Supporting Information

A constrained tetrapeptide as a model of Cu(I) binding sites involving Cu_4S_6 clusters in proteins.

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CDPPC characterization

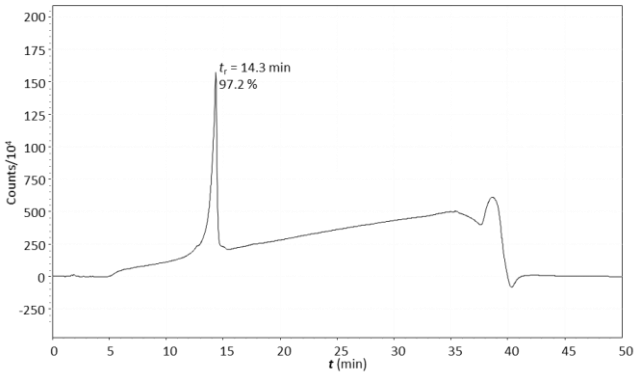

Figure S1. Analytical HPLC chromatogram of CDPPC peptide (flowrate = 1 mL/min, gradient 0-60% of AcN in 30 min), t_r (CDPPC) = 14.3 min.

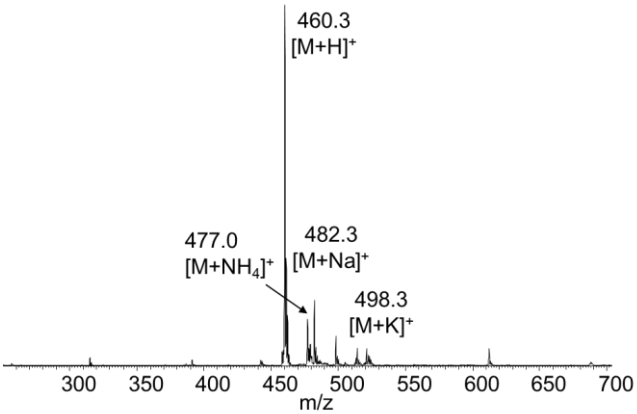

Figure S2. (+) ESI-MS spectrum of the purified CDPPC

CPGC characterization

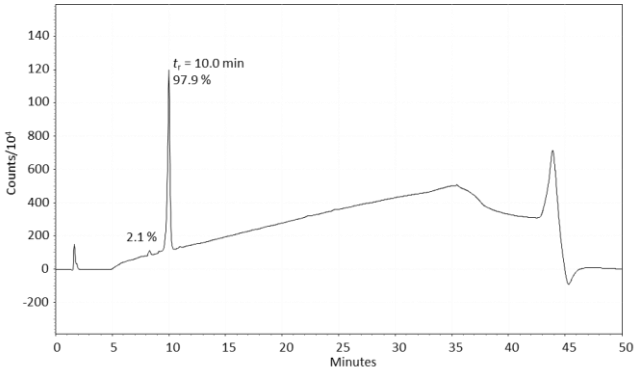

Figure S3. Analytical HPLC chromatogram of CPGC peptide (flowrate = 1 mL/min, gradient 0-60% of AcN in 30 min), t_r (CPGC) = 10 min.

