Supporting Information

A colorimetric chemosensor for the sequential detection of copper ion and amino acids (cysteine and histidine) in aqueous solution

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Table S1. Determination of Cu(II) in water samples

Sample	Cu(II) added (μmol/L)	Cu(III) found (μmol/L)	Recovery (%)	R.S.D. (n = 3) (%)
Artificial polluted solution[a]	0.00	0.00	-	-
	10.00	9.76	97.6	0.3

[a] Prepared by deionized water, 6.00 μmol/L Zn(II), 10 μmol/L Cd(II), Pb(II), Na(I), K(I), Ca(II), Mg(II). Conditions: [**1**] = 15 μmol/L in 10 mM DMF-bis-tris buffer solution (1:5, pH 7.0).

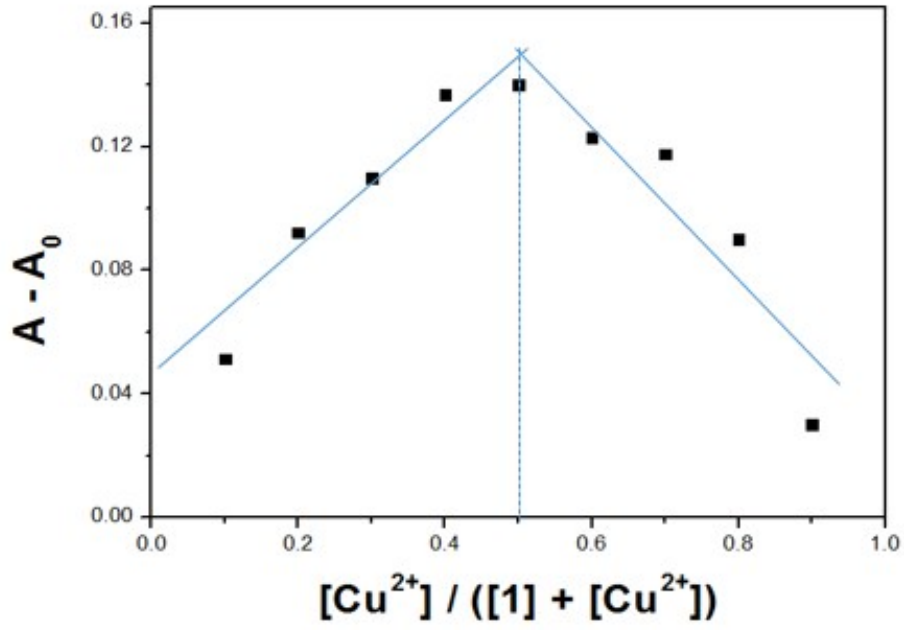


Fig. S1 Job plot for the binding of **1** with Cu^{2+}. Absorbance at 345 nm was plotted as a function of the molar ratio $[Cu^{2+}]$ / ([**1**] + $[Cu^{2+}]$). The total concentrations of copper ions with **1** were (40 μM).

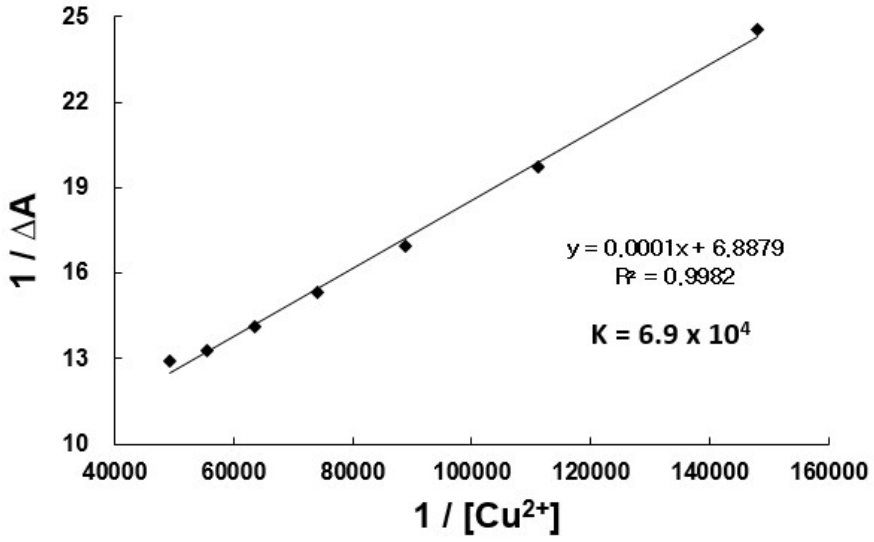


Fig. S2 Benesi-Hildebrand equation plot (absorbance at 525 nm) of **1** (15 μM), assuming 1:1 stoichiometry for association between **1** and Cu^{2+}.

