SUPPORTING INFORMATION

Influence of Stereochemistry, Affinity and Redox Potentials on Single- and Double-Strand DNA Cleavage by Copper and Nickel ATCUN Metallopeptides

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Table S1. Effect of Lys donor group and its stereochemistry on electrode potential ($M^{3+/2+}$) for Cu(II)• and Ni(II)•peptide complexes.

Peptide-Complex	E^o ($M^{3+/2+}$) (vs NHE)*					
	-COOH C-terminus		$-CONH_2$ C-terminus		$-CONH_2$ C-terminus, Lysine in D configuration	
	E^o [a]	ΔE (mV) [b]	E^o [a]	ΔE (mV) [b]	E^o [a]	ΔE (mV) [b]
Cu-GGH	1.0341	61	1.0684	100	-	-
Cu-GKH	-	-	1.0577	127	1.03255	84
Cu-KGH	-	-	1.0515	102	1.03311	66
Cu-KKH	-	-	1.0178	97	0.99368	53
Cu-KGHK	1.0488	54	1.0497	84	-	-
	E^o ($M^{3+/2+}$) (vs NHE)*					
Ni-GGH	1.007	171	1.087	-	-	-
Ni-GKH		-	1.097	-	1.157	-
Ni-KGH		-	1.097	186	1.067	151
Ni-KKH		-	1.077	-	1.047	-
Ni-KGHK	1.047	96	1.067	111	-	-

*At pH 7.4, [a] square wave voltammetry (E_s = 10 mV, E_{sw} = 25 mV, f = 100 Hz, I/E = -4) [b] Cyclic voltammetry (Scan rate = 100 mV/s, I/E = -4). 1 mM Cu/Ni-Peptide (Cu/Ni:Peptide, 1:1.1), in phosphate buffer, $[HPO_4]_t^-$ = 25 mM, pH = 7.4, μ = 0.1 M KCl. D-configuration forms of Lys-Gly-His-Lys were not studied.

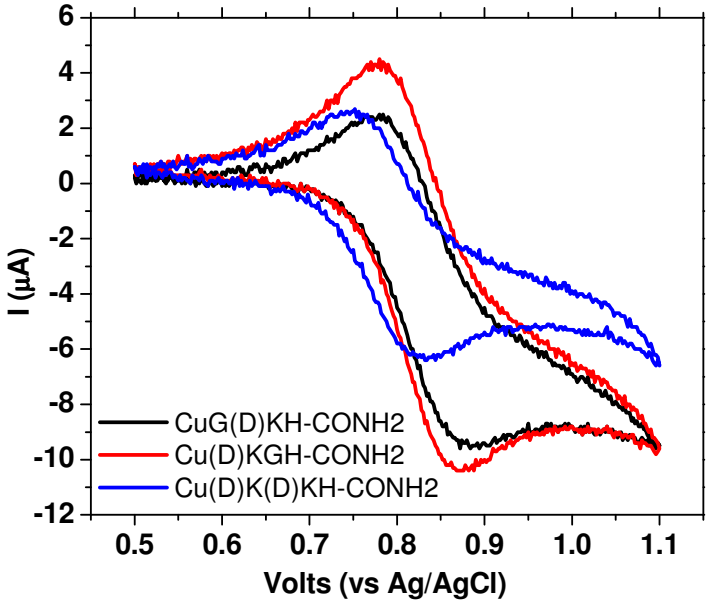

Figure S1. Cyclic voltammograms for some representative Cu(II)•peptide complexes. Conditions include: 1 mM Cu(II)•peptide (Cu:peptide, 1:1.1), in phosphate buffer, $[HPO_4]_t^-$ = 25 mM, pH 7.4, μ = 0.1 M KCl. Scan rate = 100 mV/s, I/E = -4. Buffer background was subtracted from each data.

