (1 μ M) in 50% (v/v) H₂O/CH₃CN in the presence of 14 μ M Cu²⁺ as a function of pH.



Scheme 2. The proposed reaction mechanism of SRH with Cu²⁺.

611.4, 633.3 and 673.3, which are corresponding to $[\mathbf{SRH} + \mathbf{H}]^+$, $[\mathbf{SRH} + \mathbf{Na}]^+$ and $[\mathbf{SRH} + \mathbf{Cu}-\mathbf{H}]^+$, respectively. The peak at m/z 673.3 also demonstrated the presence of **2**(SRH–Cu²⁺ complex). The reaction product of **SRH** and Cu²⁺ was separated, which was proved to be rhodamine B by TLC (Thin layer Chromatography) and ¹H NMR experiments. Moreover, the addition of Cu²⁺ into **RSH** solution in CH₃CN resulted in no obvious fluorescence and color changes, which imply the essential role of water in the detection process. Based on the above findings, we proposed that the reaction in this system may proceed according to the route depicted in Scheme 2, which is similar to that proposed by Czarnik [38].

3.5. The possible interference by other metal ions

Interference by other metal ions was further assessed through competitive experiments. The fluorescence changes of **SRH** were measured by the treatment of 5 equiv. Cu^{2+} ions in the presence of 50 equiv. other interfering metal ions including Mg^{2+} , Ce^{3+} , Cd^{2+} , Na^+ , Zn^{2+} , K^+ , Hg^{2+} , Ag^+ , Co^{2+} , Ni^{2+} , Pb^{2+} , Ba^{2+} and Ca^{2+} . As shown in Fig. 9, the tested background metal ions showed almost no interference with the detection of Cu^{2+} ion.

3.6. Preliminary analytical application

In order to examine the potential applicability of the rhodamine-B based chemodosimeter **SRH**, it was preliminarily applied in the determination of Cu^{2+} in two waste water samples from our laboratory. The probe was treated with the water samples with or



Fig. 9. Fluorescence intensity of SRH (1 $\mu M)$ upon the addition of 5 μM Cu^{2+} in the prescence of 50 μM background ions.

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Results of determination Cu2+	in waste water samples.

Sample	Proposed method	The known concentration (μM)
wast water1 wast water2	$\begin{array}{c} 0.132 \pm 0.035 \\ 0.908 \pm 0.045 \end{array}$	0.100 ± 0.004 1 000 + 0.025

Mean of three replicates.

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without addition of Cu^{2+} ions. As shown in Table 1, **SRH** was able to measure the concentrations of spiked Cu^{2+} with good recovery, revealed that **RSH** could potentially be used for detecting Cu^{2+} in real samples.

4. Conclusion

A simple and new rhodamine-B based chemodosimeter **SRH** for Cu^{2+} has been developed. Results revealed that compound **SRH** could be used as an efficient Cu^{2+} -selective "turn-on" fluorescent and chromogenic probe with an excellent selectivity and sensitivity in aqueous media. The detection limit for Cu^{2+} was determined as 10 nM and the studied background metal ions showed either no or negligible interference toward the detection of Cu^{2+} . We believe that the current developed chemodosimeter **SRH** should be highly attractive for many practical applications in chemical and biological systems.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2010.07.004.

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