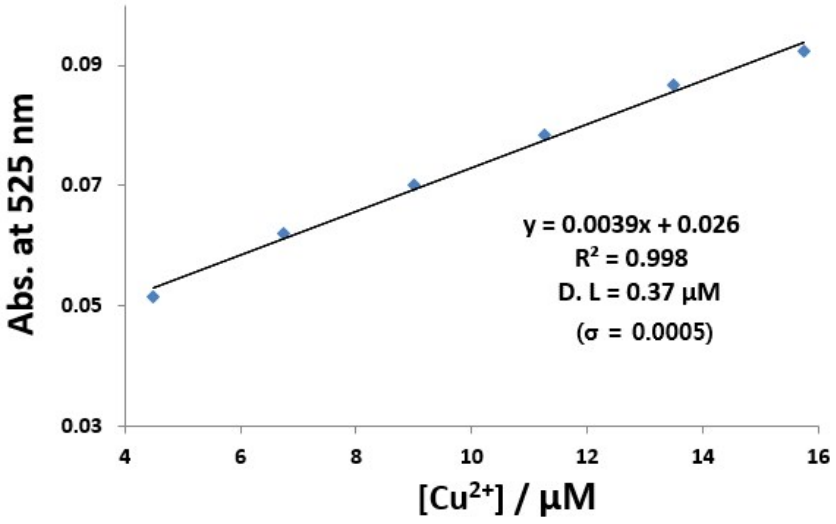
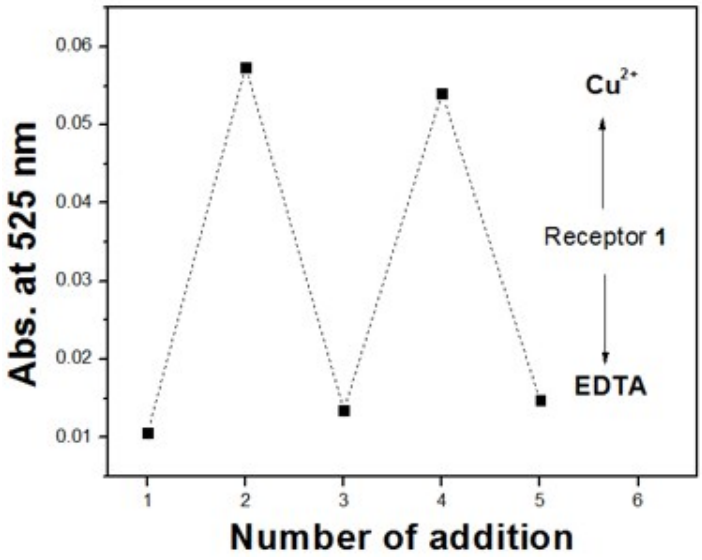


Fig. S3 Determination of the detection limit based on change in the ratio (absorbance at 525 nm) of **1** (15 μM) with Cu^{2+}.

(a)



(b)

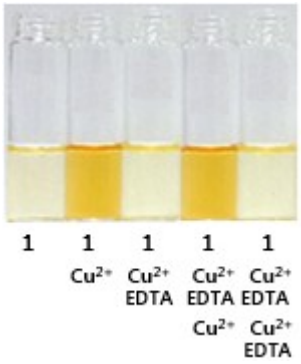


Fig. S4 (a) UV-vis spectral changes of **1** (15 μM) after the sequential addition of Cu^{2+} and EDTA in DMF-buffer solution (1:5, v/v, 10 mM, bis-tris, pH 7.0). (b) The color changes of **1** (15 μM) after the sequential addition of Cu^{2+} and EDTA.

