Molecular Cages as Spin Switches and Templates for polynuclear Clusters

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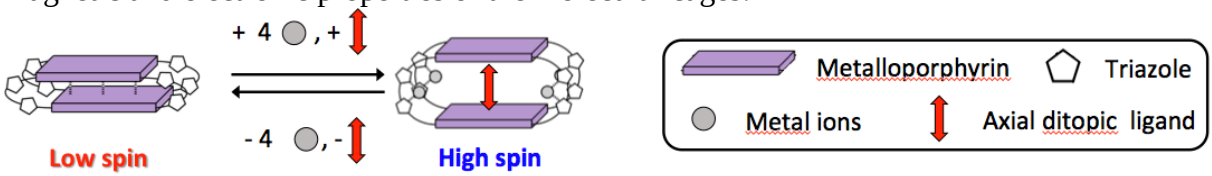
Spin states switches represent a promising field in molecular materials chemistry.[1] The spatial arrangement of the components of three-dimensional architectures can be used to optimize physical properties, such as magnetic or spin-spin interactions.[2] Metalloporphyrins are attractive constituents of molecular cages since their large aromatic cores delineate well the cavity and assist the encapsulation of π-conjugated guest molecules.[3] Furthermore, their coordination, redox, electronic, magnetic, catalytic and photophysical properties are easily tuned by the choice of the substituents or the metal ion.[3] In particular, the spin state of Ni(II)-porphyrins depends on the presence of additional axial ligands: with no ancillary ligand, the geometry around Ni(II)-porphyrins is roughly square planar and the complex is diamagnetic and low spin (S=0); with one or two axial ligands, they become a paramagnetic high spin species (S=1).[4] They thus constitute coordination-induced spin-state switches.

We recently synthesized covalent cages consisting of two porphyrins connected by four flexible linkers, each incorporating two 1,2,3-triazolyl ligands.[5] In these molecules, the components are orthogonal binding sites, metalloporphyrins for coordinating ligands and triazoles as allosteric sites for binding metal ions, and controlling the size of the cavity. These sophisticated architectures have been used so far as allosteric receptors[6a,b] and as catalysts.[6c]

The aims of this thesis project are to take advantage of the spatial arrangement of the components of such capsules to control the spin states of the supramolecular capsule. The face-to-face metalloporphyrins can fix axial ligands depending on the absence or presence of metal ions on the triazole peripheral binding sites (see Figure). Another aspect will be to explore the magnetic properties of tetra- or octanuclear clusters obtained by coordination of paramagnetic ions to the triazole ligands. An experimental approach based on EPR spectroscopy, including pulsed hyperfine spectroscopy (ESEEM, ENDOR, HYSCORE) will be used to characterize the magnetic and electronic properties of the molecular cages.[7]



The student will have the opportunity to work with groups specialized in DFT calculations, magnetic measurements and photochemical characterizations of the designed structures.

References

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