Supplementary information

A spectroelectrochemical study of copper chloro-complexes for high performance all-copper redox flow batteries

Giampaolo Lacarbonara[a§], Nicolò Albanelli[a§], Daniele Fazzi[a], Catia Arbizzani[a§*]

[a]Alma Mater Studiorum - University of Bologna, Dept. of Chemistry "Giacomo Ciamician",

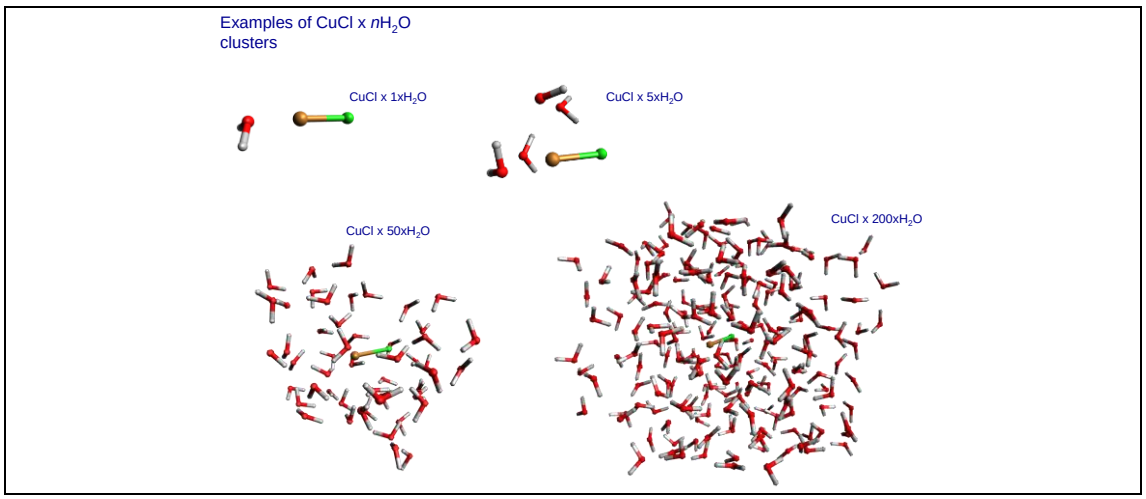
Via Francesco Selmi 2, 40126 Bologna, Italy

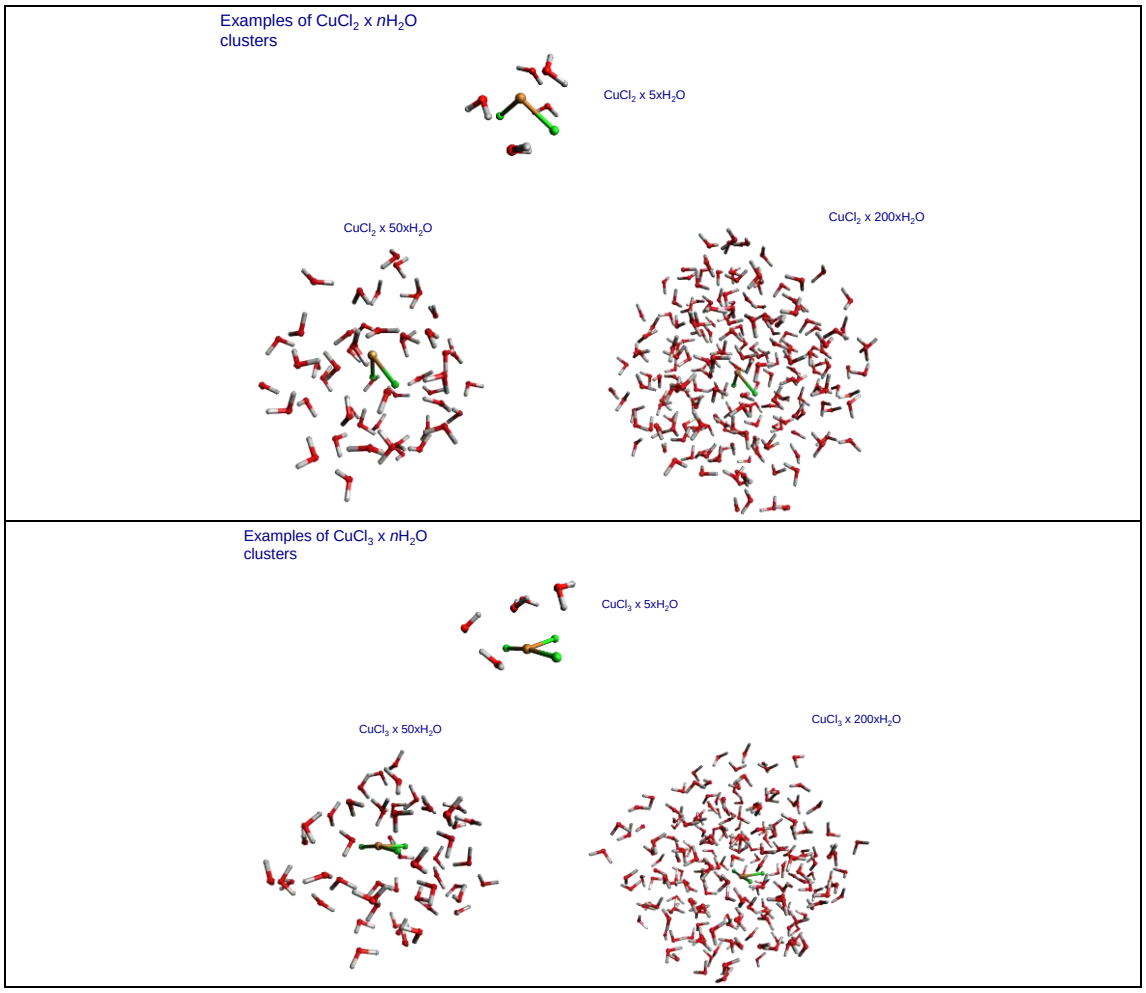
* Corresponding Author: catia.arbizzani@unibo.it

