Electronic Supplementary Material (ESI) for Dalton Transactions.

Copper ion interaction with the RNase catalytic site fragment of the Angiogenin protein: an experimental and theoretical investigation

Antonio Magrì, [a] *Giovanni Tabbì,*[a] *Raffaella Breglia,*[b] *Luca De Gioia,*[c] *Piercarlo Fantucci,*[c] *Maurizio Bruschi*[b]* *Raffaele P. Bonomo,* [d]* *Diego La Mendola* [e]*

[a]Consiglio Nazionale delle Ricerche, Istituto di Biostrutture e Bioimmagini (IBB-CNR), Via P. Gaifami 18, 95126 Catania (Italy)

[b]Dipartimento di Scienze dell'Ambiente e della Terra, Università di Milano-Bicocca, Piazza della Scienza 1 20126 Milan (Italy)

[c]Dipartimento di Biotecnologie e Bioscienze, Università di Milano-Bicocca, Piazza della Scienza 2 20126-Milan (Italy)

[d]Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale A. Doria 6, 95125 Catania, (Italy)

[e]Dipartimento di Farmacia, Università di Pisa, Via Bonanno Pisano 6, 56126 Pisa (Italy)

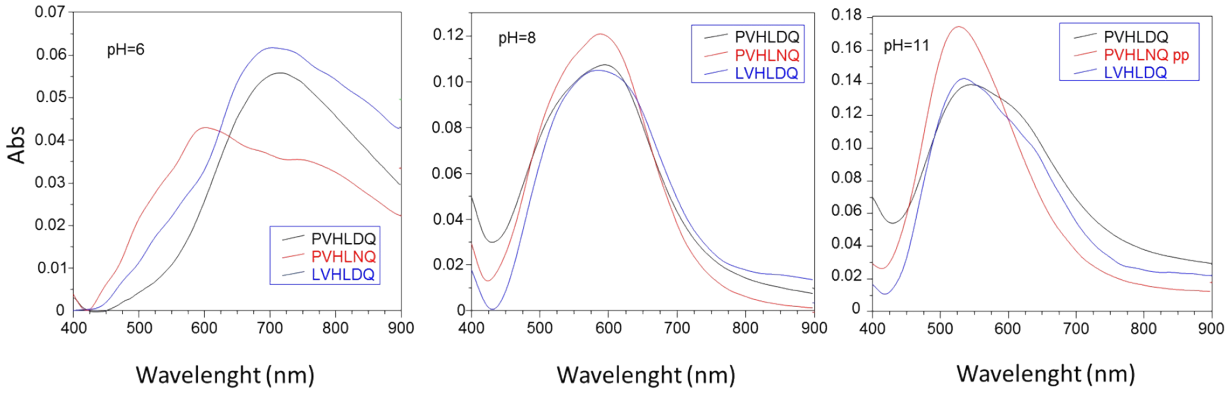

Figure S1 Uv-Vis spectra of Cu-Ac-PVHLDQ-NH_2 (black), Cu-PVHLNQ-NH_2 (red), Cu-LVHLDQ-NH_2 (blu) systems recorded at different pH values. At pH=11, in the system Cu-PVHLNQ-NH_2, a precipitation phenomenon was observed altering the Abs value.

Table S1 Relevant stabilities in (kcal mol^{-1}) of isomers of the $[Cu(Ac\text{-}PVHLDQ\text{-}NH_2)]^-$, $[Cu(Ac\text{-}PVHL\mathbf{N}Q\text{-}NH_2)]^0$, and $[Cu(Ac\text{-}\mathbf{L}VHLDQ\text{-}NH_2)]^-$ complexes computed using the BP86/SVP and the B3LYP/BS1 schemes on the geometries computed at the BP86/SVP level (for labels see the text).

Complex	ΔE BP86/SVP	ΔE B3LYP/BS1
CuL_A-1	25.3	24.7
CuL_A-2	10.3	12.6
CuL_A-3	0.0	0.0
CuL_A-W_{22}-2	39.3	26.7
CuL_A-W_{22}-3	0.0	0.0
CuL_{B1}-1	4.2	7.3
CuL_{B1}-2	0.7	4.2
CuL_{B1}-3	4.4	4.6
CuL_{B2}-1	5.3	7.3
CuL_{B2}-2	5.4	7.6
CuL_{B2}-3	0.0	0.0
CuL_{B1}-W_{22}-2	16.9	19.2
CuL_{B1}-W_{22}-3	12.3	18.3
CuL_{B2}-W_{22}-2	47.1	41.3
CuL_{B2}-W_{22}-3	0.0	0.0
CuL_C-1	16.5	19.4
CuL_C-2	7.0	7.6
CuL_C-3	0.0	0.0
CuL_C-W_{22}-2	0.0	0.0
CuL_C-W_{22}-3	1.4	4.1

