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1,8-Naphthyridine modified rhodamine B derivative and Cu^{2+} complex: colorimetric sensing of thiols in aqueous media

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ABSTRACT

A 1,8-naphthyridine modified rhodamine B derivative (**1**) has been designed and synthesized. Compound **1** is the first 1,8-naphthyridine-modified rhodamine B sensor that can detect Cu^{2+} selectively with a dramatic color change from colorless to pink. The complex of **1** and Cu^{2+} was utilized as a chemosensing ensemble for cysteine (Cys), homocysteine (Hcy), and glutathione (GSH) detection, which showed highly sensitive and selective colorimetric response to Cys, Hcy, and GSH among the tested naturally occurring α-amino acids in EtOH-HEPES (0.02 M, pH 7.4) (3:7, v/v) buffer solution.

Introduction

The recognition and sensing of biothiols are of intense interests because the intracellular thiols play an important role in maintaining biological systems. Cysteine (Cys), homocysteine (Hcy), and glutathione (GSH) as the well-known biothiols, are essential biological materials required for the growth of cells and tissues in living systems. For example, Cys deficiency is associated in many syndromes, including retarded growth, hair depigmentation, lethargy, liver damage, muscle and fat loss, and weakness.[1] Similarly, an elevated level of Hcy in human plasma is a risk factor for Alzheimer's, cardiovascular diseases, neural tube defect, inflammatory bowel disease, and osteoporosis.[2] Therefore, the optical method for the detection and sensing of Cys, Hcy, and GSH with high sensitivity is of current interest in the chemosensor research field.

Up to now, various biothiol chemosensors based on Michael addition,[3] cyclization reaction with aldehyde,[4] cleavage reaction by thiols,[5] or metal complexes-displace coordination mechanisms[6] have been synthesized.[7] In the Cys, Hcy, and GSH binding, these chemosensors show multifarious absorbance or fluorescence changes. However, relatively few examples of chemosensors for Cys/Hcy/GSH sensing showed obvious colorimetric change, which can be easily observed by naked eyes.[8] Therefore, it is still a challenge for synthesizing sensors that selectively and sensitively detect Cys, Hcy, and GSH with obvious colorimetric changes.

Rhodamine derivatives and its ring-opening reaction received a great deal of attention and have been applied as fluorescent and colorimetric metal ion sensors in organic and biological researches.[9] Recently, Li and Zhang et al. reported a sensitive colorimetric sensor toward α-amino acids based on a rhodamine B derivative and copper ion ensemble system.[10] However, the pink solution of this system changed to colorless immediately upon the addition of all kinds of the tested α-amino acids, which is showing no selectivity to any individual α-amino acid. Hence choosing an appropriate binding site in a sensor is crucial and a decisive factor for the sensor's selectivity. With the intriguing structures, good bonding properties, as well as the multiple biocompatibility and spectroscopic properties, 1,8-naphthyridine and its derivatives have been applied in the coordination chemistry and molecular recognition fields.[11] It exhibits various coordination modes with Cu^{+}, Cu^{2+}, Zn^{2+}, and many other metal ions[12] with interesting spectroscopic properties. Therefore, 1,8-naphthyridine, as a typical N-containing receptor, was introduced to a rhodamine B chromophore in company with Cu^{2+} ion to form the high selectivity sensing ensemble system for Cys, Hcy, and GSH in the present work.

Herein, we report the design and synthesis of a new1, 8-naphthyridine modified rhodamine B derivative (**1**), which displays

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a dramatic color change from colorless to pink only toward Cu^{2+} among all the examined metal ions in EtOH-HEPES (0.02 M, pH 7.4) (3:7, v/v) buffer solution. Moreover, the complex of **1** and Cu^{2+} was utilized as a chemosensing ensemble for Cys, Hcy, and GSH detection, which showed a highly sensitive and selective colorimetric response to thiols among the tested α-amino acids, including histidine (His), leucine (Leu), isoleucine (Ile), methionine (Met), lysine (Lys), threonine (Thr), tyrosine (Tyr), valine (Val), aspartic acid (Asp), arginine (Arg), alanine (Ala), serine (Ser), glutamine (Gln), proline (Pro), glutamic acid (Glu), glycine (Gly), phenylalanine (Phe), Cys, Hcy, and GSH, in the aqueous solution.

