Supplementary data to accompany:

Monomer, dimer or cyclic helicate? Coordination diversity with hard-soft *P*,*N*-donor ligands?

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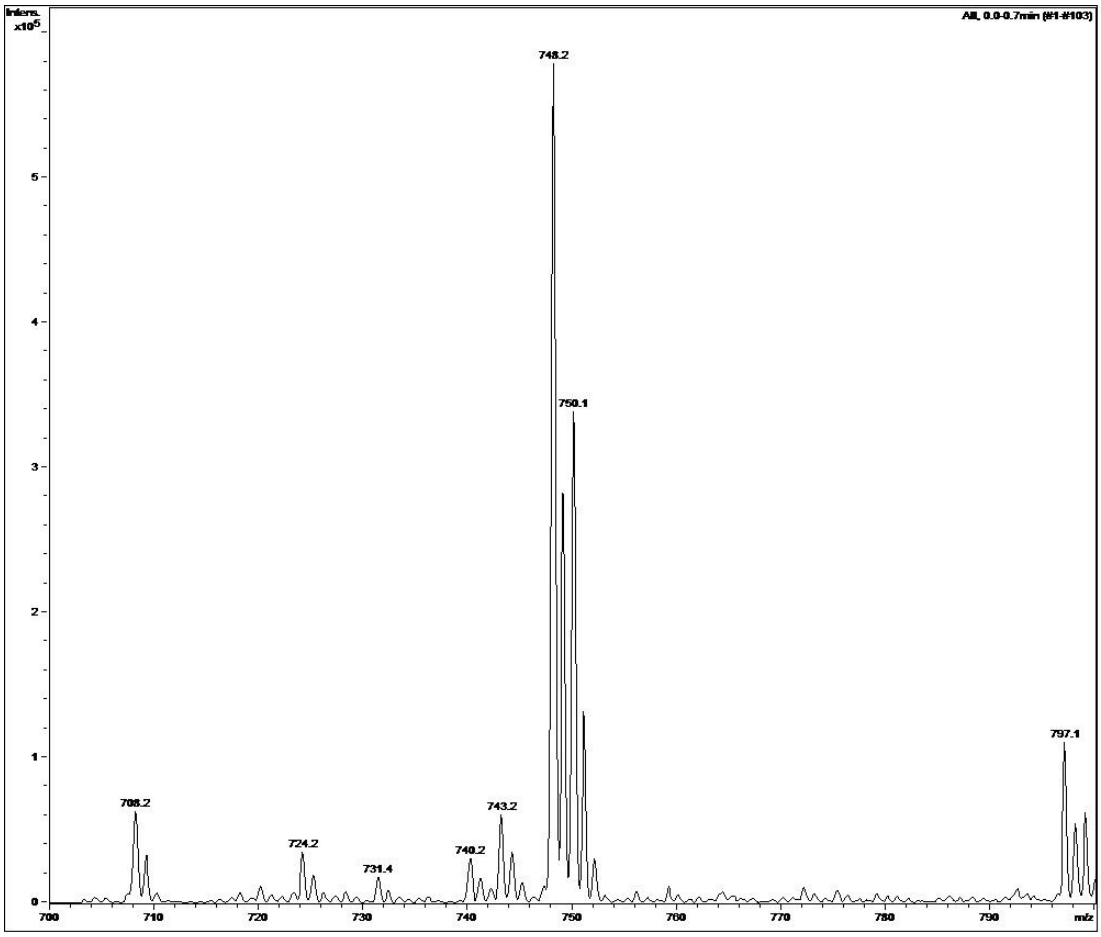

Figure S1a. ESI MS of an MeOH solution of [Cu(**1**)][PF_6] showing *m/z* 748.2 assigned to [Cu(**1**)]$^+$. The peak envelope at *m/z* 797.1 is assigned to [Cu(**1**)(MeOH)(OH)]$^+$, oxidation occurring in the mass spectrometer.