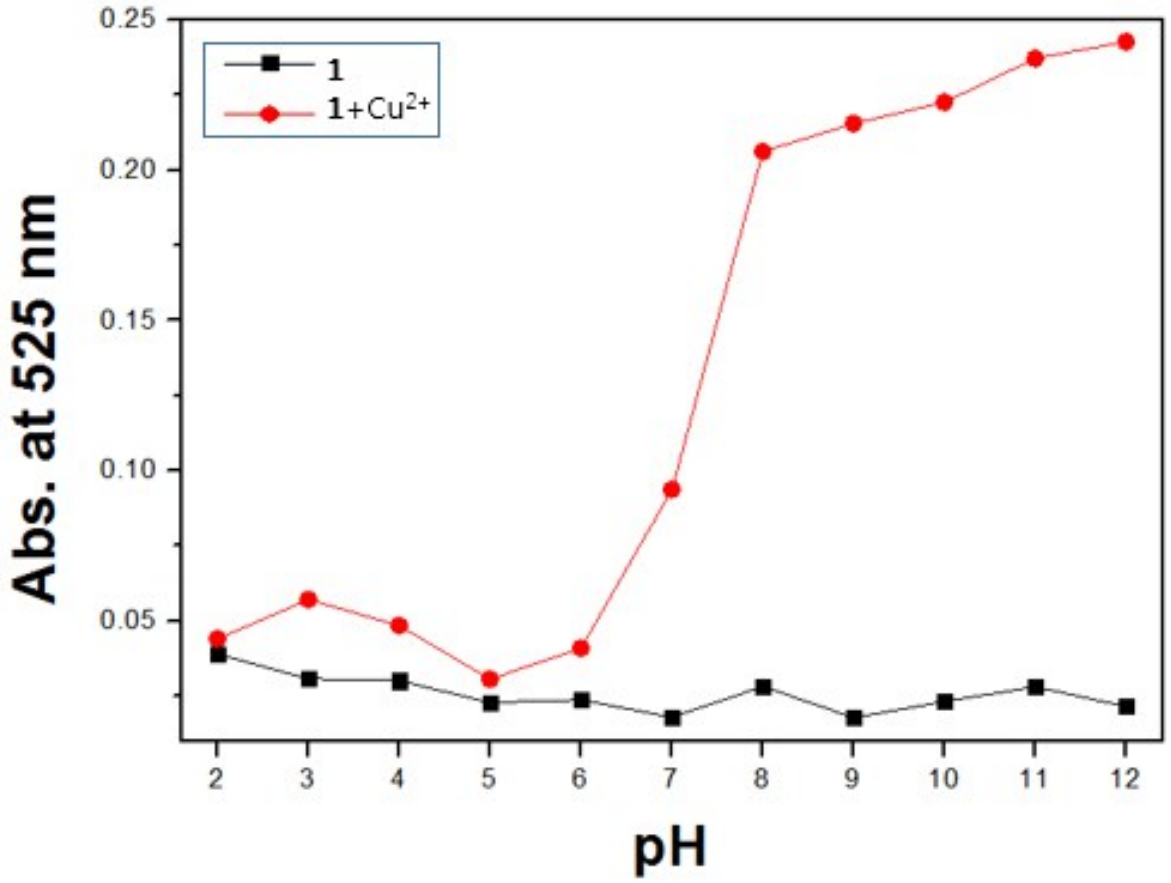


Fig. S5 UV-vis spectra of **1**-Cu^{2+} complex at various pH range (2-12) in DMF-buffer solution (1:5, v/v, 10 mM, bis-tris, pH 7.0).

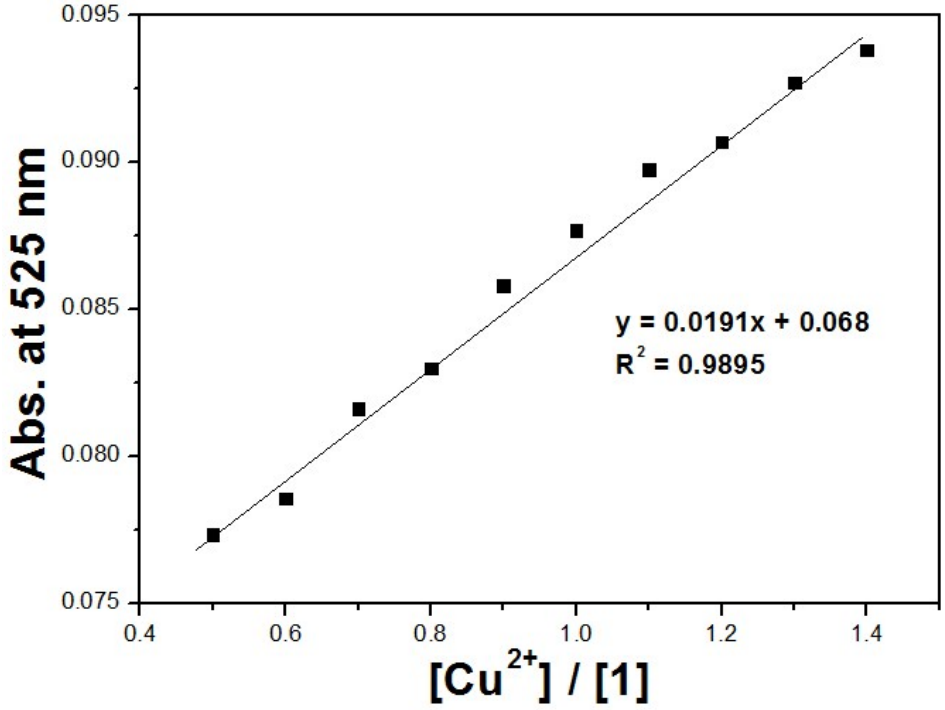
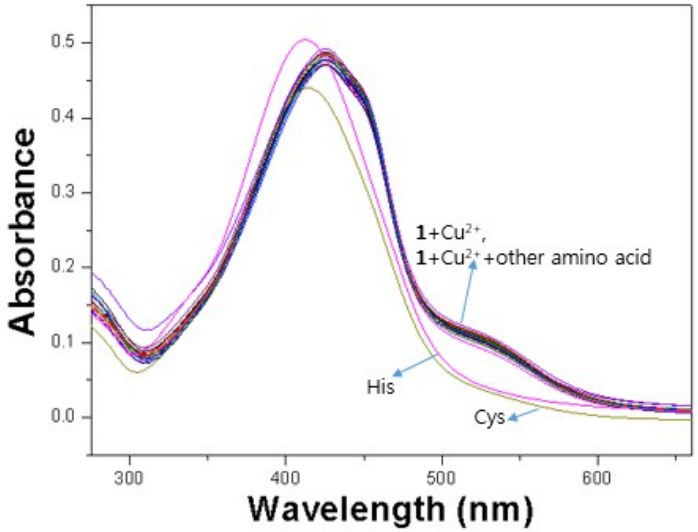


