Electronic Supplementary Material (ESI) for New Journal of Chemistry.

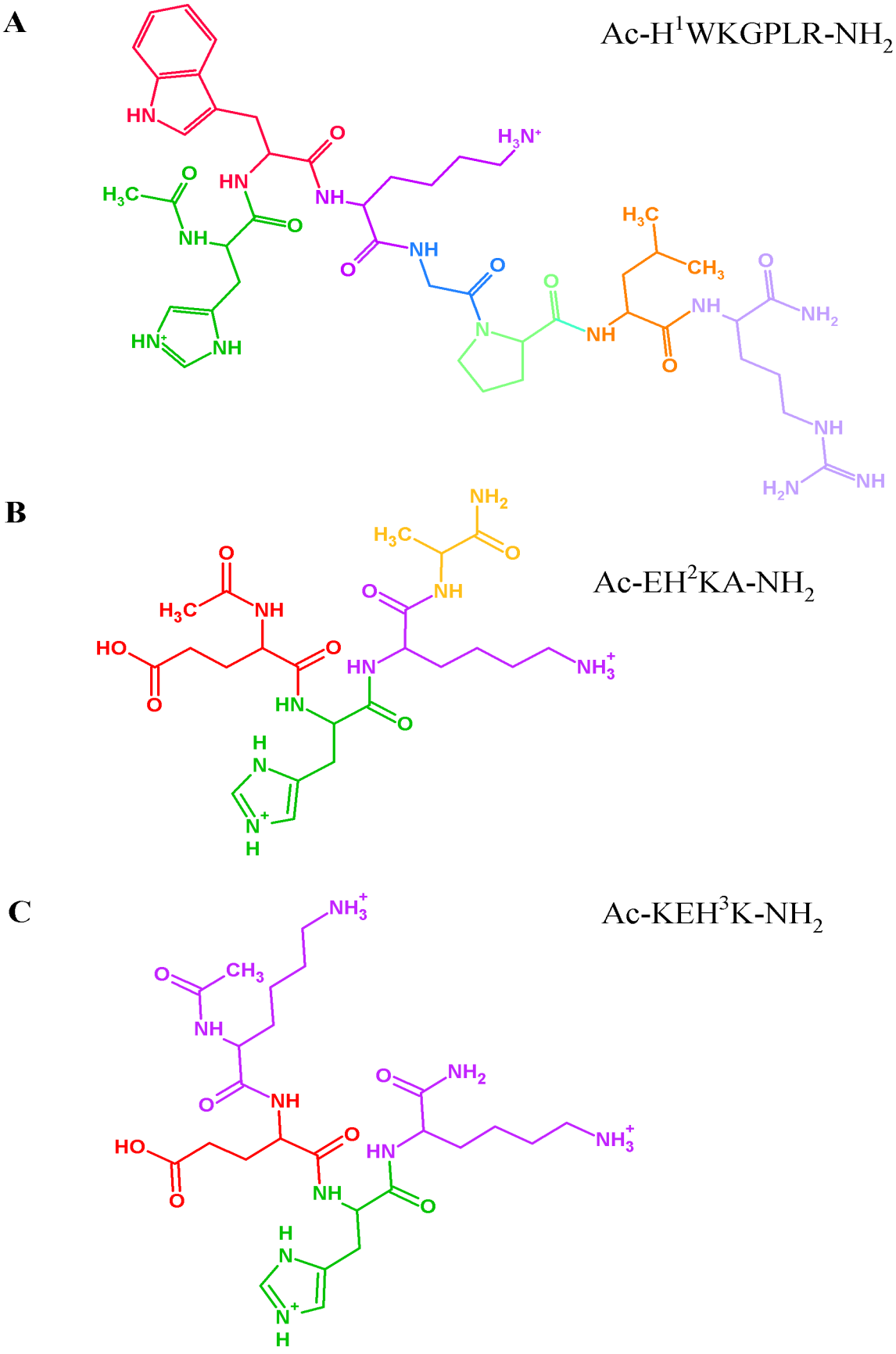

Fig. S1 The structural formulas of the studied A) Ac-**H**[1]WKGPLR-NH_2 (**L1**) B) Ac-E**H**[2]KA-NH_2 (**L2**) and C) Ac-KE**H**[3]K-NH_2 (**L3**) ligands in a fully protonated form.

