A colorimetric “naked-eye” Cu(II) chemosensor and pH indicator in an 100% aqueous solution

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ARTICLE TYPE

A colorimetric “naked-eye” Cu(II) chemosensor and pH indicator in an 100% aqueous solution

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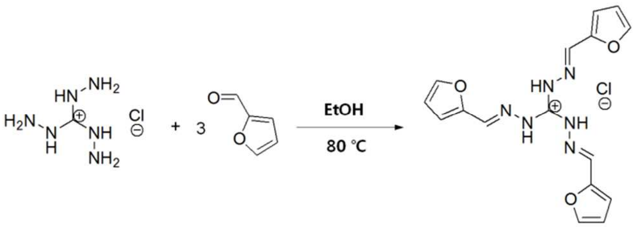
A new, highly selective and sensitive colorimetric chemosensor 1 for detection of Cu^{2+} ions in aqueous solution was developed. Receptor 1 detected Cu^{2+} ions by changing its color from colorless to yellow. Moreover, the Cu^{2+}-sensitive compound was used as a colorimetric pH detector based on a color change due to 1-Cu^{2+} complex formation identifiable via naked eye.

Copper, an essential trace element, plays a critical role in many environmental, biological, and chemical systems.[1] However, copper ion can have detrimental effects on humans and animals when overexposure to Cu^{2+}-polluted water occurs. Excess exposure to high concentrations of Cu^{2+} has been implicated in the development of Alzheimer’s and Parkinson’s disease.[2] The U.S. Environmental Protection Agency (EPA) has set the safe limit of copper in drinking water at 1.3 ppm (ca. 2.0 x 10^{-5} M).[3] Therefore, a reliable method for determination of trace amounts of Cu^{2+} in biological and environmental samples is essential.

Unlike some analytical techniques, such as atomic absorption spectrometry[4a], fluorescence techniques[4b], and electrochemical methods[4c], colorimetric methods can conveniently and easily monitor target ions in the visible range with high sensitivity, specificity, simplicity, low cost, and rapid tracking of analytes in biological, toxicological, and environmental samples.[1c,5] Therefore, the colorimetric methods have attracted considerable attention in detection of toxic metal ions, including Cu^{2+}.

In addition, determination of pH is essential in many processes in agriculture, industry, and human health.[6] While the majority of pH chemosensors reported to date are fluorescence intensity-based[7] or fluorescence ratiometry-based[8] with advantages including high sensitivity, ease of use, real-time visualization, and quick response times compared to the traditional glass pH electrodes[6a,9], pH chemosensors based on color change are relatively rare.[10] Also, the colorimetric pH sensors reported to date have suffered from limitations such as complicated synthetic procedures, high detection limits, and use of organic solvents. Thus, the development of a new sensitive colorimetric pH chemosensor working in mild environments by simple synthetic approach is of great interest.

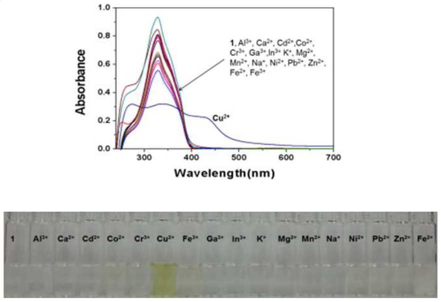
Herein, we report synthesis and characterization of a simple colorimetric sensor **1** based on combination of triaminoguanidinium and furfural moieties for selective detection of copper ions in 100% aqueous solution. The receptor **1** detected Cu^{2+} ions by color change from colorless to yellow with a fast response time. Moreover, we were able to determine a certain range of pH simply by observing the color change of the receptor **1** in the presence of Cu^{2+} ions.



Scheme 1 Synthesis of receptor **1**.

The receptor **1** was obtained by a condensation reaction of triaminoguanidinium chloride and furfural with an 85% yield in ethanol at room temperature (Scheme 1). **1** was characterized by ^{1}H-NMR, ^{13}C-NMR, ESI-mass spectrometry and elemental analysis.

