Electronic Supplementary Information for Dalton Transactions

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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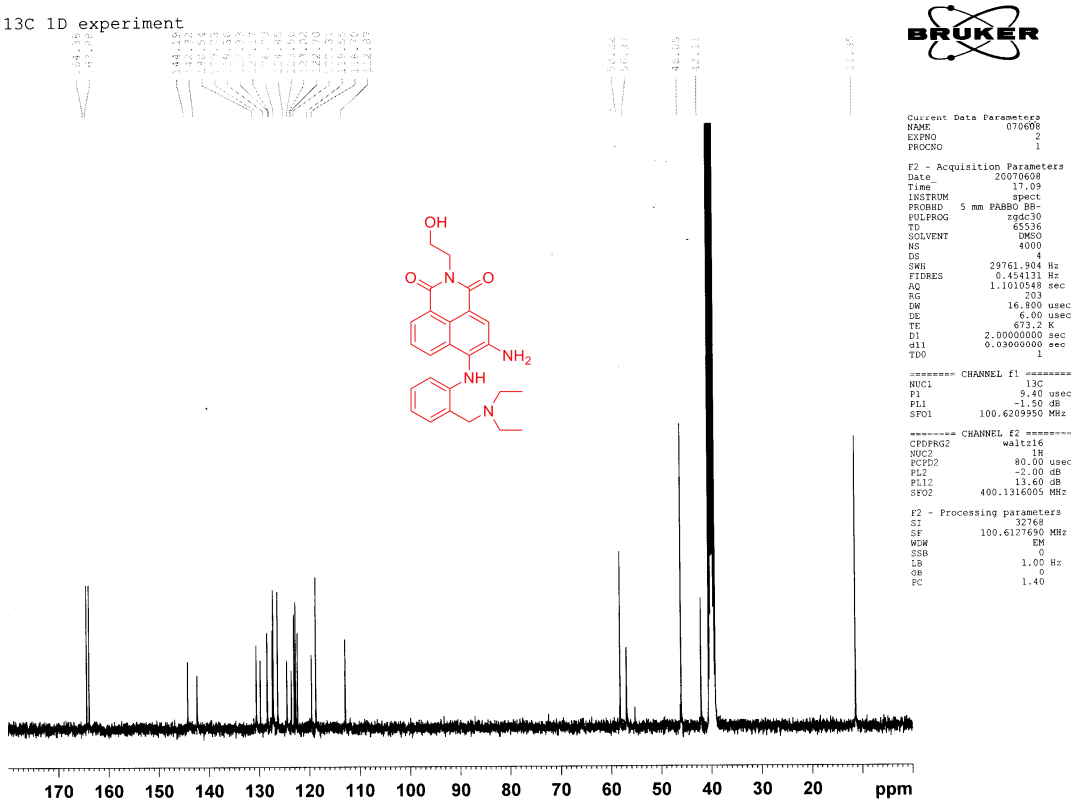
S1. Association Constants and Curve fitting