§ ISE Members

1. Calculations

a. Example of optimized (GFN2-xTB) water copper-chloride supramolecular clusters.





b. Optimized (GFN2-xTB) geometry for $[CuCl(H_2O)_5]^+$

O	-2.7599122238	-0.3335844248	-0.2996072262
Cl	0.9603619173	-1.6463921577	0.1555632251
Cu	-0.7278111628	-0.1654402697	0.2726916931
O	-0.1547980495	1.5557862806	1.4474117895
O	-0.6967317927	1.3338709274	-1.4395155435
O	1.8164179369	0.4036333442	-1.8619007240
O	2.3631818679	0.9615560708	0.9550925003
H	-2.7555813661	-1.1454356353	-0.8153441982
H	-2.7107425919	0.4019312335	-0.9236169948
H	-0.5878672332	2.1106260353	-0.8828762561
H	0.2080880910	1.0882061340	-1.7328454176
H	0.8314367040	1.4581623618	1.3320016335
H	-0.3418023401	1.3342574439	2.3619011461
H	2.1074822118	0.0176963070	-2.6894102043

H	1.6226733733	-0.3567427579	-1.2616588787
H	2.5344506442	1.1841206380	0.0329338011
H	2.1790677577	0.0037812069	0.9396047295

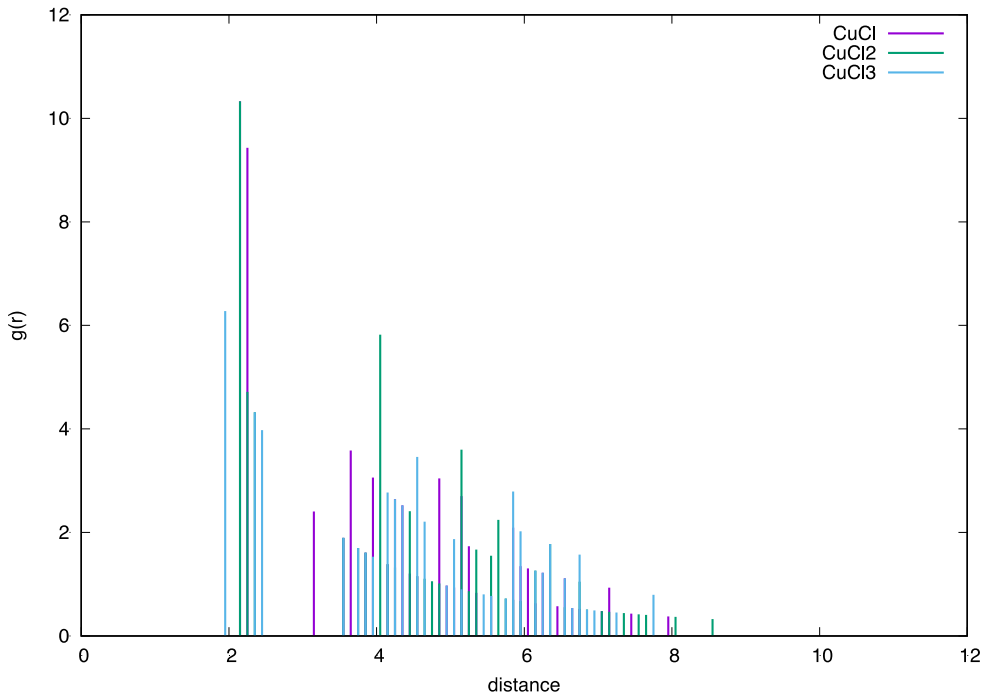
c. Optimized (GFN2-xTB) geometry for $[CuCl_2(H_2O)_4]^0$