The colorimetric sensing abilities of **1** were primarily investigated in bis-tris buffer (10 mM, pH 7.0) containing 0.1% distilled water (DW) with various metal ions (Cu^{2+}, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Fe^{2+}, Ga^{3+}, In^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+}). Upon the addition of 6 equiv of each cation, only Cu^{2+} induced a distinct spectral change, while other metal ions showed either none or minimal change in the absorption spectra relative to the free receptor **1** (Fig. 1a). Consistent with the UV-Vis spectral change, the solution of **1** in the presence of Cu^{2+} ion changed color from colorless to yellow (Fig. 1b), indicating that



(a)

(b)

Fig. 1. (a) UV-Vis spectra changes of **1** (30 µM, buffer-DW (999:1, v/v)) upon the addition of 6 equiv of metal ions. (b) Colorimetric changes of

receptor **1** (30 μM) upon the addition of various metal ions (6 equiv) in buffer-DW solution.

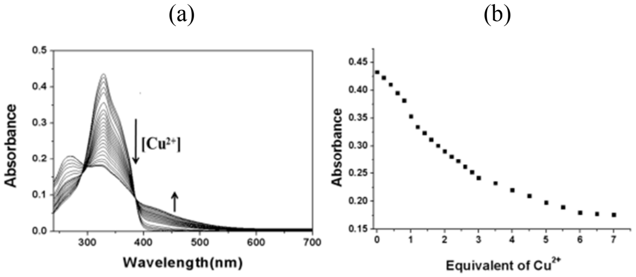
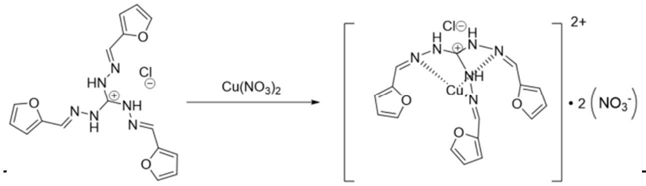


Fig. 2. (a) UV-Vis spectra changes of **1** (10 μM) in the presence of different concentrations of Cu^{2+} ions in buffer-DW (999:1, v/v) solution. (b) Absorption at 331 nm versus the number of equiv of Cu^{2+} added.

receptor **1** could serve as a potential candidate for "naked-eye" chemosensor of Cu^{2+} in aqueous solutions.

The binding properties of **1** with Cu^{2+} were further studied by UV-Vis titration experiments. Upon addition of Cu^{2+} ions to the solution of **1**, a sharp absorption band at 325 nm significantly decreased, while two new broad bands at 275 and 425 nm gradually reached maxima at 6 equiv of Cu^{2+} (Fig. 2). At the same time, a clear isosbestic point was observed at 387 nm, implying the conversion of the free receptor **1** to a copper complex. Furthermore, the new absorption peak at 425 nm ($\varepsilon = 0.8 \times 10^4\ M^{-1}cm^{-1}$) in the visible region might be due to the ligand-to-metal-charge-transfer (LMCT) and indicate the formation of a complex between receptor **1** and Cu^{2+} ions. A Job plot analysis showed a 1:1 stoichiometry for the **1**-Cu^{2+} complex (Fig. S1†).[11]

To further examine the binding mode between **1** and Cu^{2+}, a positive-ion ESI mass experiment was carried out. A peak at m/z 227.57 assigned to $[\mathbf{1}+Cu+H_2O]^{2+}$ was observed (calcd. 227.13) (Fig. S2†). In addition, Infrared (IR) spectroscopy was employed to gain a better understanding of the structure of **1**-Cu^{2+} complex. The bands at 1633 cm^{-1} and 1302 cm^{-1} of the IR spectrum of **1** (Fig. S3 (a)†) are associated with C=N group and ether group of the furan moiety, respectively. IR spectrum of the solid state **1**-Cu^{2+} complex obtained from the reaction of Cu^{2+} and **1** showed that the band 1633 cm^{-1} of the imine absorption region was shifted to 1614 cm^{-1}, while the ether group was little shifted (Fig. S3 (b)†). These results suggest that Cu^{2+} may coordinate to the nitrogen atoms of the imine moieties of **1**. In order to further confirm the coordination mode between **1** and Cu^{2+}, we took IR spectra of two **1**-Ni^{2+} and **1**-Cd^{2+} complexes, which might have the same coordination geometry as **1**-Cu^{2+} complex (Fig. S3 (c)† and Fig. S3 (d)†). IR spectra of the solid state **1**-Ni^{2+} and **1**-Cd^{2+} complexes also showed that the band 1633 cm^{-1} of imine absorption region was shifted to 1605 cm^{-1} and 1597 cm^{-1}, respectively, while the ether group band (1302 cm^{-1}) showed almost no change. These IR studies further support that Cu^{2+} might bind to the nitrogen atoms of the imine groups of **1**, not the oxygen atoms of the ether moieties. Based on the Job plot, Infrared (IR) spectra, and ESI-mass spectrometry analysis, we propose the structure for a 1:1 complex of **1** and Cu^{2+} (Scheme 2).



