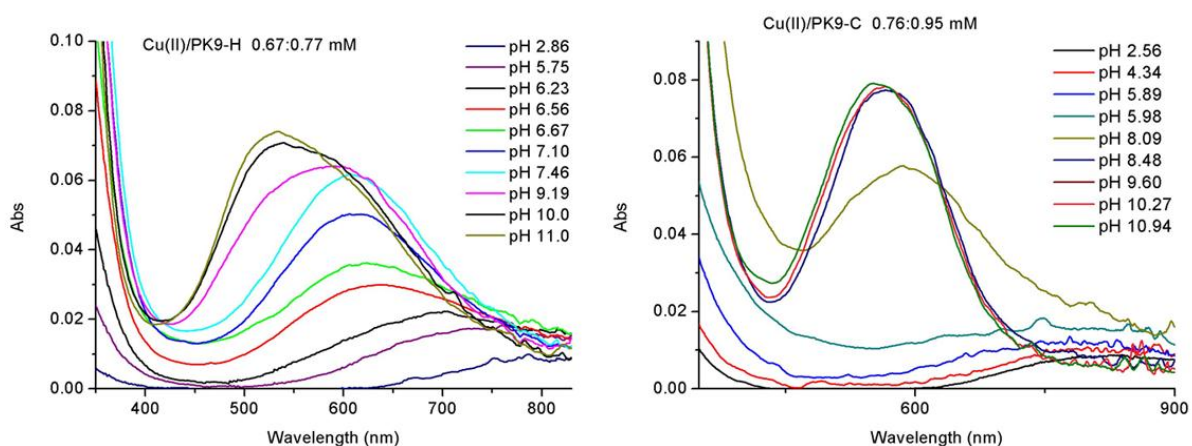
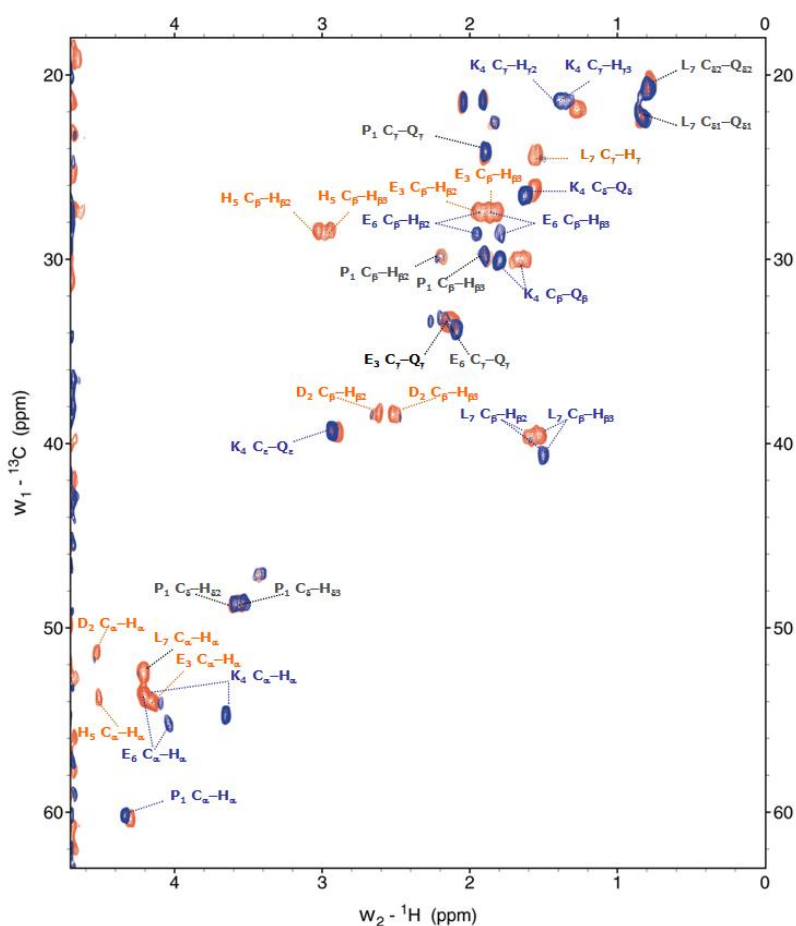


