

Fig. 1S† Concentration distribution of the complexes formed in Cu(II)-to-peptide molar ratio 1:1 as a function of pH. [Cu(II)]=0.001M. (a) Cu(II)-H1A/H9A system (b) Cu(II)-H1A/H6A system

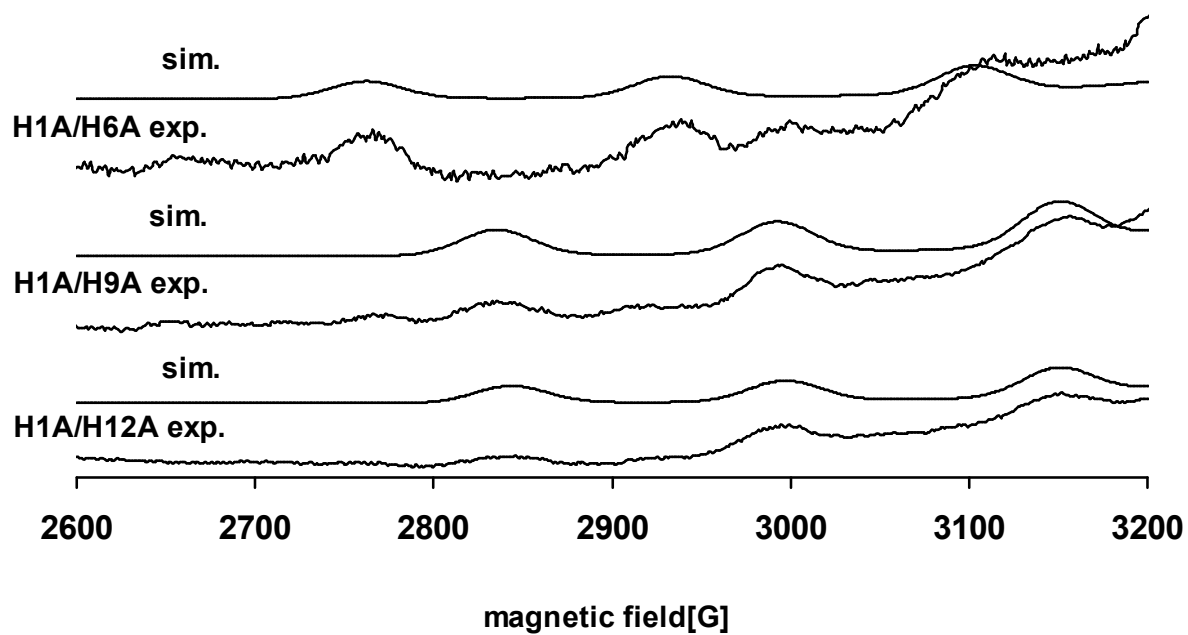


Fig. 2S† Frozen solution EPR spectra (simulated and experimental) of the CuL complexes for the Cu(II)-H1A/H12A (pH 5.5), Cu(II)-H1A/H9A (pH 5.3) and Cu(II)-H1A/H6A (pH 5.6). Metal-to-ligand molar ratio 1:1.

