



## A new rhodamine-based dual chemosensor for Al<sup>3+</sup> and Cu<sup>2+</sup>



Qiuping Hu<sup>a</sup>, Yuling Liu<sup>b</sup>, Zhengqiang Li<sup>a</sup>, Rongzheng Wen<sup>a</sup>, Yuan Gao<sup>a</sup>, Yiling Bei<sup>a</sup>, Qingzeng Zhu<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

<sup>b</sup> Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, PR China

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### ABSTRACT

A new rhodamine B derivative bearing a hydrazone group has been designed and prepared. The synthesized colorimetric and fluorescent molecular chemosensor can be used as a dual probe, selectively detecting Al<sup>3+</sup> and Cu<sup>2+</sup> in acetonitrile solution by monitoring changes in the absorption and fluorescence spectral patterns. The results show that Al<sup>3+</sup> ions can induce a greater fluorescence enhancement, while the addition of Cu<sup>2+</sup> ions induces a strong UV–vis absorption enhancement with weak fluorescence. The limits of detection of Cu<sup>2+</sup> and Al<sup>3+</sup> were estimated to be  $2.9 \times 10^{-7}$  M and  $8.3 \times 10^{-9}$  M, respectively.

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The development of selective and sensitive sensors for metal ions has attracted a great deal of attention.<sup>1</sup> Colorimetric and fluorescent methods based on molecular chemosensors have become important tools for the recognition of metal ions due to the operational simplicity and low detection limits.<sup>2</sup> Recently, the development of colorimetric and fluorescent chemosensors on a single sensor for multiple analytes has received increased attention.<sup>3</sup> Compared to one-to-one analysis methods, detection methods for numerous metal ions with differential responses have advantages of being more efficient and less expensive. For example, an excellent dual chemosensor that can detect Cu<sup>2+</sup> and Hg<sup>2+</sup> by monitoring changes in UV absorption and the fluorescence spectral pattern has been developed.<sup>4</sup>

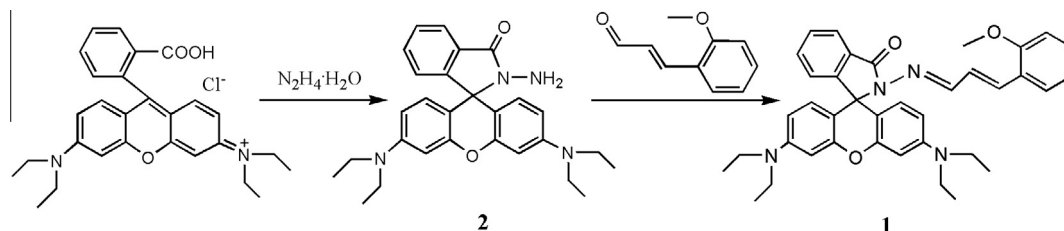
Considerable efforts have been made to develop suitable chemosensors for the detection of Cu<sup>2+</sup> and Al<sup>3+</sup> due to their biological and environmental importance.<sup>5</sup> In this regard, most methods for Cu<sup>2+</sup> detection are based on a turn-off response because of the paramagnetic nature of Cu<sup>2+</sup>.<sup>6</sup> Recently, a few groups have developed fluorescent turn-on sensors for Cu<sup>2+</sup>.<sup>7</sup> Aluminum is the third most abundant element in the earth's crust. Because of the poor coordination ability of Al<sup>3+</sup> compared to transition metal ions, only a few chemosensors with good sensitivity and selectivity for Al<sup>3+</sup> have been developed.<sup>8</sup> Therefore, the development of a new approach with high sensitivity and specificity toward Al<sup>3+</sup> and Cu<sup>2+</sup> is highly desirable.

\* Corresponding author. Tel.: +86 531 88362866; fax: +86 531 88364464.

E-mail addresses: [qzzhu@sdu.edu.cn](mailto:qzzhu@sdu.edu.cn), [q.zhu@icc.ac.cn](mailto:q.zhu@icc.ac.cn) (Q. Zhu).

