BIOINSPIRED CAGED CATALYSTS

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O_2-activating metalloproteins (containing Cu, Fe or Mn metals) perform challenging functionalization of inert C-H bonds, under physiological conditions, in a remarkably efficient manner. [1] The binding cavities found in these systems govern the selectivity and efficiency of reactions. In their hydrophobic channels, destabilizing (like steric repulsion) and stabilizing (like H-bonding) forces allow for substrate positioning and activation/stabilization of highly reactive intermediates. In order to reproduce the efficient chemistry found in nature, we therefore develop bioinspired complexes where the reactive metal center is entrapped in chiral cage architectures describing well-defined hydrophobic cavities. We have recently demonstrated that these organic supra-structures allow for protection of Cu(I) active sites, [2] control of the chirality around the metal core, and lead to enhanced oxidation catalysts (eg CH_4 oxidation). [3] On this basis, we are currently developing caged O_2-activating Cu(I) catalysts displaying an H-bonding hydrophobic cavity, [4] aiming at controlling substrate positioning and/or stabilizing metastable intermediates.

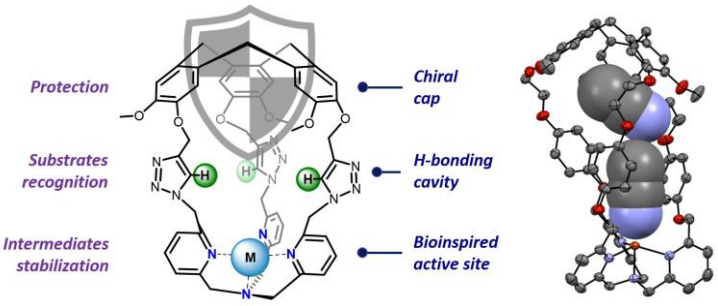

Figure 1. Schematic representation of the targeted caged catalysts along with an example of XRD structure of a caged copper complex.

Discussion about (*i*) the crucial role of these hydrophobic cavities for efficient and selective transformations and (*ii*) the unusual coordination properties of related caged complexes, will be the core of this communication, which aims at giving a better understanding of the benefits of these novel confined oxidation catalysts.

1) W. B. Tolman and co., *Chem. Rev.*, **2017**, 117, 2059.
2) G. Qiu, P. Nava, A. Martinez and C. Colomban, *Chem. Commun.*, **2021**, 57, 2281.
3) D. Diao, A. J. Simaan, A. Martinez, C. Colomban, *Chem.Commun.* **2023**, 59, 4288 (***2023 Emerging investigators***).
4) G. Qiu, D. Diao, … , A. J. Simaan, P. Nava, A. Martinez, C. Colomban, *Dalton Trans.*, **2022**, 51, 10702 (***New talent: Europe 2022*** themed issue, "***hot-article***").