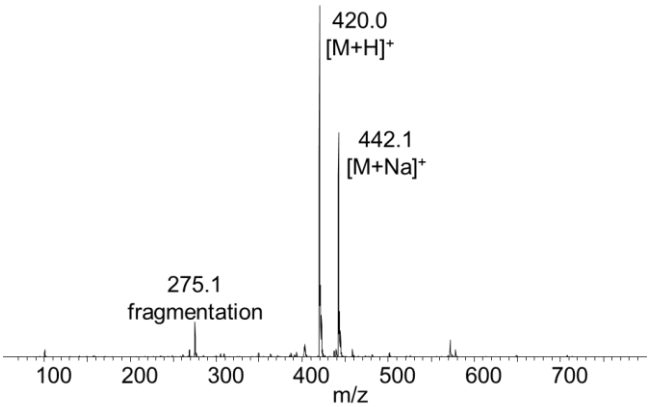

Figure S4. (+) ESI-MS spectrum of the purified CPGC

Physico-chemical experiments: supplementary figures

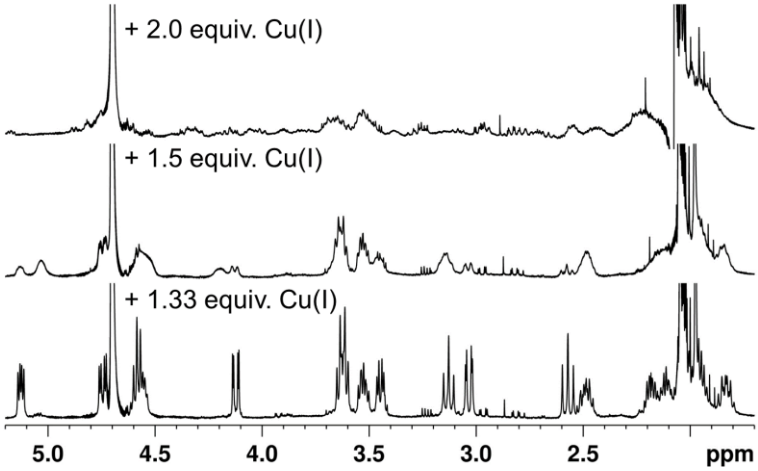

Figure S5. ^{1}H NMR (500 MHz, 298 K) spectra of the aliphatic region of CDPPC (1.58 mM) in phosphate buffer (20 mM, pD = 7.4, D_2O) with 1.33, 1.5 and 2 equiv. of $Cu(CH_3CN)_4PF_6$ in CD_3CN.

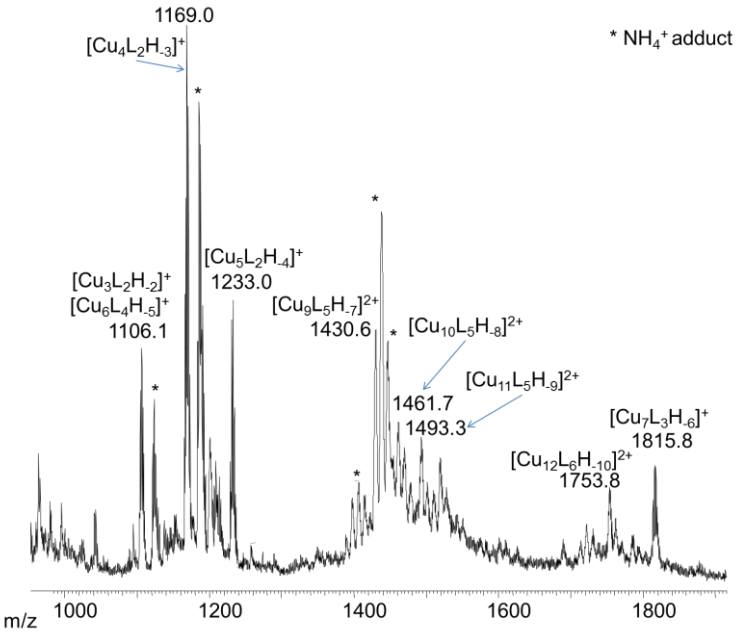

Figure S6. (+)ESI-MS spectrum of CDPPC (100 µM in NH_4AcO buffer 20 mM, pH = 6.9 / AcN, 9/1 v/v) with 2 Cu(I) equiv. showing the presence of high nuclearity species.

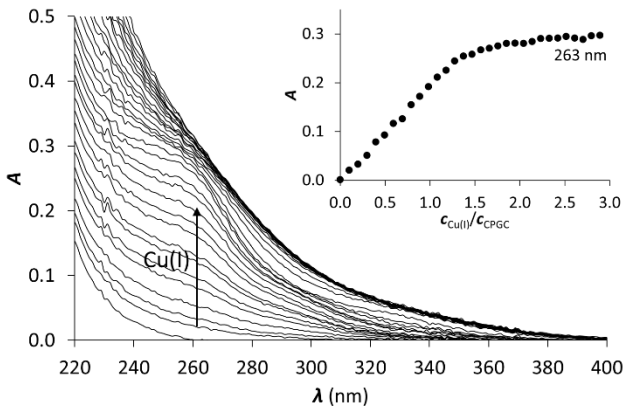

Figure S7. UV titration of CPGC (30.2 µM in phosphate buffer 20 mM, pH 7.4) with $Cu(CH_3CN)_4PF_6$ in AcN. The insert shows the evolution of the absorbance at λ = 263 nm as a function of the $c_{Cu(I)}/c_{CPGC}$ ratio.