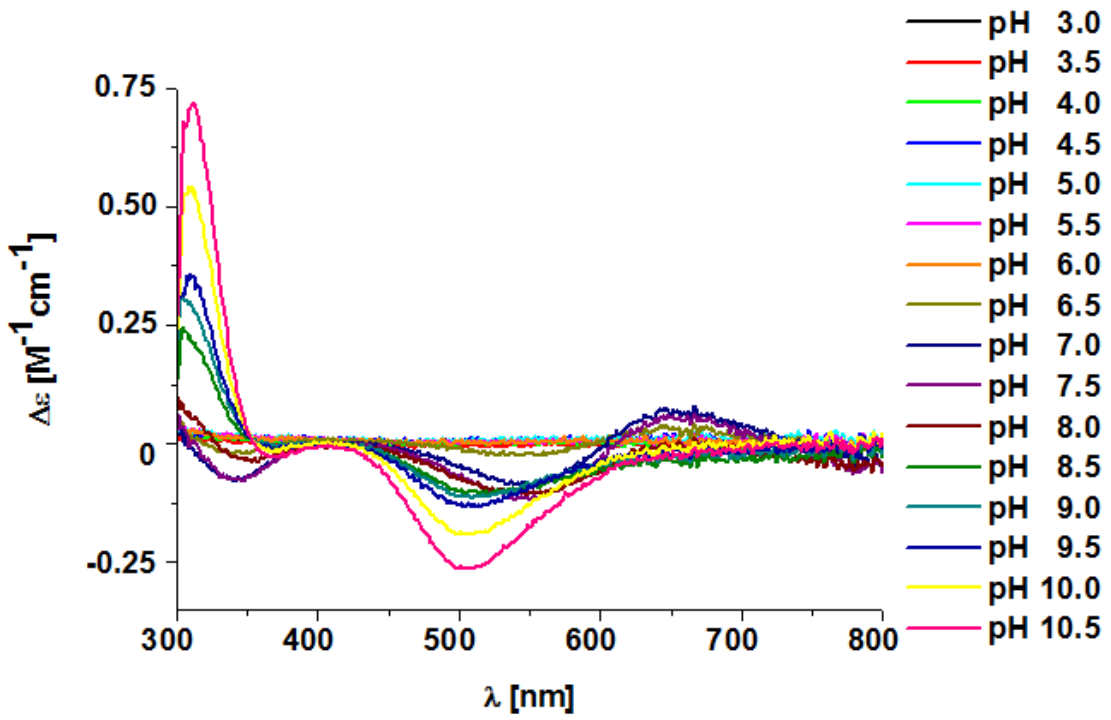

Fig. S2 CD spectra of the Cu(II)-Ac-**H**[1]WKGPLR-NH_2 (**CuL1**) system in the Vis region as a function of pH. Cu:L=1:1, [Cu(II)]=0.001M.

