WORKSHOP

"From supramolecular organization to sensing applications »

Le Jeudi 2 avril à 14h00
CINaM, Bibliothèque Raymond Kern

14:00 Growth of Metal Organic Frameworks (MOFs) onto functionalized silicon surfaces
Catherine de Villeneuve
Laboratoire de physique de la matière condensée, Palaiseau

15:00 Metal ions in Biomimetic Cavities: From Molecular Recognition to Reactivity, and vice versa
Olivia Reinaud
Laboratoire de Chimie et Biochimie, Paris

16:30 MCI's Activities on Gas Sensors
Sandrine Bernardini, Khalifa Aguir et Marc Bendahan
Institut Matériaux Microélectronique Nanosciences de Provence, Marseille

CINaM
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Campus de Luminy
Entrée libre

Growth of Metal Organic Frameworks (MOFs) onto functionalized silicon surfaces

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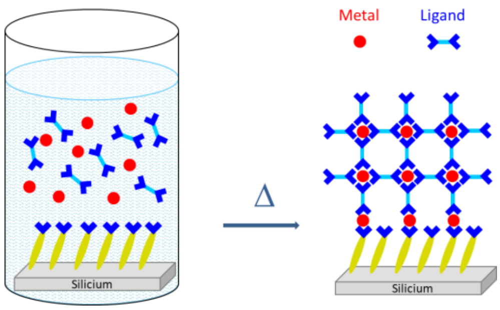
Metal Organic Frameworks (MOFs) are crystalline porous solids obtained by self-assembly of metal ions and organic linkers in solution. These materials are very attractive for a wide range of applications because of their versatile and tunable porosity (pore shape and size) and physico-chemical properties given by the precursors or host entities inserted in the porous network. Currently tremendous efforts aim at their integration in planar devices.[1,2] Within this frame, the fabrication of MOF layers with well controlled structural and/or physicochemical properties is one of the major issues but remains a challenge for a large number of these materials.

In our group we are interesting in the *direct* growth of MOFs onto functionalized silicon surfaces of tunable structure and surface chemistry. The surfaces are prepared par chemical etching and then functionalized by covalent grafting of COOH-functionalized alkyl monolayers (Si-C linkage) that subsequently can be used as primary layer for the covalent coupling of other chemical functional groups/ligands. [3-5]



The systems under investigation are Fe-based MOFs obtained from Fe^{3+} and carboxylate ligands (BDC, BTC…). The structural properties of the MOFs will be presented on the base of SEM, XRD and AFM characterizations.

(1) I. Stassen et al. Chem. Soc. Rev. 2017, 46, 3185.
(2) J. Liu et al. Chem. Soc. Rev., 2017,46, 5730-5770.
(3) A. Faucheux, et al. Langmuir 2006, 22, 153.
(4) C.H. de Villeneuve et al. Advanced Materials 2012, 25, 416.
(5) C. Henry-de-Villeneuve et al. Langmuir 2019, 35, 2547.

Metal ions in Biomimetic Cavities: From Molecular Recognition to Reactivity, and vice versa

Olivia Reinaud

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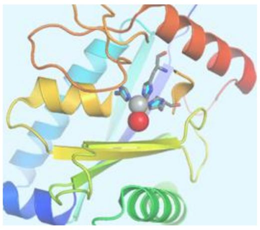
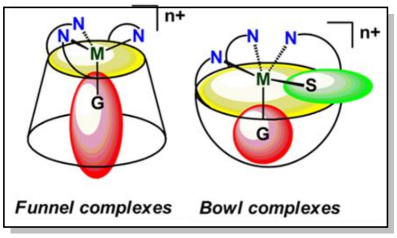
Abstract. The aim of our work is to design supramolecular systems that will mimic both the coordination core and the hydrophobic pocket of a metallo-enzyme active site. Our strategy relies on the synthesis of cavity-based ligands that allow the control of the coordination spheres of the metal ion (1^{rst}, 2^{nd} and 3^{rd}), together with the approach and the binding of an exogenous molecule. Since many years, we have been developing systems based on the calix[6]arene scaffold, giving rise to the so-called *Funnel complexes*.[1] More recently, we started to explore metal complexes based on the resorcin[4]arene scaffold, which provides a supramolecular environment different in shape, rigidity and binding properties, so-called *Bowl complexes*.
Various aspects of these cavity-complexes will be presented and the *Bowl* vs. *Funnel* supramolecular concepts for biomimetic metal complexes will be discussed, with a special focus on recent results obtained with *Bowl complexes*.[2]



