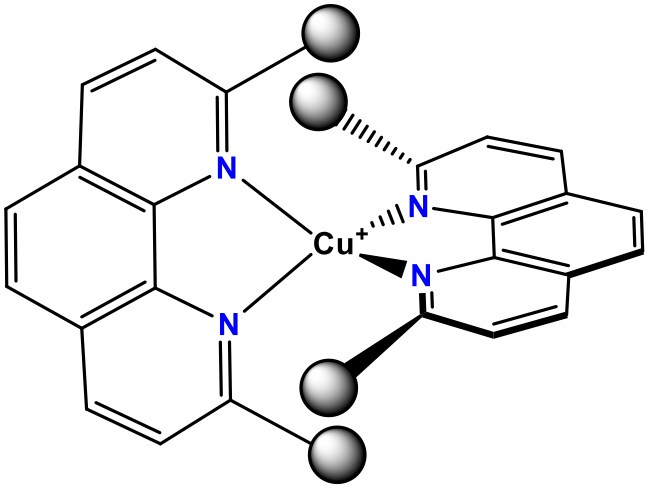

Figure S1. Bulky phenantroline-based ligands inducing Td geometry.

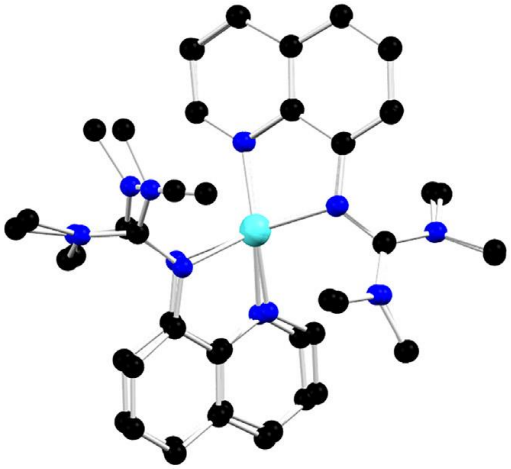

Figure S2. Superimposition of the molecular structures of $[Cu^{I/II}(TMGqu)_2]^{+/2+}$. From ref. [1]

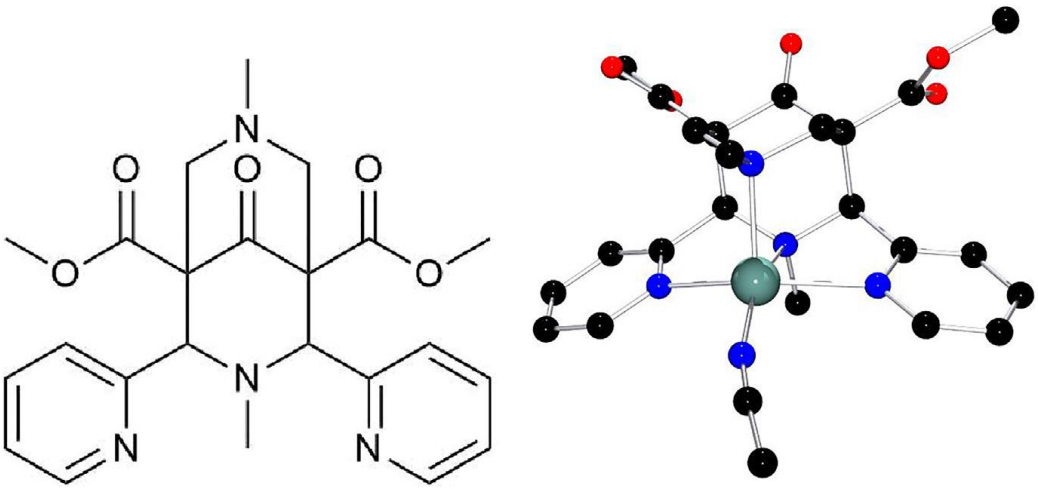

Figure S3. Scheme of a bispidine ligand and the corresponding cuprous complex that adopts a Cu(II) like SBP geometry. From [2].