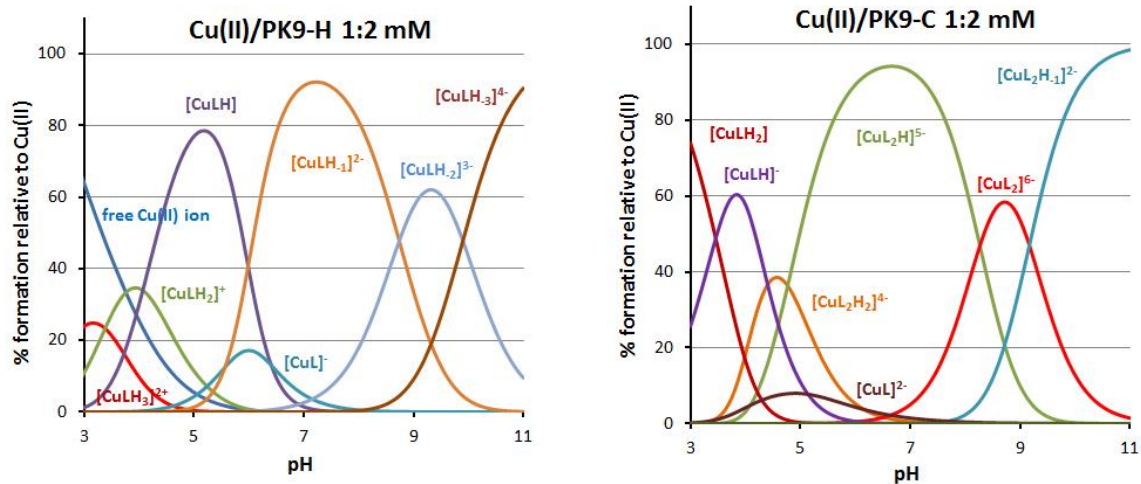
## Supplementary materials



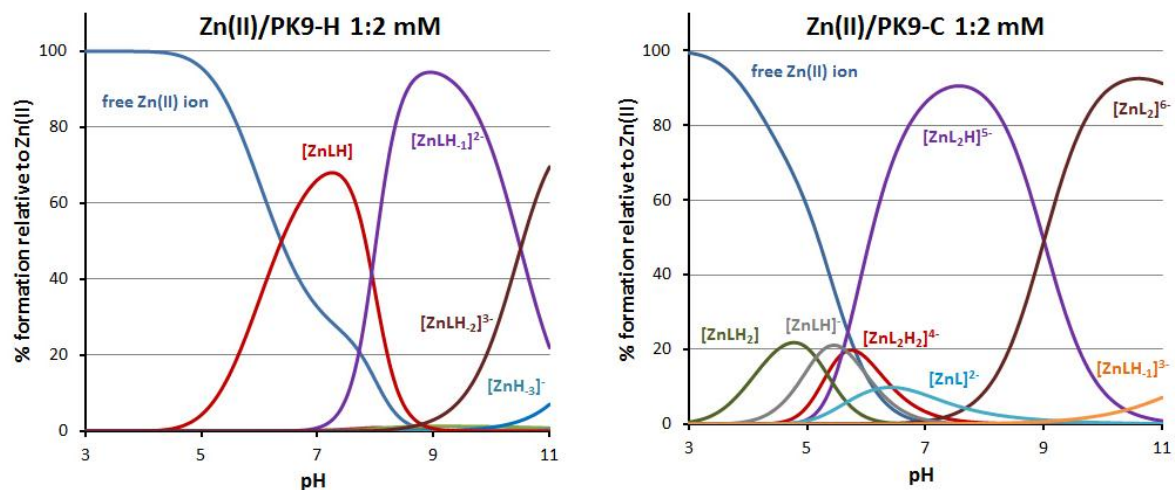
**Fig. S1** UV-Vis spectra, at different pH values, for the system Cu(II)/PK9-H and Cu(II)/PK9-C at 25°C and  $I = 0.1$  M (KCl).  $C_M = 1 \cdot 10^{-3}$  M, M/L molar ratio = 1:1



