

PhD position: Supramolecular Embedment of Metalloenzyme Model Complexes in a Giant Hydrogen-bonded Capsule

Supervisor: Dr. Benoit Colasson, Université de Paris, UMR 8601.

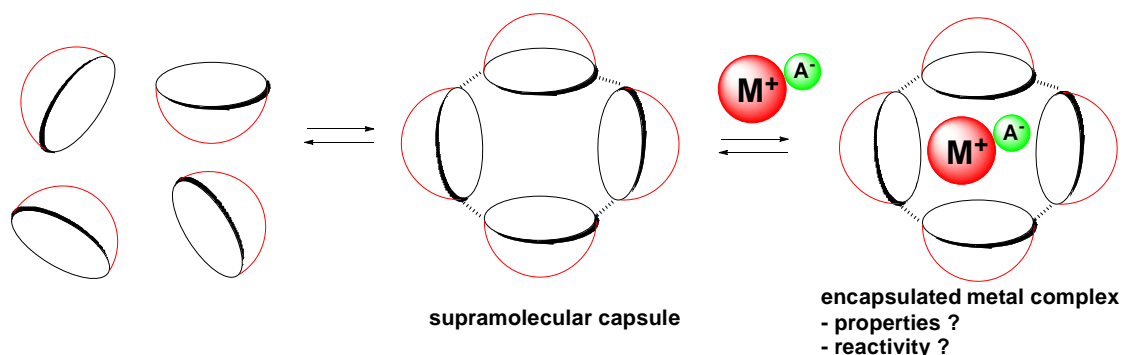
Contact: benoit.colasson@parisdescartes.fr

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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 CH₄ in CH₃OH).



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) and the reactivity of this supramolecular biomimetic system in catalytic reactions (oxidation, hydrolysis).

Work plan. The first part of the work will be devoted to the synthesis of some N-ligands and their metal complexes [Cu(I), 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). This work will pave the way for the next step which will be the use of this complex/cage tandem in catalysis.

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 2020.

To apply, please send to benoit.colasson@parisdescartes.fr a CV and the contact details of two former advisors.

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. Renaud, Y. Le Mest, *Chem. Sci.*, **2018**, 9, 8282-8290 ; b) N. Le Poul, Y. Le Mest, I. Jabin, O. Renaud, *Acc. Chem. Res.*, **2015**, 48, 2097-2016.
- 2- J.-N. Rebilly, B. Colasson, O. Bistri, D. Over, O. Renaud, *Chem. Soc. Rev.*, **2015**, 44, 467-489.