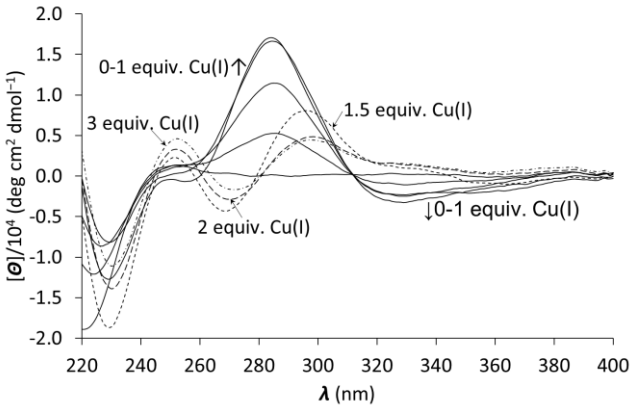

Figure S8. CD titration of CPGC (30.2 µM in phosphate buffer 20 mM, pH 7.4) with $Cu(CH_3CN)_4PF_6$ in AcN.

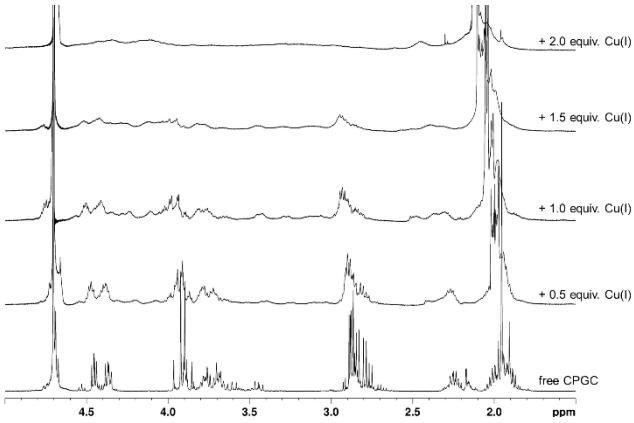

Figure S9. ^{1}H NMR spectra (500 MHz, 298 K) of the aliphatic region of CPGC (1.91 mM) in phosphate buffer (20 mM, pD = 7.4, D_2O) with increasing amounts of $Cu(CH_3CN)_4PF_6$ in CD_3CN.

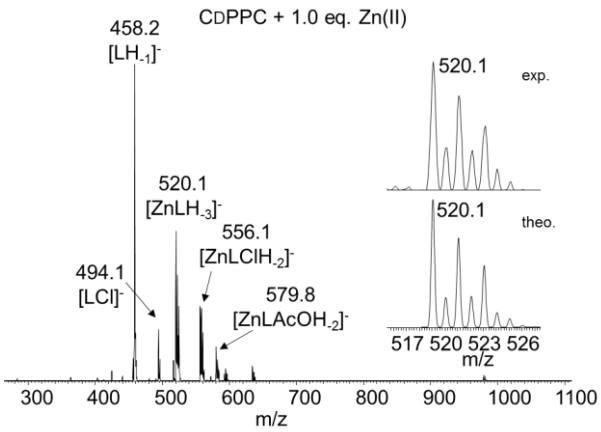

Figure S10. (−)ESI-MS spectrum of Zn·CDPPC ($c_{peptide}$ = 100 µM, in NH_4AcO buffer 20 mM, pH = 6.9). The insert gives the comparison of the experimental and theoretical isotopic pattern of the ion $[ZnLH_{-3}]^-$ with m/z = 520.1.