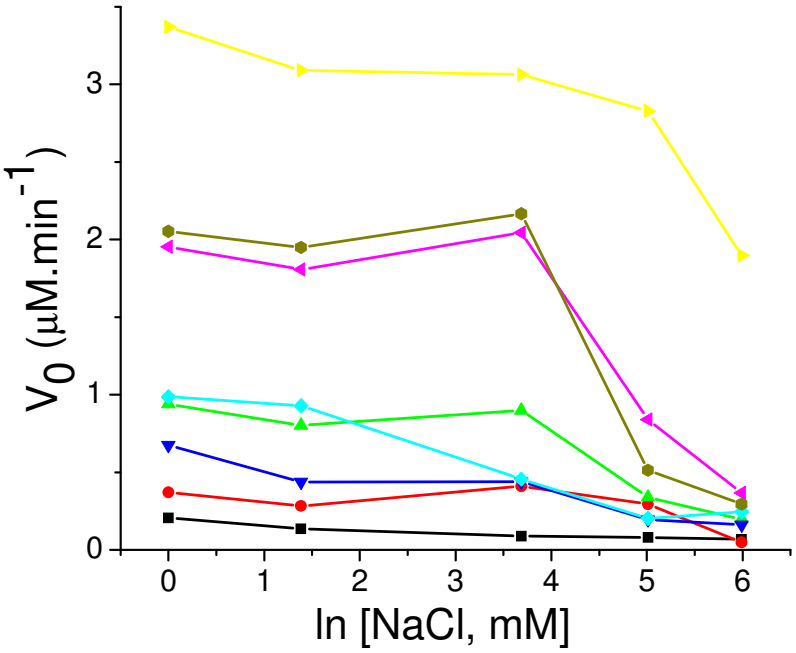

Figure 2S. Salt-dependent influence on the dsDNA cleavage reactivity of Cu^{2+}-ATCUN complexes. Cleavage activities of Cu^{2+}-GGH, Cu^{2+}-GKH, Cu^{2+}-KGH, Cu^{2+}-GdKH, Cu^{2+}-dKGH, Cu^{2+}-KKH, Cu^{2+}-dKdKH and Cu^{2+}-KGHK were studied, where [DNA] = 50 μM, [Cu^{2+}-ATCUN] = 40 μM, [ascorbate] = 500 μM in 20 mM Tris buffer, pH = 7.4, 37°C for 15 min, at 0 mM, 4 mM, 40 mM, 150 mM and 400 mM final NaCl concentrations.

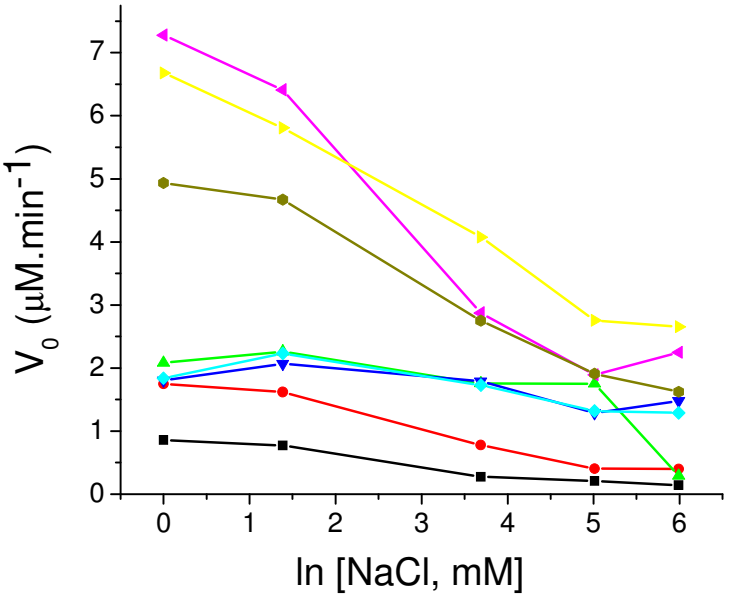

Figure 3S. Salt-dependent influence on the dsDNA cleavage reactivity of Ni^{2+}-ATCUN complexes. Cleavage activities of Ni^{2+}-GGH, Ni^{2+}-GKH, Ni^{2+}-KGH, Ni^{2+}-GdKH, Ni^{2+}-dKGH, Ni^{2+}-KKH, Ni^{2+}-dKdKH and Ni^{2+}-KGHK were studied, where [DNA] = 50 μM; [Ni^{2+}-ATCUN] = 4 μM, [KSO_5] = 50 μM in 20 mM Na Cacodylate buffer, pH = 7.4, 37 °C for 15 min, at 0 mM, 4 mM, 40 mM, 150 mM and 400 mM final NaCl concentrations.