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# Cu<sup>2+</sup>-selective colorimetric signaling by sequential hydrolysis and oxidative coupling of a Schiff base

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## ABSTRACT

A new Cu<sup>2+</sup>-selective probe was developed based on the Cu<sup>2+</sup>-induced sequential hydrolysis and oxidative coupling reactions of 4-aminoantipyrine-appended 8-hydroxyquinoline derivative **1**. Cu<sup>2+</sup>-assisted hydrolysis of the enamine moiety of Schiff base **1** afforded its constituents, 4-aminoantipyrine and 8-hydroxyquinoline-2-carboxaldehyde. The Cu<sup>2+</sup>-induced oxidative coupling between these *in situ* generated compounds afforded a quinoneimine dye. Prominent naked-eye-detectable selective signaling of Cu<sup>2+</sup> ions, assisted by EDTA, was realized through a color change from faint yellow to pink with a detection limit of  $1.81 \times 10^{-6}$  M.

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The development of selective and sensitive reaction-based signaling systems for chemically and biologically important species has attracted much recent research interest.<sup>1</sup> Because of the extensive use of copper in modern industry, the demand for sensitive and selective determination of Cu<sup>2+</sup> has increased recently. Various chemosensors and probes have been developed for this purpose.<sup>2</sup> In particular, chemodosimeters or probes utilizing a reaction-based signaling approach have recently attracted considerable interest.<sup>3</sup> The main advantages of this strategy are cumulative signaling and specific chemical reactions between the probe molecule and analytes, which allows for high sensitivity and excellent selectivity in signaling.<sup>1a</sup> This approach has been successfully utilized to design various reaction-based probes for the signaling of important metal ions, anions, and biologically important neutral species.

The structural transformation of the designed probe induced by the redox activity of Cu<sup>2+</sup>, which leads to changes in the optical properties, can be a useful design tool. Currently, copper-catalyzed reactions are very important in organic synthesis as one of the more powerful tools for selective synthetic reactions, such as condensation, oxidation, alkyne coupling, and Diels–Alder reactions.<sup>4</sup> In particular, the Cu-induced oxidation of organic compounds is well established in organic synthesis. A wide range of oxidation and oxidative coupling reactions have been reported exploiting the versatile oxidant properties of  $Cu^{2+.5}$  Recently, a number of probes based on  $Cu^{2+}$ -induced oxidation processes, such as the oxidative cyclization of azoaromatics and thiosemicarbazone,<sup>6</sup> oxidation and subsequent hydrolysis of fluorescein hydrazido 2-iminophenyl boronic ester,<sup>7</sup> oxidative dehydrogenation of a boron-dipyrromethene (BODIPY)-based amine,<sup>8</sup> and oxidation of dihydrorosamine<sup>9</sup> have been reported. In addition,  $Cu^{2+}$  is known to act as an oxidant in the coupling of catechol and iminodibenzyls with 4-aminoantipyrine (AAP).<sup>10</sup> We have recently reported simple  $Cu^{2+}$ -selective probes that utilize the oxidative coupling of AAP with phenols and anilines.<sup>11</sup> On the other hand, metal-ion-induced hydrolysis is particularly useful for the design of  $Cu^{2+}$ -selective probes<sup>12</sup> because  $Cu^{2+}$  can induce the hydrolysis of various functional groups, such as acetyls,<sup>13</sup> picolinates,<sup>14</sup> lactones,<sup>15</sup> and hydrazones.<sup>16</sup> Moreover, the  $Cu^{2+}$ -induced hydrolysis of Schiff bases is also a well-known process in organic synthesis.<sup>17</sup>

As a reaction-based chromogenic indicator for signaling of the biologically important analyte hydrogen peroxide, AAP has been uniquely employed.<sup>18</sup> This well-established and widely used assay is based on the oxidative coupling of AAP with phenolic compounds to yield highly colored quinoneimine dyes.<sup>19</sup> AAP has also been utilized as an efficient ligating subunit for the construction of sensors for transition metal ions,<sup>20</sup> such as  $Al^{3+,21}$  Fe<sup>3+,22</sup> and Cu<sup>2+,23</sup> In addition to metal sensors, a fluorescent probe capable of detecting intracellular arsenate (H<sub>2</sub>AsO<sub>4</sub>)<sup>24</sup> and a piezoelectric quartz crystal sensor for the detection of sulfur dioxide in air have been developed by using AAP.<sup>25</sup> AAP has also been employed for