Fig. S6 UV-vis absorbance of **1** as a function of Cu(II) concentration. [**1**] = 15 μM and [Cu^{2+}] = 7.5-21.0 μM in DMF-buffer solution (1:5, v/v, 10 mM, bis-tris, pH 7.0).

(a)



(b)

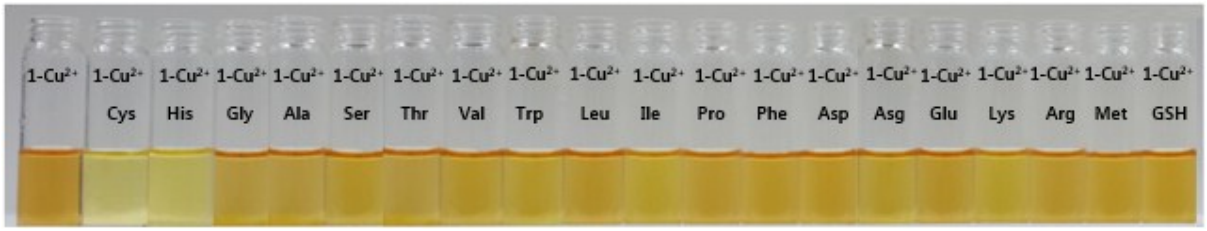
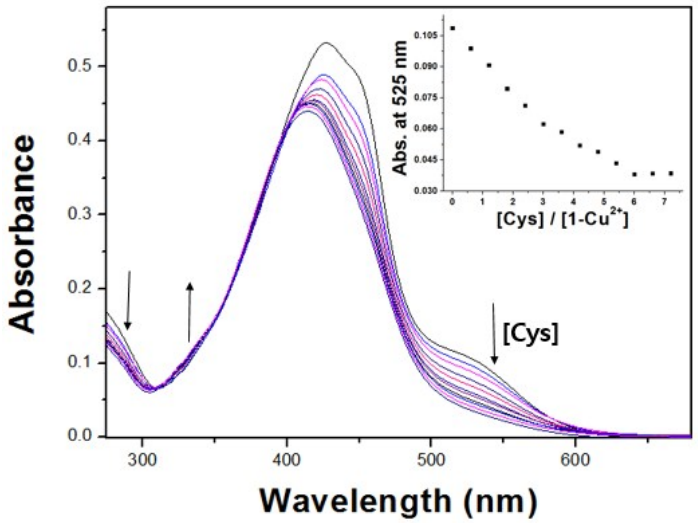


Fig. S7 (a) UV-vis spectra of **1**-Cu^{2+} complex (15 μM) upon addition of 7.5 equiv of various amino acids (Cys, His, Gly, Ala, Ser, Thr, Val, Trp, Leu, Ile, Pro, Phe, Asp, Arg, Glu, Lys, Arg, Met and GSH). (b) Color changes observed for **1**-Cu^{2+} complex (30 μM) upon the addition of Cys, His, Gly, Ala, Ser, Thr, Val, Trp, Leu, Ile, Pro, Phe, Asp, Arg, Glu, Lys, Arg, Met and GSH (7.5 equiv).

(a)



(b)

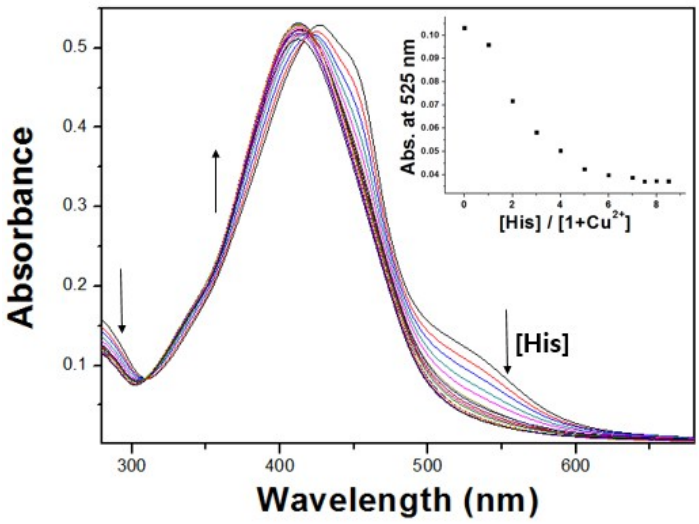
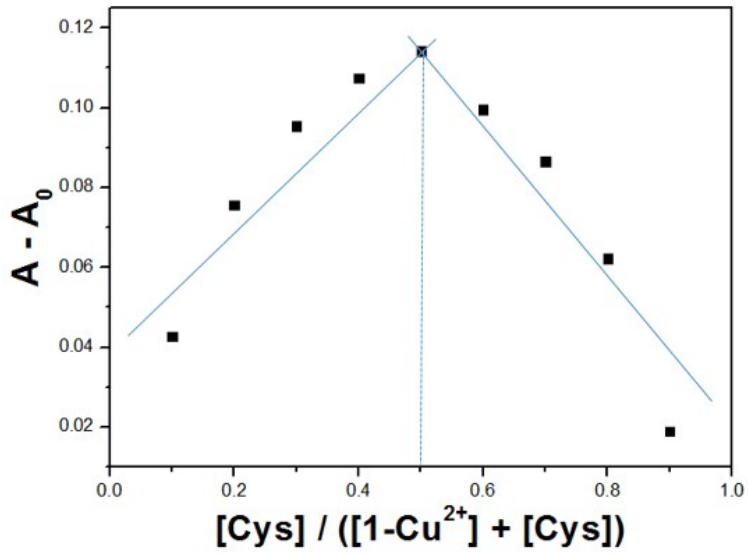


