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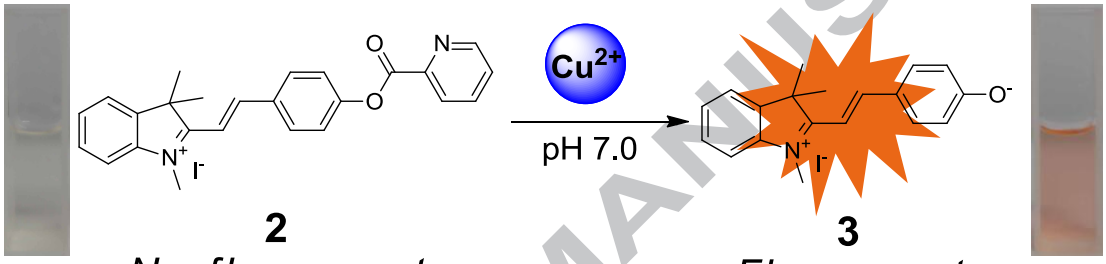

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Research Institute of Food Science & Engineering Technology, Hezhou University, Hezhou 542899, P. R. China

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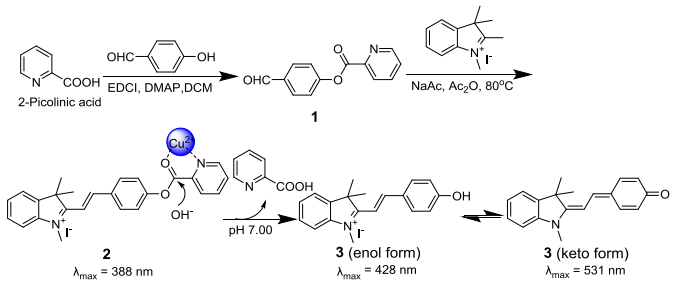
ABSTRACT

A hemicyanine-based colorimetric and fluorescent turn-on probe **2** was designed and synthesized. The probe displayed a rapid response time, high sensitivity, and high selectivity for Cu^{2+} over other metal ions. Moreover, the probe can detect Cu^{2+} in the presence of 15 species metal ions by absorption spectra, fluorescence spectra and naked-eye in aqueous media.

Copper is the third most abundant indispensable trace element (following iron and zinc) in human body and plays a crucial role in various physiological processes.[1] However, abnormal levels of copper are implicated in a variety of diseases. Definitely, copper deficiency may cause coronary heart disease.[2] An excess amount of copper could lead to harmful effects by causing oxidative stress and disorders,[3] which are associated with neurodegenerative diseases including Alzheimer's,[4] Menke's,[5] Parkinson's,[6] Wilson's,[7] and prion diseases.[8] In addition, copper has become an important metal pollutant[9] due to its widespread applications. Therefore, development of sensitive and selective methods for detection of copper ions in biological and environmental systems is strongly desired.

Although traditional methods such as atomic absorption spectrometry (AAS),[10] atomic emission spectrometry (AES),[11] inductively coupled plasma mass spectrometry (ICP-MS),[12] voltammetry,[13] and electrochemicalmethods[14] have been used for detection of copper ions, these methods often require expensive instruments and tedious sample preparation procedures, which preclude their application for real-time and *in vivo* analysis. In contrast, fluorescence probe because of its specificity, high sensitivity, real-time detection, and simple instrumentation[15] has attracted much attention. As a consequence, a number of fluorescent probes have been developed to detect copper ions in recent years.[16]

Among the reported probes for copper ions, colorimetric and fluorescent probes have drawn increasing attraction,[17] because they not only have the advantages of the fluorescent probes, but also have the characteristics of the colorimetric measurements, such as low cost, simplicity, visualization and analysis *in situ* using simple apparatus.[18] So far, only a few rhodamine-based[19] and BODIPY-based[20] colorimetric and fluorescent turn-on probes for copper ions have been reported. Nevertheless, some of them exhibited cross-sensitivities toward other metal ions. Therefore, developing selective and sensitive colorimetric and fluorescent turn-on probe for Cu^{2+} detection under physiological conditions is highly demanded.