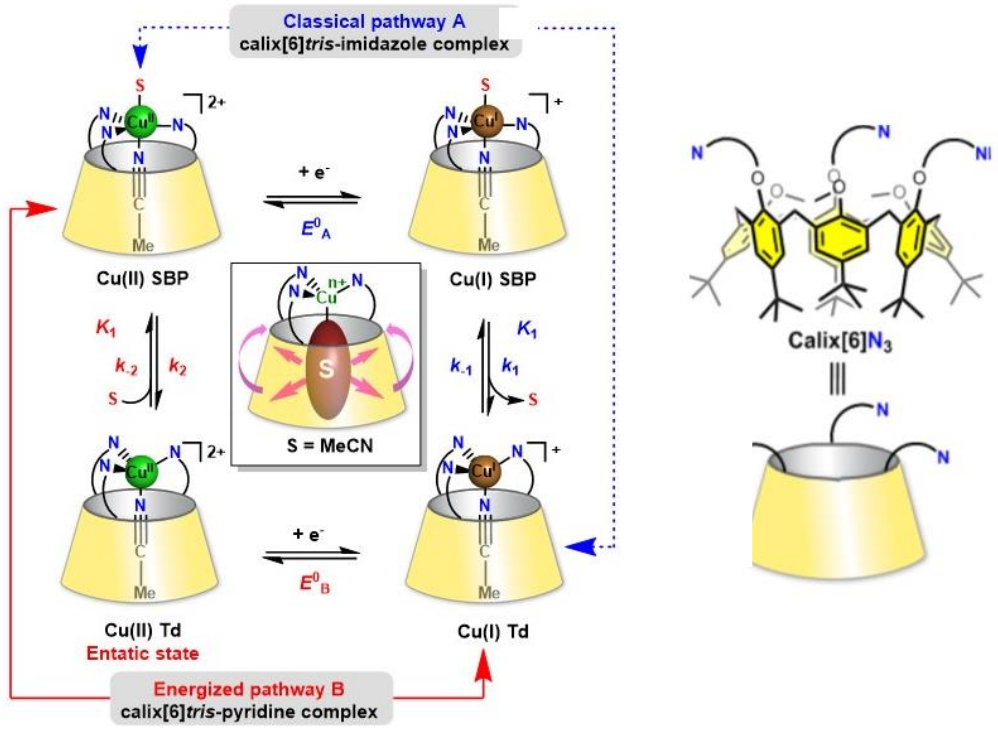

Figure S4. Supramolecular control of the electrochemical – chemical pathways by the calixarene cavity. With N-ligand = imidazole, pathway A: first reduction top Cu(I), then change in geometry from SBP to Td is observed. With N-ligand = pyridine, 'entatic-like' pathway B: first change in geometry from SBP to Td and then reduction to Cu(I). From ref. [3].

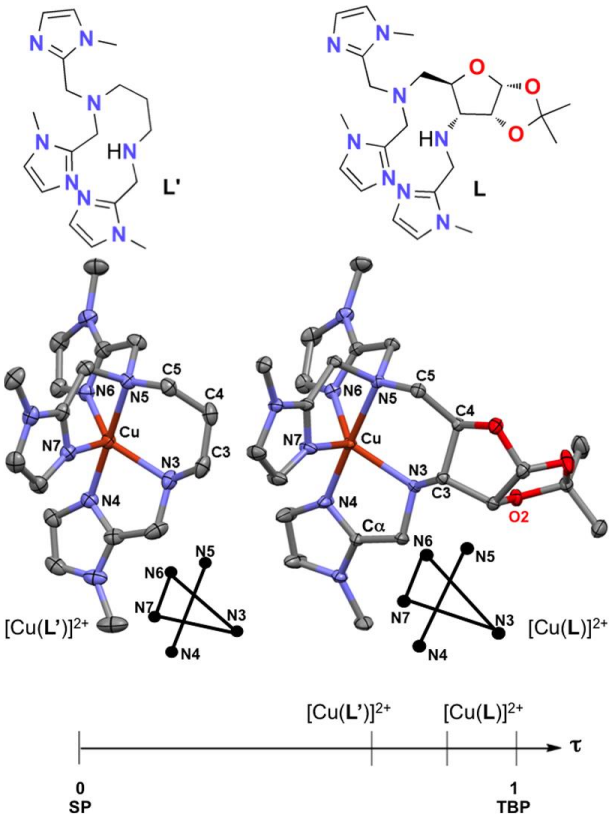

Figure S5. Structure of the glycoligand (L) and linear analogue (L') and of the corresponding X-ray $[Cu^{II}(L/L')]^{2+}$ structures. From ref. [4].

