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ORIGINAL PAPER

A Novel Colorimetric and Fluorescent "Off-On" Chemosensor for Cu^{2+} Based on a Rhodamine Derivative Bearing Naphthyridine Group

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Abstract A new rhodamine-based derivative bearing a naphthyridine group (compound **1**) was synthesized as a colorimetric and fluorescent "off-on" chemosensor for Cu^{2+} in aqueous solutions. The sensing behaviors of **1** toward various metal ions in neutral aqueous solutions were investigated by absorption and fluorescence spectroscopies. Compound **1** is found to exhibit a significant increase in absorbance at 561 nm and an amplified fluorescence at 590 nm toward Cu^{2+} in a selective, sensitive and rapid manner. The quantification of Cu^{2+} by **1** using an absorption spectroscopy method was satisfactory in the linear working range 0.9–10 μM, with a detection limit of 5.4×10^{-8}M for Cu^{2+} and good tolerance of other metal ions. Upon addition of Cu^{2+}, the spirolactam ring (colorless and nonfluorescent) of **1** was opened to ring-opened amide (red color and fluorescent) and a 1:1 stoichiochemetry for the **1**-Cu^{2+} complex was formed with an association constant of $1.57\times10^{4}M^{-1}$.

Keywords Chemosensor · Rhodamine-based derivative · Naphthyridine group · Cu^{2+} recognition · Fluorescence sensing

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Introduction

The design and synthesis of new chemosensors for monitoring ionic species, especially heavy and transition metal ions in aqueous solutions, is of great interest due to their significance in chemical, biological, and environmental analyses [1–3]. Cu^{2+} is an essential trace element in biological systems [4]. However, under overloading conditions, copper exhibits toxicity, because it causes neurodegenerative diseases (e.g., Alzheimer's and Wilson's diseases) [5, 6]. Copper is also a significant metal pollutant due to its widespread use. The toxicity of copper ions for humans is rather low compared to other heavy metals, but certain microorganisms are affected by low concentration of Cu^{2+} [7]. Therefore effort has been made to design and develop probes for detection of Cu^{2+} in biological, toxicological and environmental systems. Even though fluorescent probes for copper ion have been extensively explored [8, 9], there is still a demand for new fluorescent probes in the spectral visible region, especially for "off-on" type fluorescent sensors in aqueous systems, due to the fluorescence quenching nature of paramagnetic Cu^{2+} [10].

Rhodamine-based dyes have been found applications in complicated biological systems such as molecular probes [11], and chemosensors [12, 13], due to their excellent spectroscopic properties of large molar extinction coefficient and high fluorescence quantum yield, great photostability and relatively long absorption wavelengths. The introduction of the rhodamine skeletal to construct probes of the "off-on" type is a reliable method due to the well-known spirolactam ("off") to ring-opened amide ("on") equilibrium of rhodamine derivatives. The spirolactam moiety of rhodamine served as a signal switcher, which was observed to turn on when a metal ion was bound. Addition of a specific metal ion to an appropriate rhodamine derivative bearing a spirolactam ring can cause color change as well as fluorescent change of the

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receptor. Recently, the spirolactam forms for rhodamine derivatives have been utilized for the detection of metal ions such as Hg^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, Zn^{2+} and Pb^{2+} etc. in aqueous solutions via ring-opening processes of spirolactam amides or hydrazides [14–32].

Herein, a 1,8-naphthyridine group was introduced into the rhodamine fluorophore (compound **1**), which was utilized as a selective colorimetric and fluorescent sensor for Cu^{2+} in aqueous solutions. 1,8-naphthyridine derivatives have been used as rigid bidentate ligands [33]. Compound **1** is proposed to chelate with Cu^{2+} via its carbonyl O, imino N, and naphthyridinyl N atoms. The spectroscopic studies suggested that **1** is a perspective colorimetric and fluorescent chemosensor for Cu^{2+} with high selectivity and sensitivity in aqueous solutions.

Experimental

General Apparatus and Experiments

NMR spectra were recorded with a 400 MHz Varian spectrometer. Electrospray ionization mass spectra (ESI-MS) were measured on a micrOTOF-Q II system. Absorption spectra were obtained on a TU1901 UV–visible spectrophotometer. The fluorescence spectra were measured with a Cary Eclipse fluorescence spectrometer. The pH values were measured with a pH S-3C pH meter.