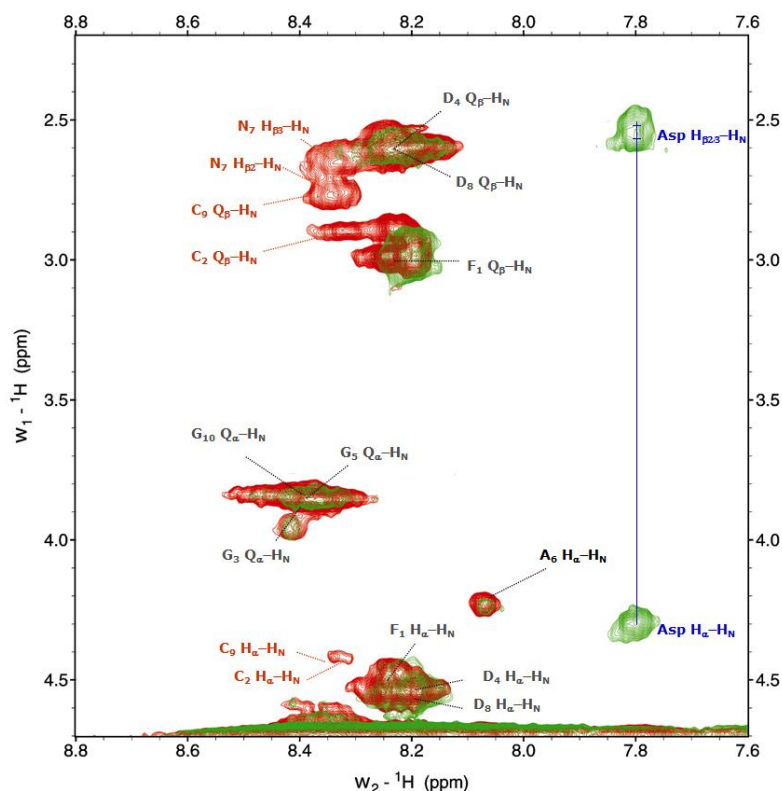
**Fig. S2** Selected aliphatic regions of  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum for PK9-H peptide, 2.5 mM, pH 7.7, T 298 K, in the absence (orange) and in the presence (blue) of 0.05 equivalents of Cu(II). Disappearing peaks are orange-labeled. The signals experiencing chemical shift changes are indicated by blue color.



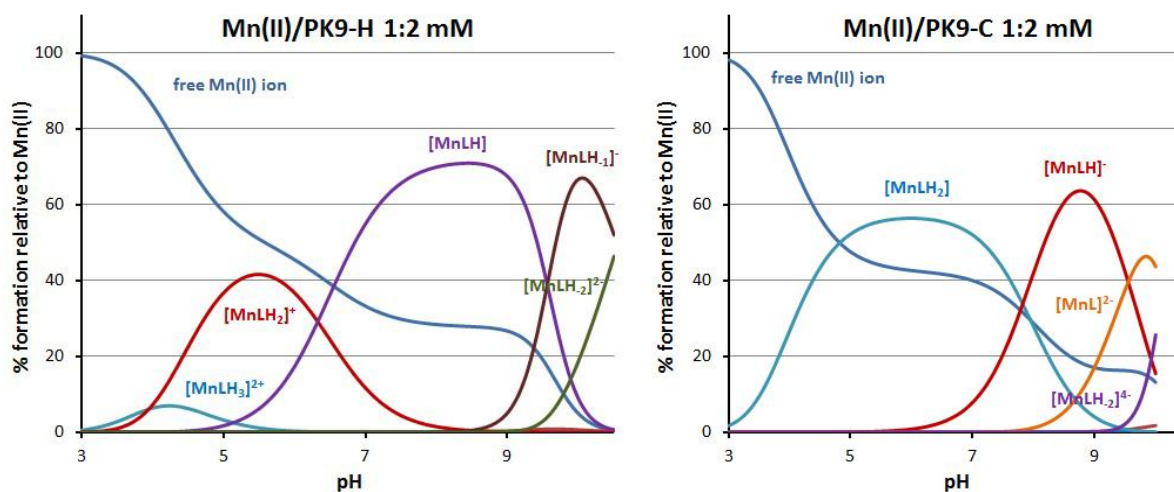
**Fig. S3** Representative distribution diagrams.  $[\text{Cu(II)}]_{\text{tot}} = 1.0 \text{ mM}$ ; Cu(II)/L ratio = 1:2.