Fig. S8 (a) UV-vis titration of **1**-Cu^{2+} (15 μM) with Cys (0-6 equiv) in DMF-buffer solution (1:5, v/v, 10 mM, bis-tris, pH 7.0). Inset: Absorption titration profile of **1**-Cu^{2+} with Cys at 525 nm. (b) UV-vis titration of **1**-Cu^{2+} (15 μM) with His (0-7.5 equiv) in DMF-buffer solution (1:5, v/v, 10 mM, bis-tris, pH 7.0). Inset: Absorption titration profile of **1**-Cu^{2+} with His at 525 nm.

(a)



(b)

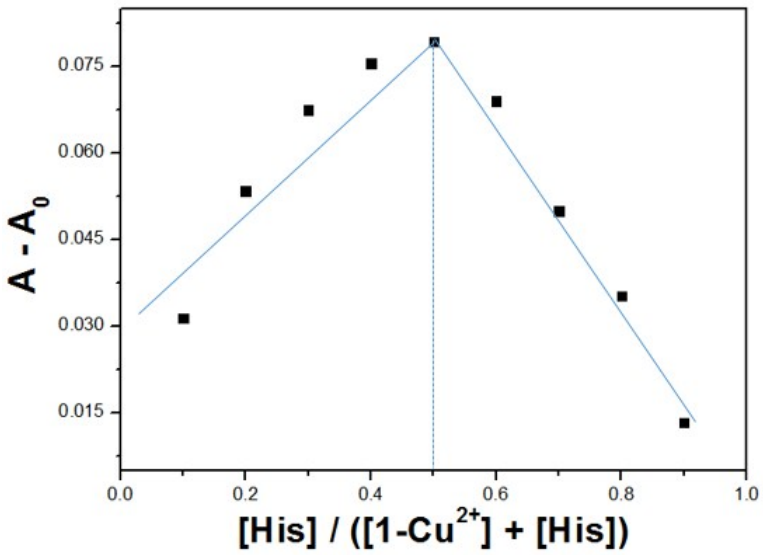
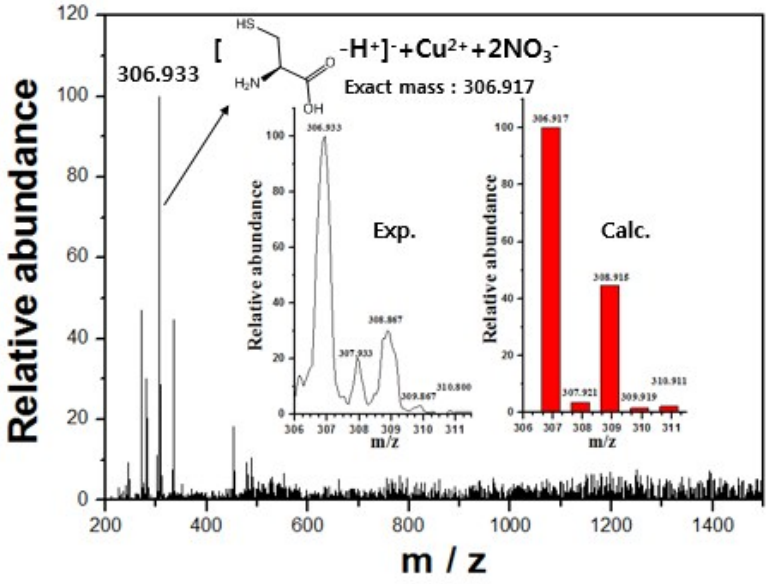


Fig. S9 (a) Job plot for the reaction of **1**-Cu^{2+} with Cys. Absorbance at 525 nm was plotted as a function of the molar ratio [Cys] / ([**1**-Cu^{2+}] + [Cys]). The total concentrations of Cys with **1**-Cu^{2+} complex were 40 μM. (b) Job plot for the reaction of **1**-Cu^{2+} with His. Absorbance at 525 nm was plotted as a function of the molar ratio [His] / ([**1**-Cu^{2+}] + [His]). The total concentrations of His with **1**-Cu^{2+} were 40 μM.