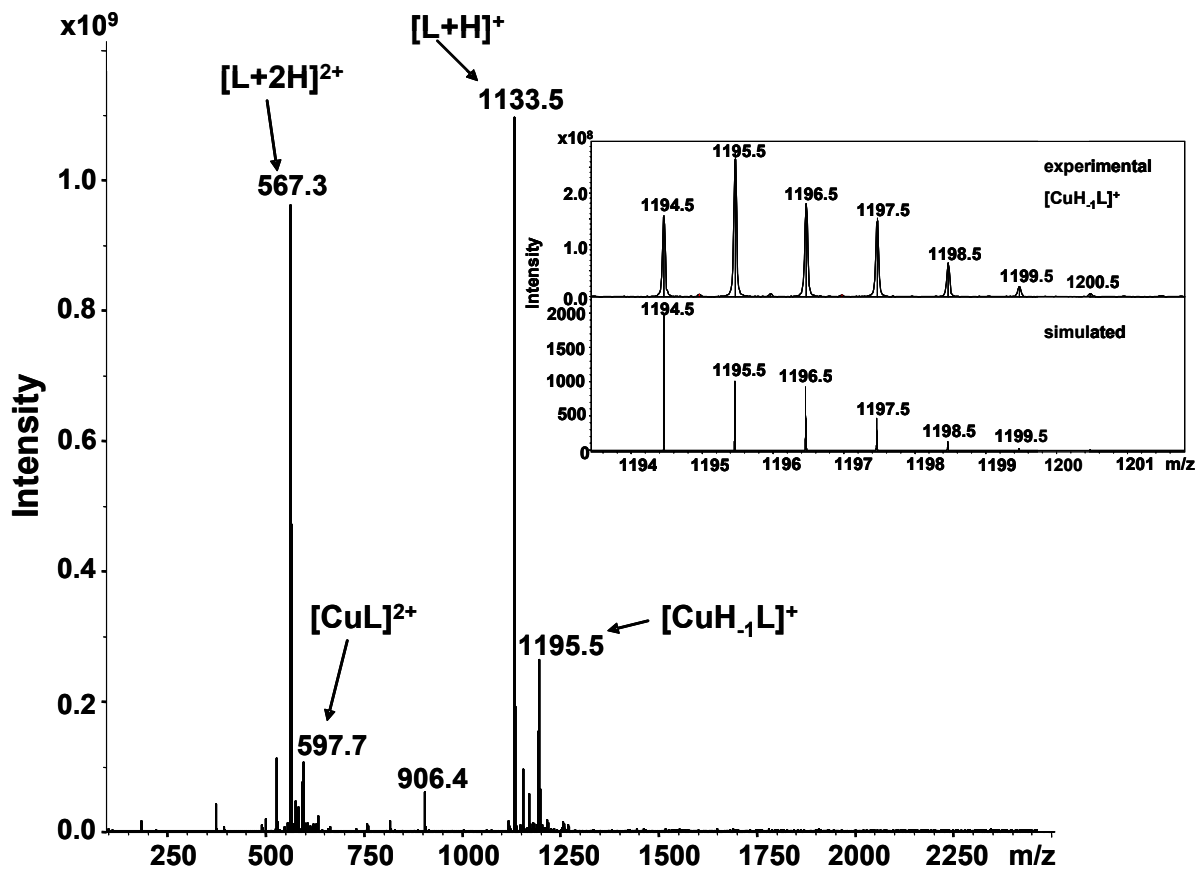


Fig. 3S† ESI mass spectrum for the Cu(II)-H1A/H12A system at 1:1 molar ratio in water solution. Experimental and simulated spectra for the $[CuH_{-1}L]^+$ molecular ion with m/z 1195.5 Da.

