PhD position: Encapsulation in a supramolecular cage of metal transition complexes for bioinspired oxidation catalysis

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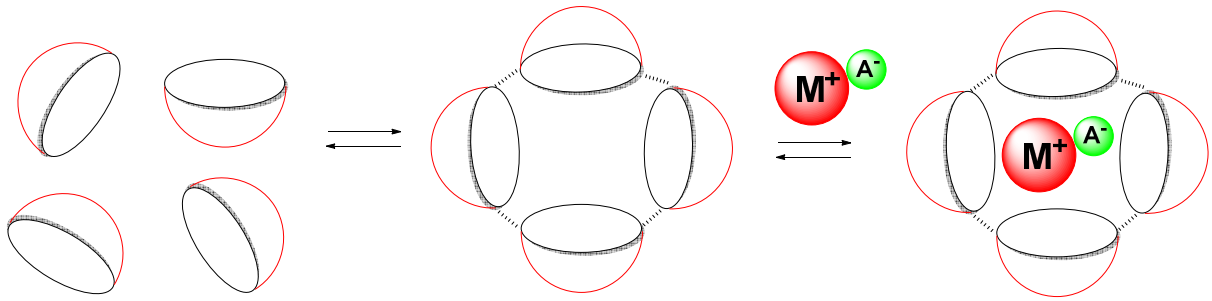
Context. Biomimetic inorganic chemistry aims at reproducing structural and spectroscopic properties and ultimately the reactivity of metallic enzymes. In this context, our group has acquired a strong expertise in using simple and well-studied ligands covalently attached to a molecular cavity (e.g. calix[6]arene or resorcinarene).[1] The presence of the molecular cavity is reminiscent of the enzyme pocket. Depending on the design of the molecular systems, different synergetic effects between the metal complex and this artificial pocket can be found illustrating the importance of the confinement of the complex model in a control environment.[2]
We want now to follow another approach in which a coordination complex is fully embedded in a supramolecular capsule. The capsule is obtained from the self assembly of multiple bricks and its volume is large enough to encapsulate a coordination complex.
The supramolecular embedment will enable to study the intrinsic properties of a metal cation. Moreover, by addressing some aspects of the biological systems (isolation of the catalyst from the bulk, catalyst-substrate pre-organization, stabilization of intermediates…), this strategy opens new perspectives for challenging reactions (e.g. oxidation of CH_4 in CH_3OH).



supramolecular capsule

encapsulated metal complex
- properties ?
- reactivity ?

Objectives. The objectives of this thesis will be to study the parameters for a successful encapsulation, the influence of this encapsulation on the properties of the metal complexes (structural, electrochemical, spectroscopic), the interaction with O_2 and the reactivity of this supramolecular biomimetic system in oxidation reactions.
Work plan. Following some preliminary results recently published on one particular complex,[3] the first part of the work will be devoted to the synthesis of some other N-ligands and their metal complexes [Cu(I), Cu(II), Zn(II), Fe(II)]. Then the encapsulation of these complexes in the supramolecular capsule will be studied (mainly by NMR, UV-vis and EPR spectroscopies) and the parameters influencing the encapsulation will be determined (e.g. charge, role of the anion, steric hindrance). Then, the Cu/O_2 and Fe/O_2 chemistry within this particular biomimetic environment will be scrutinized. Finally, this complex/cage tandem will be used in catalyzed oxidation reactions.
Requirement. We are looking for a motivated and creative candidate with knowledge in coordination and supramolecular chemistry. Experimental skills: experience in organic and metal complex synthesis (schlenk line, glovebox), use of spectroscopies such as NMR, UV-vis or EPR and electrochemistry.

The position will start in October 2021.
To apply, send to benoit.colasson@parisdescartes.fr your CV, the letters of reference of two former advisors and the transcript of the marks of your Master degree (1st and 2nd years).

References.

1-a) N. Le Poul, B. Colasson, G. Thiabaud, D. Jeanne Dit Fouque, C. Iacobucci, A. Memboeuf, B. Douziech, J. Řezáč, T. Prangé, A.de la Lande, O. Reinaud, Y. Le Mest, *Chem. Sci.*, **2018**, *9*, 8282-8290 ; b) N. Le Poul, Y. Le Mest, I. Jabin, O. Reinaud, *Acc. Chem. Res.*, **2015**, *48*, 2097-2016.
2- J.-N. Rebilly, B. Colasson, O. Bistri, D. Over, O. Reinaud, *Chem. Soc. Rev.*, **2015**, *44*, 467-489.
3- T. Zhang, L. Le Corre, O. Reinaud, B. Colasson, *Chem. Eur. J.*, **2021**, *27*, 434-443.