Scheme 1. Synthetic strategy for **2** and proposed reaction mechanism for Cu^{2+}.

Based on our previous research,[21] it is necessary to choose an efficient fluorophore in the design of fluorescent probes. Merocyanine dyes show strong intramolecular charge transfer (ICT) with "push-pull" substituent pairs,[22] when ICT process was affected by a certain sensing event, both colour and fluorescence changes were observed.[23] Thus, merocyanine is an attractive platform for the design of colorimetric and fluorescent turn-on probes. With these facts in mind, we develop a selective and sensitive colorimetric and fluorescent turn-on probe **2** for Cu^{2+} (Scheme 1), which employs merocyanine as the fluorophore and

∗ Corresponding author. Tel.: 86-774-5229756; e-mail: zhudongjian@iccas.ac.cn and 250581250@qq.com

picolinate as recognition unit. The synthetic strategy for preparing probe **2** is outlined in Scheme 1. For comparison, compound **3** was also synthesized. The detailed experimental procedures and ^{1}H and ^{13}C NMR spectroscopy and ESI mass spectrometry are explained in the Supporting Information.

With **2** in hand, we carried out optimizations on experimental conditions such as pH and solubility. At room temperature (25°C), the fluorescence intensity at 557 nm of **2** in the absence and presence of Cu^{2+} at different pH was studied (Fig. S1). It could be seen that the fluorescence intensity increased slightly in the pH ranging from 4.0 to 7.0 in the absence of Cu^{2+}. However, the fluorescence intensity remarkably increased with pH increasing in the range of 7.0 - 9.5 in the absence of Cu^{2+}. On the other hand, in the presence of Cu^{2+}, the fluorescence intensity was increased in the region of pH 6.0 - 8.0. These findings indicated that alkaline condition (>7.0) could cause the hydrolysis of **2**, which increased background fluorescence. Thus, pH 7.0 is suggested to be suitable for Cu^{2+} detection. In addition, **2** and **3** exhibit good solubility in HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution containing acetonitrile as a cosolvent (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0) at room temperature according to the absorption spectra (Fig. S2). Based on the above observations, buffer solution of HEPES (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C) was selected as the optimized conditions for further spectral investigation.

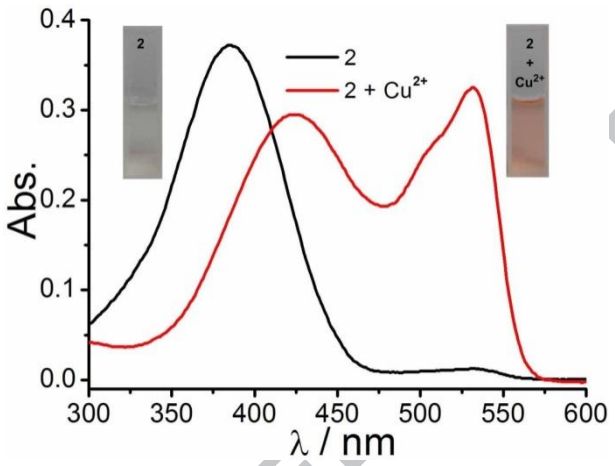


Figure 1. Absorption spectra of **2** (10 μM) (black line) before and (red line) after reaction with Cu^{2+} (20 μM) in HEPES buffer (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C). The colour change of **2** before and after the reaction are shown in the insets.