Table S2 EPR g-tensors of the $[Cu(Ac\text{-}PVHLDQ\text{-}NH_2)]^-$, $[Cu(Ac\text{-}PVHL\mathbf{N}Q\text{-}NH_2)]^0$ and $[Cu(Ac\text{-}\mathbf{L}VHLDQ\text{-}NH_2)]^-$ complexes computed using the B3LYP functional and the BS1 basis set on geometries optimized at the RI-BP86/SVP level of theory (for labels see the text)

Complex	$g_z \equiv g_{\|\|}$	g_x	g_y	g_{iso}
CuL_A-1	2.179	2.036	2.084	2.099
CuL_A-3	2.146	2.040	2.046	2.077
CuL_A-W_{22}-2	2.177	2.051	2.062	2.096
CuL_A-22W-3	2.168	2.045	2.065	2.093
Expt.	2.224			
CuL_{B1}-1	2.166	2.029	2.089	2.095
CuL_{B1}-2	2.153	2.037	2.062	2.084
CuL_{B1}-3	2.145	2.041	2.050	2.079
CuL_{B2}-1	2.152	2.042	2.054	2.083
CuL_{B2}-2	2.167	2.046	2.060	2.091
CuL_{B2}-3	2.138	2.041	2.044	2.074
CuL_{B1}-W_{22}-2	2.159	2.048	2.053	2.087
CuL_{B1}-W_{22}-3	2.174	2.056	2.058	2.096
CuL_{B2}-W_{22}-2	2.156	2.047	2.051	2.085
CuL_{B2}-W_{22}-3	2.152	2.045	2.051	2.083
Expt.	2.220			
CuL_C-1	2.160	2.027	2.074	2.087
CuL_C-2	2.153	2.047	2.049	2.083
CuL_C-3	2.144	2.037	2.047	2.076
CuL_C-W_{22}-2	2.156	2.036	2.059	2.084
CuL_C-W_{22}-3	2.163	2.043	2.061	2.089
Expt.	2.230			

Table S3 Mulliken atomic spin densities for the Cu ion and ligand atoms of $[Cu(Ac\text{-}PVHLDQ\text{-}NH_2)]^-$, $[Cu(Ac\text{-}PVHLNQ\text{-}NH_2)]$ and $[Cu(Ac\text{-}LVHLDQ\text{-}NH_2)]^-$ complexes computed using the B3LYP functional and the BS1 basis set on geometries optimized at the RI-BP86/SVP level of theory (for complex labels see the main text)

Complex	Cu	N_{His}	N_{Leu}	N_{Asp}	O_{Asp}; $O1_{Asn}$; $O2_{Asn}$	O_{Val}; O_w
CuL_A-1	0.60	0.03	0.11	0.12	0.11	0.01
CuL_A-2	0.57	0.06	0.09	0.12	0.11	0.00
CuL_A-3	0.56	0.05	0.12	0.13	0.09	0.00
CuL_A-W_{22}-2	0.52	0.06	0.14	0.11	0.06	0.00
CuL_A-W_{22}-3	0.61	0.06	0.10	0.13	006	0.00
CuL_{B1}-1	0.60	0.04	0.18	0.10	0.03	0.01
CuL_{B1}-2	0.57	0.05	0.15	0.12	0.04	0.00
CuL_{B1}-3	0.55	0.05	0.18	0.12	0.04	0.00
CuL_{B2}-1	0.58	0.04	0.16	0.15	0.04	0.00
CuL_{B2}-2	0.58	0.04	0.16	0.15	0.04	0.00
CuL_{B2}-3	0.60	0.04	0.13	0.12	0.05	0.00
CuL_{B1}-W_{22}-2	0.59	0.06	0.12	0.12	0.06	0.00
CuL_{B1}-W_{22}-3	0.62	0.05	0.15	0.12	0.04	0.00
CuL_{B2}-W_{22}-2	0.60	0.05	0.15	0.12	0.04	0.00
CuL_{B2}-W_{22}-3	0.59	0.06	0.13	0.12	0.06	0.00
CuL_C-1	0.59	0.05	0.10	0.12	0.11	0.00
CuL_C-2	0.57	0.05	0.08	0.13	0.10	0.00
CuL_C-3	0.55	0.04	0.09	0.15	0.13	0.00
CuL_C-W_{22}-2	0.59	0.05	0.12	0.15	0.06	0.00
CuL_C-W_{22}-3	0.61	0.06	0.11	0.13	0.07	0.00