(a)



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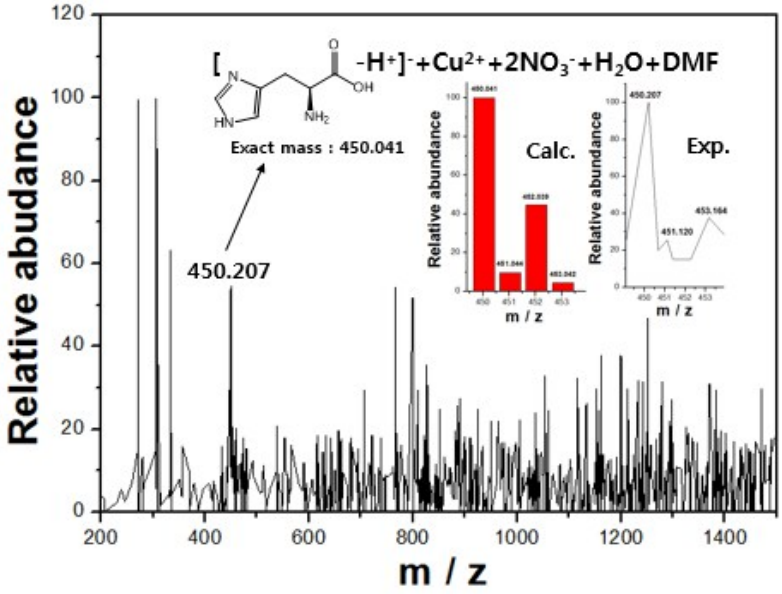
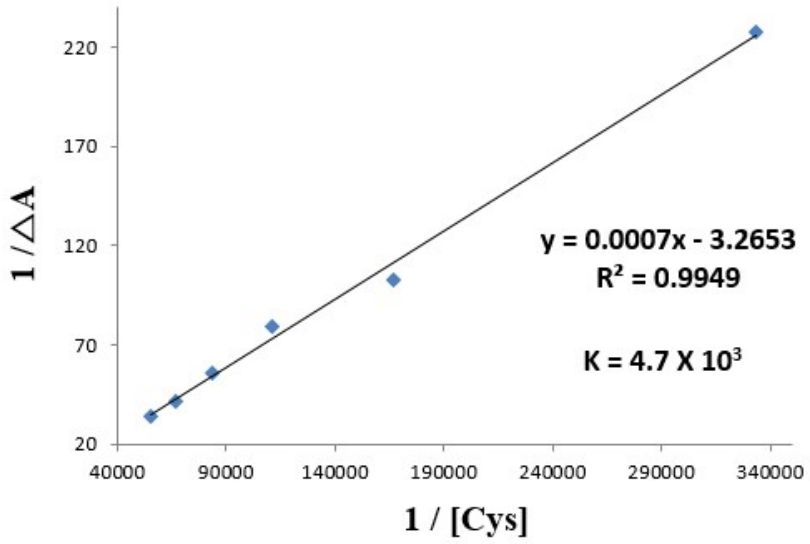


Fig. S10 (a) Negative-ion ESI-mass spectrum of **1**-Cu^{2+} complex (100 μM) upon addition of 1 equiv of Cys. (b) Negative-ion ESI-mass spectrum of **1**-Cu^{2+} complex (100 μM) upon addition of 1 equiv of His.

(a)



(b)

