Supporting Information for "Copper(II) complexes with peptides based on the second cell binding site of fibronectin: metal coordination and ligand exchange kinetics" by Silvia Pizzanelli, Claudia Forte, Calogero Pinzino, Antonio Magrì and Diego La Mendola

Potentiometric titrations: definition of the stability constant β_{pqr} for the complex $Cu_pL_rH_q$

The species formed in the investigated systems can be characterized by the general equilibrium process (charges omitted):

$$pCu + qH + rL = Cu_pL_rH_q \quad (1)$$

in which L represents the free peptide and $Cu_pL_rH_q$ the complex.

The stability constant β_{pqr} is defined as:

$$\beta_{pqr} = [Cu_pL_rH_q] / [Cu]^p \,.\, [H]^q \,.\, [L]^r \quad (2)$$

Note that q may have negative values ($CuLH_{-1}$ in the simplest case) due to the progressive deprotonation of the amide NH groups.

Table S1. Selected proton signals and relative line width for PHSFN in D_2O at pD=5.2 before and after the addition of copper ion at room temperature. The peptide concentration was 29.7 mM.

PHSFN				
residue	proton	chemical shift (ppm);[a] J coupling (Hz)	line width (Hz) with no Cu(II)	line width (Hz) with 0.016 mole-equivalents of Cu(II)
P	δ	3.73; $J_{\delta\gamma}$=6.8	2.5	3.2
H	β', β''	3.26, 3.36; $J_{\alpha\beta'}$=9.0 $J_{\alpha\beta''}$=5.4 $J_{\beta'\beta''}$=-15.5	3.0	4.0
	δ	7.36;	1.8	4.0
	ε	8.71; $J_{\delta\varepsilon}$=1.4	0.8	4.0
S	β	3.91; $J_{\alpha\beta}$=5.8	3.0	3.2
F	β', β''	3.19, 3.24; $J_{\alpha\beta'}$=8.0 $J_{\alpha\beta''}$=6.9 $J_{\beta'\beta''}$=-13.6	3.0	4.0
	aromatic	~7.4		
N	β', β''	2.77, 2.87; $J_{\alpha\beta'}$=8.0 $J_{\alpha\beta''}$=5.6 $J_{\beta'\beta''}$=-15.6	1.5	2.0

Table S2. Selected proton signals and relative line width for PHSEN in D_2O at pD=5.2 before and after the addition of copper ion at room temperature. The peptide concentration was 33.6 mM.

PHSEN				
residue	proton	chemical shift (ppm);[a] J coupling (Hz)	line width (Hz) with no Cu(II)	line width (Hz) with 0.036 mole-equivalents of Cu(II)
P	δ	3.74; $J_{\delta\gamma}$=6.7	3.0	3.5
H	β', β''	3.31, 3.43; $J_{\alpha\beta'}$=8.7 $J_{\alpha\beta''}$=5.6 $J_{\beta'\beta''}$=-15.4	2.5	3.2
	δ	7.43;	2.0	2.7
	ε	8.74; $J_{\delta\varepsilon}$=1.4	1.2	2.0
S	β', β''	3.96, 3.99; $J_{\alpha\beta'}$=5.3 $J_{\alpha\beta''}$=5.9 $J_{\beta'\beta''}$=-11.6	2.5	3.2
E	γ	2.61 $J_{\gamma\beta}$=7.2	3.5	4.3
N	β', β''	2.85, 2.94; $J_{\alpha\beta'}$=8.0 $J_{\alpha\beta''}$=5.6 $J_{\beta'\beta''}$=-15.6	2.0	3.0

[a] The ^1H frequency scale was externally referenced to the signal of acetone in D_2O (2.22 ppm)[1].

[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.,* 1997, **62,** 7512-7515.