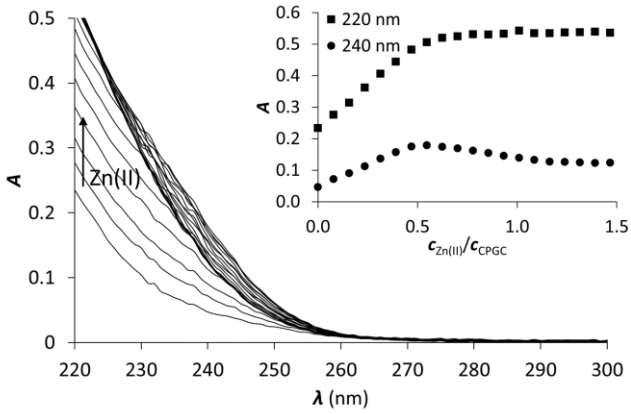

Figure S11. UV titration of CPGC (38.2 µM in phosphate buffer 20 mM, pH = 7.4) with Zn(II). The insert shows the evolution of the absorbance at λ = 220 and 240 nm as a function of the $c_{Zn(II)}/c_{CPGC}$ ratio

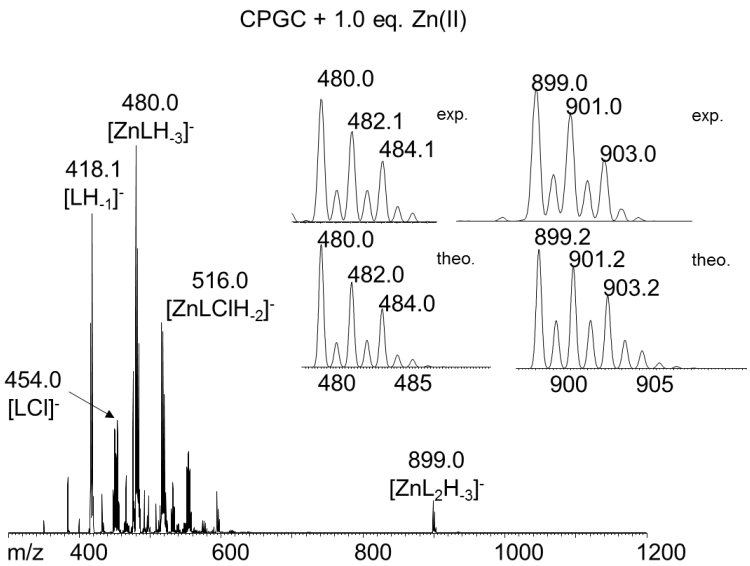

Figure S12. (−)ESI-MS spectrum of Zn·CPGC ($c_{peptide}$ = 100 µM, in NH_4AcO buffer 20 mM, pH 6.9). Inserts give the comparison of the experimental and theoretical isotopic pattern of the main ions.

^{1}H NMR Tables

Table S1. Assignments of the ^{1}H NMR resonances (δ, ppm) of CDPPC (major conformation) in H_2O/D_2O 9/1 v/v at 298 K, 500 MHz.

	NH	Hα	Hβ	Others
Cys1	8.21	4.77	2.77	(Ac) 1.95
DPro2	–	4.41	2.01; 2.23	(γ) 2.02
				(δ) 3.64; 3.89
Pro3	–	4.64	1.86; 2.28	(γ) 2.03
				(δ) 3.74
Cys4	7.87	4.32	2.87; 3.02	(NH_2) 7.07; 7.14

Table S2. Assignments of the ^{1}H NMR resonances (δ, ppm) of Cu_4(CDPPC)$_3$ in phosphate buffer (c_{buffer} = 20 mM, pH = 7.4, H_2O/D_2O 9/1 v/v) at 298 K, 500 MHz.

	NH	Hα	Hβ	Others
Cys1	7.81	4.74	3.12; 3.44	(Ac) 2.02
DPro2	–	4.54	2.04 ; 2.11	(γ) 1.85
				(δ) 3.62
Pro3	–	5.08	2.18 ; 2.50	(γ) 1.87 ; 2.02
				(δ) 3.52 ; 3.61
Cys4	9.24	4.10	2.54; 3.10	(NH_2) 6.96; 7.45

Table S3. Assignments of the ^{1}H NMR resonances (δ, ppm) of CPGC in H_2O/D_2O 9/1 v/v at 298 K, 500 MHz.

	NH	Hα	Hβ	Others
Cys1	8.28	4.67	2.82	(Ac) 1.97
Pro2	–	4.38	1.93; 2.26	(γ) 2.00
				(δ) 3.70; 3.78
Gly3	8.46	3.93	–	
Cys4	8.09	4.47	2.88	(NH_2) 7.14; 7.63