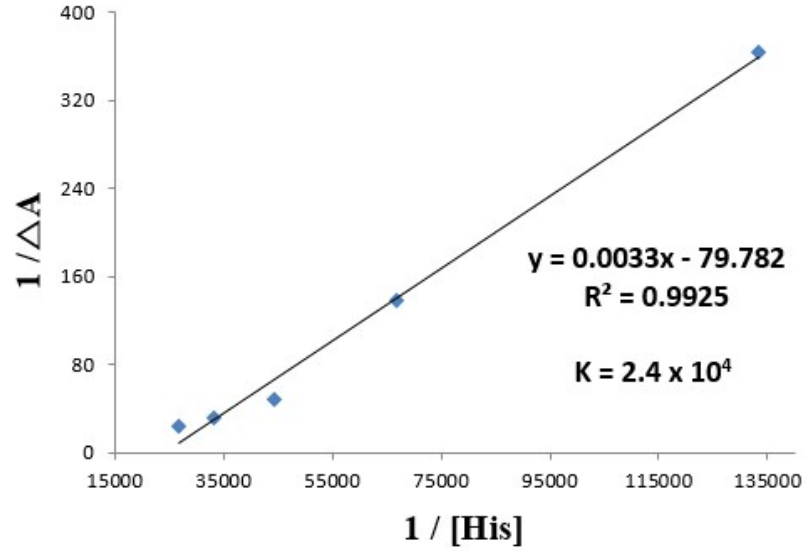
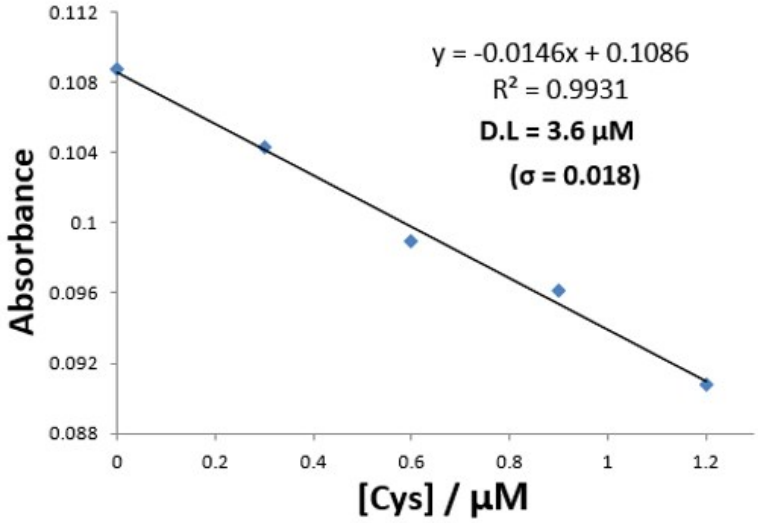


Fig. S11 (a) Benesi-Hildebrand equation plot (absorbance at 525 nm) of **1**-Cu^{2+}, assuming 1:1 stoichiometry for interaction between **1**-Cu^{2+} with Cys. (b) Benesi-Hildebrand equation plot (absorbance at 525 nm) of **1**-Cu^{2+}, assuming 1:1 stoichiometry for interaction between **1**-Cu^{2+} with His.

(a)



(b)

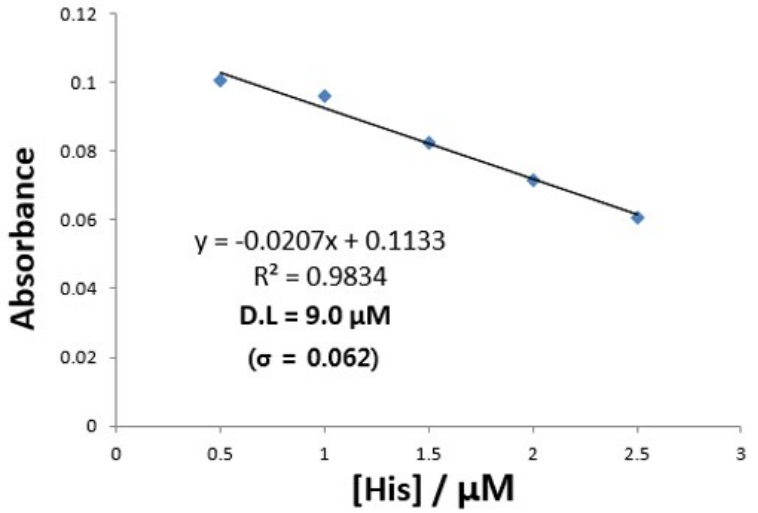
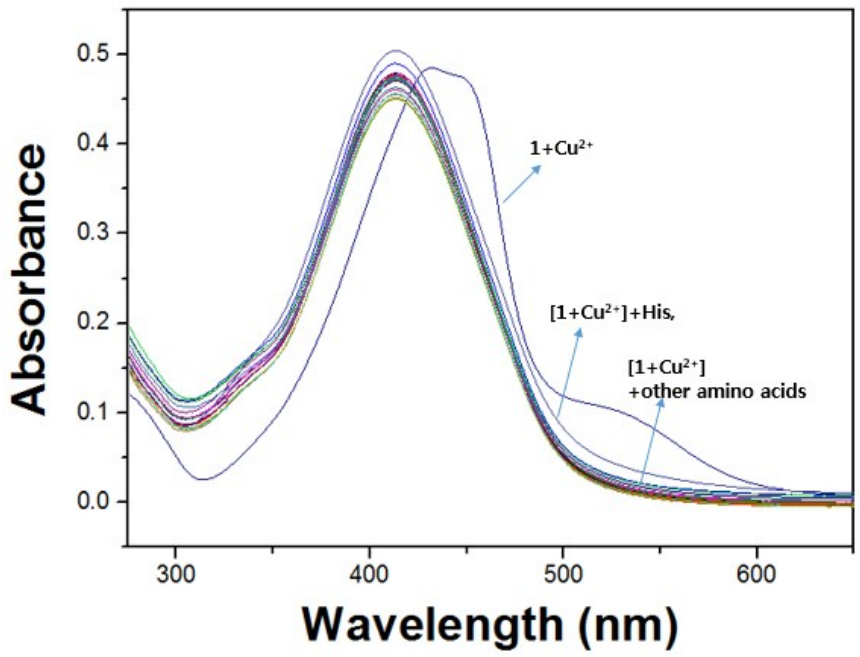


Fig. S12 (a) Determination of the detection limit based on change in the ratio (absorbance at 525 nm) of **1**-Cu^{2+} (15 µM) with Cys. (b) Determination of the detection limit based on change in the ratio (absorbance at 525 nm) of **1**-Cu^{2+} (15 µM) with His.