Then, we assessed the photophysical properties of **2** under the optimized conditions (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C). The absorption spectra and colour change of **2** before and after reaction with Cu^{2+} are shown in Fig. 1. A solution of **2** exhibited an absorption band at 388 nm. Upon addition of Cu^{2+}, the band at 388 nm disappeared, while two new absorption bands centered at 428 nm and 531 nm emerged, which were ascribed to the fluorescent product **3** enol form and keto form, respectively (Figs. S3 and S4). The colour of the solution dramatically turned from pale yellow to pink, which is similar to the colour of **3** in HEPES buffer (Fig. S4), thus allowing colorimetric detection of Cu^{2+} by the naked eye. Time course studies showed that the absorbance of 388 nm decreased and the absorbance of 428 nm and 531 nm reached a plateau within 72 s (Fig. S5), indicating that the probe reacted rapidly with Cu^{2+} under optimized conditions.

Based on the colour change of the solution, the colorimetric analysis of **2** toward various metal ions was studied. As shown in Fig. 2, Cu^{2+}, whether present alone or in the presence of mixed metal ions, displays the expected pink, but the other metal ions including Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Al^{3+} ions, do not show any colour change, indicating that **2** exhibits high selectivity to Cu^{2+} over other metal ions. It is worth noted that **2** has excellent selectivity to Cu^{2+} even in the presence of 15 species metal ions.

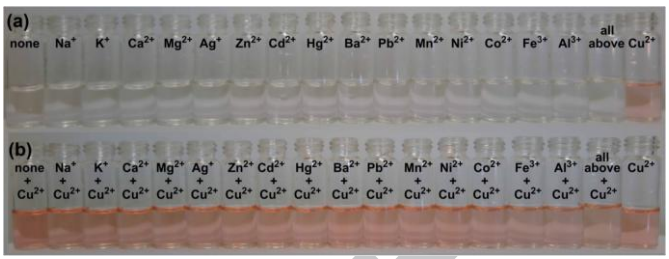


Figure 2. Colour change observed before (a) and after (b) the addition of Cu^{2+} (20 μM) to the solution of **2** (10 μM) in HEPES buffer (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C) in the presence of different metal ions: Na^{+} (1 mM), K^{+} (1 mM), Ca^{2+} (1 mM), Mg^{2+} (1 mM), Ag^{+} (20 μM), Zn^{2+} (20 μM), Cd^{2+} (20 μM), Hg^{2+} (20 μM), Ba^{2+} (20 μM), Pb^{2+} (20 μM), Mn^{2+} (20 μM), Ni^{2+} (20 μM), Co^{2+} (20 μM), Fe^{3+} (20 μM), Al^{3+} (20 μM), Cu^{2+} (20 μM).

The selectivity of **2** for Cu^{2+} detection was also investigated by absorption spectra. As shown in Fig. 3, **2** exhibits high selectivity to Cu^{2+}, which is in good agreement with the result of colour change.

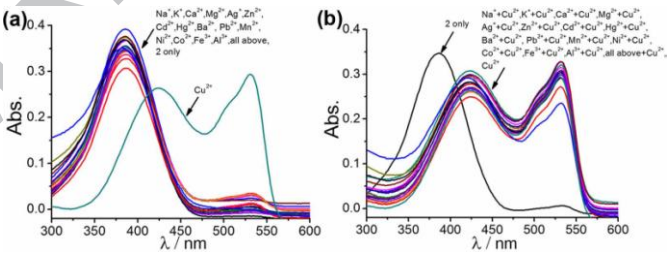


Figure 3. Absorption spectra of **2** (10 μM) in the absence and presence of different metal ions: Na^{+} (1 mM), K^{+} (1 mM), Ca^{2+} (1 mM), Mg^{2+} (1 mM), Ag^{+} (20 μM), Zn^{2+} (20 μM), Cd^{2+} (20 μM), Hg^{2+} (20 μM), Ba^{2+} (20 μM), Pb^{2+} (20 μM), Mn^{2+} (20 μM), Ni^{2+} (20 μM), Co^{2+} (20 μM), Fe^{3+} (20 μM), Al^{3+} (20 μM), Cu^{2+} (20 μM). (a): free probe and probe treated with the marked metal ions. (b): probe treated with the marked metal ions followed by Cu^{2+} (20 μM) and free probe. Data were acquired in HEPES buffer (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C).