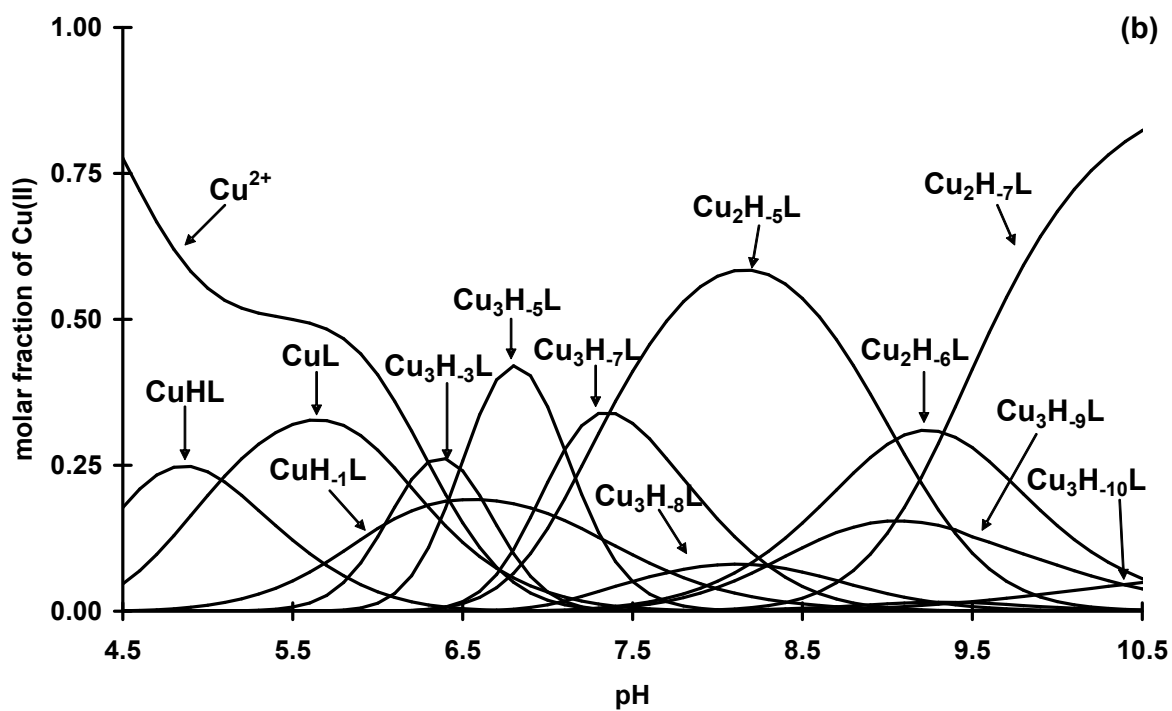
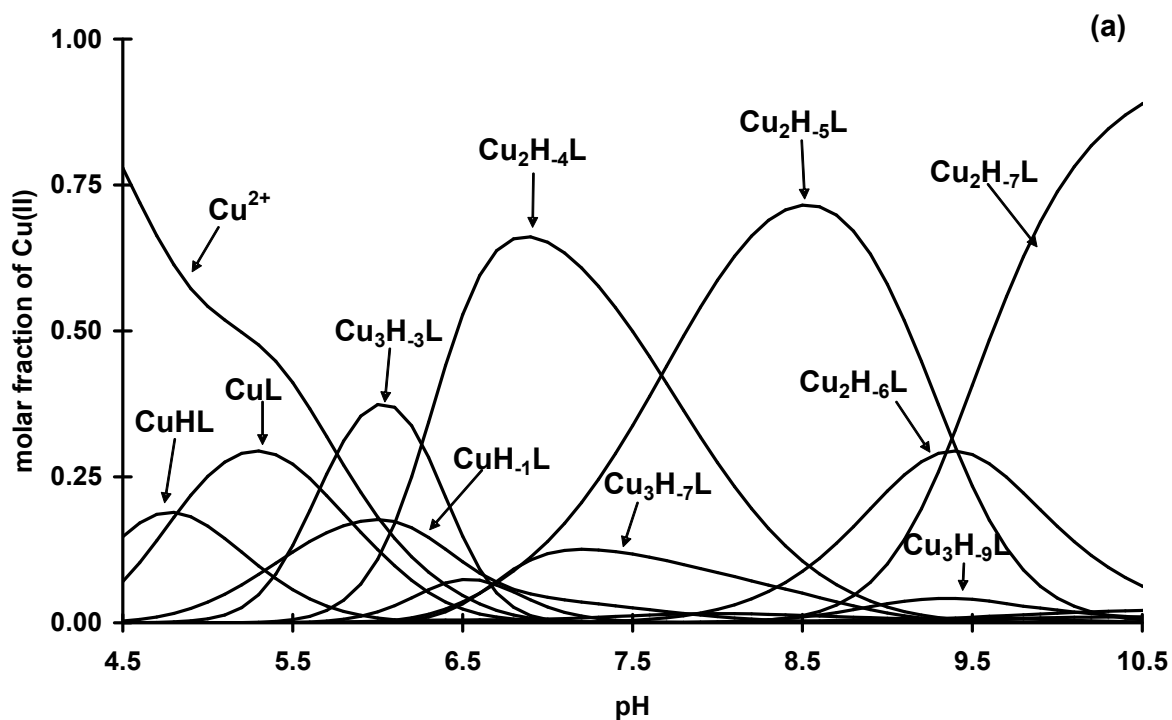