The nitrates or chlorides of metal ions were used to evaluate the metal ion binding property and selectivity of **1** in ethanol-Tris–HCl buffer (0.02 M, pH 7.2) (1:1, v/v). Stock solutions of the metal ions (5 mM) were prepared in deionized water. Stock solutions of **1** (1 mM) were prepared in ethanol respectively. In titration experiments, 3 mL solution of **1**, which was diluted to a certain concentration with ethanol-Tris–HCl (0.02 M, pH 7.2) (1:1, v/v), was added into a quartz optical cell with an optical path length of 1 cm. The stock solution of each metal ion was added into the quartz optical cell step by step via a syringe.

Synthesis of Spirolactam Rhodamine B Derivative 1

Compound **1** was synthesized by condensing rhodamine B hydrazide [29] with N-(2-formyl-4-methyl-1,8-naphthyridin-7-yl)acetamide referring the procedure [31] with some modifications (Scheme 1). 0.0913 g (0.2 mmol) rhodamine B hydrazide and 0.0550 g (0.24 mmol) N-(2-formyl-4-methyl-1,8-naphthyridin-7-yl)acetamide were dissolved in 25 ml of anhydrous ethanol. The mixture was refluxed under N_2 for 10 h. Then the solvent was removed in vacuo. The resulting precipitate was purified by column chromatography on silica gel with ethyl acetate/hexanes (1:8, v:v) to afford a yellow solid of 0.072 g (yield 54 %). ^{1}H NMR in DMSO-d_6 (Fig. S1, Supplementary material), δ (ppm): 1.05 (t, J=7.2 Hz, 12H); 2.25 (s, 3H); 2.60 (s, 3H); 3.27–3.32 (m, 8H); 6.32–6.35 (m, 2H); 6.46–6.46 (m, 4H); 7.08 (d, J=7.6 Hz, 1H); 7.57–7.66 (m, 3H); 7.98 (d, J=7.2 Hz, 1H), 8.18 (s, 1H); 8.29 (d, J=8.8 Hz, 1H); 8.44 (d, J=8.8 Hz, 1H); 10.98 (s, 1H). ^{13}C NMR in DMSO-d_6 (Fig. S2, Supplementary material), δ (ppm): 12.85, 14.54, 18.33, 21.22, 24.62, 44.10, 60.22, 65.44, 97.77, 104.85, 108.68, 120.35, 123.78, 124.29, 127.97, 129.35, 135.03, 144.82, 146.91, 149.17, 152.59, 152.78, 154.65, 154.84, 156.35, 164.75, 170.51, 170.81. MS (ESI-MS): m/z calculated for $[M+H]^+$, $C_{40}H_{41}N_7O_3$, 667.8. Found: 668.4, 690.3 $[M+Na]^+$ (Fig. S3, Supplementary material).

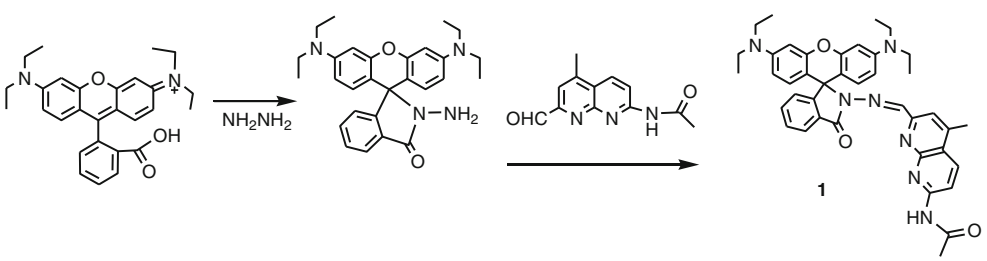
The intermediate N-(2-formyl-4-methyl-1,8-naphthyridin-7-yl)acetamide was prepared as follows. 0.5 g (2.89 mmol) 5,7-dimethyl-1,8-naphthyridin-2-amine in 9.5 mL acetic anhydride was refluxed for 40 min. After it was cooled to 0 °C, 0.42 g 5,7-dimethyl-1,8-naphthyridin-2-acetamide was obtained by filtration. Then 0.4 g (1.86 mmol) 5,7-dimethyl-1,8-naphthyridin-2-acetamide and 0.25 g (2.25 mmol) SeO_2 in 50 mL 1,4-dioxane was refluxed for 6 h. The hot mixture was filtered. Then the filtrate was removed in vacuo. The crude product was recrystallized with ethanol to give 3 gN-(2-formyl-4-methyl-1,8-naphthyridin-7-yl)acetamide. ^{1}H NMR($CDCl_3$) (Fig. S4, Supplementary material): 2.34 (s, 3H), 2.81 (s, 3H), 7.89 (s, 1H), 8.47 (d, J=8.8 Hz, 1H), 8.64 (s, 1H), 8.68 (d, J=8.8 Hz, 1H), 10.22 (s, 1H).

