Aix*Marseille université

Ecole Doctorale des Sciences Chimiques ED250

cnrs

Exploring metallopeptides as oxidation catalysts

Laboratory : Institut des Sciences Moléculaires de Marseille UMR CNRS 7313

Aix-Marseille Université, Campus Scientifique de Saint Jérôme

Avenue Escadrille Normandie-Niemen, F-13397 MARSEILLE CEDEX 20

Thesis supervisor: Dr. Olga Iranzo

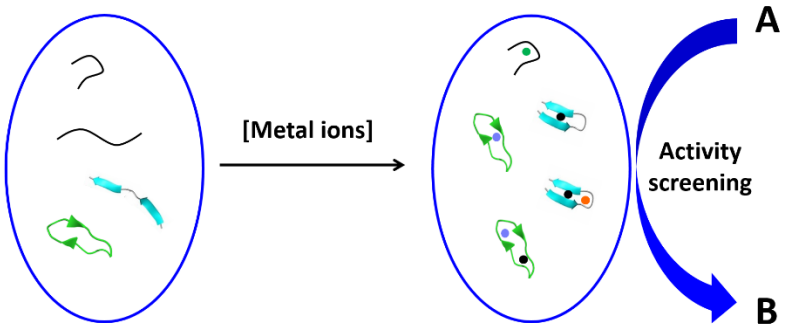
Thesis co-supervisor: Dr. Thierry Tron

Project Description:

The development of sustainable, more efficient and selective organic synthesis is one of the fundamental research goals in chemistry. In this respect, catalysis is a central technology since the majority of chemical and pharmaceutical products on an industrial scale rely on catalysis for their synthesis. Due to the increasing price of energy and limited supplies of fossil feedstock, a transition towards a sustainable supply of energy and raw materials is compelling. In this context, new catalytic transformations and more efficient catalysts are still required to unveil potential applications of otherwise unreactive molecules.

Copper-containing enzymes are known to participate in a variety of O_2-processing reactions acting either as oxygenases, which mediate oxygen-atom transfer to organic substrates, or as oxidases, which couple the reduction of O_2 to H_2O (or H_2O_2) to the oxidation of diverse substrates.[1,2] These enzymes produce a diverse range of natural products that are significant to the pharmaceutical and chemical industries. For example, methane monooxygenases convert methane, a greenhouse gas, into methanol, a valuable feedstock and potential fuel source. Inspired by these copper enzymes, chemists have been developing synthetic inorganic models that could catalyze O_2 activation reactions and become established synthetic tool for the production of both fine and bulk chemicals.[3-6] Despite the large number of systems designed, few examples exist where metal complexes based on small peptides have been employed. Yet, peptide frameworks constitute a very attractive and versatile platform for the development of new catalysts. Among these attractive features are their structural diversity, their chiral intrinsic character and their accessible synthesis by well-established solid-phase methodologies. Additionally, the inherent modularity of peptides makes it possible to readily adjust their metal coordination properties and reactivity to attain tailored made functionalities.

The goal of this project is to produce peptide-based scaffolds capable to 1) coordinate one or several copper ions,[7] 2) stabilize different copper oxidation states and 3) generate different outer-coordination spheres. Subsequently, their properties as catalysts for oxidation reactions using O_2 and H_2O_2.will be explored and the mechanisms of action studied using different spectroscopic and electrochemical methodologies. The studies will be also extended to other redox active transition metal ions.



References:

1. J.P. Klinman, *Chem. Rev.* **1996**, 96, 2541
2. E.I. Solomon, D.E. Heppner, E.M. Johnston, J.W. Ginsbach, J. Cirera, M. Qayyum, M.T. Kieber-Emmons, C.H. Kjaergaard, R.G. Hadt, L. Tian, *Chem. Rev.* **2014**, 114, 3659
3. P. Gamez, P.G. Aubel, W.L. Driessen, J. Reedijk, *Chem. Soc. Rev.*, **2001**, 30, 376
4. L.M. Mirica, X. Ottenwaelder, T.D.P. Stack, *Chem. Rev.* **2004**, 104, 1013
5. E.A. Lewis, W.B. Tolman, *Chem. Rev.* **2004**, 104, 1047
6. S. Fukuzumi, K.D. Karlin, Coord. *Chem. Rev.* **2013**, 257, 187
7. A. Fragoso, P. Lamosa, R. Delgado, O. Iranzo, *Chem. Eur. J.*, **2013**, 19, 2076

Desired profile:

The candidate must have a Master degree in Chemistry and high motivation for research. A good competence in written and spoken English is needed to work in an international environment. Experience in organic/inorganic synthesis and spectroscopic methodologies (NMR, EPR, UV-Vis, CD) will be positively evaluated.

Application documents and deadline:

The candidate must send a complete CV, a copy of the Bachelor and Master transcripts, a motivation letter and the contact information of two referees to the following email addresses: olga.iranzo@univ-amu.fr and thierry.tron@univ-amu.fr.

The deadline for application is **1st June 2015**.

Selection process:

The candidates will be contacted for a first interview based on the candidacy documents. The selected candidate(s) will have a second interview with the "École doctorale des Sciences Chimiques - ED250".