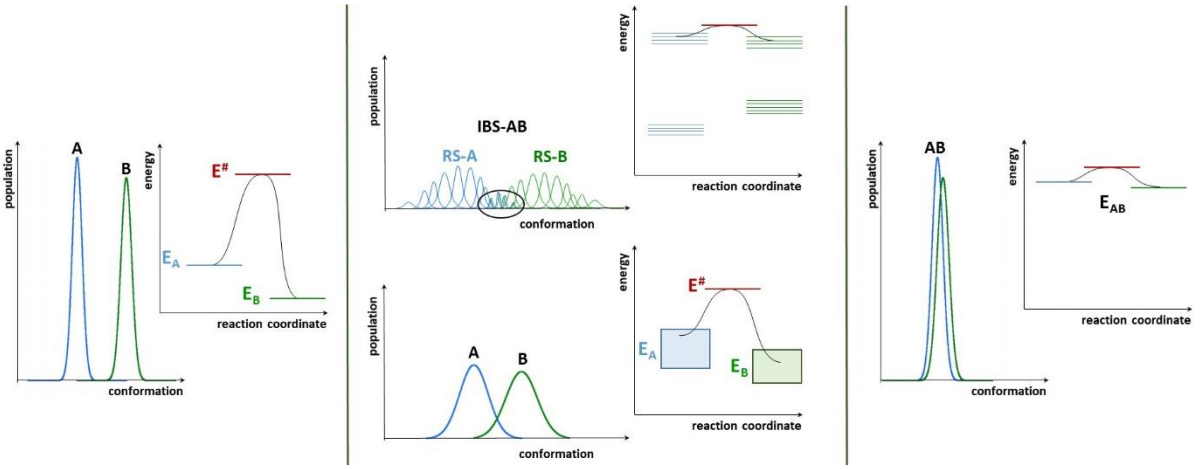

Figure S6. Different cases of Cu(I) - Cu(II) redox process in copper complexes. Left: classical case, middle: IBS mechanism (top) and ecstatic case (bottom), Right: Panel: Entatic. Two data are given: the population as a function of the conformation and the energy as function of a reaction coordinate. Subscripts A and B corresponds to the preferred environment for Cu(I) and Cu(II), respectively. AB to a geometry intermediate between A and B, RS to resting state, IBS to In-Between State, and # to the transition state.

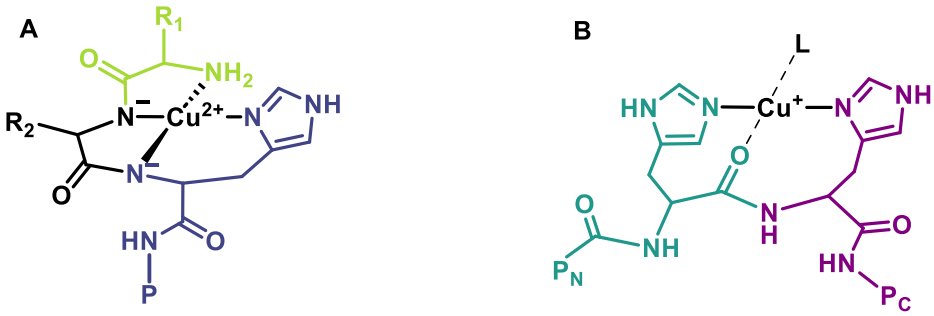

Figure S7. A: scheme of an ATCUN motif.[5] R_1, R_2 and P represent the side-chains of the first and second amino-acid residues and the C-terminal part of the peptide respectively. B: scheme of a bis-His binding motif. P_N and P_C represent the N-terminal and C-terminal sequence of the peptide, respectively. L is a possible additional ligand from the peptide. R_1, R_2, P, P_N and P_C depends on the peptide under focus (human Ctr1 or histatins). For more details, see refs.[6-9]

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