O	-0.3038060950	1.0320559058	-1.7117699988
Cu	0.2703833903	0.1667054970	0.3113748432
Cl	-1.0249183703	-1.6187053839	0.4696427171
Cl	2.1208999465	-0.8421134306	-0.4914698328
O	1.5067718223	1.8002388522	0.6198349273
O	-1.3692837260	1.3124795095	1.0902061582
O	-2.8610350287	0.2354960323	-0.9750845115
H	0.1142288018	0.4080800740	-2.3144609005
H	-1.2608299675	0.8585328511	-1.7357329980
H	2.3246481054	1.3995554051	0.2809646219
H	1.1963545267	2.4339644838	-0.0376496511
H	-2.4429918568	-0.5704412145	-0.5941370703
H	-3.7613780492	-0.0008695975	-1.2065160057
H	-1.6685826435	0.8083188331	1.8548600582
H	-2.0436512332	1.1796220229	0.3948384840

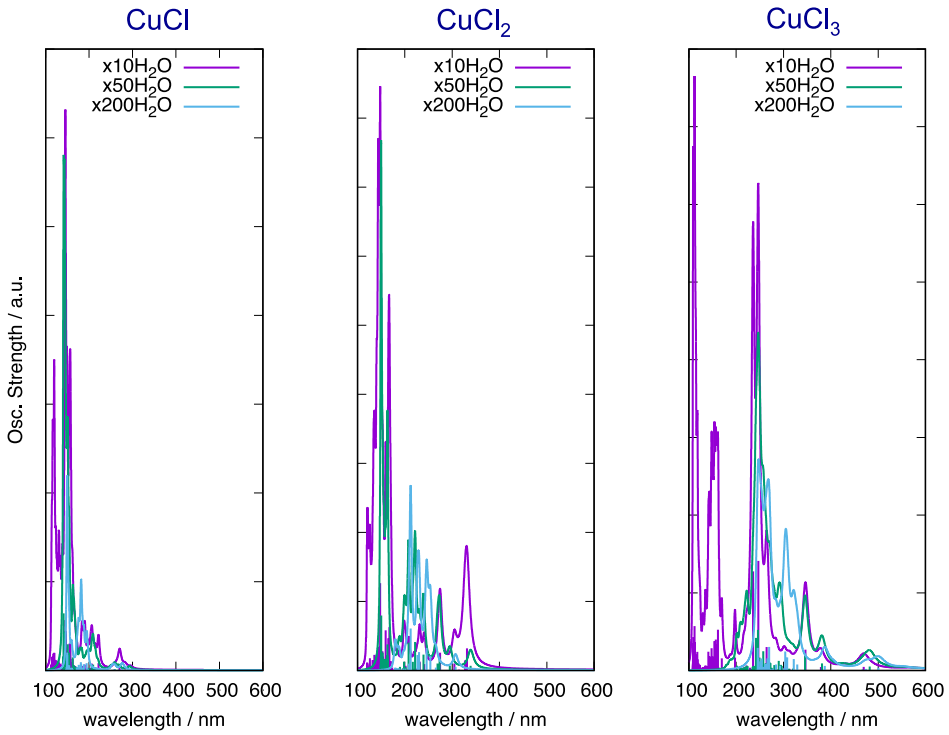
d. Optimized (GFN2-xTB) geometry for $[CuCl_3(H_2O)_3]^-$