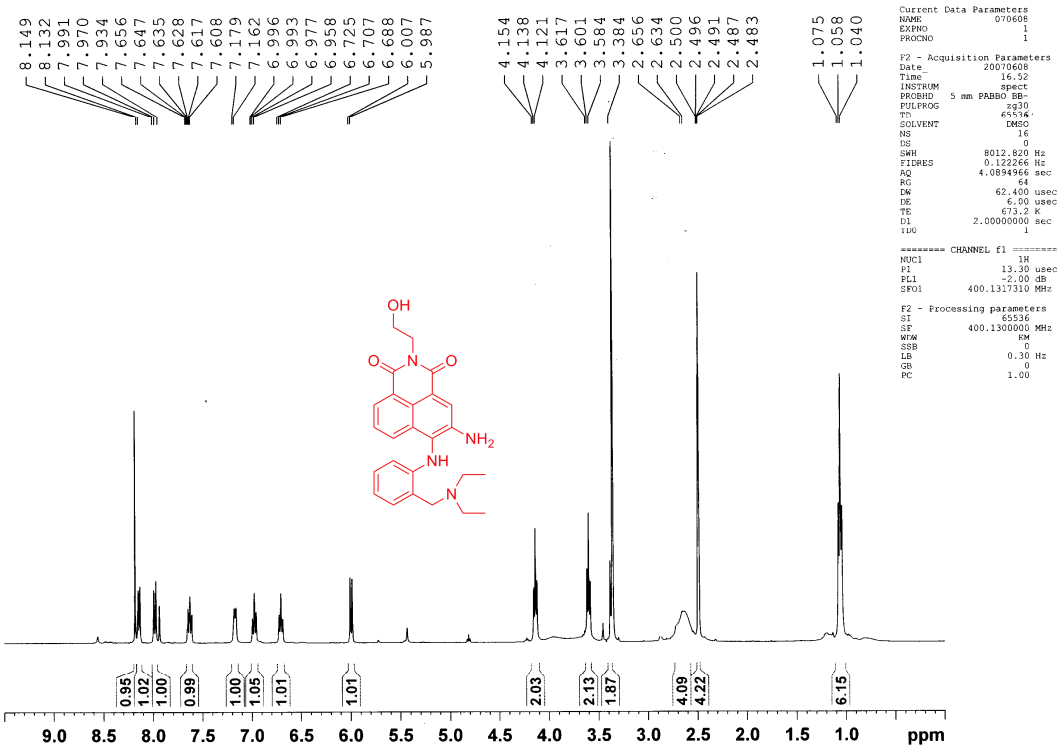
The following equation was used for the nonlinear least squares analysis to determine the Ka:

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

Y was the recorded absorbance intensity, Y_0 was the start value without the addition of target molecule (metal ions, amino acids), Y_{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