Results and discussion

N-(7-formyl-1,8-naphthyridine-2-yl) acetamide (**2**)[13] and Rhodamine B-hydrazide (**3**)[14] were synthesized by modifying the reported procedure. The synthesis of **1** is outlined in Scheme 1. Reaction of **2** and **3** in ethanol at reflux for 12 h afforded **1** in 41% yield. The detailed experimental procedures and ^{1}H and ^{13}C NMR spectra are summarized in Supporting Information.

The photophysical properties of **1** was evaluated in EtOH-HEPES buffer (0.02 M, pH 7.4) (3:7, v/v) solution. As shown in Figure 1, compound **1** (2×10^{-5} M) showed a strong absorption at around 370 nm, which is attributed to the intraligand (IL) Π → Π* transition of 1,8-naphthyridine. Additions of Li^{+}, Na^{+}, K^{+}, Ag^{+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, and Cr^{3+} showed little or no effect on the absorption of **1** besides Cu^{2+}. Upon addition of 2 equiv Cu^{2+} ions, a new absorption peak centered at 562 nm appeared because of the rhodamine B ring-opening process. The above result induced a clear colorimetric change from colorless to pink that enabled detection simply by naked eyes.

The changes in the fluorescence emission of **1** were next investigated. As shown in Figure S1, when excited with 360 nm, there was a wide band centered at around 415 nm corresponding to the emission of 1,8-naphthyridine intraligand fluorescence. Additions of Li^{+}, Na^{+}, K^{+}, Ag^{+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}, and Cr^{3+} exerted a slight enhancement or quenching

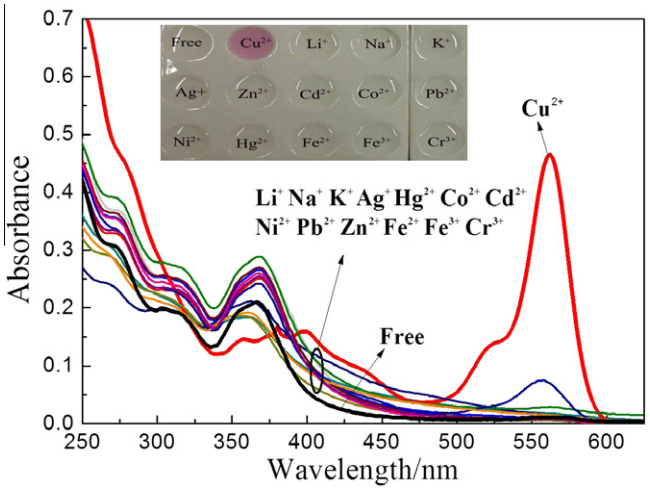
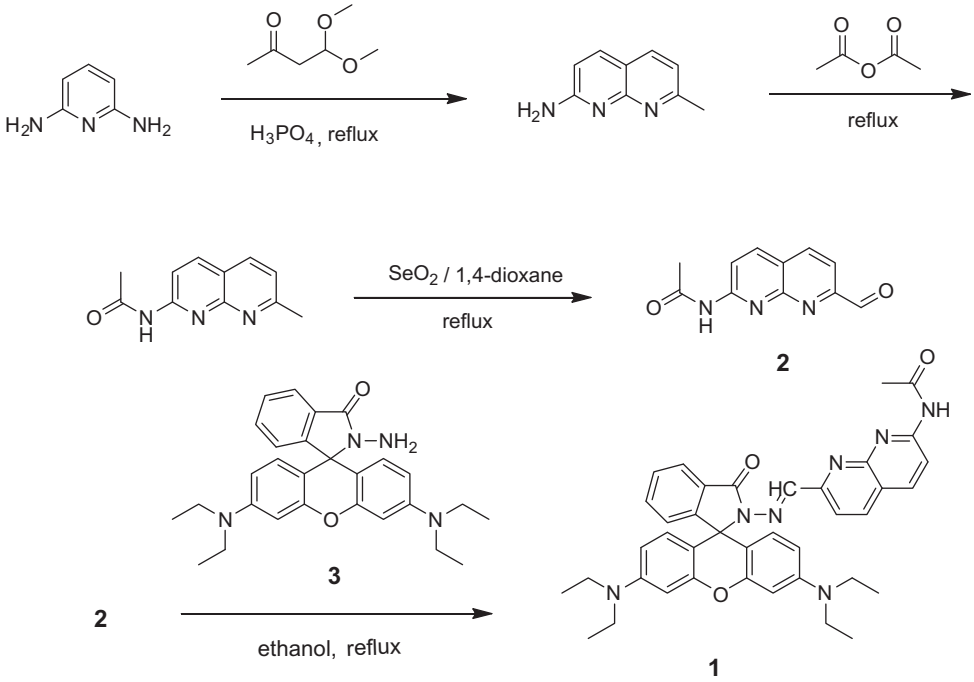


