Supporting information

A Colorimetric Sensor for Cu$^{2+}$ in Aqueous Solution Based on Metal Ion-induced Deprotonation: Deprotonation/protonation Mediated by Cu$^{2+}$-ligand Interactions

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S1. Association Constants and Curve fitting

The following equation was used for the nonlinear least squares analysis to determine the $K_a$:

$$Y = Y_0 + \frac{Y_{\text{lim}} - Y_0}{2} \left\{ 1 + \frac{C_M}{c_L} + \frac{1}{K_M c_L} - \left[ \left( 1 + \frac{C_M}{c_L} + \frac{1}{K_M c_L} \right)^2 - 4 \frac{C_M}{c_L} \right]^{1/2} \right\}$$

$Y$ was the recorded absorbance intensity, $Y_0$ was the start value without the addition of target molecule (metal ions, amino acids), $Y_{\text{lim}}$ was the limiting value (left as a floating parameter), $C_M$ was the target molecule concentration, and $C_L$ was the sensor concentration.1

S2 Partial spectra of NMR, HR-MS

13C 1D experiment
S3. The Job's plot of 3 with Cu$^{2+}$ ion

Figure S3. Job's plots of 3 in Tris buffer (pH6.98) solution, the total concentration of sensors and Cu$^{2+}$ ion is $2 \times 10^{-5}$ M.
S4. ESI-Mass spectra of 3/Cu$^{2+}$ complex

Fig. S4. ES$^+$ mass spectra of 3 ($1 \times 10^{-5}$ M) in the presence of Cu$^{2+}$ in ethanol/water (2/8) solution (cautions: buffer salts could not be used).

[Image of mass spectra diagram]

[3-H+Cu]$^+$ and isotopic peak

[3+H]$^+$

S5. The UV/vis responses of 3 in a diluted solution

Fig. S5. Cu$^{2+}$-titration induced the absorption changes of sensor 3 ($5.0 \times 10^{-6}$ M) in 10 mM Tris buffer (pH 6.98) solution. Inset showed the changes at 540 nm as a function of Cu$^{2+}$ concentration at $10^{-7}$ M.

[Image of UV/vis spectrum diagram]

Cu$^{2+}$/10$^{-6}$ M
S6. Curve fitting and Binding constant

Curve fitting to determinate the association constant according the equation 1 in S1. In order to avoid the $K_S C_L >> 1$, the dates acquired in diluted solution ($5 \times 10^{-6}$ M).

Curve fitting to determinate the association constant according the equation 1 in S1. A solution of $2 (2 \times 10^{-5}$ M) was used to determine the association constant ($K_a$).

S7. The UV/vis responses of 3 to different cations
Fig.S7a. UV-Vis absorption spectra of 3 (2 × 10⁻⁵ M) in buffer (10 mM Tris, pH 6.98) solution upon addition of different concentrations of various metal ions. Note: the UV/vis (300 nm to 400 nm) changes-induced by FeCl₃ came from the absorption itself of FeCl₃.
Figure S7b. The UV changes of 3 (2 × 10⁻⁵ M) in the presence of Co²⁺ (0 to 10 equiv) in 10 mM Tris (pH 6.98) buffer solution. The result indicated that Cu²⁺ could induce the absorption band red shift without interference from Co²⁺, but the UV intensity at 540 nm decreased 40% compared to the intensity in the absence Co²⁺.

References and notes