Results and Discussion

Absorption Spectroscopic Studies

The absorption spectra of **1** upon titration of Cu^{2+} are shown in Fig. 1. The solution of **1** without any metal ions is almost

Scheme 1 Synthesis of compound 1



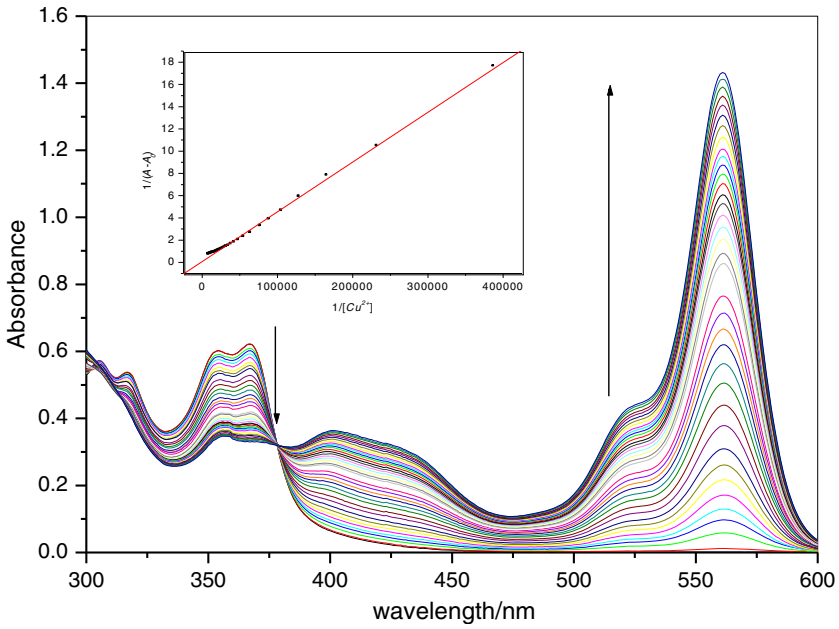


Fig. 1 Absorption spectra of **1** (20 μmol/L) upon addition of Cu^{2+} in ethanol-Tris–HCl (0.02 mol/L, pH 7.2) (1:1, v/v) solution. Insert: Benesi-Hildebrand plot (absorbance at 561 nm) of **1** using Eq. 1, assuming 1:1 stoichiometry for association between **1** and Cu^{2+}

colorless and exhibits almost no absorption in the visible wavelength range (450–600 nm), indicating that **1** is predominantly in the form of spirolactam. The characteristic peak of the spiro-carbon of **1** near 65.4 ppm in the ^{13}C NMR spectrum also supports this consideration [34] (Fig. S2). Free **1** displays absorption bands of naphthyridine chromophore at 353 nm and 367 nm. Upon addition of Cu^{2+}, a new absorption peak at 561 nm and a new absorption shoulder in the wavelength range (400–450 nm) appear. Figure 1 was basically dominated by the absorption bands that belong to the rhodamine chromophore upon addition of Cu^{2+}. The absorbance at 561 nm and the shoulder increases gradually with the increase of Cu^{2+} concentration, while the peaks at 353 nm and 367 nm decrease. The absorbance at 561 nm increases about 42 times upon addition of one equivalent of Cu^{2+}, suggesting the formation of the ring-opened tautomer of the rhodamine chromophore and the obvious interaction of Cu^{2+} and **1**. There is a concomitant isosbestic absorption point at 378 nm, indicating the existence of only one intermediate complex [35]. The shoulder in wavelength range (400–450 nm) became prominent presumably due to the contribution from the naphthyridine moiety in **1**, with significant bathochromic shift due to the Cu^{2+}-binding. Accordingly, the titration solution exhibits an obvious and characteristic color change from light yellow to red, indicating that probe **1** can serve as a 'naked-eye' indicator for Cu^{2+} ion. Job's plot evaluated from the absorption spectra of **1** and Cu^{2+} with a total concentration of 60 μM (Fig. 2) according to the method for continuous variations [36] indicates that **1** binds with Cu^{2+} in a 1:1 stoichiometry. The stability constant of the complex was calculated by the linear Benesi–Hildebrand expression (Eq. 1) [37]:

$$\frac{1}{A-A_0}=\frac{1}{K_a(A_{\max}-A_0)[Cu^{2+}]}+\frac{1}{A_{\max}-A_0} \quad (1)$$

where A_0 is the absorbance of **1** at 561 nm without Cu^{2+}. A is the absorbance of **1** obtained with Cu^{2+}. A_{max} is the absorbance of **1** in the presence of excess amount of Cu^{2+}. K_a is the association constant. $[Cu^{2+}]$ is the concentration of Cu^{2+}. On the basis of the plot of $1/(A-A_0)$ and $1/[Cu^{2+}]$, the association constant was determined from the slope to be $1.57\times10^4 M^{-1}$ (Insert in Fig. 1). The absorbance of **1** at 561 nm increases linearly with the increasing of Cu^{2+} concentration in

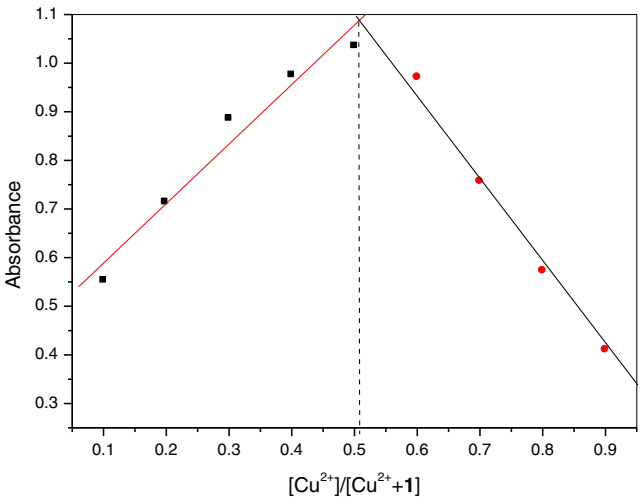


Fig. 2 Job's plot evaluated from the absorption spectra of **1** and Cu^{2+} at 561 nm in 6×10^{-5} mol/L in ethanol-Tris–HCl (0.02 mol/L, pH 7.2) (1:1, v/v) solution

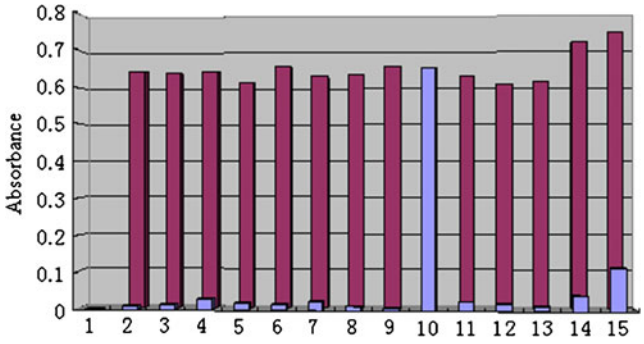


Fig. 3 The absorbance of **1** (20 μM) at 561 nm in the presence of 140 μM different metal ions or 25.6 μM Cu^{2+} (blue bars), and upon further addition of 25.6 μM Cu^{2+}. 1: no ions, 2: Zn^{2+}, 3: Pb^{2+}, 4: Hg^{2+}, 5: Ni^{2+}, 6: Mn^{2+}, 7: Cd^{2+}, 8: Ag^{+}, 9: Cr^{3+}, 10: Cu^{2+}, 11: Mg^{2+}, 12: Co^{2+}, 13: K^{+}, 14: Fe^{2+}, 15: Fe^{3+}

the range of 9×10^{-7}–1×10^{-5} mol/L (Fig. S5, Supplementary material). The relationship between the absorbance at 561 nm and Cu^{2+} concentration was: $A=2.32\times10^{4}C$-5.48×10^{-3}, where A was the absorbance at 561 nm and C was the concentration of Cu^{2+} in mol/L with a correlation coefficient of $R^2=0.9988$. The detection limit, based on the definition by IUPAC was found to be 5.4×10^{-8} mol/L from 11 blank solutions.