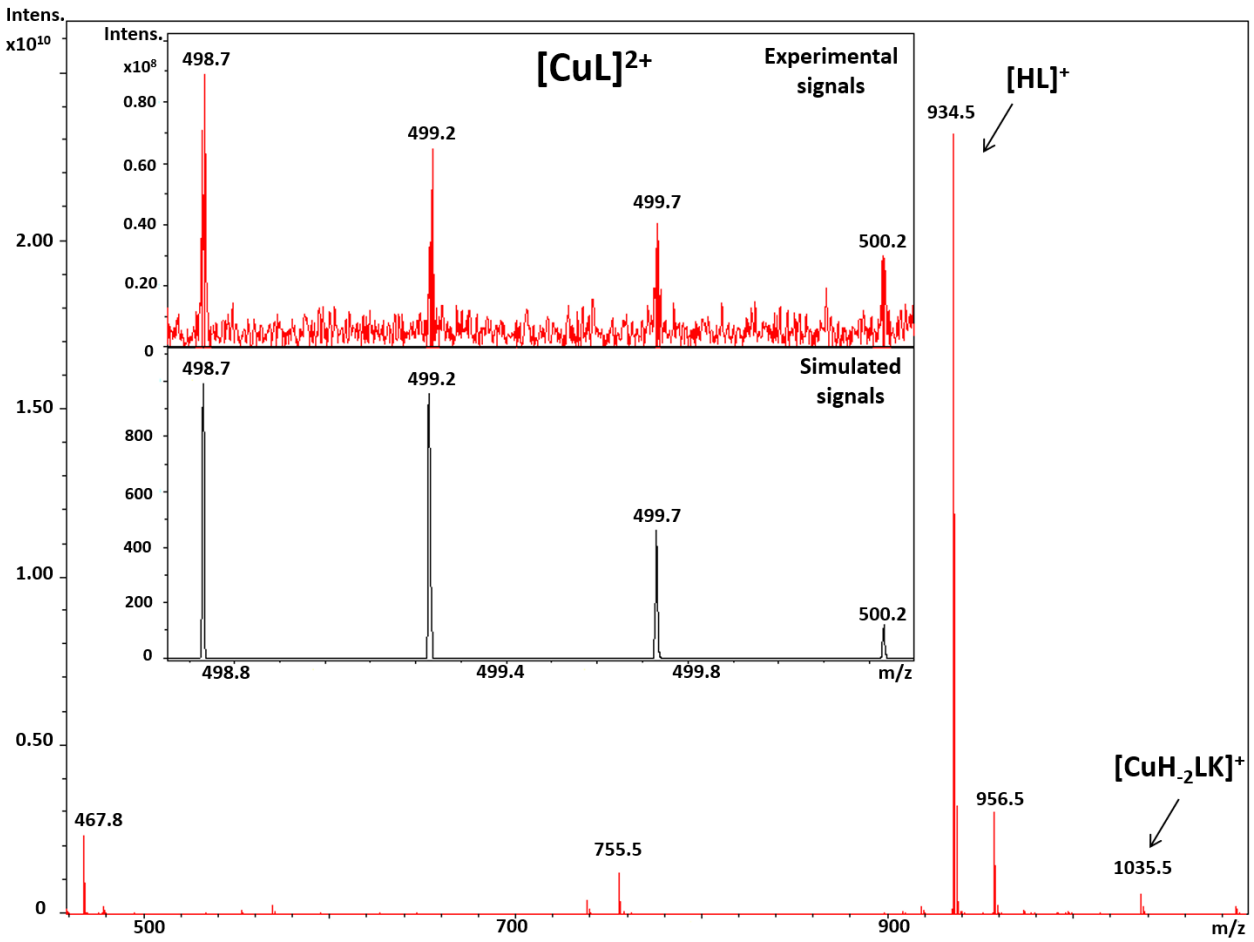

Fig. S3 ESI mass spectrum of the **CuL1** complex (Cu:L=1:1) in aqueous solution (pH ~ 7). As an insert experimental and simulated spectrum of the $[CuL]^{2+}$ ion (*m/z*=498.7 Da) are shown.