O	-0.8837196322	-1.3536342608	1.0492810436
Cu	0.1803511293	0.0122251617	0.2996706058
Cl	-1.4530229176	1.4060568265	0.4441310985
Cl	1.8246931265	-1.3915790290	0.1835006193
Cl	1.4209939154	1.5505215876	-0.3764847997
O	-0.4292691232	-0.6124687687	-1.9532050608
O	-2.8908107878	-1.1768048658	-0.5434552430
H	-0.4150571484	-2.1988372335	0.9754966824
H	-1.7537380734	-1.4050590241	0.5131388640
H	-0.2883251402	0.2180301037	-2.4224183067
H	0.3032059889	-1.1938587482	-2.1908160997
H	-2.3586911708	-1.0572325278	-1.3416525492
H	-3.1842330760	-0.2923438365	-0.2857877478

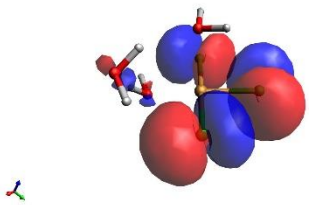
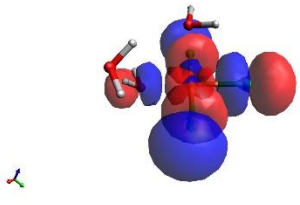
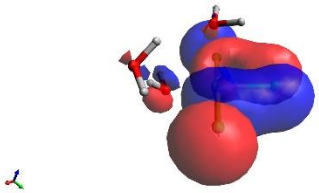
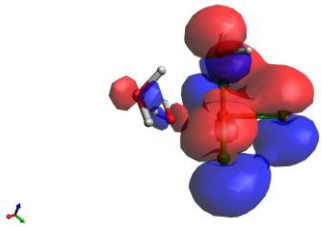
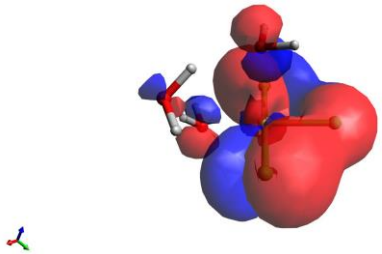
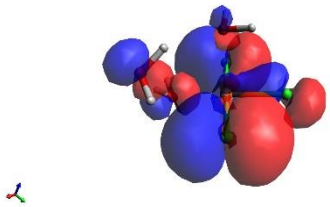
e. Cu-O radial distribution function $g_{Cu\text{-}O}(r)$ computed for clusters containing 50 water molecules.



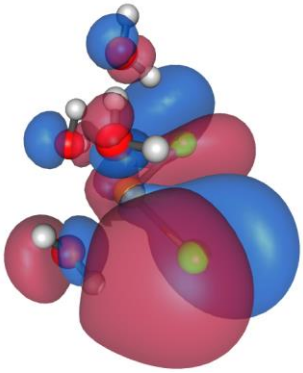
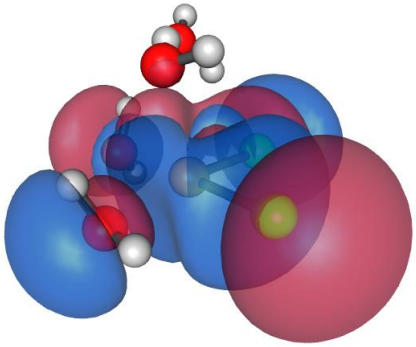
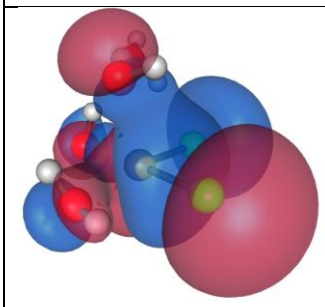
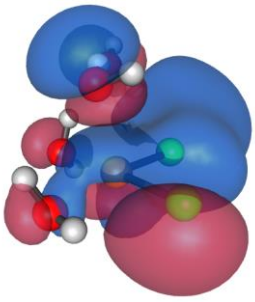
f. TDDFT calculations on water copper-chloride supramolecular clusters by varying the number of water molecules, e.g. 10, 50 and 200.