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the determination of the activity of angiotensin-l converting enzyme in serum<sup>26</sup> and as a reagent for the synthesis of gold nanoparticles and colorimetric sensing of triptan-family drugs.<sup>27</sup>

In this paper, we report a new colorimetric signaling system for  $Cu^{2+}$  using sequential  $Cu^{2+}$ -induced hydrolysis of a Schiff base and oxidative coupling. The hydrolysis of designed Schiff base **1** with  $Cu^{2+}$  afforded its constituents, AAP and 8-hydroxyquinoline-2-carboxaldehyde. Subsequently, the  $Cu^{2+}$ -induced oxidative coupling between the *in situ* generated products afforded quinoneimine dye **2** with a prominent color change from faint yellow to pink.

The condensation of 8-hydroxyquinoline-2-carboxaldehyde with AAP afforded 1 in good yield (acetonitrile, 77%) (Scheme 1). Control compounds 3 and 4, derived from 2-pyridinecarboxaldehvde and salicylaldehvde, respectively, with similar structures were also prepared by reported procedures.<sup>28</sup> Compound **1** in a 90% aqueous acetonitrile solution exhibited a faint vellow color with very weak fluorescence. Originally, we aimed to achieve enhanced signaling behavior by combining the chelating subunit 8-hydroxyquinoline with the AAP moiety, which can induce additional chromogenic behavior and/or ligation. However, we observed that the designed Schiff base was selectively hydrolyzed by Cu<sup>2+</sup>, and subsequent oxidative coupling afforded a prominent pink-colored quinoneimine dye (vide infra). Based on this finding, we investigated the colorimetric signaling of  $Cu^{2+}$  by the above mentioned consecutive reactions of prepared Schiff base 1. The  $Cu^{2+}$ -induced transformation was unique to probe **1**; it was not observed for similarly structured 3 and 4 with pyridine and phenol subunits, respectively.<sup>29</sup>

Compound 1 exhibited an absorption maximum at 373 nm in a 90% aqueous acetonitrile solution (buffered at pH 5.6 with an acetate buffer). By treating 1 with various metal ions, noticeable responses toward multiple metal ions such as Cu<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> were observed (Fig. S1, Supplementary data). Owing to the presence of the rather universal 8-hydroxyguinoline chelating subunit and the extra AAP binding site, compound **1** exhibited significant spectral changes in the presence of several transition metal ions. However, the most pronounced spectral change was observed for Cu<sup>2+</sup>. With Cu<sup>2+</sup>, a new significantly red-shifted absorption maximum was observed at 497 nm, and the absorbance of this solution was also significantly increased. Such prominent Cu<sup>2+</sup>selective signaling is due to the consecutive Cu<sup>2+</sup>-assisted reactions of 1 to form quinoneimine dye 2 (vide infra). On the other hand, 1 did not show any considerable fluorescence responses toward the surveyed metal ions (Fig. S2, Supplementary data).

The prominent chromogenic signaling of  $Cu^{2+}$  by probe **1** is due to sequential hydrolysis and oxidative coupling, which can be summarized as a two-step process (Scheme 2). First, the enamine moiety of Schiff base **1** is hydrolyzed by  $Cu^{2+}$  to yield its constituents, 8-hydroxyquinoline-2-carboxaldehyde and AAP. Second, thusgenerated 8-hydroxyquinoline-2-carboxaldehyde is oxidatively coupled with AAP with the assistance of  $Cu^{2+}$  to yield quinoneimine dye **2**.<sup>30</sup> Comparable colorimetric signaling of  $Cu^{2+}$  was



Scheme 2. Colorimetric signaling process of 1 for Cu<sup>2+</sup>.