Fig. 4S† Concentration distribution of the complexes formed in Cu(II)-to-peptide molar ratio 2:1 as a function of pH. $[\text{Cu(II)}]=0.002\text{M}$. (a) Cu(II)-H1A/H9A system (b) Cu(II)-H1A/H6A system

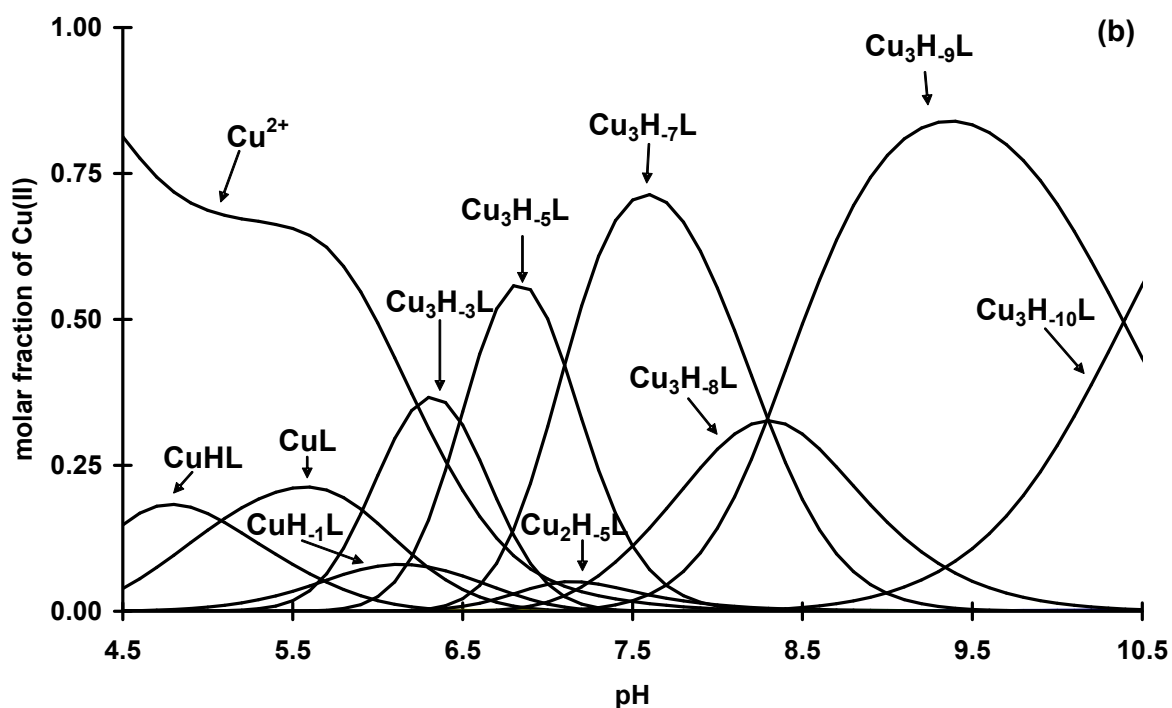
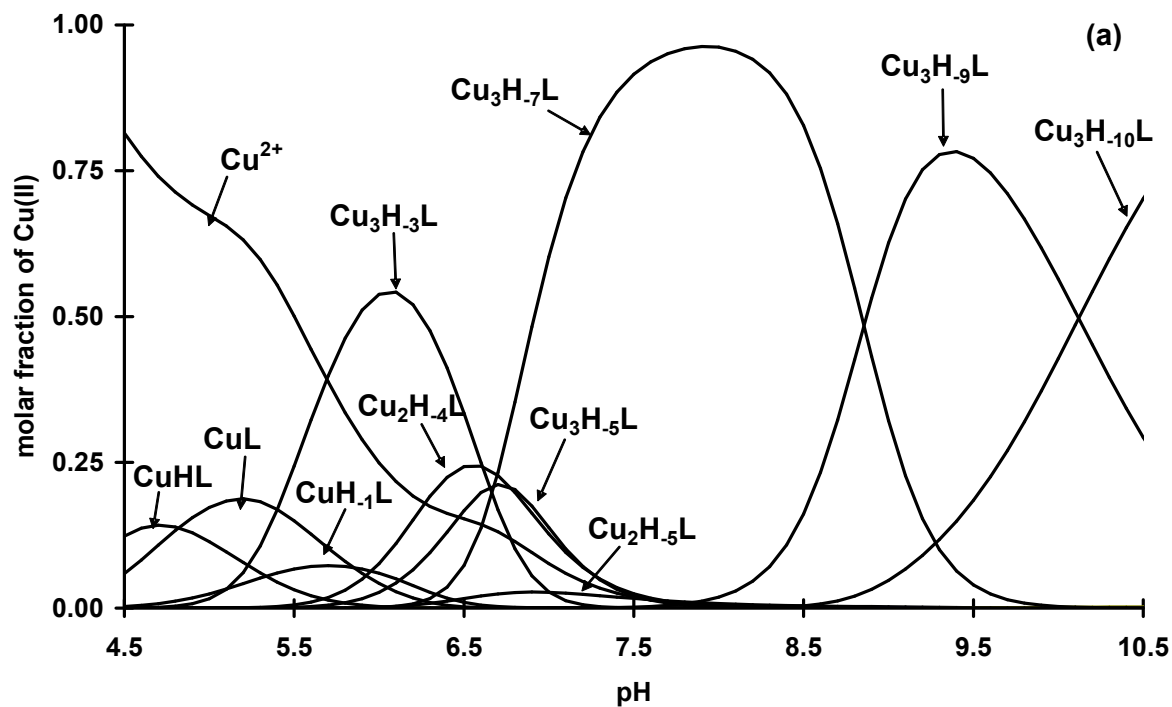