Scheme 2 Proposed structure of a 1:1 complex of **1** and Cu^{2+}

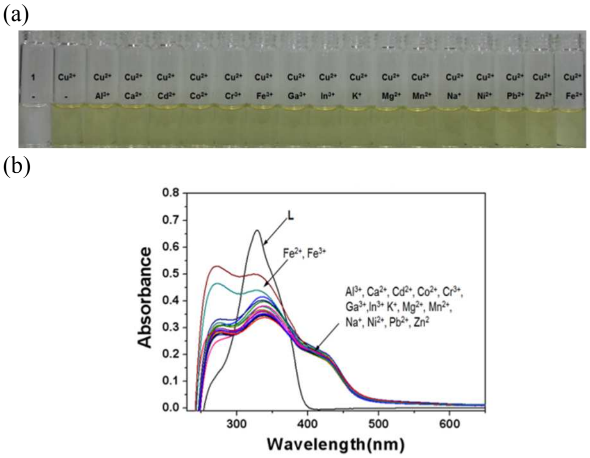


Fig. 3. (a) Colorimetric competitive experiment of **1** (30 μM) in the presence of Cu^{2+} (6 equiv) and other metal ions (6 equiv) in buffer-DW (999:1, v/v) solution. (b) Competitive selectivity of **1** (30 μM) towards Cu^{2+} (6 equiv) in the presence of other metal ions (6 equiv) in buffer-DW solution.

Based on UV-Vis titration, the association constant (K_a) of **1** with Cu^{2+} ion was calculated using Benesi-Hildebrand equation (Fig. S4†).[12] The K_a value turned out to be $1.1 \times 10^5\ M^{-1}$, which is within the values ($10^4 \sim 10^5$) previously reported for Cu^{2+}-binding chemosensors.[2b,13] For a comparison, we carried out Job plot and UV-vis titration of **1** toward Ni^{2+} to obtain the association constant K_a (Fig. S5† and Fig. S6†),[14] because it is well known that Cu^{2+} and Ni^{2+} may have a very similar coordination geometry. Based on this UV-vis titration experiment, we calculated the association constant ($7.14 \times 10^2\ M^{-1}$) of **1** and Ni^{2+} (Fig. S7†). The K_a value of **1**-Ni^{2+} complex is much lower than that of **1**-Cu^{2+} complex, which imply the high selectivity of **1** toward Cu^{2+} among other metal ions. The detection limit of receptor **1** as a colorimetric sensor for the analysis of Cu^{2+} ions was found to be 2.7×10^{-6} M (Fig. S8†).[15] The U. S. Environmental Protection Agency (EPA) has set the

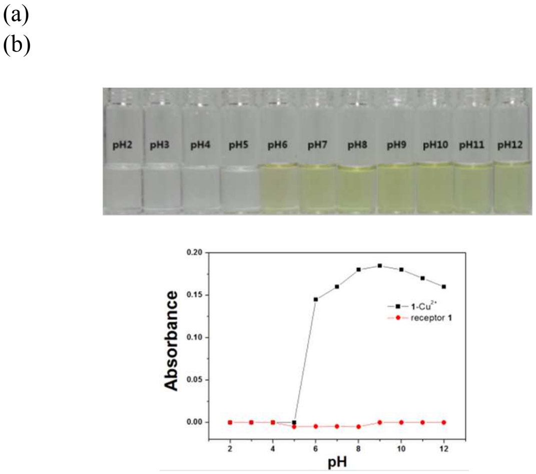


Fig. 4. (a) The color changes of **1**-Cu^{2+} complex at different pH (2-12) in buffer solution. (b) UV-vis spectra of **1**-Cu^{2+} complex at different pH values (2-12) in buffer solution.