Figure 1. Absorbance spectra of **1** (2×10^{-5} M) upon addition of 2 equiv of Cu^{2+} and other cations in EtOH-HEPES (0.02 M, pH 7.4) (3:7, v/v) buffer solutions. Inset: color changes of **1** in the presence of different cation perchlorates (10 equiv) in EtOH-HEPES (0.02 M, pH 7.4) (3:7, v/v).

effect on the emission of **1**. Commonly, the fluorescence intensity at around 550 nm would be enhanced because of the rhodamine B ring-opening process. However, no new emission peak was observed because of the strong fluorescence quench effect of Cu^{2+} ion.

Beside the high sensitivity, another important feature of **1** is its high selectivity toward Cu^{2+} over other competitive species. As shown in Figure S2 in Supplementary data, the absorption changes upon the addition of excess amount of competitive metal ions were measured. The unique absorption change with appearance of pink of **1** was observed only by the addition of Cu^{2+}, which can be ascribed to the spirolactam bond cleavage of the rhodamine B group. The other competitive metal ions such as Li^{+}, Na^{+}, K^{+}, Ag^{+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+}, and Cu^{+} (Fig. S19) gave



Scheme 1. Synthesis route of compound **1**.

negligible changes in the UV spectra, indicating the selective binding of **1** to Cu^{2+}.

To get a further insight into the binding of Cu^{2+} with **1**, the absorbance spectra of **1** upon titration with Cu^{2+} were recorded (Fig. 2). Upon addition of increasing amounts of Cu^{2+} ions, a new absorption band centered at 562 nm appeared with increasing intensity. Meanwhile, the absorption band centered at 366 nm decreased gradually with an isosbestic point observed at 385 nm. A C-curve dependence of the absorbance intensity at 562 nm as a function of Cu^{2+} concentration was observed, which indicated that **1** forms a 2:1 complex with Cu^{2+}, whose association constant (K_a) was determined to be about $4.44 \times 10^9\ M^{-2}$ from the titration experiments.[15] Moreover, Job's plot (Fig. 3) and FAB mass (Fig. S10) confirmed the 2:1 stoichiometry for the **1**-Cu^{2+} complex, which also strongly supports the above conclusions.

The sensitivity of **1**-Cu^{2+} complex for 20 naturally occurring α-amino acids was determined. As shown in Figure 4, upon additions of α-amino acids, including His, Leu, Ile, Met, Lys, Thr, Tyr, Val, Asp, Arg, Ala, Ser, Gln, Pro, Glu, Gly, Phe, Cys, Hcy, and GSH to the solutions of **1**-Cu^{2+}, respectively, only Cys, Hcy, and GSH (Fig. S14) caused a significant decrease of the absorption at around 562 nm along with the color change from pink to colorless instantaneously (Fig. 4 inset).

A relative stronger binding ability of Cys/Hcy/GSH and Cu^{2+} over that of **1** toward Cu^{2+} in the ensemble of **1**-Cu^{2+} clearly contributes to high sensitivity in the detection of Cys/Hcy/GSH, and is also responsible for a good selectivity over other amino acids. Titration of **1**-Cu^{2+} complex with Cys/Hcy/GSH was then conducted by UV–vis spectroscopy. As shown in Figure 5, Figure 6 and Figure S14, upon addition of increasing amounts of Cys/Hcy/GSH to a solution of **1**-Cu^{2+} (2×10^{-5} M) in spectroscopic grade EtOH and HEPES buffer (0.02 M, pH 7.4) (3:7, v/v), the absorption band at 562 nm disappeared with decreasing intensity and reached its minimum upon addition of 4.0 equiv Cys/Hcy/GSH. The clear color change from pink to colorless was easily observed by naked eyes. The binding constants for Cys/Hcy/GSH and **1**-Cu^{2+} were then calculated and found to be in accordance with the observed selectivity trend. The binding constants of Cys/Hcy/GSH and **1**-Cu^{2+} ($6.30 \times 10^{10}\ M^{-2}$, $1.39 \times 10^{11}\ M^{-2}$ and $3.74 \times 10^{12}\ M^{-2}$) (Fig. S23–S25) are larger than that of **1** with Cu^{2+} ($4.44 \times 10^9\ M^{-2}$).[15] Therefore, the ligand **1** in **1**-Cu^{2+} complex can be replaced by Cys/Hcy/GSH, and **1**-Cu^{2+} is able to selectively discriminate Cys, Hcy, or GSH among other analogs (Scheme 2).