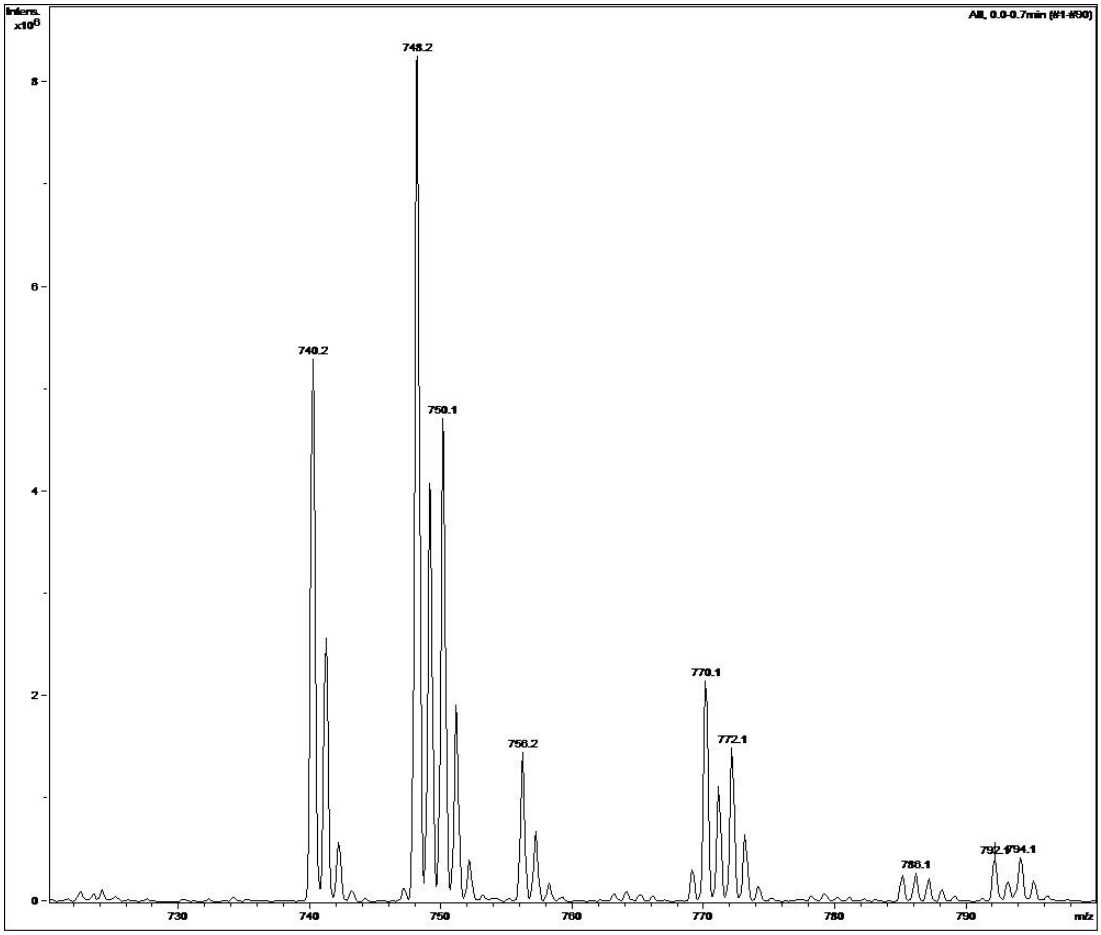

Fig. 1b ESI MS of a solution of [Cu(**1**)][PF_6] in a 1 : 1 mixture of MeOH and CH_2Cl_2; peak assignments: *m/z* 740.2 [**1** + 2O + Na]$^+$, 756.2 [**1** + 2O + K]$^+$, 748.2 [Cu(**1**)]$^+$, 770.1 [Cu(**1**) – H + Na]$^+$. The peak at *m/z* 792.1 is tentatively assigned to [Cu(**1**) – 2H + 2Na]$^+$.