observed with a 1:1 mixture of AAP and 8-hydroxyguinoline-2carboxaldehyde under the same conditions. The formation of a coupling product between AAP and phenols promoted by oxidants, such as hydrogen peroxide and persulfate, has already been reported.<sup>31</sup> We have also reported a simple  $Cu^{2+}$ -selective signaling probe system based on the coupling of AAP with phenols or anilines.<sup>11</sup> However, to the best of our knowledge, there are no studies on sequential Cu2+-assisted enamine hydrolysis and oxidative coupling reactions to yield quinoneimine dyes. The proposed signaling by oxidative coupling was proven by NMR spectroscopy and UV-vis measurements. As a reference compound for this purpose, the postulated signaling product 2 was independently prepared by the reaction of 8-hydroxyquinoline-2-carboxaldehyde with AAP by using ammonium persulfate as the oxidant.<sup>11a</sup> The structure of quinoneimine dye **2** was confirmed by <sup>1</sup>H NMR and mass measurements. After purification of the  $Cu^{2+}$ -signaling product of **1** by passing it through a silica plug, its <sup>1</sup>H NMR spectrum was found to be the same as that of independently prepared 2 (Fig. 1). ESI mass measurements also confirmed the formation of quinoneimine dye 2, with an intense peak observed at m/z = 373.1289 for  $[2+H]^+ (C_{21}H_{17}N_4O_3)$  (Fig. S3, Supplementary data).

Although **1** exhibited the most prominent signaling behavior toward  $Cu^{2+}$ , it is not satisfactory as a selective probe for  $Cu^{2+}$ because  $Hg^{2+}$ ,  $Cd^{2+}$ , and  $Pb^{2+}$  ions also induced considerable UV-vis spectral responses (Fig. S1, Supplementary data). We noticed that the prominent difference in the response of probe **1** toward  $Cu^{2+}$ and the other metal ions was the irreversible structural transformation induced by the former and the formation of reversible complexes with the latter. Hence, to increase the selectivity toward  $Cu^{2+}$ , a chelating agent EDTA, which could complex most of the surveyed metal ions, was added (Fig. 2). We surmised that, upon treatment of the signaling solution containing probe **1** and various metal ions with EDTA, most of the interfering metal ions would be sequestered by complex formation with EDTA to release free **1**. On the other hand, in the case of  $Cu^{2+}$  ions, the probe has already been irreversibly transformed to quinoneimine dye **2**, and the



Scheme 1. Preparation of aminoantipyrine-appended 8-hydroxyquinoline-based probe 1 and structures of control compounds 3 and 4.



**Figure 1.** Partial <sup>1</sup>H NMR spectra of (a) **1** only and (b) the purified Cu<sup>2+</sup> signaling product of **1** in CDCl<sub>3</sub>. [**1**] = 10 mM.

Tonly L' Nar K' Mg<sup>a</sup> Ca<sup>la</sup> Ba<sup>ja</sup> Al<sup>a</sup> Mn<sup>a</sup> Fe<sup>a</sup> Co<sup>ja</sup> N<sup>a</sup> Cu<sup>ja</sup> Zn<sup>a</sup> Agʻ Cd<sup>a</sup> Hg<sup>a</sup> Pb<sup>ja</sup>



**Figure 2.** Cu<sup>2+</sup>-selective ratiometric signaling of **1** measured at 497 nm with an additional post-treatment with EDTA. [**1**] =  $4.0 \times 10^{-5}$  M, [M<sup>n+</sup>] =  $2.0 \times 10^{-4}$  M, and [EDTA] =  $4.0 \times 10^{-4}$  M in a mixture (1:9, v/v) of CH<sub>3</sub>CN and an acetate buffer solution (pH 5.6, 10 mM).

solution properties would not be significantly affected by the addition of EDTA. A preliminary investigation was conducted by additional post-treatment with EDTA of the signaling solution **1** in the presence of the surveyed metal ions. As expected, the addition of EDTA to the signaling solution of **1** containing Cu<sup>2+</sup> did not significantly change the UV-vis spectrum. On the other hand, when the solutions of **1** containing the other metal ions were treated with EDTA, the complexed metal ions were effectively sequestered, and the spectrum of **1** was completely recovered.