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DE 6.00 usec
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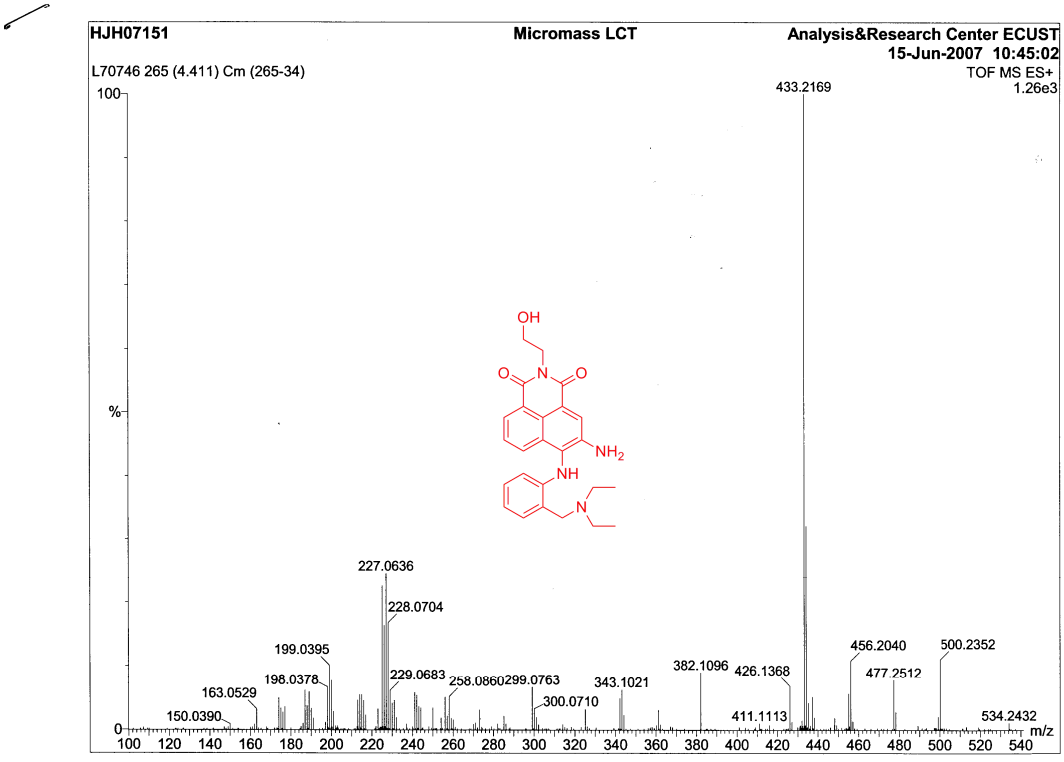