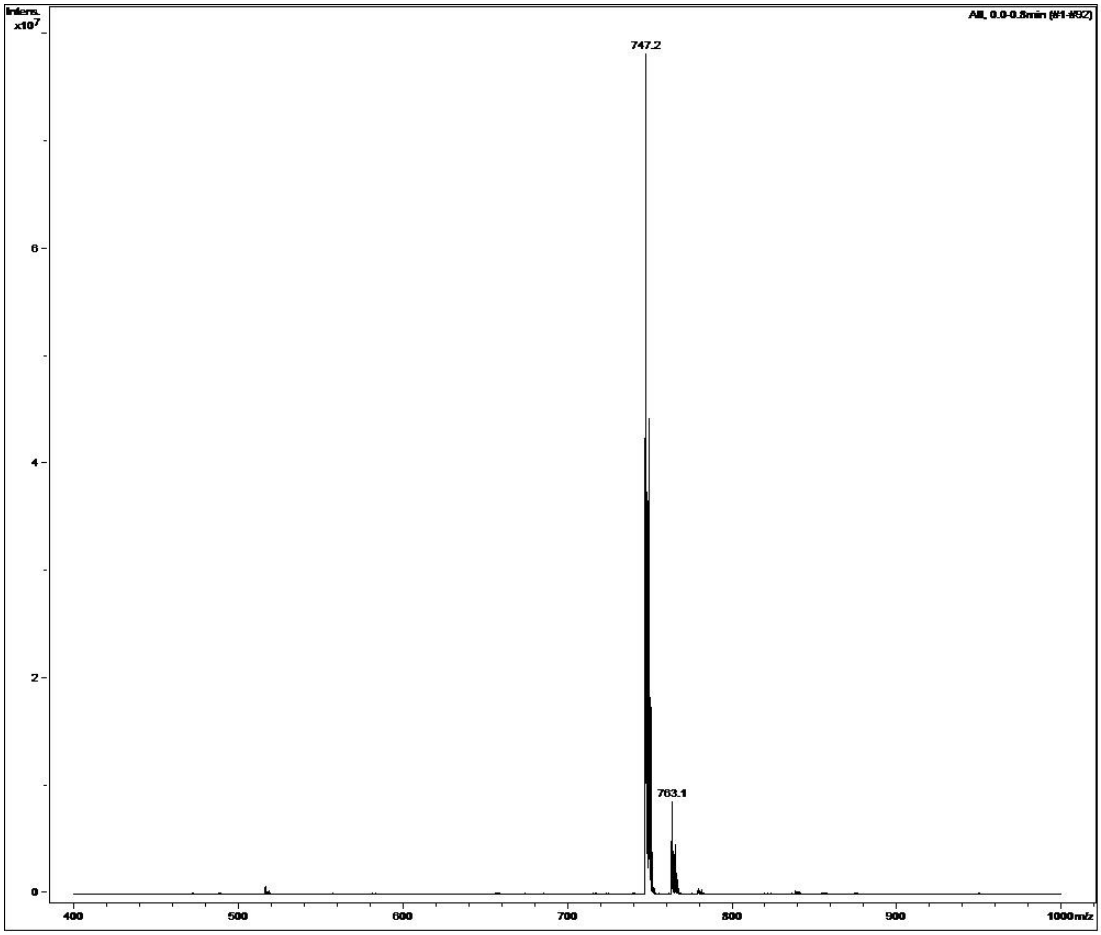

Figure S2. ESI MS of an MeCN solution of [Cu(**2**)][PF_6]: *m/z* 747.2 corresponds to [Cu(**2**)]$^+$ and *m/z* 763.1 to [Cu(**2** + O)]$^+$.

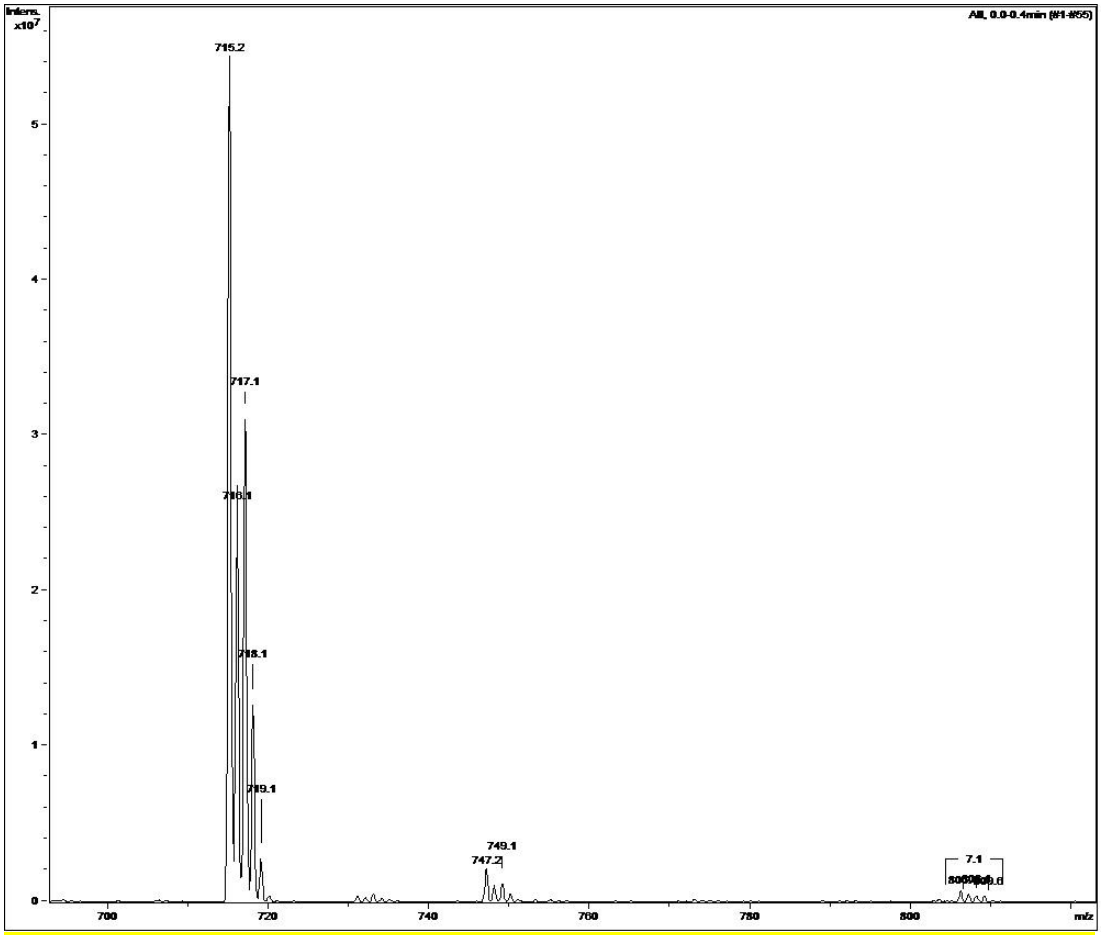

Figure S3 ESI MS of a MeOH solution of [Cu(**3**)][PF_6]: *m/z* 715.2 corresponds to [Cu(**3**)]$^+$.

