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研究課題名(和文) Surface Functionalization and Materials Integration of Metal-Organic Polyhedra

研究課題名(英文) Surface Functionalization and Materials Integration of Metal-organic Polyhedra

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研究成果の概要(和文)：Metal-organic polyhedra where assembled with either polyoxometalates or enzymes, to prepare functional porous composites. Both types of systems lead to very efficient composites, with performances enhanced due to MOPs' porosity. See English section for detailed outline.

研究成果の学術的意義や社会的意義

At a fundamental level, this project helped understanding the modes of assembly between MOPs and diverse nanometer-sized object. Focusing on applicability, it also lead to the preparation of highly active composites, benefitting from improved performances thanks to MOPs' porosity.

研究成果の概要(英文)：This project involved the use of metal-organic polyhedra (MOPs) as elementary building block with porosity for the preparation of functional composite materials. I mainly focused on the use of ionic MOPs, using electrostatic interactions as the main mode of assembly with diverse objects. In particular, I focused on the assembly of MOPs with polyoxometalates (POMs) and with enzymes. Thanks to their high symmetry, POMs formed crystalline network when assembled with MOPs. The structure could be modulated by adjusting either POM nature/charge and MOP shape. The resulting materials maintained POM activity (e.g. as redox-active material or catalyst), while benefitting from the MOPs' porosity. Enzymes were also immobilized by co-assembly with MOPs. This required the development of a reliable water-based MOP chemistry, that allowed the assembly in extremely mild conditions. Diverse enzymes, either positively or negatively charged, were immobilized, and maintained a high catalytic activity.

研究分野：Chemistry

キーワード：Metal-organic polyhedra Porous material Composite material Polyoxometalate Enzyme immobilization

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1. 研究開始当初の背景

Modular materials design is a powerful approach to access new functional composites for targeted applications. It consists in the use of various elementary bricks, assembled together in a controlled fashion, to reach new systems with functionalities that are a combination of those bricks, often with performance enhancement. Metal-organic polyhedra (MOPs) are especially useful for this approach, because they are cage-shaped molecular entities measuring a few nanometer diameter, that can be dispersed in solution and recombined in a controlled manner, by themselves or with a co-assembled species. New porous functional materials can thus be built from their supra-MOP assembly.

While MOP synthesis was well-understood at the beginning of this project, with several archetypal structure well described, relatively few articles discussed their modes of assembly to access new materials with designable properties. Some articles focused for instance on the effect of solvent on the crystalline packing of MOPs, and consequences on their porous properties. The use of MOPs as elementary nodes connected by organic linkers to build an extended network, either crystalline or as a gel, was only recently developed at the time. However, almost no report concerned the assembly of MOPs with other types of chemical objects, notably at the length scale of a few nanometers. This scale is however extremely relevant, because it is also the typical size of MOPs, so complex organized structure could be expected. Among these very limited number, even fewer relied on ionic interaction to drive the assembly.

2. 研究の目的

During this project, I focused on the development of new composites materials, relying on the association of MOPs with different chemical objects. I notably aimed toward the development of a chemistry relying on ionic MOPs, a field barely studied so far but extremely rich. The aim was thus to assemble MOPs of one charge with entities of the opposite charge to build complex mesoscale salts with functional properties. Indeed, charged species to be assembled with ionic MOPs exist at all scale of chemistry, so a rich variety of composites and multiscale assembly was expected. Ionic interactions also possess good properties in terms of strength, directionality and dynamics that makes them interesting to build extended functional salts.

The list of potential counter-ions that can potentially be assembled (and have been effectively assembled during the project) ranges from monoatomic ions to long polymers, I focused mainly on the assembly of MOPs with (i) polyoxometalates (POMs) and (ii) enzymes and other proteins. While clearly different, both are charged objects having a size of a few nanometers.

POMs are metal-oxoclusters, typically anionic, that have recently found applications as catalysts or as redox-active centers for sensors or battery applications. Meanwhile, enzymes are long chains of amino acids, essentially obtained from biological systems, that catalyzes chemical reactions with unparalleled activities and selectivities. In both cases, the immobilization of these catalytic centers in a network of porous cages was expected to bring significantly improved performances thanks to the high accessibility, while also benefitting from the advantages of solid-state catalysis.

3. 研究の方法

In this project, I used already reported MOPs structures (or slight modifications of known MOPs structures) to prepare ionic MOPs, and assembled them with either POMs or proteins.