Rhodamine derivatives, which are ideal chemosensors due to their particular spiroactam structures and excellent photophysical properties, offer a 'naked-eye' straightforward detection method used extensively in the detection of metal ions. The spiroactam structure of rhodamine derivatives provides very weak fluorescence strength and UV absorption, while ring-opening of the spiroactam brings about strong UV absorption and fluorescence enhancement along with an apparent color change.<sup>9</sup> Based on this mechanism, chemosensors based on rhodamine have been developed extensively.<sup>10</sup> However, the simultaneous selective detection of Al<sup>3+</sup> and Cu<sup>2+</sup> by a molecular chemosensor based on a rhodamine scaffold is rare.<sup>11</sup> Recently, Luo reported a colorimetric and fluorescent double-sensor prepared from rhodamine B. This chemosensor can be used to detect Al<sup>3+</sup> in ethanol–H<sub>2</sub>O (2:3, v/v) systems and Cu<sup>2+</sup> in CH<sub>3</sub>CN–H<sub>2</sub>O (3:2, v/v) systems.<sup>11c</sup> In our previous work, we have reported a rhodamine-based fluorescent probe for Al<sup>3+</sup>.<sup>12</sup> Herein, we developed a dual chemosensor capable of selectively sensing Cu<sup>2+</sup> and Al<sup>3+</sup> ions in an acetonitrile solution. The synthesized chemosensor showed 'naked-eye' color change, strong visible light absorption in the presence of Cu<sup>2+</sup>, and weak fluorescence. Meanwhile, upon addition of Al<sup>3+</sup>, the synthesized chemosensor exhibited a distinct fluorometric enhancement and color change in the ultraviolet light. The sensitivity of the synthesized chemosensor is higher than that of many single-channel sensors based on rhodamine for Al<sup>3+</sup>.<sup>10g,f,13</sup>

As depicted in Scheme 1, compound **1** was synthesized as a light-yellow powder in 72.8% yield through the reaction of rhodamine B hydrazide<sup>14</sup> with 2-methoxycinnamaldehyde in an equal

Scheme 1. Synthetic route of **1**.

molar ratio. The structure of **1** was well characterized using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and mass spectra (Figs. S1–S4). The spirolactam form of **1** was verified by the existence of a peak at 65.62 ppm in the  $^{13}\text{C}$  NMR spectrum. The solution of **1** in acetonitrile was colorless and stable for more than three months.

The free **1** exhibited notably weak absorption and fluorescence above 500 nm, indicating that the spirolactam form was predominant. Upon addition of 2.0 equiv of  $\text{Cu}^{2+}$  ions to the colorless solution of **1** (12  $\mu\text{M}$ ), the system of **1**+ $\text{Cu}^{2+}$  became pink and showed a strong absorption band centered at 554 nm, which suggested the formation of an open-ring form.<sup>15</sup> To ascertain the selectivity of **1** toward various metal ions, such as  $\text{Al}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mg}^{2+}$ , the absorption spectra and fluorescence spectra of **1** toward other metal ions were recorded. As shown in Figure 1, the tested metal ions exhibited no color changes in the visible light. The absorption spectra indicated that the **1**+ $\text{Al}^{3+}$  and **1**+ $\text{Co}^{2+}$  systems afforded a very weak absorption band at 565 nm, which was red-shifted relative to that of the **1**+ $\text{Cu}^{2+}$  system. The other metal cations exhibited negligible variations in the absorption spectra.

To obtain more insight into the properties of chemosensor **1** toward  $\text{Cu}^{2+}$ , absorption titration was performed with various amounts of  $\text{Cu}^{2+}$ . Figure 2 shows the absorption spectra of chemosensor **1** in the visible region with increasing concentrations of  $\text{Cu}^{2+}$  in acetonitrile. The results showed that the absorbance of **1**+ $\text{Cu}^{2+}$  solution increased with increasing amounts of  $\text{Cu}^{2+}$ . The

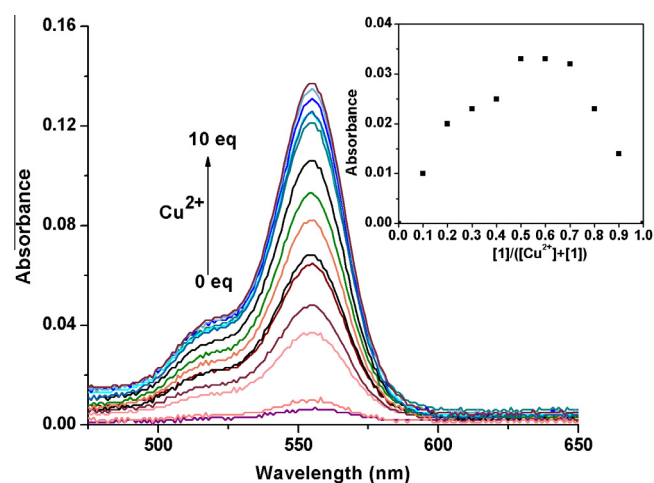


Figure 2. Absorption spectra of **1** (5  $\mu\text{M}$ ) in acetonitrile in the presence of different amounts of  $\text{Cu}^{2+}$ . The inset shows the Job plot of **1** and  $\text{Cu}^{2+}$  in acetonitrile ( $[\mathbf{1}]+[\text{Cu}^{2+}] = 30 \mu\text{M}$ ).