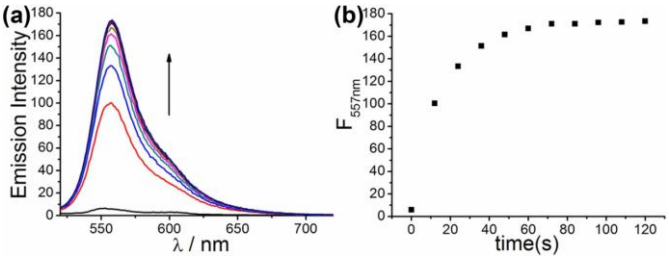


Figure 4. (a) Fluorescence spectra of **2** (10 μM) recorded every 12 s within 2 min after the addition of Cu^{2+} (20 μM) in HEPES buffer (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C, λ_{ex} = 500 nm). (b) The fluorescence intensity at 557 nm changes as a function of time.

We next tested fluorescence response of **2** to Cu^{2+}. A solution of **2** (10 μM) has almost no fluorescence upon excitation at 500 nm. However, upon addition of Cu^{2+} (20 μM) for 2 min, the solution of **2** showed significant fluorescent emission, and the fluorescence intensity at 557 nm reached a plateau within 72 s with a 29-fold enhancement (Fig. 4). The fluorescent emission change clearly demonstrated that the hydrolysis of **2** was triggered by Cu^{2+} and subsequently liberated the fluorescent

product **3** (Fig. S6). The reaction product of **2** was also checked by ESI analysis to explore the reaction mechanism. The ESI spectrum of the reaction solution of **2** with Cu^{2+} shows a major peak at m/z = 278.2 $[M-I]^+$, which is characteristic of the mass of **3** (Fig. S7). All these results clearly demonstrate that reaction of **2** with Cu^{2+} causes the hydrolysis of the picolinate moiety, thus validating our proposed mechanism (Scheme 1).

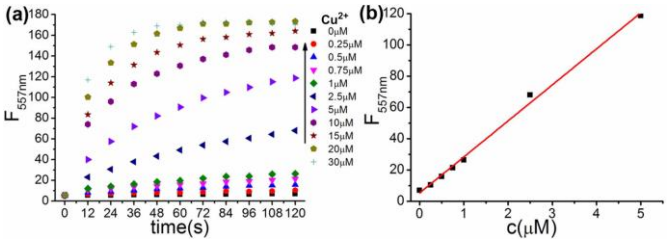


Figure 5. (a) Plot of fluorescence intensity at 557 nm *vs.* the reaction time in the presence of varied concentrations of Cu^{2+}. (b) The fluorescence intensity at 557 nm as a function of the concentrations of Cu^{2+} in the range of 0 - 5 μM. Data were acquired in HEPES buffer (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C, λ_{ex} = 500 nm).

To test sensitivity, the time-dependent fluorescence spectra of **2** in the presence of varied concentrations of Cu^{2+} were studied and the hydrolysis was traced by measuring the fluorescence at 557 nm (Fig. 5a). It can be seen that the fluorescence intensity at 557 nm of **2** (10 μM) increased gradually with the increasing of the concentration of Cu^{2+} from 0 μM to 30 μM and then reached a plateau. The fluorescence at 557 nm was stable at about 20 μM of Cu^{2+} (Fig. S8). However, negligible changes in fluorescence were detected in the absence of Cu^{2+} for the same interval of time. Moreover, a good linearity between the fluorescence intensity at 557 nm and the Cu^{2+} concentration in the range of 0 - 5 μM is observed, as depicted in Fig. 5b. The detection limit of the probe for Cu^{2+} was thus calculated to be 0.2 μM (Fig. S9),[24] which is much lower than the limit of copper in drinking water (~20 μM) set by the U. S. Environmental Protection Agency.[25]

The fluorescence intensity at 557 nm reached a plateau within 72 s in the presence of Cu^{2+} (20 μM), which is in accordance with that in the above absorption spectra studies. The above findings indicated that the hydrolysis reaction of **2** by Cu^{2+} was very fast (within 72 s) under optimized conditions with fluorescence enhancement. Therefore, this reaction time of 72 s and the safety limit of copper (20 μM) in drinking water were used for the following experiments.