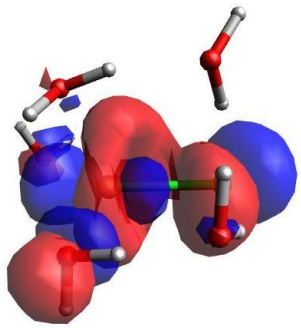
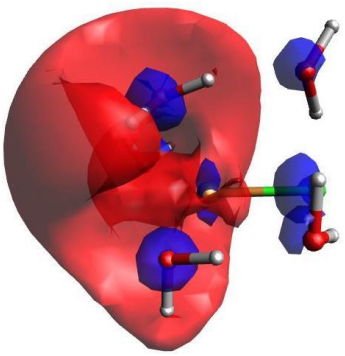
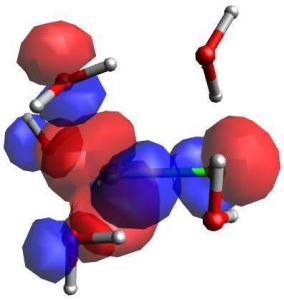
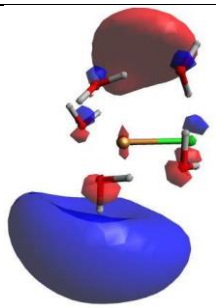
g. Molecular orbitals involved in the electronic transitions: $[CuCl_3(H_2O)_3]^-$

 HOMO	 LUMO
 HOMO-7	 HOMO-5
 HOMO-6	 HOMO-3

h. Molecular orbitals involved in the electronic transitions: $[CuCl_2(H_2O)_4]$

 HOMO	 LUMO
 HOMO-4	 HOMO-3

h. Molecular orbitals involved in the electronic transitions: $[CuCl(H_2O)_5]^+$

 HOMO	 LUMO
 HOMO-4	 LUMO+1

2. Cu(II) speciation dependence from Cl^- concentration

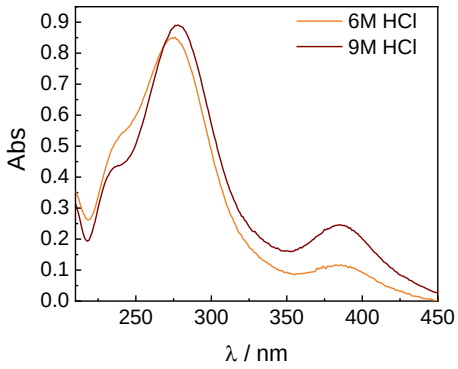


Figure S1. UV/Vis absorption spectra of 50 mM $CuCl_2$ electrolytes with different concentrations of HCl in a quartz cuvette with 50 μm optical path.

3. Cu(II) voltammetric dependence from Cu(II) concentration

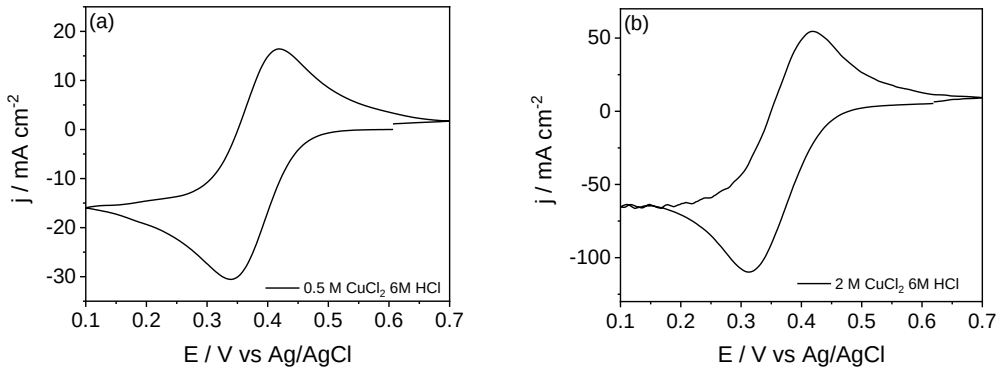


Figure S2. CV at 0.01 V s^{-1} of (a) 0.5 M $CuCl_2$ 6 M HCl and (b) 2 M $CuCl_2$ 6 M HCl electrolytes in three-electrode conventional cell, WE: Pt disk, CE: Pt wire, RE: Ag/AgCl.