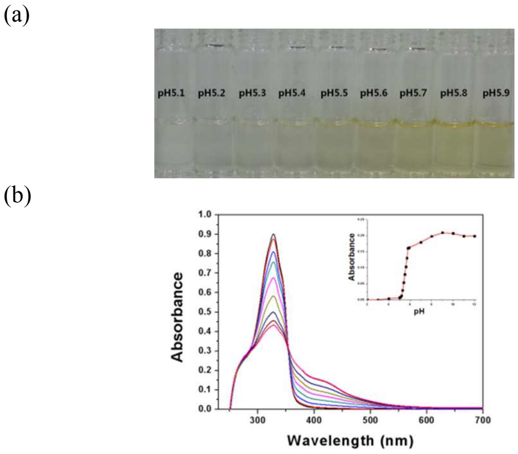


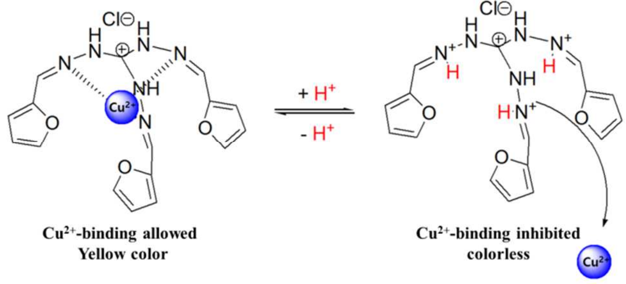
Fig. 5. (a) The color changes of **1**-Cu^{2+} complex at different pH values (5.1-5.9) in buffer-DW (999:1, v/v) solution. (b) UV-vis spectra changes of receptor **1** (30 μM) after the addition of 6 equiv of copper (II) ions at different pH values (pH 5.1-5.9). Inset: Change of the absorption intensities with pH increase from 2.0 to 12.0.

safe limit of copper in drinking water at 2.0 x 10^{-5} M. Hence with its much lower detection limit for Cu^{2+} ions, receptor **1** could be a powerful tool for the detection of copper ions in drinking water.

The preferential selectivity of **1** as a colorimetric chemosensor for the detection of Cu^{2+} was studied in the presence of various competing metal ions. For competition studies, receptor **1** was treated with 6 equiv of Cu^{2+} in the presence of 6 equiv of other metal ions, as indicated in Fig. 3. There was no interference for detection of Cu^{2+} in the presence of Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Fe^{2+}, Ga^{3+}, In^{3+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. Thus, receptor **1** could be used as a selective colorimetric sensor for Cu^{2+} in the presence of most competing metal ions.

The effect of pH on the absorption response of receptor **1** to Cu^{2+} ions was investigated in the pH range of 2 to 12 (Fig. 4). The color of **1**-Cu^{2+} complex remained in yellow color between pH 6 and 12, while its color changed to colorless between pH 2 and 5 (Fig. 4a). These results indicate that Cu^{2+} could be clearly detected by the naked eye or UV-Vis absorption measurements using receptor **1** over a wide pH range of 6.0-12.0.

In order to measure the exact pH value showing the color change, we conducted pH titration from pH 5.1 to 5.9 (Fig. 5a). The solution of **1** in the presence of Cu^{2+} ion began to change color at pH 5.4. Thus, one can practically discern whether the pH of a certain solution is lower than 5.4 by observing the color change in the presence of the **1**-Cu^{2+} complex. As shown in Fig. 5b with the pH increase from 5.1 to 5.9, the absorption peak at 325 nm of the **1**-Cu^{2+} complex significantly decreased, and concomitantly a new absorption band at 425 nm was formed. There is a well-defined isosbestic point at 350 nm. The inset of Fig. 5b shows the UV-Vis spectral changes in absorbance at 425 nm of **1**-Cu^{2+} complex as a function of pH. A steep increase of absorbance was observed between pH 5 and 6. The changes in the UV-Vis spectrum with the decrease of pH could be possibly explained by the protonation of the imine moieties of receptor **1** (Scheme 3). At low pH, three protons bind to the nitrogen atoms of the three-imine moiety of receptor **1**, which likely inhibits the binding of Cu^{2+} to **1**, resulting in generation of the colorless solution of **1**. To further understand this phenomenon, we analysed absorbance change at 366 nm as a function of pH by using the Henderson-Hasselbach-type mass action equation[16] (Fig. S9†). The pK$_a$ of **1** from the plot was determined to be 6.25 which is in the range of pKa values (5.5-7.6)[17] reported for the protonated imines. This result further confirms the proposed structure of the **1**-Cu^{2+} complex as shown in Scheme 3. Importantly, the pH-dependent changes in the solution color (Fig. 6a) and the UV-Vis absorption (Fig. 6b) were reversible even after several cycles of sequential alternative addition of HCl and NaOH. These results indicate that the **1**-Cu^{2+} complex could be used as a novel and reversible optical pH indicator in a fully aqueous solution.