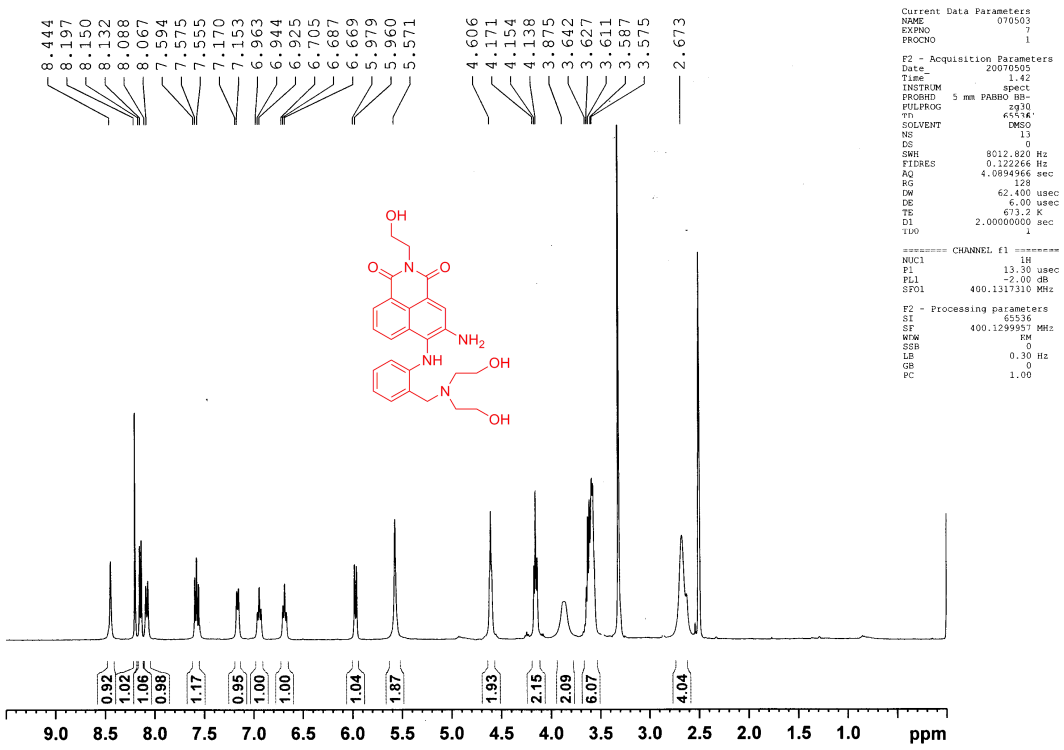
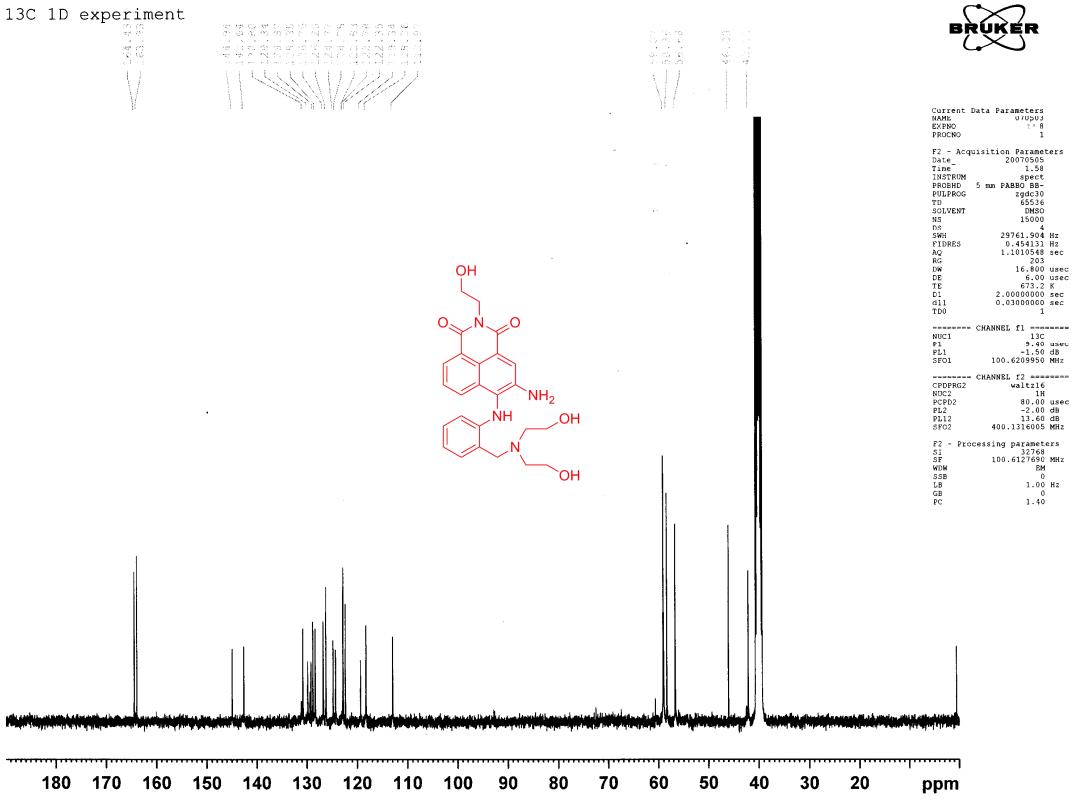
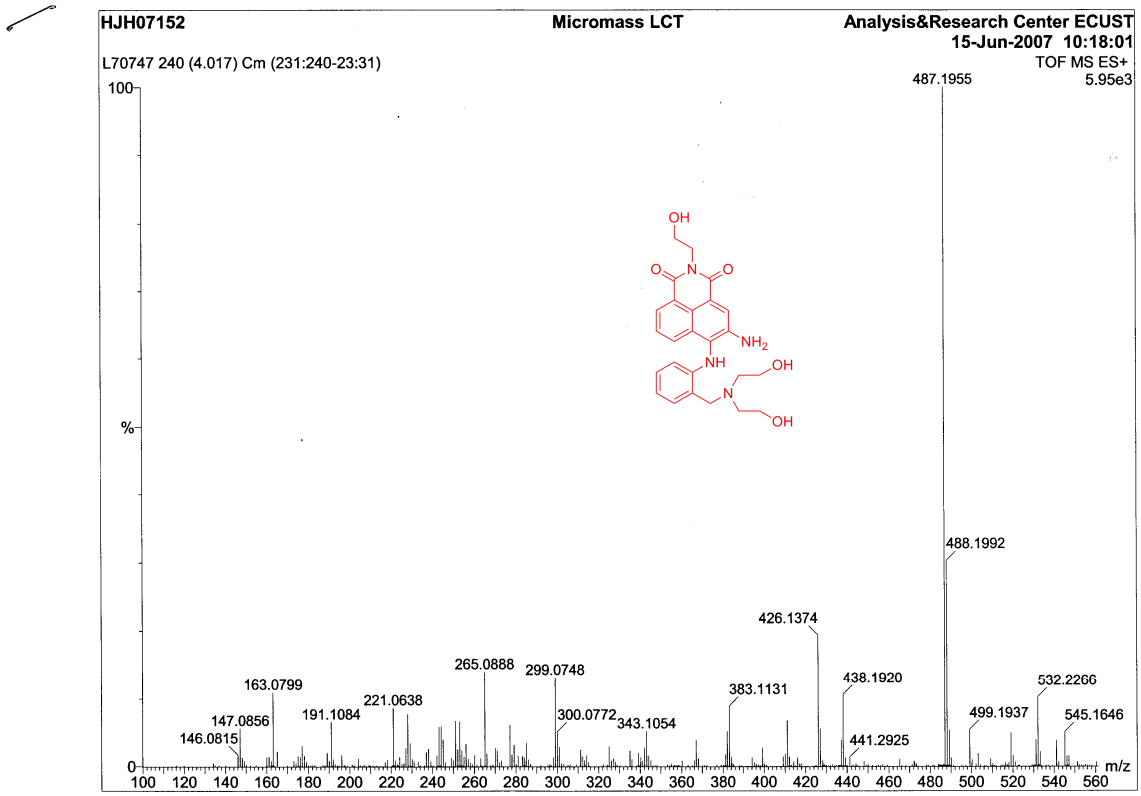