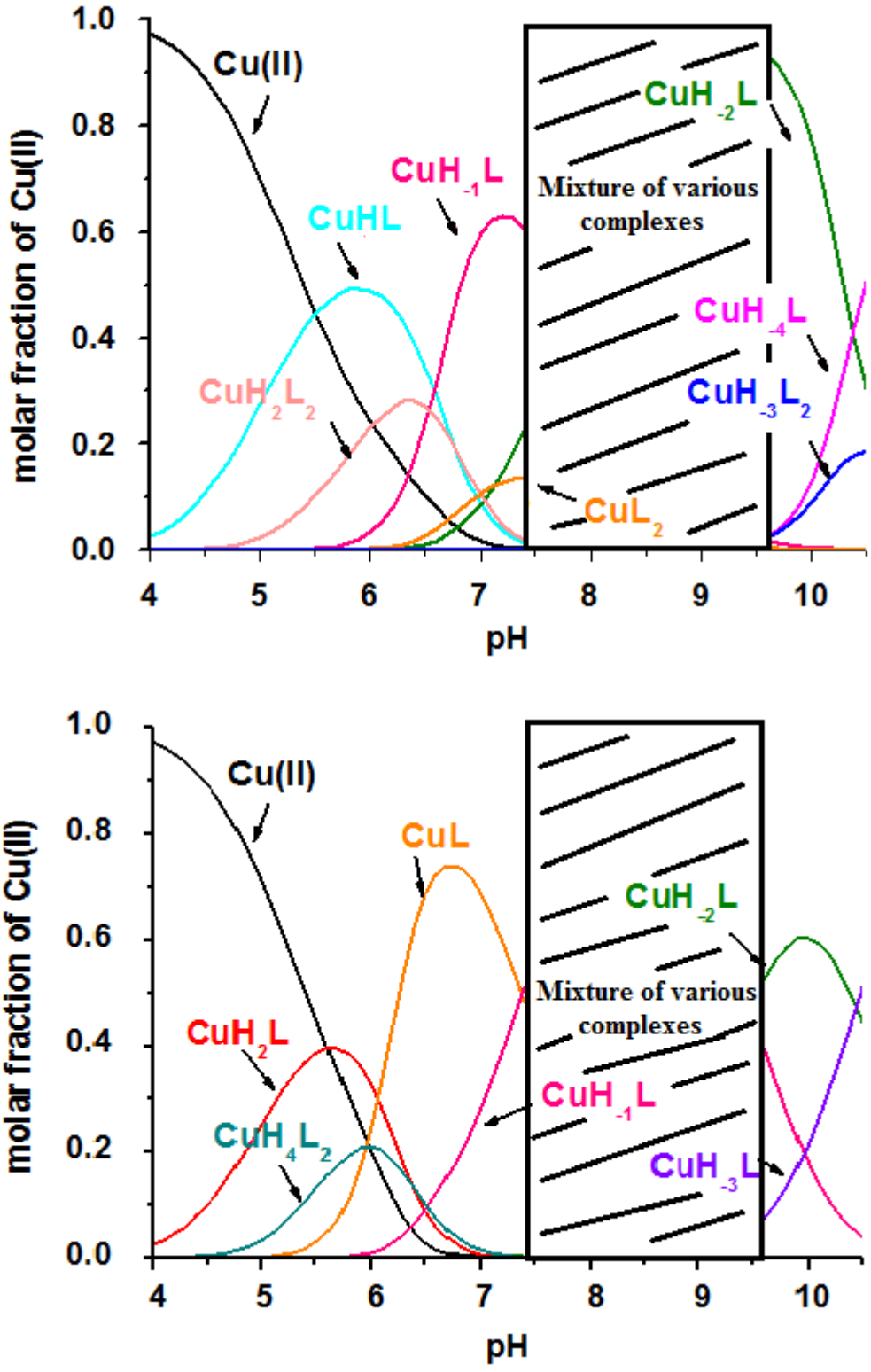

Fig. S4 Species distribution diagram of Cu(II) bis-complexes with A) Ac-E**H**^{2}KA-NH_2 (**L2**) and B) Ac-KE**H**^{3}K-NH_2 (**L3**) ligands as a function of pH. Molar ratio Cu:L=1:2, [Cu(II)]=0.001 M.