association constant ( $K_a$ ) was estimated to be  $1.66 \times 10^9 \text{ M}^{-2}$  from the absorbance titration curve assuming a 2:1 stoichiometry for the **1**+ $\text{Cu}^{2+}$  complex (Fig. S5).<sup>16</sup> This coordination mode was supported by the Job plot evaluated from the absorption spectra of **1** and  $\text{Cu}^{2+}$  with a total concentration of 30  $\mu\text{M}$  (inset in Fig. 2).<sup>17</sup> The detection limit ( $S/N = 3$ ) for  $\text{Cu}^{2+}$  was determined to be  $2.9 \times 10^{-7} \text{ M}$  based on absorbance data (Fig. S6),<sup>18</sup> which satisfied the limit for drinking water.

A high selectivity toward analytes over other potentially competitive species is an important trait of an available chemosensor. Therefore, metal ion competition experiments were conducted by adding  $\text{Cu}^{2+}$  to **1** solution in the presence of other metal ions. As shown in Figure 3, the absorption intensities of **1**+ $\text{Cu}^{2+}$  with other metal ions were different. On the one hand, some tested metal ions in **1** solution showed variant weak absorption, for example, **1**+ $\text{Al}^{3+}$  and **1**+ $\text{Co}^{2+}$  systems gave a very little absorption at 565 nm, **1**+ $\text{Fe}^{3+}$  and **1**+ $\text{Fe}^{2+}$  systems gave a fairly weak absorption at 554 nm, and other metal ions behaved negligible variations in the absorption spectra. The different absorption intensities of **1** with the tested metal ions may affect the absorbance of **1**+ $\text{Cu}^{2+}$  solution; on the other hand, the interaction between  $\text{Cu}^{2+}$  and the coexisting metal ions may also influence the absorption intensity of **1**+ $\text{Cu}^{2+}$ . Therefore, the absorption intensities for  $\text{Cu}^{2+}$  with other metal ions in **1** solution were not the same. However, the metal ion competition experiments showed that the interference from other common metal ions was very weak.

The fluorescent spectra of **1** in response to metal ions were also recorded. Figure 4 shows the fluorescence spectra of **1** (12  $\mu\text{M}$ ) with the addition of  $\text{Al}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mg}^{2+}$  (2.0 equiv) in acetonitrile solution. Interestingly, the solution of **1**+ $\text{Al}^{3+}$  exhibited a significant fluorescence enhancement (437-fold) when excited at 550 nm. However, the

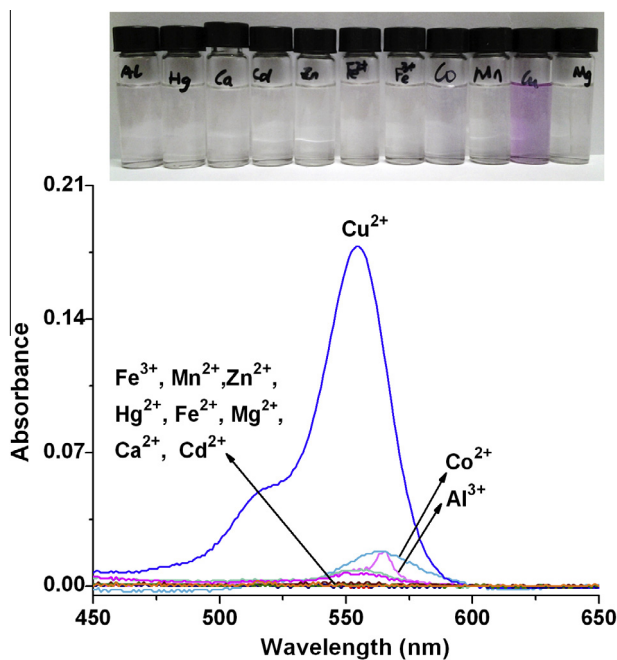


Figure 1. The color changes of **1** (12  $\mu\text{M}$  in acetonitrile) with 2.0 equiv metal ions (top); absorption spectra of **1** upon the addition of chlorate salts of  $\text{Al}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mg}^{2+}$  in acetonitrile (bottom).

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