S3. The Job's plot of 3 with Cu^{2+} ion

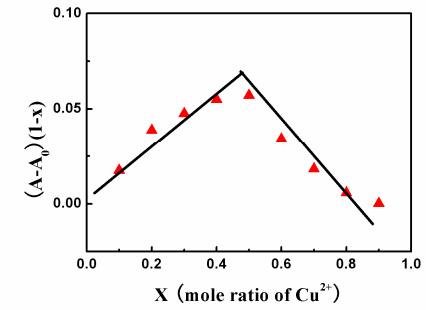


Figure S3. Job's plots of **3** in Tris buffer (pH6.98) solution, the total concentration of sensors and Cu^{2+} ion is 2×10^{-5} M.

S4. ESI-Mass spectra of 3/Cu^{2+} complex

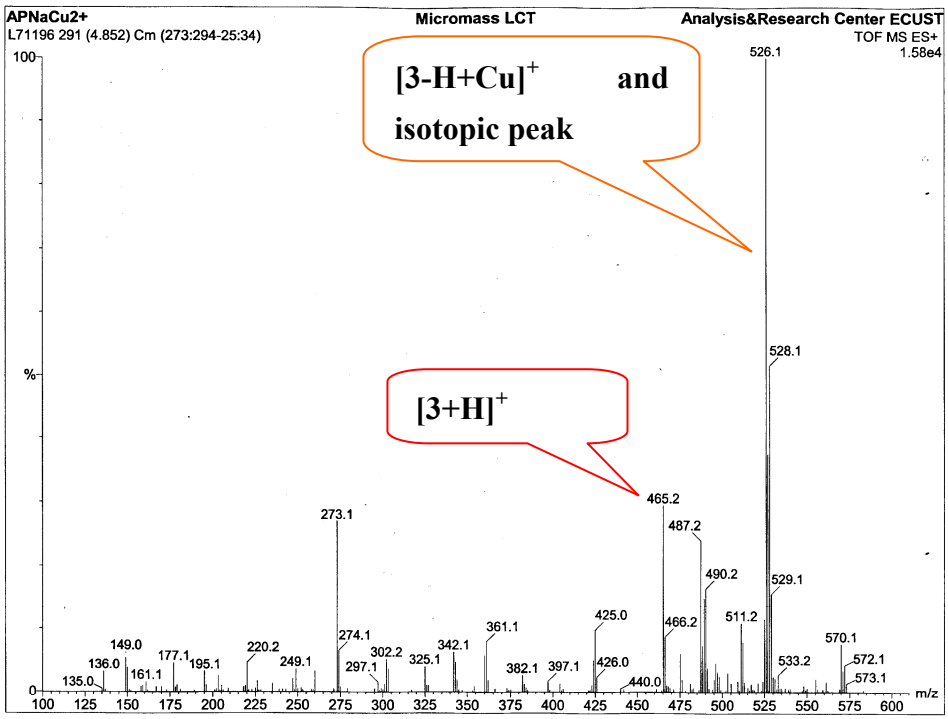


Fig. S4. ES+ mass spectra of **3** (1×10^{-5} M) in the presence of Cu^{2+} in ethanol/water (2/8) solution (cautions: buffer salts could not be used).

