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

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<tr>
<th>Journal:</th>
<th><em>Dalton Transactions</em></th>
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<tbody>
<tr>
<td>Manuscript ID:</td>
<td>DT-COM-12-2013-053637.R2</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Communication</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>03-Feb-2014</td>
</tr>
</tbody>
</table>
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A colorimetric “naked-eye” Cu(II) chemosensor and pH indicator in an 100% aqueous solution

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A new, highly selective and sensitive colorimetric chemosensor 1 for detection of Cu²⁺ ions in aqueous solution was developed. Receptor 1 detected Cu²⁺ ions by changing its color from colorless to yellow. Moreover, the Cu²⁺-sensitive compound was used as a colorimetric pH detector based on a color change due to 1-Cu²⁺ complex formation identifiable via naked eye.

Copper, an essential trace element, plays a critical role in many environmental, biological, and chemical systems. However, copper ion can have detrimental effects on humans and animals when overexposure to Cu²⁺-polluted water occurs. Excess exposure to high concentrations of Cu²⁺ has been implicated in the development of Alzheimer’s and Parkinson’s disease. The U.S. Environmental Protection Agency (EPA) has set the safe limit of copper in drinking water at 1.3 ppm (ca. 2 x 10⁻⁶ M). Therefore, a reliable method for determination of trace amounts of Cu²⁺ in biological and environmental samples is essential.

Unlike some analytical techniques, such as atomic absorption spectroscopy, fluorescence techniques, and electrochemical methods, 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. Therefore, the colorimetric methods have attracted considerable attention in detection of toxic metal ions, including Cu²⁺.

In addition, determination of pH is essential in many processes in agriculture, industry, and human health. While the majority of pH chemosensors reported to date are fluorescence intensity-based or fluorescence ratiometry-based with advantages including high sensitivity, ease of use, real-time visualization, and quick response times compared to the traditional glass pH electrodes, pH chemosensors based on color change are relatively rare. 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 Cu²⁺ 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 Cu²⁺ ions.

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 ¹H-NMR, ¹³C-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 (Cu²⁺, Al³⁺, Ca²⁺, Cd²⁺, Co²⁺, Cr³⁺, Fe³⁺, Fe²⁺, Ga³⁺, In³⁺, K⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺ and Zn²⁺). Upon the addition of 6 equiv of each cation, only Cu²⁺ 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 Cu²⁺ ion changed color from colorless to yellow (Fig. 1b), indicating that...
receptor I (30 µM) upon the addition of various metal ions (6 equiv) in buffer-DW solution.

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**Fig. 2.** (a) UV-Vis spectra changes of I (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.

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

(a)

(b)

 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 I and Cu$^{2+}$ (Scheme 2).

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**Fig. 3.** (a) Colorimetric competitive experiment of I (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 I (30 µM) towards Cu$^{2+}$ (6 equiv) in the presence of other metal ions (6 equiv) in buffer-DW solution.

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

(a)

(b)
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 \[ \frac{[\text{Cu}^{2+}]}{[\text{Cu}^{2+}]} = K_{\text{eq}} \times [\text{H}^{+}]^{3} \] (Fig. S9†). The $pK_{a}$ of 1 from the plot was determined to be 6.25 which is in the range of $pK_{a}$ 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.

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 were expected to be greater than 5.4. 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.

Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012001725 and 2012008875) are gratefully acknowledged. We thank Prof. Mi Sook Seo (Ewha Womans University) for ESI-mass running and helpful comments.

Notes and references

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| 31 | Electronic Supplementary Information (ESI) available: [Experimental procedure, Job plots, Benesi-Hildebrand equation plot and detection limit]. See DOI: 10.1039/b000000x/
| 45 | 14 A Job plot analysis showed a 1:1 stoichiometry for the 1-Ni\(^{2+}\) complex (Fig. S5f). UV-vis titration of I toward Ni\(^{2+}\) was carried out at high concentration (120 µM) of I, because there is little absorbance change at its low concentration. See Fig. S6 in supporting information.
A highly selective and sensitive colorimetric Cu²⁺-chemosensor and pH probe for practical use in water solution has been developed.