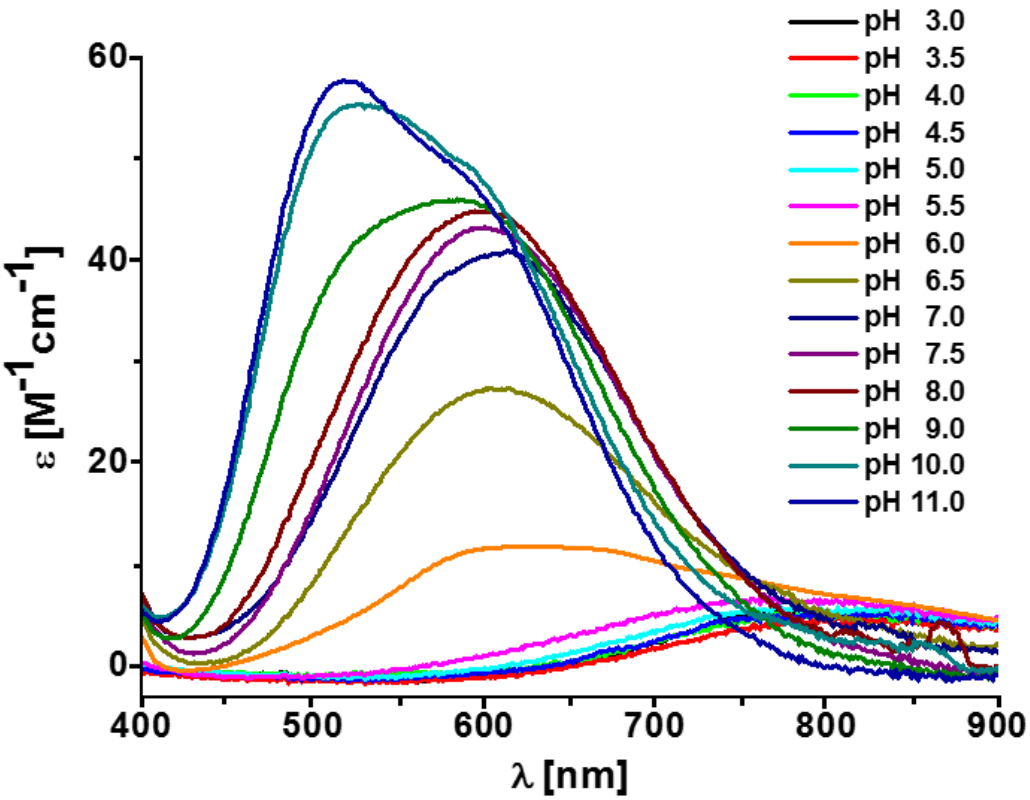

Fig. S5 Electronic absorption spectra of the Cu(II)-Ac-KE**H**^{3}K-NH_2 (**CuL3**) complex as a function of pH. Cu:L=1:1, [Cu(II)]=0.001 M.

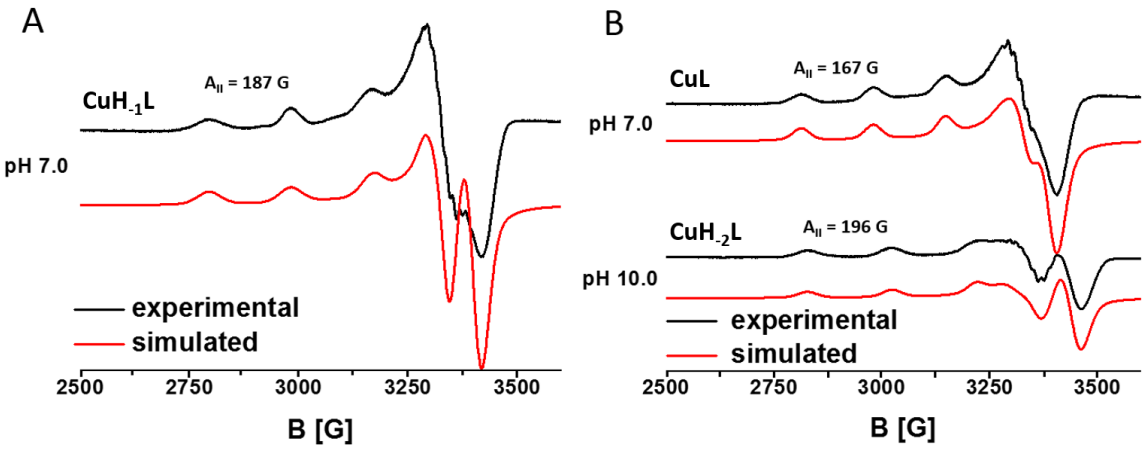

Fig. S6 EPR spectra of a frozen solution of A) Cu(II)-Ac-E**H²**KA-NH_2 (**CuL2**) and B) Cu(II)-Ac-KE**H³**K-NH_2 (**CuL3**) complexes at various pH values. Cu:L=1:1, [Cu(II)]=0.001 M.