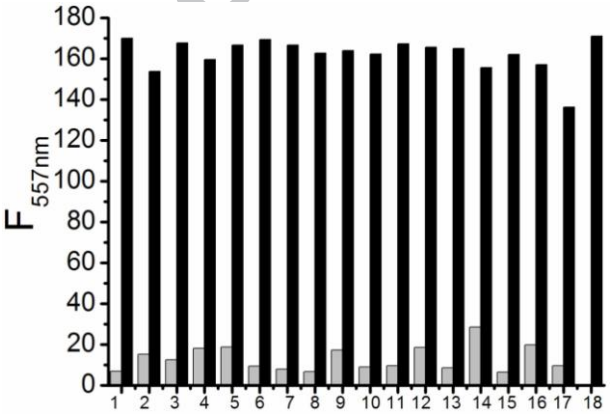


Figure 6. Fluorescence intensity at 557 nm for **2** determined in the absence and presence of different metal ions: 1, none; 2, Na^+ (1 mM); 3, K^+ (1 mM); 4, Ca^{2+} (1 mM); 5, Mg^{2+} (1 mM); 6, Ag^+ (20 μM); 7, Zn^{2+} (20 μM); 8, Cd^{2+} (20 μM); 9, Hg^{2+} (20 μM); 10, Ba^{2+} (20 μM); 11, Pb^{2+} (20 μM); 12, Mn^{2+} (20 μM); 13, Ni^{2+} (20 μM); 14, Co^{2+} (20 μM); 15, Fe^{3+} (20 μM); 16, Al^{3+} (20 μM); 17, all mentioned above metal ions; 18, Cu^{2+} (20 μM). Gray bars: free probe and probe treated with the marked metal ions. Black bars: probe treated with the marked metal ions followed by Cu^{2+} (20 μM). Data were acquired in HEPES buffer (10 mM, H_2O/CH_3CN, 4:1, v/v, pH 7.0, 25°C, λ_{ex} = 500 nm).

We then proceeded to examine the selectivity of **2**. As shown in Fig. 6 and Fig. S10, the fluorescence responses of **2** (10 μM) exhibited excellent selectivity toward Cu^{2+} over other metal ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Al^{3+} ions. Competition experiments revealed that the Cu^{2+}-induced fluorescence was almost unaffected in the presence of the metal ions mentioned above. Moreover, the fluorescence response of **2** to Cu^{2+} was almost unaffected even in the presence of 15 species metal ions (Fig. 6 17). The probe has high selectivity for Cu^{2+} over the other metal ions, which can be ascribed to the specific hydrolysis of the picolinate moiety by Cu^{2+}.[26]

In summary, we designed, synthesized and characterized a hemicyanine-based colorimetric and fluorescent turn-on probe **2**. The probe displayed a rapid response time (within 72 s), high sensitivity (detection limit of 0.2 μM), and high selectivity for Cu^{2+} over other metal ions. Moreover, the probe can detect Cu^{2+} in the presence of 15 species metal ions by absorption spectra, fluorescence spectra and an obvious colour change which was observed easily by naked-eye in aqueous media.

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Supplementary Material

Supplementary materials including synthetic procedures and characterization of compounds **1**, **2**, and **3**, and additional spectroscopic data.

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Highlights

- A novel hemicyanine-based colorimetric and fluorescent turn-on probe **2** for Cu^{2+} was developed.
- The probe can detect Cu^{2+} in the presence of 15 species metal ions by absorption spectra, fluorescence spectra and naked-eye.
- The probe exhibited a rapid response of Cu^{2+} within 72 s.
- The detection limit of **2** for Cu^{2+} was found to be 0.2 μM.