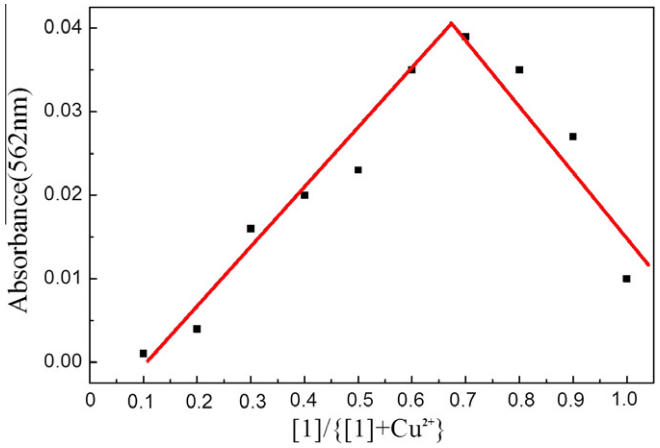


Figure 3. Job's plot showing the 2:1 binding of **1** to Cu^{2+} ions.

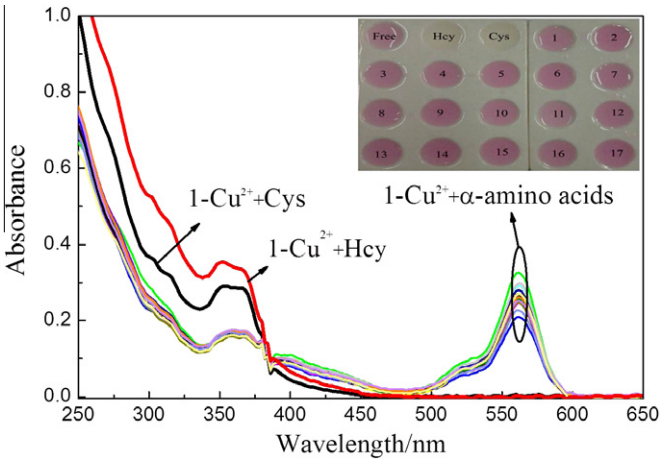


Figure 4. Absorbance spectra of **1**-Cu^{2+}(2×10^{-5} M of **1** with addition of 2.0 equiv of Cu^{2+}) in EtOH-HEPES (0.02 M, pH 7.4) (3:7, v/v) upon addition of different amino acids (6.0 equiv). Inset: color changes of **1**-Cu^{2+} upon addition of different amino acids (6 equiv) (Free:**1**-Cu^{2+}; 1:Phe; 2:Ala; 3:Met; 4:Gly; 5:Glu; 6:Gln; 7:Arg; 8:Lys; 9:Leu; 10:Pro; 11:Ser; 12:Thr; 13:Asp; 14:Tyr; 15:Val; 16:Ile; and 17:His).

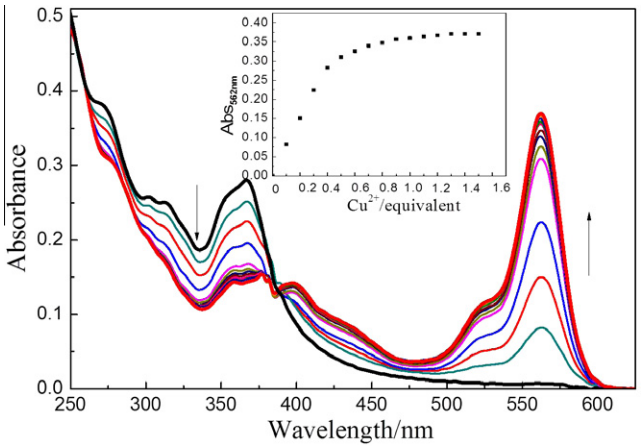


Figure 2. UV titrations of **1** (2×10^{-5} M) in EtOH -HEPES (0.02 M, pH 7.4) (3:7, v/v) upon addition of amounts of Cu^{2+} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, and 1.5 equiv). Inset: absorption intensity of **1** at 562 nm as a function of Cu^{2+} concentration.