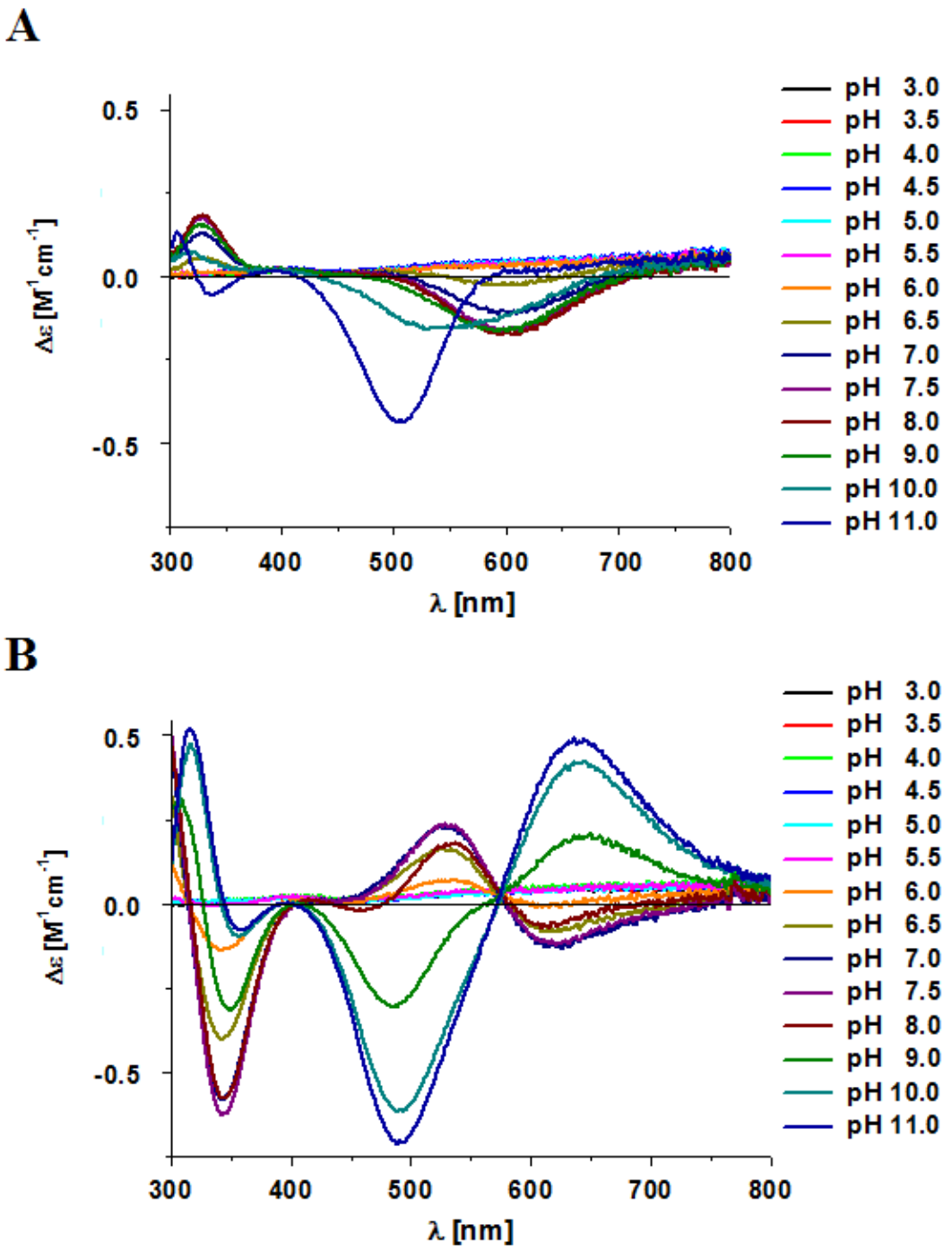

Fig. S7 CD spectra of A) Cu(II)-Ac-E**H**^{2}KA-NH_2 (**CuL2**) and B) Cu(II)-Ac-KE**H**^{3}K-NH_2 (**CuL3**) complexes in the Vis region as a function of pH. Cu:L=1:1, [Cu(II)]=0.001 M.