The time course of the response of 20 μM **1** to 25 μM Cu^{2+} in ethanol-Tris buffer (0.02 M, pH 7.2) (1:1, v/v) was investigated. The interaction of **1** with Cu^{2+} was completed in less than 2 min (Fig. S6, Supplementary material). The acidity was chosen to pH 7.2 because it is close to physiological pH conditions. Both the organic compound and inorganic salts must be dissolved in a suitable solvent. As ethanol is more environmentally friendly and cheap than other water-soluble solvents as acetone, acetonitrile, DMSO, DMF and THF, the effect of ethanol fraction was investigated by using 10 %, 30 %, 50 %, 70 % (v/v) in ethanol-Tris buffer (0.02 M, pH 7.2) for Cu^{2+} determination by 20 μM **1** (Fig. S7, Supplementary material). 50 % ethanol was found to efficiently monitor Cu^{2+}.

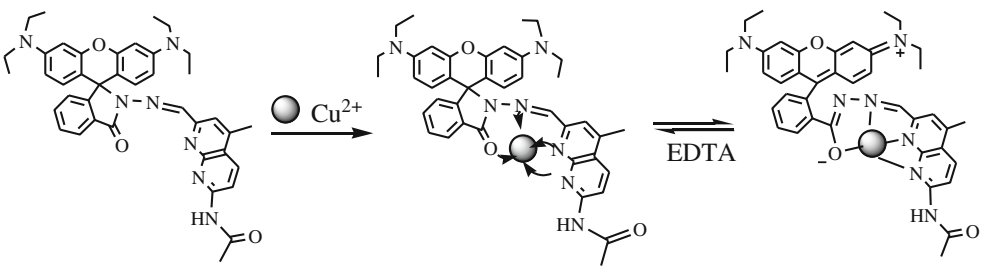
Selectivity Studies

The selective sensory studies of **1** were then extended to other metal ions. The changes in color of 20 μM **1** in presence of different cations are illustrated in Fig. S8, Supplementary material. Among the metal ions being investigated, 25.6 μM Cu^{2+} can induce an obvious red color in 20 μM **1**. 140 μM Fe^{3+} can induce a faint pink color in 20 μM **1**. 140 μM metal ions such as Pb^{2+}, Mg^{2+}, K^{+}, Ni^{2+}, Cd^{2+}, Ag^{+}, Mn^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, Fe^{2+} and Cr^{3+} cannot induce any color change of 20 μM **1**. The results indicate that **1** does not bind these metal ions. Spectrophotometric responses of 20 μM **1** in ethanol-Tris buffer (0.02 M, pH 7.2) (1:1, v/v) solutions to 140 μM various metal ions and further to 25.6 μM Cu^{2+} are shown in Fig. 3. Addition of other tested metal ions such as Pb^{2+}, Mg^{2+}, K^{+}, Ni^{2+}, Cd^{2+}, Ag^{+}, Mn^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, $Fe^{2+}$and Cr^{3+} with 7-fold can not cause any apparent absorbance increase of **1** at 561 nm. Fe^{3+} with 7-fold showed a slight increase in absorbance of **1** at 561 nm. However, Fe^{3+} induced absorbance enhancement is far below that caused by Cu^{2+} with 1.28-fold under the same conditions. Upon addition of Cu^{2+} (25.6 μM) into **1** (20 μM) containing interfering metal ions (140 μM for each), a significant absorbance at 561 nm was determined. The results indicated the tested metal ions with 7-fold that of Cu^{2+} did not interfere with the interaction of **1** with Cu^{2+}.