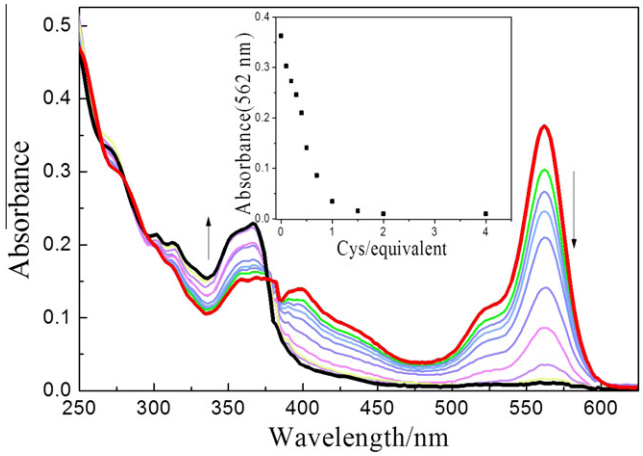


Figure 5. UV titrations of **1**-Cu^{2+} (2×10^{-5} M) in EtOH-HEPES buffer (0.02 M, pH 7.4) (3:7, v/v) in the presence of different amounts of Cys (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1.0, 1.5, 2.0, and 4.0 equiv) Inset: absorption intensity of **1**-Cu^{2+} at 562 nm as a function of Cys concentration.

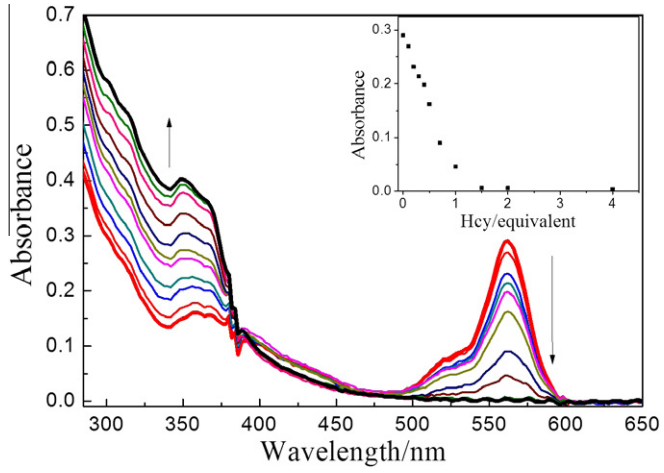
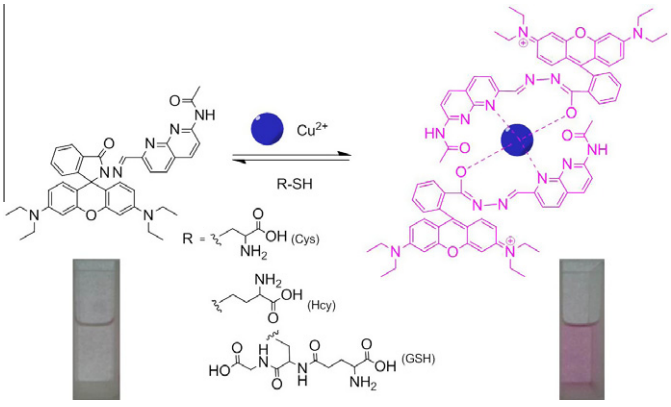


Figure 6. UV titrations of **1**- Cu^{2+}(2×10^{-5} M) in EtOH-HEPES buffer (0.02 M, pH 7.4) (3:7, v/v) in the presence of different amounts of Hcy (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1.0, 1.5, 2.0, and 4.0 equiv). Inset: absorption intensity of **1**-Cu^{2+} at 562 nm as a function of Hcy concentration.



Scheme 2. Proposed mode of **1**-Cu^{2+} and Cys/Hcy/GSH.

In conclusion, a 1,8-naphthyridine modified rhodamine B-based receptor ensemble bearing a Cu^{2+} center was investigated as a selective chemosensor for Cys/Hcy/GSH over other naturally occurring α-amino acids in a 70% aqueous solution. It was demonstrated that a relative stronger binding ability of Cys/Hcy/GSH and Cu^{2+} over that of **1** toward Cu^{2+} in the ensemble of **1**-Cu^{2+} contributed to the high sensitivity and selectivity in the detection of Cys/Hcy/GSH. The present system provided an easy, rapid, and selective detection of Cys/Hcy/GSH with dramatic color changes, from colorless to pink with Cu^{2+} and finally to colorless in the presence of Cys/Hcy/GSH, which was easily observed by naked eyes.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.09.089.

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