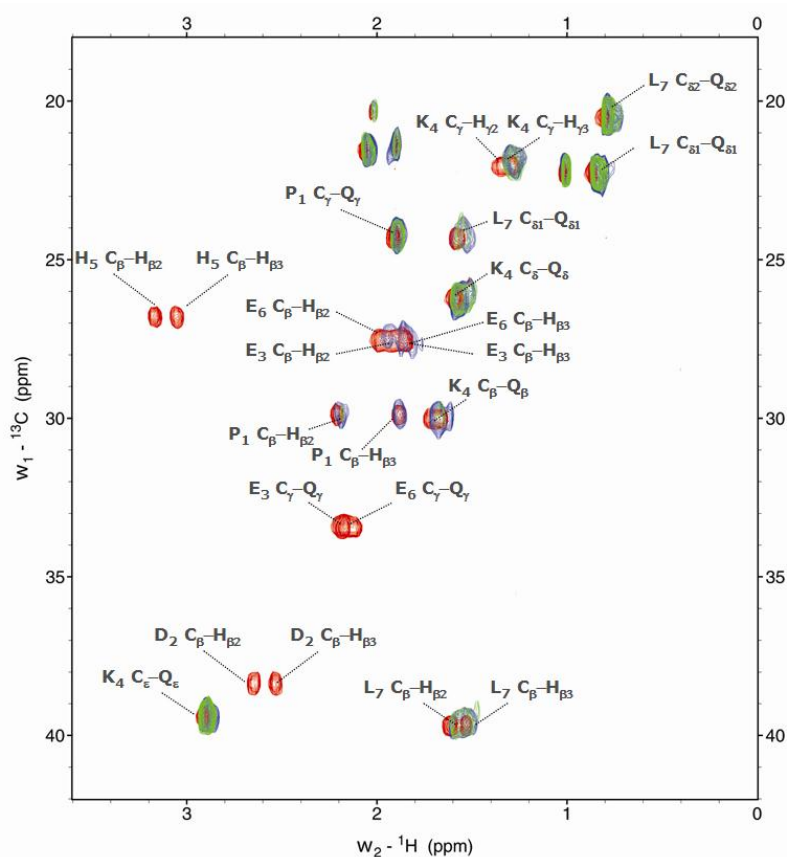
**Fig. S4** Representative distribution diagrams.  $[\text{Zn(II)}]_{\text{tot}} = 1.0 \text{ mM}$ ; Zn(II)/L ratio = 1:2.



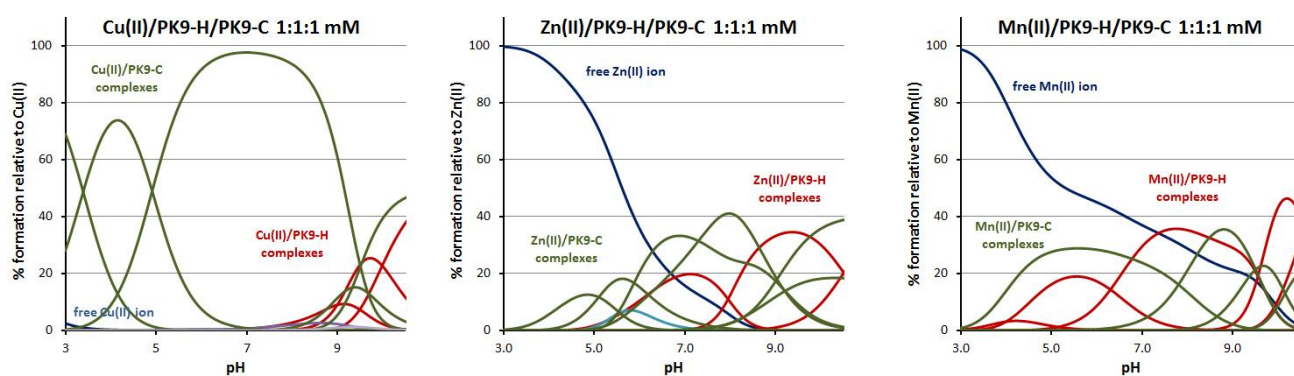
**Fig. S5** Selected aromatic regions of  $^1\text{H}$ - $^1\text{H}$  TOCSY NMR spectra of the PK9-C peptide, 2.5 mM, pH 7.2, T 298 K, in the absence (red) and in the presence (green) of 0.5 equivalents of Zn(II). Disappearing peaks are red-labeled. The new spin system for Asp residue are indicated.



**Fig. S6** Representative distribution diagrams.  $[\text{Mn(II)}]_{\text{tot}} = 1.0 \text{ mM}$ ; Mn(II)/L ratio = 1:2.



**Fig. S7** Selected aliphatic regions of  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum for PK9-H peptide, 2.5 mM, pH 7.8, T 298 K, in the absence (red) and in the presence of 0.1 equivalents of Mn(II) at pH 7.8 (green) and pH 9 (blue).



**Fig. S8.** Representative competition diagrams for ternary solution containing the metal ion (either Cu(II) or Zn(II) or Mn(II)) and the two ligands. The total concentrations of the three components are equal (1.0 mM).