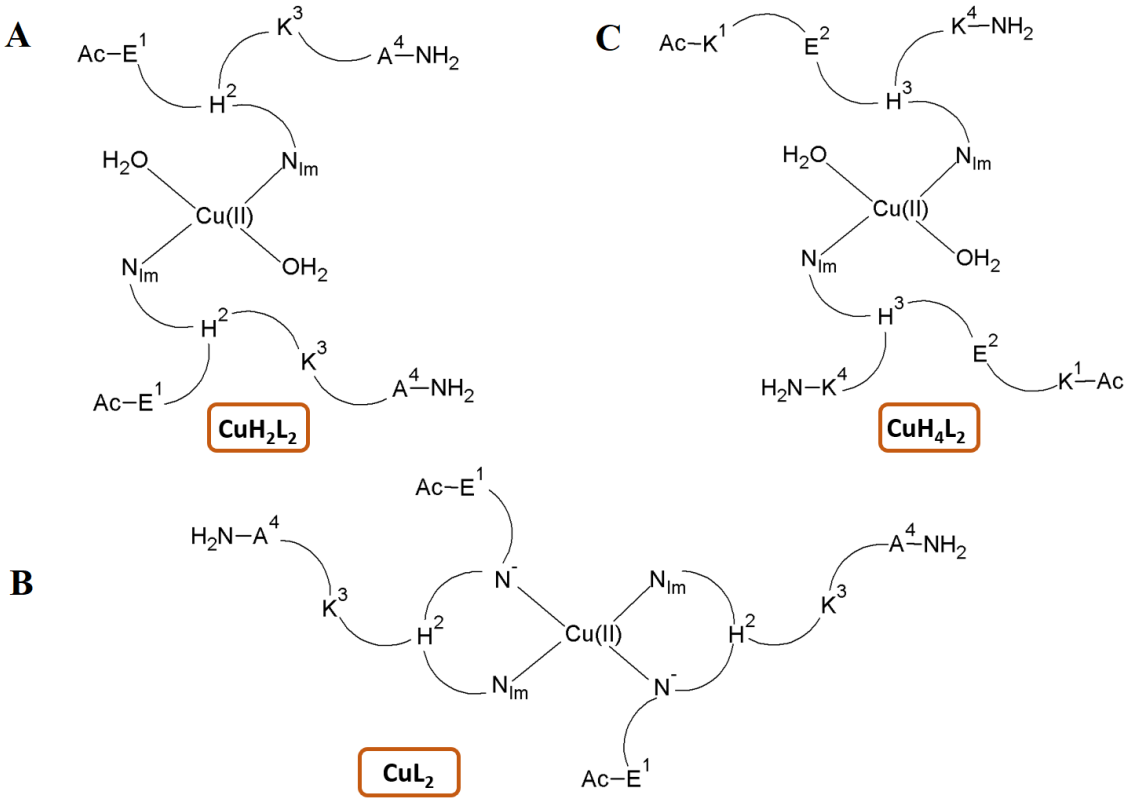

Fig. S8 Schematic representation of the proposed bis-complexes structures: A) CuH_2L_2, B) CuL_2 of the **CuL2** complex and C) CuH_4L_2 of the **CuL3** complex.