Recognition Mechanism

An evidence is obtained by determining the ESI mass spectra of **1**-Cu(II) in ethanol -Tris–HCl (0.02 M, pH 7.2) (1:1, v/v) solution (Fig. S9, Supplementary material). The peak at (m/z=731.3) for $C_{40}H_{41}CuN_7O_3$ (calcd 731.34) corresponding to $[\mathbf{1}+Cu+H]^{+}$ is clearly observed when 30 μM Cu^{2+} is added to 20 μM **1**, whereas **1** without Cu^{2+} exhibited peaks at m/z= 668.4 (calcd 668.3) and 690.3 (calcd 690.3) which corresponded to $[\mathbf{1}+H]^{+}$ and $[M+Na]^{+}$, respectively (Fig. S3). To achieve the 1:1 stoichiometry, carbonyl O, imino N, and naphthyridinyl N atoms of **1** are the most possible binding sites for Cu^{2+}. The absorption spectra responses of **1** to Cu^{2+} were reversible, which was confirmed by the reversible titration of **1**-Cu^{2+} using ethylenediamine tetraacetic acid disodium salt (EDTA) (Fig. S10, Supplementary material). And the color of **1**-Cu(II) disappeared instantly upon the addition of 1-fold EDTA due to competitive binding of Cu^{2+} from **1** by EDTA, moreover, further addition of Cu^{2+} can recover the red color. Therefore the response of **1** to Cu^{2+} is proposed to be a reversible recognition process rather than an irreversible Cu^{2+}-catalyzed reaction [29]. The proposed mechanism is shown in Scheme 2.

Scheme 2 Proposed recognition mechanism of **1** to Cu^{2+}



Fluorescence Spectroscopic Studies

Highly selective probes for Cu^{2+}, which give positive responses rather than fluorescent quenching upon Cu^{2+} binding, are usually preferred to promote the sensitivity. From the fluorescence titration experiments (Fig. 4), "off-on" fluorescence changes of **1** to Cu^{2+} were observed. Upon the addition of $CuCl_2$ into the ethanol -Tris–HCl (0.02 M, pH 7.2) (1:1, v/v) solution of **1**, a new emission band centered at 580 nm (with an excitation wavelength at 520 nm) developed and finally attained an equilibrium with the emission band slightly red-shifted to 590 nm after 7 equiv of Cu^{2+} were added. The typical emission peaks could be ascribed to the Cu^{2+} induced ring-opening of the spirolactam moiety to the delocalized xanthene moiety of the rhodamine group. The red-shift of the emission peak can be ascribed to the recombination of the orbitals after the formation of ring-opened **1**-Cu^{2+} complex. Plotting of $1/(I\text{-}I_0)$ versus $1/[Cu^{2+}]$ showed also a linear relationship (Fig. 5). The fluorescence intensity at 590 nm has a 4.2-fold enhancement, which is much weaker compared with the enhancement of the absorbance.

No significant fluorescence intensity change of **1** (20 μM) occurred in the presence of 140 μM metal ions such as Pb^{2+}, Mg^{2+}, K^{+}, Ni^{2+}, Cd^{2+}, Ag^{+}, Mn^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+} and Cr^{3+}. In contrast, upon the addition of Cu^{2+} (140 μM) into **1** (20 μM) containing the interfering metal ions (140 μM for each), a remarkable fluorescence intensity centered at 590 nm was observed (Fig. 6). These results indicated that the recognition of Cu^{2+} by **1** is not obviously interfered by other coexisting metal ions. Therefore, **1** exhibits a high selectivity toward Cu^{2+}. It is likely that there are several factors achieving the unique selectivity of **1** toward Cu^{2+}, including the suitable coordination conformation of the chelating Schiff-based receptor bearing a rigid and coplanar naphthyridine group, the nitrogen and oxygen-affinities character of the Cu^{2+} and the radius of Cu^{2+}.

The enhancement of absorbance is found to be much more significant than that of fluorescence intensity upon addition of Cu^{2+} to **1**. However, the ring-opening of the spirolactam form of rhodamine derivatives generally results in comparable amplifications of absorption and fluorescence signals [38]. Cu^{2+} does open the spirolactam ring of **1**, but at the same time the fluorescence of the Cu(II) complex is probably partially quenched by Cu^{2+} due to the paramagnetic nature of the copper ion [39, 40].