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

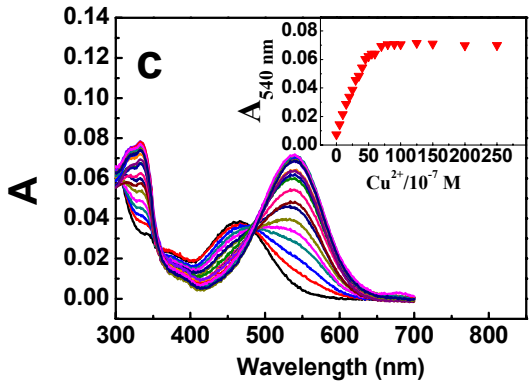
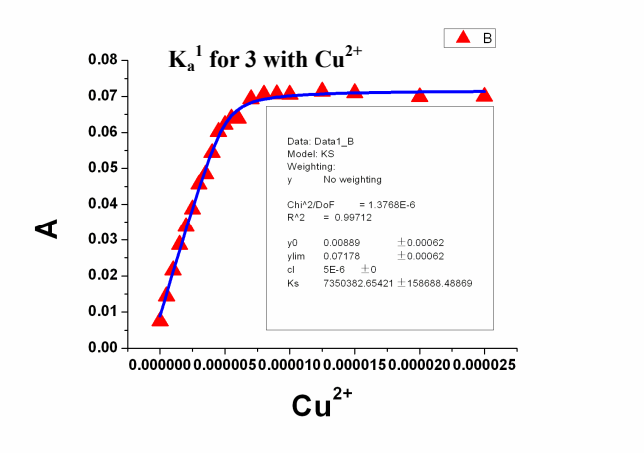
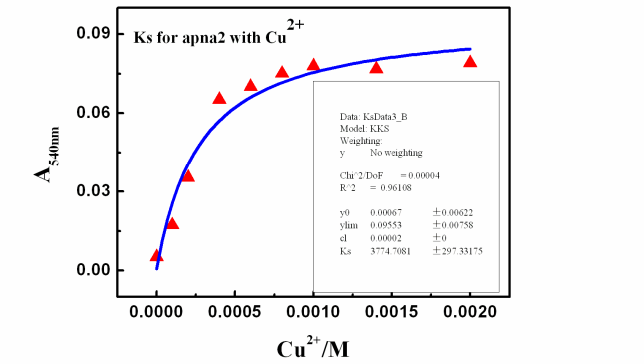


Fig. S5. Cu^{2+}-titration induced the absorption changes of sensor **3** (5.0×10^{-6} M) in 10 mM Tris buffer (pH 6.98) solution. Inset showed the changes at 540 nm as a function of Cu^{2+} concentration at 10^{-7} M

S6. Curve fitting and Binding constant

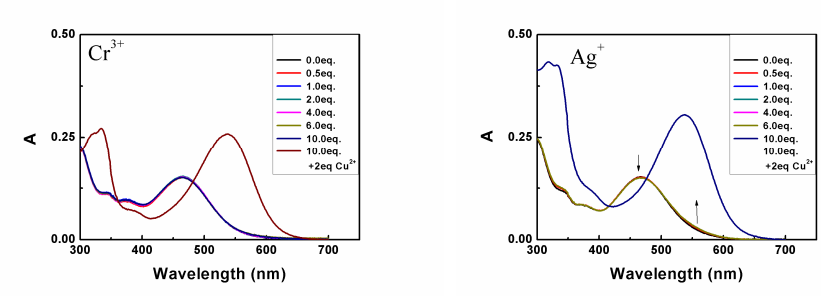


Curve fitting to determinate the association constant according the equation 1 in S1. In order to avoid the $KsC_L >> 1$, the dates acquired in diluted solution (5×10^{-6} M).