Scheme 3 Mechanism of pH response by protonation and deprotonation of the receptor

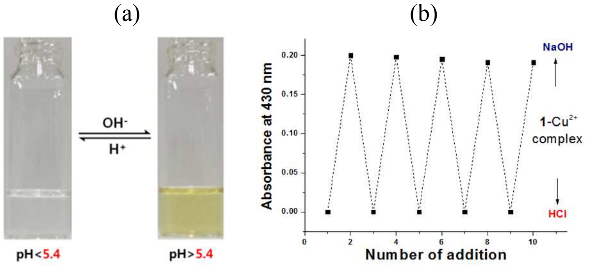


Fig. 6. (a) Reversible color changes of **1**-Cu^{2+} (30 μM) after the sequential addition of HCl and NaOH in bis-tris buffer solution. (b) Reversible changes in absorbance of **1**-Cu^{2+} complex (30 μM) at 430 nm after the sequential addition of HCl and NaOH in bis-tris buffer solution.

Since the color change of the **1**-Cu^{2+} complex was observed above pH 5.4 in 100% aqueous solution, we expected that **1**-Cu^{2+} complex might be a novel candidate for a pH probe. Therefore, we have further tested the practical use of the **1**-Cu^{2+} complex as a pH indicator by observing the color change in real environmental samples. As shown in Fig. 7, the colorimetric experiments were conducted with three samples to estimate their approximate pH values. The colors of distilled and tap water

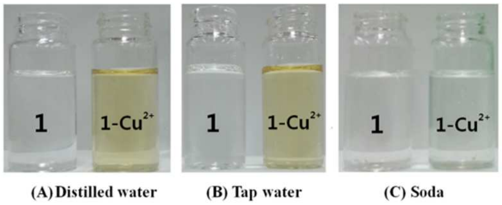


Fig. 7. The color changes of the three samples (A: distilled water, B: tap water, and C: Soda) in the presence of the **1**-Cu^{2+} complex (30 μM).

samples in the presence of **1**-Cu^{2+} complex changed from colorless to yellow, while no color change was observed in a soda sample. Based on these results, the pH of the soda sample was expected to be lower than 5.4, and those of the distilled and tap water samples were expected to be greater than 5.4. A pH meter showed that the soda had a pH of 3.15, while the distilled and tap water samples had pHs of 6.18 and 7.09, respectively. These results indicate that **1**-Cu^{2+} complex could be used as a reliable pH indicator for environmental analyses.

In conclusion, we prepared a simple colorimetric receptor **1** with high selectivity and sensitivity for Cu^{2+} in water solution. Importantly, the detection limit (2.7 μM) of **1** for Cu^{2+} falls sufficiently below the limit criterion of drinking water (20 μM). Moreover, we showed that **1**-Cu^{2+} complex can also be used as a colorimetric pH indicator in real environmental samples. Based on these results, we believe that receptor **1** will be an excellent prototype for the development of a novel colorimetric Cu^{2+}-chemosensor and pH probe.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedure, Job plots, Benesi-Hildebrand equation plot and detection limit]. See DOI: 10.1039/b000000x/

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14 A Job plot analysis showed a 1:1 stoichiometry for the **1**-Ni^{2+} complex (Fig. S5†). UV-vis titration of **1** toward Ni^{2+} was carried out at high concentration (120 μM) of **1**, because there is little absorbance change at its low concentration. See Fig. S6 in supporting information.

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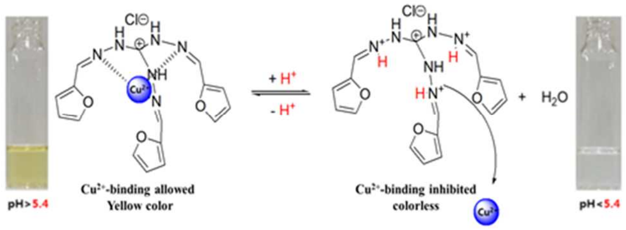
Graphical Abstract for TOC



A highly selective and sensitive colorimetric Cu^{2+}-chemosensor and pH probe for practical use in water soultion has been developed.