Fig. 5S† Concentration distribution of the complexes formed in Cu(II)-to-peptide molar ratio 3:1 as a function of pH. $[\text{Cu(II)}]=0.003\text{M}$. (a) Cu(II)-H1A/H9A system (b) Cu(II)-H1A/H6A system

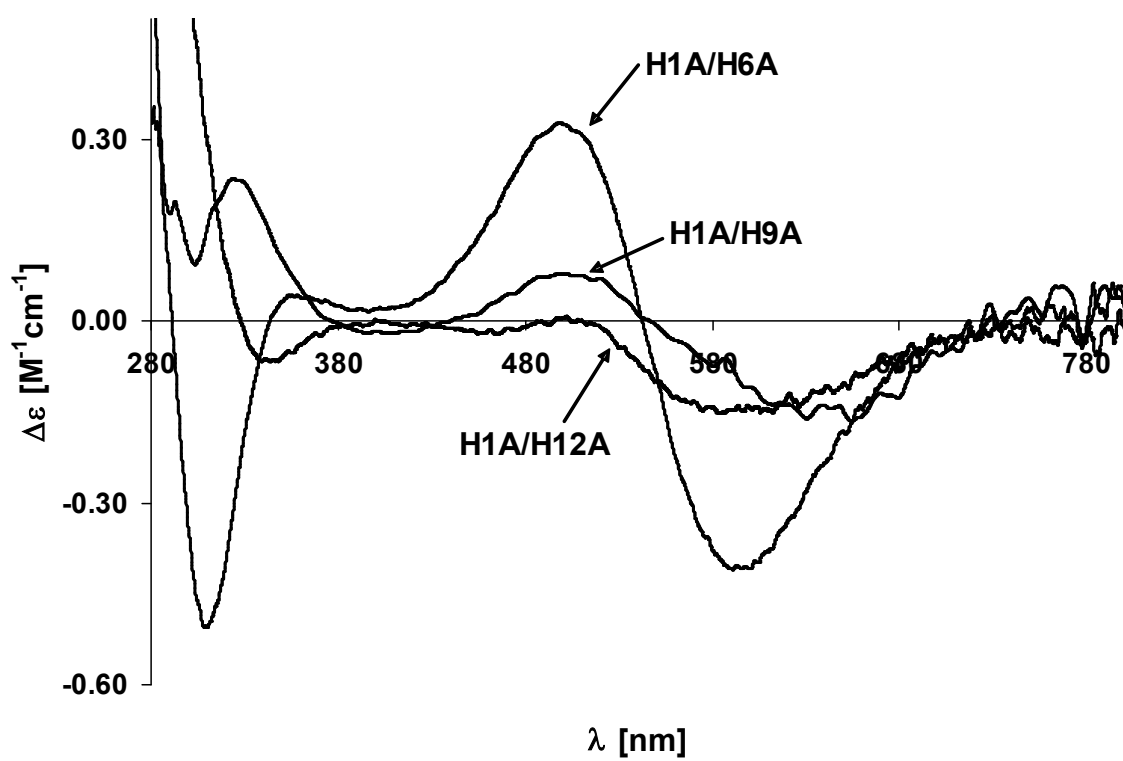


Fig. 6S† CD spectra of the Cu(II)-H1A/H12A, Cu(II)-H1A/H9A and Cu(II)-H1A/H6A systems of the Cu_2H_5L complexes