Proteic metallo-site



Supramolecular modeling

References

[1] **Reviews on the subject :** *Calixarenes and resorcinarenes as scaffolds for supramolecular metallo-enzyme mimicry*, J.-N. Rebilly, O. Reinaud, *Supramol. Chem.*, **2014**, *26*, 454-479. DOI: 10.1080/10610278.2013.877137**;** *Biomimetic Cavity-Based Metal Complexes,* J.-N. Rebilly, B. Colasson, O. Bistri, D. Over, O. Reinaud, *Chem. Soc. Rev.* **2015**, *44*, 467-489. DOI: 10.1039/c4cs00211c**;** *Supramolecular Control of Transition Metal Complexes in Water by a Hydrophobic Cavity: a Bio-Inspired Strategy,* O. Bistri and O. Reinaud, *Org. Biomol. Chem*., **2015**, *13*, 2849–2865. DOI: 10.1039/C4OB02511C**;** *Supramolecular Modeling of Mono-Copper Enzyme Active Sites with Funnel-Complexes,* N. Le Poul, Y. Le Mest, I. Jabin, O Reinaud*, Acc. Chem. Res.,* **2015***, 48,* 2097–2106. DOI: 10.1021/acs.accounts.5b00152.

[2] *The 3^{rd} degree of biomimetism: associating the cavity effect, Zn^{II} coordination and internal base assistance for guest binding and activation,* A. Parrot, S. Collin, G. Bruylants, O. Reinaud, *Chem. Sci.* **2018,** *9*, 5479–5487. DOI: 10.1039/c8sc01129j. *Submerging a Biomimetic Metallo-Receptor in Water for Molecular Recognition: Micellar Incorporation or Water Solubilization? A Case Study*, S. Collin, A. Parrot, L. Marcelis, E. Brunetti, I. Jabin, G. Bruylants, K. Bartik, and O. Reinaud, *Chem. Eur. J.* **2018**, *24*, 17964 – 17974. DOI: 10.1002/chem.201804768. *A biomimetic strategy for the selective recognition of organophosphates in 100% water: synergies of electrostatic interactions, cavity embedment and metal coordination*, S. Collin, N. Giraud, E. Dumont, O. Reinaud, *Org. Chem. Front.*, **2019**, *6*, 1627–1636. DOI: 10.1039/c9qo00263d.

MCI's Activities on Gas Sensors

Sandrine Bernardini, Khalifa Aguir et Marc Bendahan

Advanced materials have a huge potential of providing sensing data on air quality environment and individual health. Advanced materials have a key role in providing sensitive layers on Metal Oxide gas sensors. Therefore, low-cost sensors for monitoring continuously air quality around people are needed. Metal OXide (MOX) materials offer an alternative way to develop miniaturized resistive gas sensors with repeatable, reliable and reproducible sensing results. In 1962, T. Seiyama *et al.* have demonstrated Zinc Oxide (ZnO) thin layer conductivity changes with the adsorption or the desorption of gas on a metal oxide surface. Then, tin oxide (SnO_2), tungsten oxide (WO3) and Zinc Oxide (ZnO) have been demonstrated to be good gas-sensing materials for several gases such as O_3, NO_2, NH_3, CO, and ethanol. This talk will present the work being carried out in Microsensors and Instrumentation group in the Institute of Materials Microelectronic Nanoscience of Provence (IM2NP) at Aix-Marseille University (France). We will discuss the results on design and the conception of the transducer, the heater integration and the sensor's power consumption. Then, we will move on to the metal oxide nanoparticles used in our gas microsensors and will open up the discussion on material selectivity.