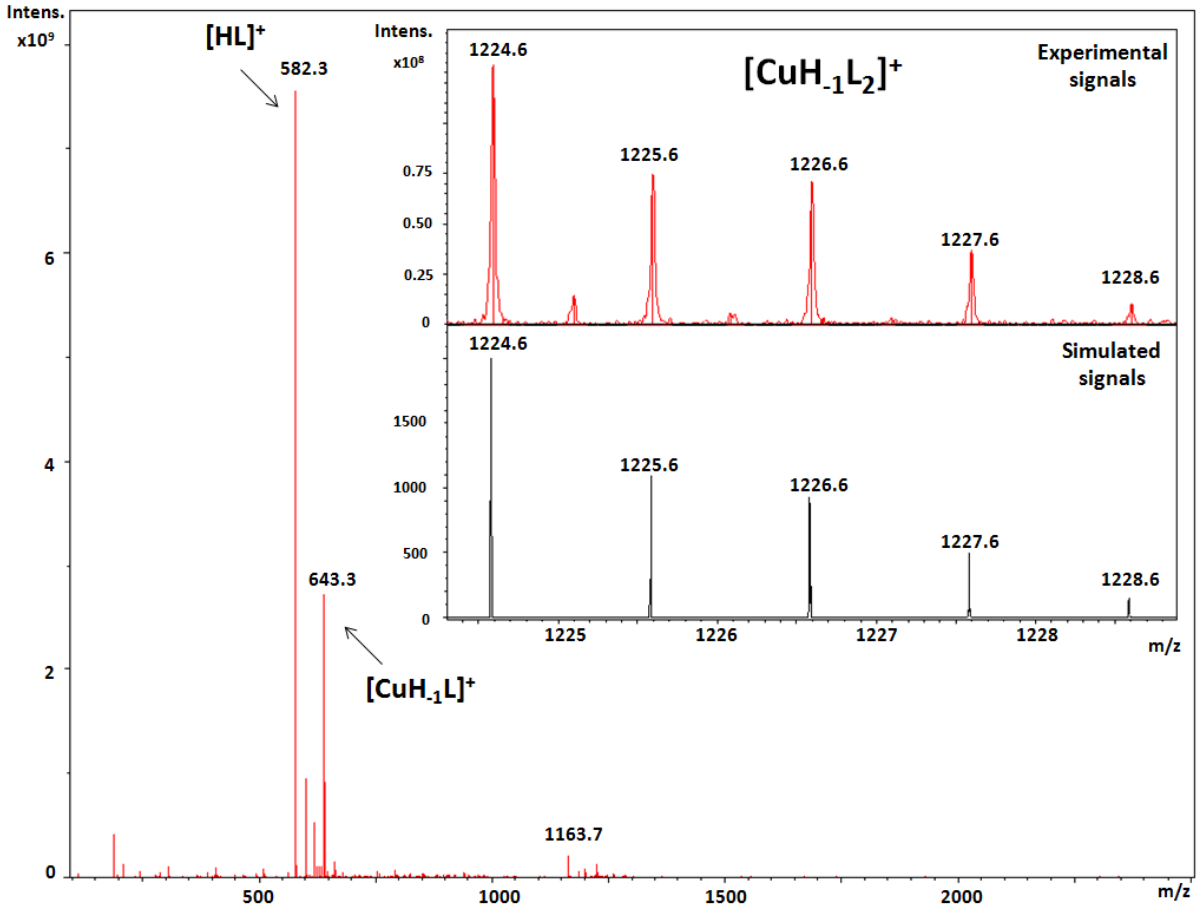

Fig. S9 ESI mass spectrum of the **CuL3** complex (Cu:L=1:2) in aqueous solution (pH ~ 7). As an insert experimental and simulated spectra of the $[CuH_{-1}L_2]^+$ ion (*m/z* = 1224.6 Da) are shown.

Table S1 The deprotonation constants for amide protons (pK_a values) for Cu(II) complexes with studied ligands and peptides found in the literature.

Peptide	p$K_{1(amide)}$	p$K_{2(amide)}$	p$K_{3(amide)}$ or p$K_{H2Ocoord.}$
H^1			
Ac-H^1WKGPLR-NH_2 (L1)	6.42	6.66	7.33
Ac-H^1GGG[a]	6.60	6.96	8.92
Ac- H^1GGGWGQ-NH_2[b]	6.49	6.19	8.98
H^2			
Ac-EH^2KA-NH_2 (L2)	-	-	7.83
Ac-GH^2GG[a]	6.11	6.12	10.76
Ac-PH^2SFN[c]	6.48	6.62	8.38
Ac-PH^2SRN[c]	6.66	6.44	8.93
H^3			
Ac-KEH^3K-NH_2 (L3)	-	-	7.38
Ac-GGH^3G[a]	6.05	6.43	8.95
Ac-LAH^3YNK[d]	5.75	-	9.04
Ac-GGH^3[e]	6.50	7.35	9.25
Ac-YIH^3[f]	6.99	7.34	8.92
Ac-GTH^3S-NH_2[g]	6.08	6.08	7.97
Ac-FKH^3V-NH_2[g]	5.93	5.93	8.52
Ac-MKH^3M-NH_2[g]	5.64	5.64	8.96
Ac-KGH^3GNG-NH_2[h]	5.56	6.06	8.90
Ac-SKH^3M-NH_2[i]	-	-	7.75

[a]ref. [28]
[b]ref. [45]
[c]ref. [46]
[d]ref. [47]
[e]ref. [48]
[f]ref. [49]
[g]ref. [50]
[h]ref. [44]
[i]ref. [58]

Table S2 The calculated logK^* values of Cu(II) bis-complexes with **L2** and **L3** peptides.

[a]**logK^***	**2N** **{2N_{Im}}**	**4N** **{2N_{Im}, 2N^-}**
Ac-EH^2KA-NH_2 (L2)	-5.67	-19.65
Ac-KEH^3K-NH_2 (L2)	-5.66	-

[a]The logK^*=logβ(CuH_jL_2)-logβ(H_nL) where the *j* corresponds to the number of protons in the coordinated ligand to metal ion and the *n* correspond to the number protons of the coordinated ligand and released from ligand during complexation.