Supporting Information

A new Schiff-based chemosensor for selective detection of Cu$^{2+}$ and Co$^{2+}$ and its copper complex for colorimetric sensing of S$^{2-}$ in aqueous solution

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Fig. S1 $^1$H NMR spectrum of 1.
Fig. S2 $^{13}$C NMR spectrum of 1.
Fig. S3 Job’s plot for the binding of 1 with Cu²⁺. Absorbance at 460 nm was plotted as a function of the molar ratio of [Cu²⁺]/([1]+[Cu²⁺]). The total concentration of Cu²⁺ ions with receptor 1 was 5.0 x 10⁻⁵ M.
**Fig. S4** Li’s plot (at 460 nm) of 1 (10 μM), assuming 2:1 stoichiometry for association between 1 and Cu²⁺.
Determination of the detection limit of 1 (10 μM) for Cu$^{2+}$ based on change of absorbance at 460 nm.
Fig. S6 (a) Absorption spectral changes of 1 (10 μM) upon addition of Cu$^{2+}$ (1 equiv) in the absence and presence of 1 equiv of various metal ions in buffer/DMF solution (4:1; v/v, 10 mM bis-tris, pH 7.0). (b) The color changes of 1 (10 μM) upon addition of Cu$^{2+}$ (1 equiv) in the absence and presence of 1 equiv of various metal ions in buffer/DMF solution (4:1; v/v, 10 mM bis-tris, pH 7.0).
**Fig. S7** UV-vis absorbance (at 460 nm) of 1 and Cu^{2+}-2·1 complex at different pH values (2-12).
Fig. S8 Absorbance (at 460 nm) of 1 as a function of Cu(II) concentration ([I] = 10 μmol/L and [Cu(II)] = 0.0-2.4 μmol/L). Conditions: all samples were conducted in bis-tris buffer/DMF (4:1; v/v).
Fig. S9 Job’s plot for the binding of 1 with Cu$^{2+}$. Absorbance at 460 nm was plotted as a function of the molar ratio of $[\text{Co}^{2+}]/([1]+[\text{Co}^{2+}])$. The total concentration of Co$^{2+}$ ions with receptor 1 was $1.0 \times 10^{-5}$ M.
Fig. S10 Absorption spectra of 1 (10 μM), Co$^{2+}$-2·1 complex under the degassed and exposure-to-air conditions, and Co$^{2+}$-2·1 complex under aerobic conditions, respectively.
**Fig. S11** Li’s plot (at 460 nm) of 1 (10 μM), assuming 2:1 stoichiometry for association between 1 and Co²⁺.
Fig. S12 Determination of the detection limit of 1 (10 μM) for Co$^{2+}$ based on change of absorbance at 460 nm.
Fig. S13 (a) Absorption spectral changes of I (10 μM) upon addition of Co$^{2+}$ (1.8 equiv) in the absence and presence of 1.8 equiv of various metal ions in buffer/DMF solution (4:1; v/v, 10 mM bis-tris, pH 7.0). (b) The color changes of I (10 μM) upon addition of Co$^{2+}$ (1.8 equiv) in the absence and presence of 1.8 equiv of various metal ions in buffer/DMF solution (4:1; v/v, 10 mM bis-tris, pH 7.0).
Fig. S14 UV-vis absorbance (at 460 nm) of 1 and Co$^{2+}$-2·1 complex at different pH values (2-12).
Fig. S15 (a) The theoretical excitation energies and the experimental UV-vis spectrum of 1. (b) The major electronic transition energies and molecular orbital contributions for 1 (H = HOMO and L = LUMO).

<table>
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<th>Excited state 1</th>
<th>Wavelength (nm)</th>
<th>Percent (%)</th>
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<td>H → L</td>
<td>355.03</td>
<td>97</td>
<td>π → π*</td>
<td>0.8072</td>
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Fig. S16 (a) The theoretical excitation energies and the experimental UV-vis spectrum of Cu$^{2+}$-2·1. (b) The major electronic transition energies and molecular orbital contributions for Cu$^{2+}$-2·1 (H = HOMO and L = LUMO).
Fig. S17 Molecular orbital diagrams and excitation energies of 1 and Cu$^{2+}$-2·1.
**Fig. S18** (a) The theoretical excitation energies and the experimental UV-vis spectrum of Co$^{3+}$-2·1. (b) The major electronic transition energies and molecular orbital contributions for Co$^{3+}$-2·1 (H = HOMO and L = LUMO).
Fig. S19 Molecular orbital diagrams and excitation energies of 1 and Co$^{3+}$-2·1.
**Fig. S20** UV-vis spectra of 1 (10 μM), Cu$^{2+}$·2·1 (10 μM), and Cu$^{2+}$·2·1 (10 μM) + S$^{2-}$ (1.7 equiv) in buffer/DMF (4:1; v/v, 10 mM bis-tris, pH = 7.0).
Fig. S21 Positive-ion electrospray ionization mass spectrum of Cu$^{2+}$-2·1 (0.1 mM) upon addition of 1 equiv of S$^{2-}$. 
Fig. S22 Benesi-Hildebrand plot (at 460 nm) of Cu$^{2+}$-2·1 (10 μM), assuming 1:1 stoichiometry for association between Cu$^{2+}$-2·1 and S$^{2-}$. 

$y = 0.0003x + 5.221$

$R^2 = 0.9987$

$K = 1.7 \times 10^4$
**Fig. S23** Determination of the detection limit of Cu$^{2+}$-2·1 (10 μM) for S$^{2-}$ based on change of absorbance at 460 nm.
Fig. S24 UV-vis absorbance (at 460 nm) of Cu$^{2+}$-2·1 and Cu$^{2+}$-2·1 + S$^{2-}$ at different pH values (2-12).