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Self-Assembled Multifunctional Metallocages : Luminescence and Recognition

The design and the synthesis of self-assembled coordination cages possessing nanocavities are a major focus due to their promising applications in catalysis, guest binding, drug delivery, and chemical separation. Moreover, there is an increasing interest in integrating physical properties into such metallocages especially optical because of their potential use as molecular switches, sensors and responsive materials.[1] In this regard, the photophysical properties of such metallocages can change drastically upon changing their environment and electronic structure such as through their host-guest chemistry, through intermolecular interactions or by another metal coordination with an adjacent linker. These advanced levels of control will open new opportunities for the creation of pore networked soft materials and bring a new world to this field, which may potentially increase their application scope.

In this context, we have described various self-assembling metallocages for host-guest chemistry.[2] Subsequently, the use of a luminescent rigid *bis*(ethynylpyridine)aniline and *bis*(ethynylpyridine)benzene-based ligands has led to the formation of nanocapsules of type M_2L_4 (M = Pd, Pt).[3] These capsules have limited emissive properties but are able to accommodate organic molecule, especially anionic complexes, in their cavity.

Alternatively, the group of Ortega-Alfaro has developed modular synthetic strategies for obtaining push-pull azo-photo switches that isomerize under visible light stimulus or under biphotonic conditions using a cyanine as fluorescent antenna. These azo-compounds can be used as an efficient tool for drug delivery applications. [4] Parallelly, they have also put a point, synthetic methodologies for obtaining luminescent motifs based on heterocyclic compounds with a ring-junction nitrogen atom that behaves as selective and sensitive sensors for the detection of metal as iron(III) in water-compatible mediums.[5]

In this PhD project, we wish to design new self-assembled luminescent metallocages as sensors or responsive materials. (Figure 1) For this purpose, our approach will be to enhance the photophysical properties of our cages by their post-functionalization with highly light-emitting units.

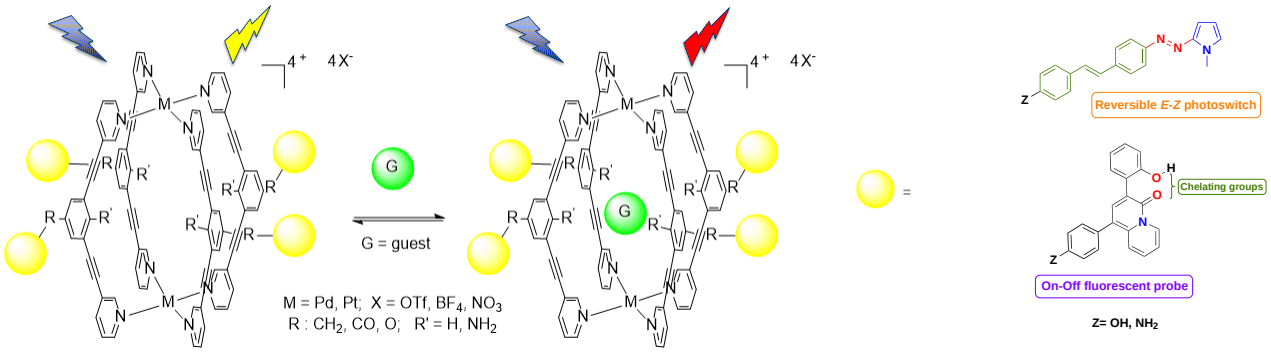

Figure 1. Design of new self-assembled luminescent metallacages as sensor or responsive materials

Their ability to encapsulate complexes will be studied, distinct photophysical properties could be obtained. Moreover, weak supramolecular interactions, such as metal-metal d-d interactions between the nanocapsule and the guest or π–π stacking between emissive units can be potentially observed, which can at the same time significantly influence the photophysical properties and lead to extended emissive metallocages-based frameworks. In addition, the incorporation of units such as reversible photo-izomerisable azo-pyrrole dyes and/or functionalized sensors based on quinolizine, allows us to consider the recognition of multiple guests through their multiple binding domains. These luminescent structures rarely reported so far can be promising for various applications including guest regulation. Preliminary

results on the functionalization of number of metallocages and emissive units have already been carried out allowing them reasonable to be combined and demonstrate the measured risks of the project.

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Impact, benefits and organization of the project :

This project offers interesting developments, is ambitious and challenging in a highly competitive international context. The aim is to advance the knowledge in the field with original concepts. This research project covers in particular the conception, the synthesis of self-assembled architectures, which possess properties beyond those of their constituents, in particular luminescence and recognition properties. Although primarily fundamental in nature, this project is able to lead potentially to applications and technological advances particularly in the domains of molecular switches and sensors. In order to better understand and illustrate the issues, the global color detection sensors market size reached approximately USD 2.18 billion in 2023. Demand in the market is expected to increase with rising application of color detection sensors in diverse industries such as automotive, healthcare, industrial automation, and others. The market is further projected to grow at a CAGR of 7.3% between 2024 and 2032, reaching a value of USD 4.08 billion by 2032.

More over in terms of methodology, recently preliminary results (functionalization of metallocages and emissive units) have demonstrated the feasibility of our approach. These results will enable us to initiate the work before considering new metallocages and emissive bricks, which will be prepared by the PhD student in Paris and Mexico.The research consortium relies on highly synergistic teamwork and has the potential for a broad impact. The involved researchers have each a specific and complementary expertise in different fields, all being essential for the development and completeness of the project. Dr. C. Desmarets (SU associate professor, 50%) will bring his expertise in the organic and inorganic synthesis, characterization, and properties (recognition) of metallocages, while Dr. Ma. Carmen Ortega Alfaro (UNAM professor, 50%) has a recognized expertise in luminescence of organic and organometallic compounds. It is important to notice that this project results from scientific discussions and exchanges related to their joint participation in the Webinar Chemistry SU-UNAM program in 2021 and as speakers in the Catalysis Summer School held last June in Mexico City.

Finally, the PhD candidate need have expertise in organic and inorganic synthesis (Ligand synthesis, Coordination chemistry, Schlenk techniques) and characterization. (NMR, IR-FT, X-Ray). Skills in luminescence will be also appreciated.