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Redox controlling the binding ability of coordination cages grafted on monolayered surfaces

The coordination-driven self-assembly strategy is remarkably efficient in building discrete polygons and cages, unreachable through usual covalent chemistry. This approach, directed through thermodynamic control, is supported by both the highly predictable directionality of the metal-ligand coordination sphere and the reversible nature of the coordination bonds.[1,2] We have actively contributed to this field through the preparation of the first electroactive discrete metalla-cages able to trigger the binding or the expulsion of a guest, through an external redox stimulus.[3–6] Nevertheless, the development of such electron-rich stimuli responsive architectures is currently restricted to conceptual studies in solution. To target applications, their integration into nanofunctionalized devices is highly desirable. This could be achieved by immobilizing the cages on a substrate allowing a redox stimulation.[7,8]

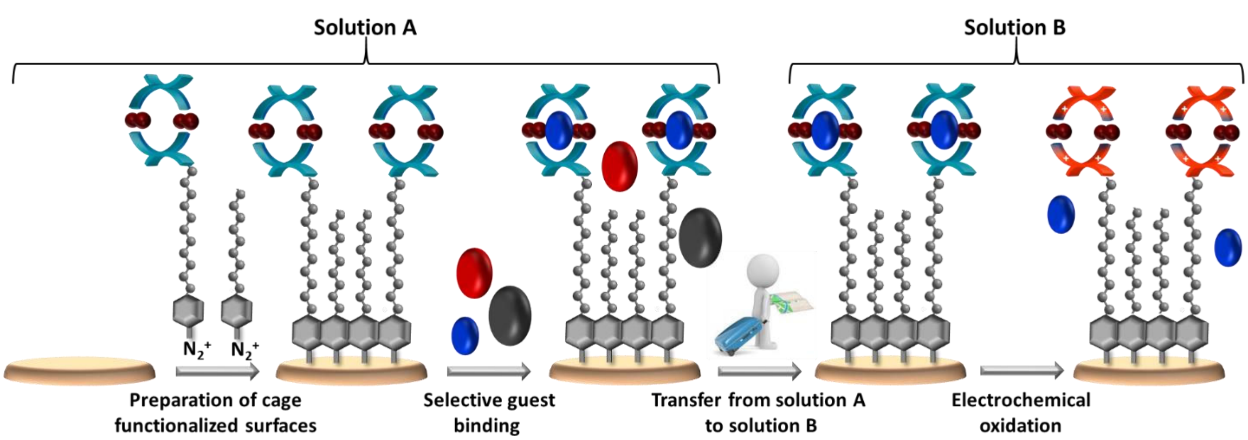

Figure 1. Cartoon illustrating the objectives of the PhD project.

Through designing new families of self-assembled coordination cages, featuring both a cavity for host-guest purposes and a grafting function, this project aspires to: 1) address the basics for the formation of cages on surfaces, 2) enable a selective guest binding and 3) control delivery of guests through redox stimulation (Figure 1).

Desired skills

A first part of the research project will be dedicated to the synthesis of electroactive organic ligands and organometallic complexes. The self-assembly conditions will then be optimized in solution and the supramolecular structures will be characterized and studied by different analytical methods (depending on the case: X-ray, multinuclear NMR, DOSY NMR, mass spectrometry, electrochemical and spectroelectrochemical characterizations). Once the target molecules synthesized, organic monolayers will be prepared and physico-chemical characterization will be undertaken on the functionalized surfaces (electrochemical and spectroelectrochemical characterizations, surface characterization techniques such as XPS and quartz crystal microbalance measurements).

These characterizations will be carried out in partnership with members of the laboratory and external collaborators, while leaving the PhD student at the center of the project in order to perfect his training.

The candidate should have a Master degree in chemistry and a strong interest in organic synthesis as well as in physical chemistry.

Application

All applications should include a cover letter, a CV and at least one recommendation letter and should be sent to sebastien.goeb@univ-angers.fr and christelle.gautier@univ-angers.fr.

References

(1) Sun, Y.; Chen, C.; Liu, J.; Stang, P. J. Recent Developments in the Construction and Applications of Platinum-Based Metallacycles and Metallacages via Coordination. *Chem. Soc. Rev.* **2020**, *49* (12), 3889–3919.

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(3) Goeb, S.; Sallé, M. Electron-Rich Coordination Receptors Based on Tetrathiafulvalene Derivatives: Controlling the Host–Guest Binding. *Acc. Chem. Res.* **2021**, *54* (4), 1043–1055.

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(5) Szalóki, G.; Croué, V.; Carré, V.; Aubriet, F.; Alévêque, O.; Levillain, E.; Allain, M.; Aragó, J.; Ortí, E.; Goeb, S.; Sallé, M. Controlling the Host–Guest Interaction Mode through a Redox Stimulus. *Angew. Chem. Int. Ed.* **2017**, *56* (51), 16272–16276.

(6) Croué, V.; Goeb, S.; Szalóki, G.; Allain, M.; Sallé, M. Reversible Guest Uptake/Release by Redox-Controlled Assembly/Disassembly of a Coordination Cage. *Angew. Chem. Int. Ed.* **2016**, *55* (5), 1746–1750.

(7) Shkirskiy, V.; Billon, J.; Levillain, E.; Gautier, C. From Monolayer to Multilayer: Perylenediimide Diazonium Derivative Acting Either as a Growth Inhibitor or a Growth Enhancer. *Langmuir* **2021**, *37* (44), 12834–12841.

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