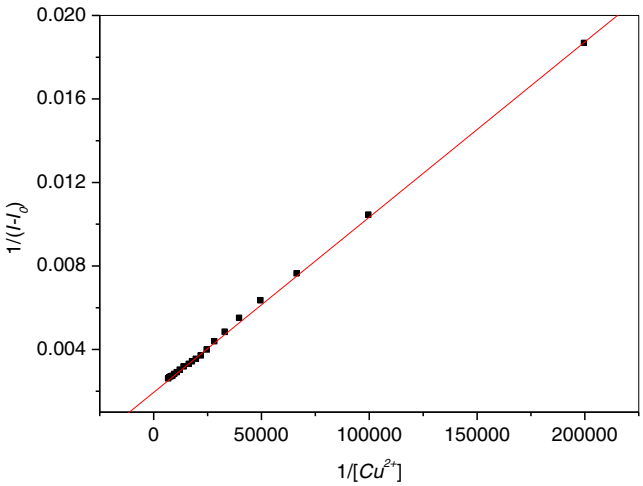


Fig. 5 Benesi-Hildebrand plot Benesi-Hildebrand plot (emission at 590 nm) of **1** using Eq. 1, assuming 1:1 stoichiometry for association between **1** and Cu^{2+}

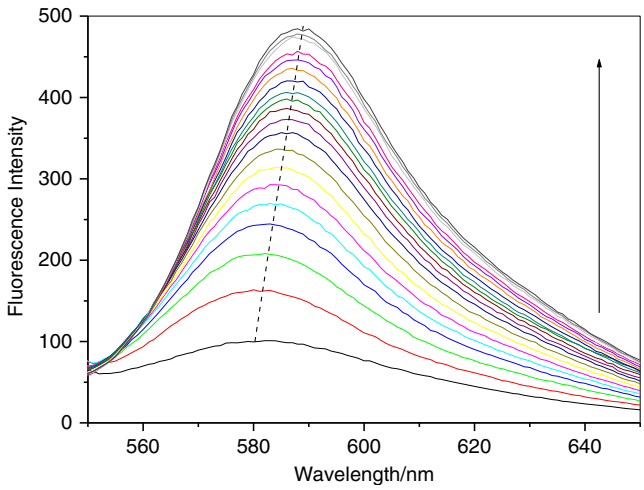


Fig. 4 Fluorescence spectra of 1 (20 μM) in ethanol -Tris–HCl (0.02 M, pH 7.2) (1:1, v/v) solution upon addition of increasing concentrations of $CuCl_2$ with an excitation wavelength at 520 nm

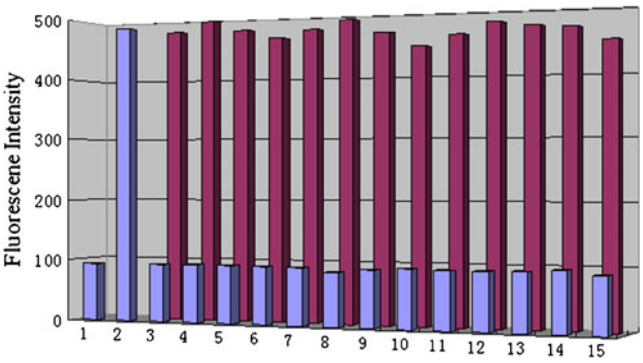


Fig. 6 Fluorescence intensity of **1** (20 μM) 590 nm in the presence of 140 μM different metal ions (*blue bars*), and upon further addition of 140 μM Cu^{2+} (*red bars*). 1: no ions, 2: Cu^{2+}, 3: Zn^{2+}, 4: Pb^{2+}, 5: Hg^{2+}, 6: Ni^{2+}, 7: Mn^{2+}, 8: Cd^{2+}, 9: Ag^{+}, 10: Cr^{3+}, 11: Mg^{2+}, 12: Co^{2+}, 13: K^{+}, 14: Fe^{2+}, 15: Fe^{3+}

Conclusions

A new spirolactam form of a rhodamine fluorophore bearing a 1,8-naphthyridine group (**1**) has been synthesized as a chemosensor for the recognition of copper ion in aqueous solutions. This compound displays a selective, sensitive absorbance change and amplified fluorescence with rapid response to Cu^{2+} via a 1:1 binding mode. A reversible ring-open process of spirolactam (off) to the delocalized hydrazone (on) process are proposed in the spectroscopic response of **1** toward Cu^{2+}.

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