Crystallographic data for 2{[Cu_2(3**)$_2$][PF_6]$_2$}·C_5H_{12}·5H_2O**

$C_{181}H_{158}Cu_4F_{24}N_8O_5P_{12}$, M = 3607.02, yellow block, monoclinic, space group $P2_1/c$, a = 12.9676(14), b = 47.180(5), c = 18.0286(15) Å, β = 128.169(5)°, U = 8671.8(15) Å^3, Z = 2, D_c = 1.378 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.677 mm^{-1}, T = 123 K. Total 70538 reflections, 19083 unique, R_{int} = 0.0600. Refinement of 12947 reflections (1119 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0831 ($R1$ all data = 0.1296), $wR2$ = 0.2258 ($wR2$ all data = 0.2623), gof = 1.160. CCDC 907594.

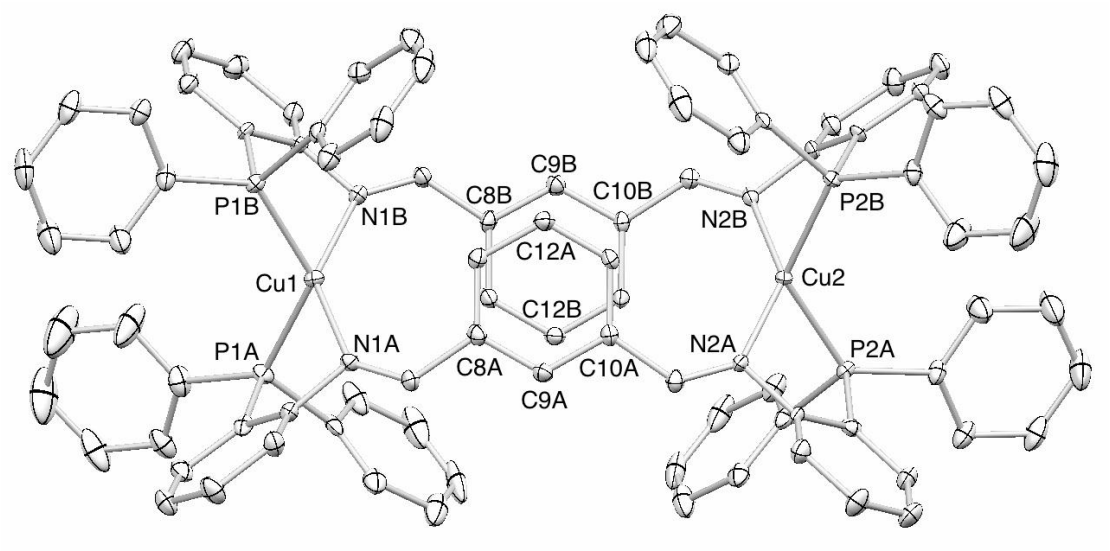

Fig. S4 The structure of the $[Cu_2(\mathbf{3})_2]^{2+}$ cation in $2\{[Cu_2(\mathbf{3})_2][PF_6]_2\}\cdot C_5H_{12}\cdot 5H_2O$ (ellipsoids plotted at 40% probability level and H atoms omitted). Selected bond parameters: Cu1-N1A = 2.119(3), Cu1-N1B = 2.120(4), Cu1-P1A = 2.2441(9), Cu1-P1B = 2.2442(9), Cu2-N2A = 2.089(3), Cu2-N2B = 2.138(3), Cu2-P2B = 2.2332(9), Cu2-P2A = 2.2531(9) Å; N1A-Cu1-N1B = 140.15(12), N1A-Cu1-P1A = 83.36(8), N1B-Cu1-P1A = 114.38(9), N1A-Cu1-P1B = 115.00(8), N1B-Cu1-P1B = 83.28(8), P1A-Cu1-P1B = 127.51(4), N2A-Cu2-N2B = 140.74(12), N2A-Cu2-P2B = 119.53(9), N2B-Cu2-P2B = 81.96(8), N2A-Cu2-P2A = 83.69(8), N2B-Cu2-P2A = 110.29(8), P2B-Cu2-P2A = 127.07(4) .