Based on this background, we measured the selective signaling behavior of **1** for  $Cu^{2+}$  with an additional post-treatment of the signaling solution with EDTA. As shown in Figure 2, the interference from Hg<sup>2+</sup> and Pb<sup>2+</sup> ions was completely removed by the effective sequestering effect of EDTA, and exclusive signaling of **1** toward  $Cu^{2+}$  was realized. The absorbance ratio in the presence and absence of metal ions ( $A/A_0$ ) of **1** measured at 497 nm was particularly large (60.6) for  $Cu^{2+}$ , whereas the remaining metal ions exhibited small and nearly constant ratios ranging between 0.70 for Fe<sup>3+</sup> and 2.3 for Co<sup>2+</sup> and Hg<sup>2+</sup>. In general, the Cu<sup>2+</sup>-selective signaling property of **1** was not significantly affected by the presence of other metal ions as background (Fig. 3). The signaling of **1** toward Cu<sup>2+</sup> was fast and completed within 10 min (Fig. S4,



**Figure 3.** Competitive signaling of  $Cu^{2+}$  by **1** in the presence of other metal ions as background with an additional post-treatment with EDTA. **[1]** =  $4.0 \times 10^{-5}$  M,  $[Cu^{2+}] = [M^{n+}] = 2.0 \times 10^{-4}$  M, and [EDTA] =  $4.0 \times 10^{-4}$  M in a mixture (1:9, v/v) of CH<sub>3</sub>CN and an acetate buffer solution (pH 5.6, 10 mM).

Supplementary data). In addition, efficient signaling was observed at a neutral pH range between 5.6 and 7; at higher (>7.5) and lower pH (<5.0), signaling became less pronounced (Fig. 4). The pH-dependency of the Cu<sup>2+</sup>-selective chromogenic behavior of the probe **1** and a mixture of its constituents, 8-hydroxyquinoline-2-carboxaldehyde and AAP, was found to be similar (Fig. S5, Supplementary data). The coupling of phenols with AAP is known to proceed with electrophilic attack of deprotonated phenolate form on AAP,<sup>32</sup> thus the coupling reaction would be facilitated with increasing the pH of the reaction medium (estimated pK<sub>a</sub> of 8-hydroxyquinoline-2-carboxaldehyde = 9.27).<sup>33</sup> However, the signaling is believed to be dwindled at higher pH region (pH > 7.0), presumably due to the instability of the resulting dye **2** in alkaline medium.<sup>34</sup>

Finally, the quantitative analytical behavior of **1** for Cu<sup>2+</sup> signaling was elucidated by UV-vis titration. As the Cu<sup>2+</sup> concentration increased, the absorption band at 497 nm increased progressively (Fig. 5). A linear calibration curve was obtained up to  $2.0 \times 10^{-4}$  M. A detection limit of  $1.81 \times 10^{-6}$  M was estimated for the determination of Cu<sup>2+</sup> by **1** in a 90% aqueous acetonitrile solution.<sup>35</sup>

In summary, a new reaction-based colorimetric probe based on the 8-hydroxyquinoline-based Schiff base was developed for the selective signaling of  $Cu^{2+}$  ions. A Schiff base prepared from AAP and 8-hydroxyquinoline-2-carboxaldehyde exhibited pronounced  $Cu^{2+}$ -selective, naked-eye-discernible chromogenic signaling with a color change from faint yellow to pink. The observed chromogenic



**Figure 4.** pH-dependency of  $Cu^{2+}$  signaling by **1.** [**1**] =  $4.0 \times 10^{-5}$  M, [ $Cu^{2+}$ ] =  $2.0 \times 10^{-4}$  M, [buffer] =  $1.0 \times 10^{-2}$  M, and [EDTA] =  $4.0 \times 10^{-4}$  M in 90% aqueous acetonitrile. Acetate buffer (pH 3.6–6.0), HEPES buffer (pH 7.0–7.5), tris buffer (pH 8.0–8.5), and borate buffer (pH 9.0–10.0) were used.



**Figure 5.** UV-vis titration of **1** with  $Cu^{2*}$ . Inset: Changes in absorbance at 497 nm as a function of  $[Cu^{2*}]$ . [**1**] =  $4.0 \times 10^{-5}$  M and  $[Cu^{2*}]$  =  $0-4.0 \times 10^{-4}$  M in a mixture (1:9, v/v) of CH<sub>3</sub>CN and an acetate buffer solution (pH 5.6, 10 mM). After signaling the solution was treated with EDTA ( $4.0 \times 10^{-4}$  M).

signaling is attributed to the Cu<sup>2+</sup>-induced hydrolysis of the enamine of the probe followed by oxidative coupling of the hydrolysis products to yield a highly colored quinoneimine dye. By utilizing EDTA as a post-treatment masking agent, selectivity toward Cu<sup>2+</sup> could be greatly enhanced.

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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.2015.10. 071. These data include MOL files and InChiKeys of the most important compounds described in this article.

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