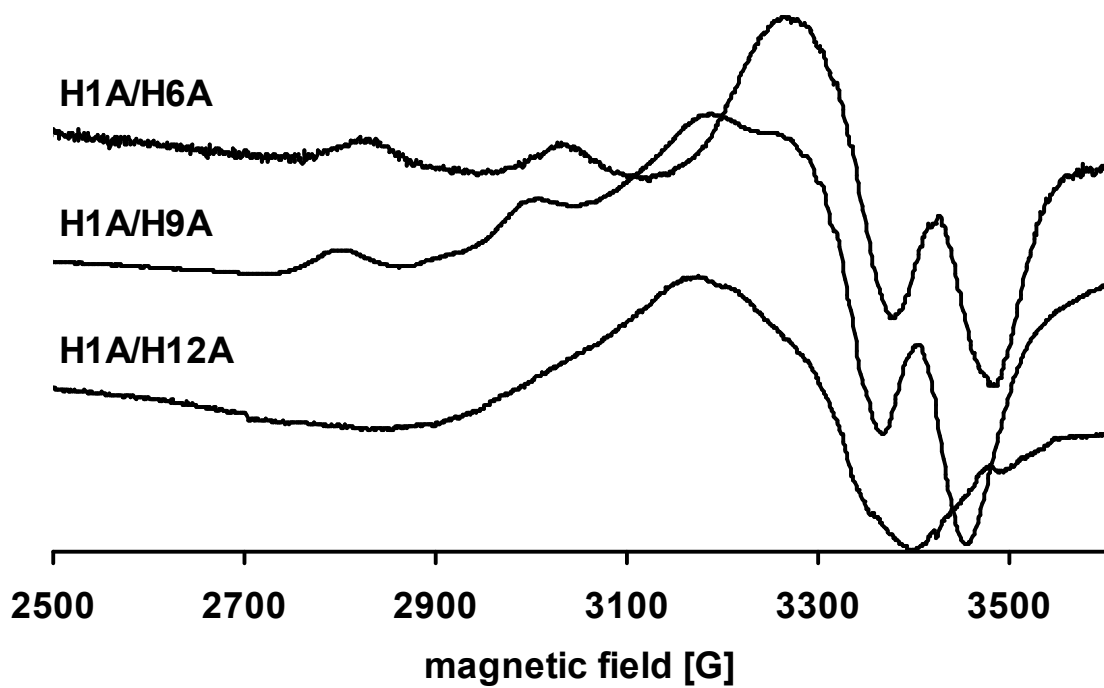


Fig. 7S† Frozen solution EPR spectra of the Cu(II)-H1A/H6A, Cu(II)-H1A/H9A and Cu(II)-H1A/H12A systems of the $\text{Cu}_3\text{H}_9\text{L}$ or $\text{Cu}_3\text{H}_{10}\text{L}$ complexes formed in 3:1 metal-to ligand molar ratio at pH about 11