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

S7. The UV/vis responses of 3 to different cations



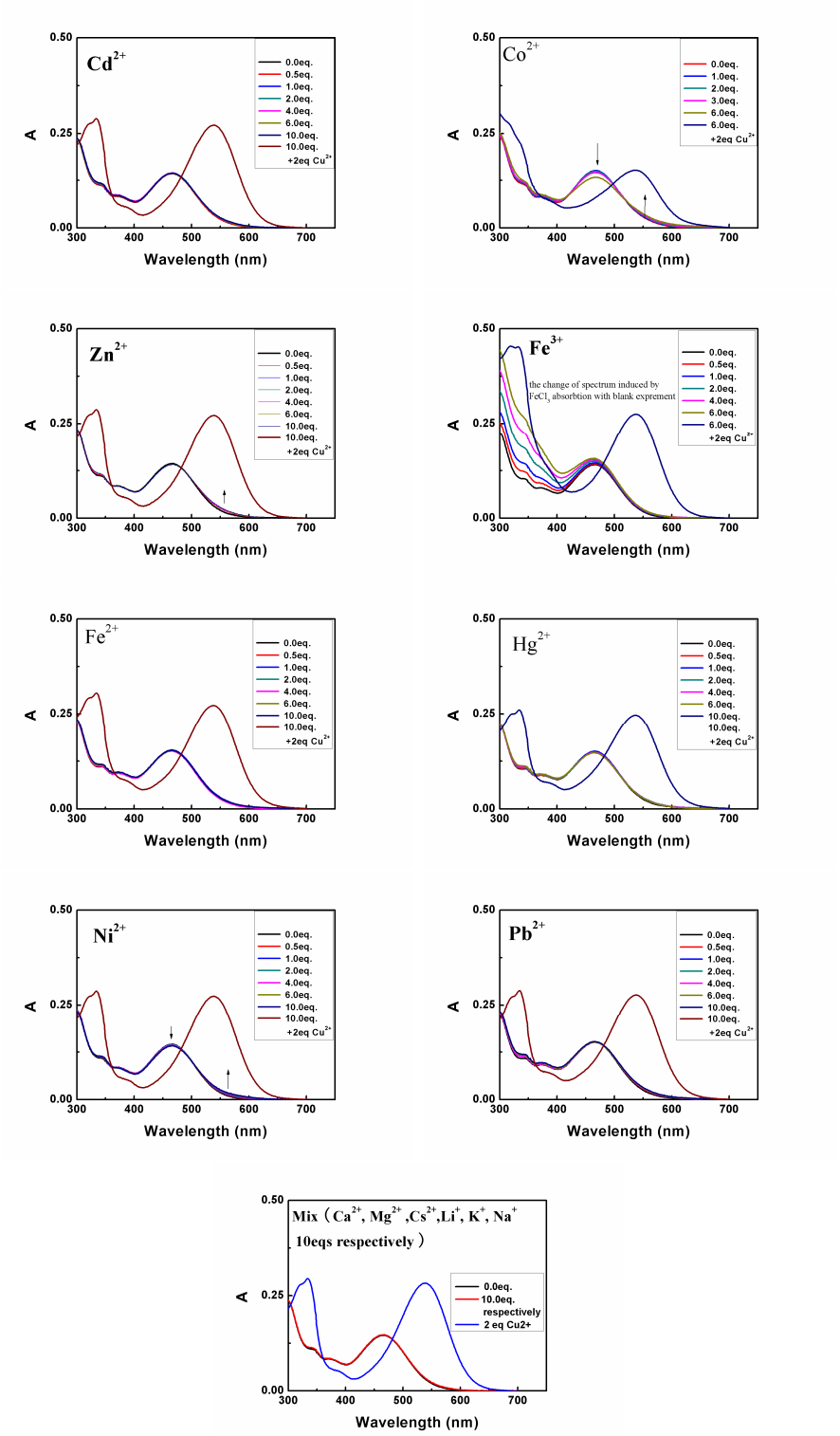


Fig.S7a. UV-Vis absorption spectra of **3** (2×10^{-5} M) in buffer (10 mM Tris, pH6.98) solution upon addition of different concentrations of various metal ions. Note: the UV/vis (300 nm to 400 nm) changes-induced by $FeCl_3$ came from the absorption itself of $FeCl_3$.

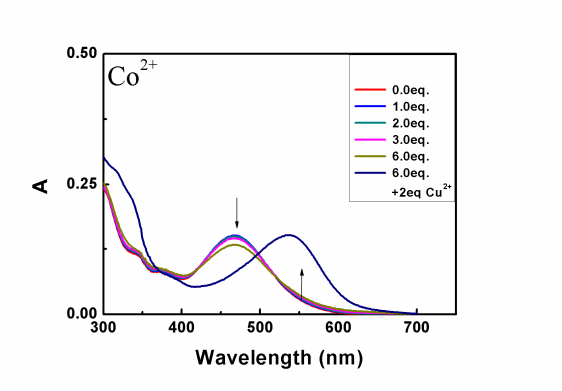


Figure S7b. The UV changes of **3** (2×10^{-5} M) in the presence of Co^{2+} (0 to 10 equiv) in 10 mM Tris (pH6.98) buffer solution. The result indicated that Cu^{2+} could induce the absorption band red shift without interference from Co^{2+}, but the UV intensity at 540 nm decreased 40% compared to the intensity in the absence Co^{2+}.

References and notes

1. B. Valeur, *Molecular Fluorescence. Principles and Applications*; Wiley-VCH: Weinheim, 2002