(a)



(b)

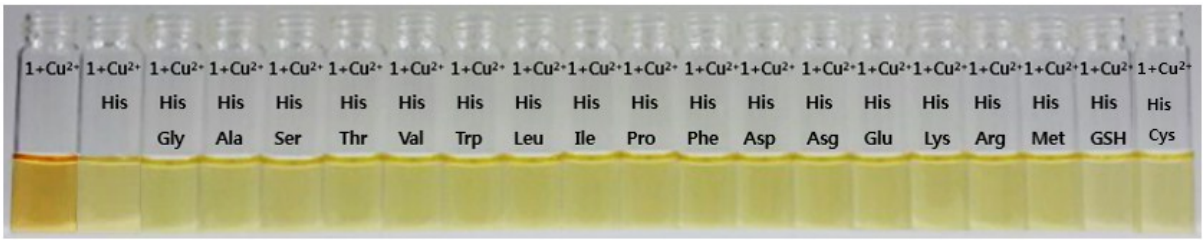
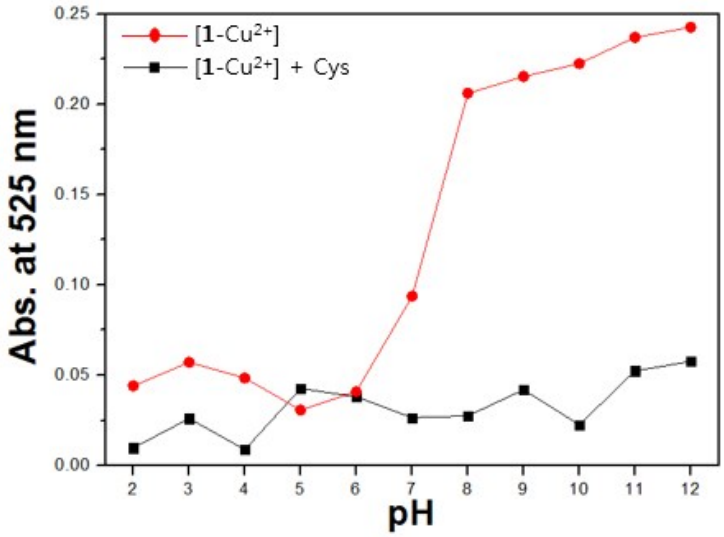


Fig. S13 (a) Competitive selectivity of **1**-Cu^{2+} complex (15 μM) toward His (7.5 equiv) in the presence of other amino acids (7.5 equiv). (b) Color changes of **1**-Cu^{2+} complex (30 μM) in the presence of His (7.5 equiv) and other amino acids (7.5 equiv).

(a)



(b)

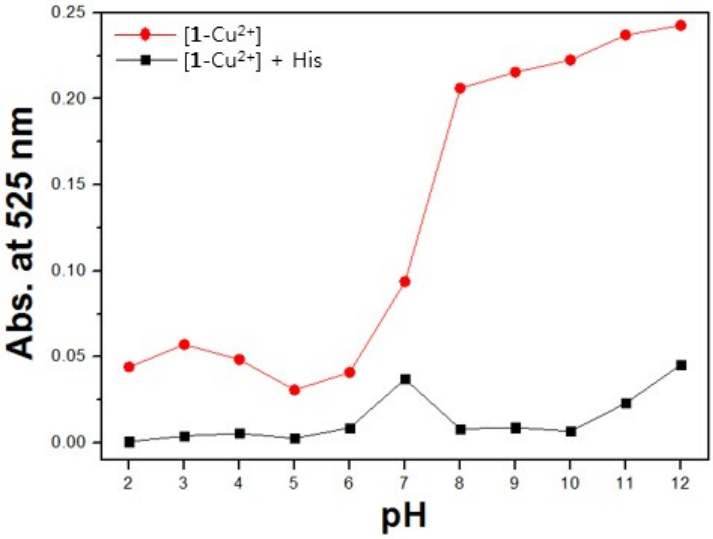


Fig. S14 (a) UV-vis absorbance of **1**-Cu^{2+} complex with Cys at various pH range (2-12) in DMF-buffer solution (1:5, v/v, 10 mM, bis-tris, pH 7.0). (b) UV-vis absorbance of **1**-Cu^{2+} complex with His at various pH range (2-12) in DMF-buffer solution (1:5, v/v, 10 mM, bis-tris, pH 7.0).