- POM-assembly can be performed in a wide variety of solvent. Due to the high symmetry of POMs, crystalline assemblies can typically be obtained. The characterization of the samples essentially mirrors that of metal-organic frameworks (MOFs). In addition, reactivity of the POMs with reducers or as catalysts is evaluated.

- By contrast, enzymes need to be processed in mild aqueous conditions to avoid denaturation and loss of activity. For this reason, water-soluble and hydrolytically-stable MOPs have been developed. MOP-enzyme composites are prepared simply by co-assembly. Catalytic activity using model substrate is also characterized.

4. 研究成果

MOPs have been successfully assembled with POMs and with enzymes (as well as other types of ionic species, such as molecular polyanions, as preliminary results), with maintenance of chemical reactivity. These constitutes the two main axes of the project.

Since POMs are macro-anions, zirconium-based cationic tetrahedron-shaped cages (**ZrTd**, charge: +4) was selected to perform the assembly. I notably studied the assembly with Keggin-type POMs of formula $\text{SiM}_{12}\text{O}_{40}^{4-}$ (**SiM₁₂**; M = W or Mo). Taken independently, both POMs and MOPs are readily soluble in common solvents such as ethanol. However, their mixing resulted instantly in the precipitation of microcrystalline powders we called POM-MOP composites (Figure 1). These POM-MOP composites maintained the high porosity of the **ZrTd** cages, while also preserving the red-ox activity of **SiM₁₂**. These results have been published (*Chem. Commun.* **2021**, *57*, 5187). Other structures, using other MOPs and POMs are currently under investigation and will be reported soon.

In addition to POMs, MOPs have also been assembled with proteins and notably enzymes, as a way to prepare supported biocatalysts. In this case, a rhodium-carboxylate MOP was selected to guarantee

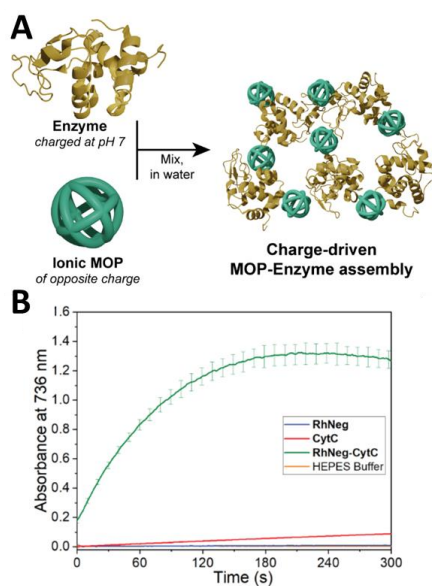


Figure 2. **A:** Principle of the charge-driven MOP-enzyme assembly. **B:** Catalytic activity of free (red) and immobilized (green) **CytC** (reaction: oxidation of ABTS substrate by H_2O_2).

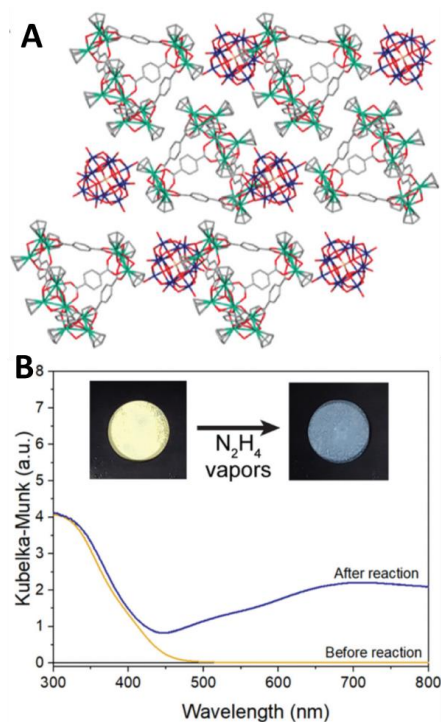


Figure 1. **A:** Crystal structure of the POM-MOP $\text{SiMo}_{12}\text{-ZrTd}$. **B:** UV-visible spectra response of $\text{SiMo}_{12}\text{-ZrTd}$ upon reduction by hydrazine vapors.

hydrolytic stability of the MOP. Two variants of this MOP, one anionic and the other cationic, were achieved through ligand modification of this core MOP. Assembly can thus be achieved with a wide variety of enzymes, with isoelectric point either above or below 7 (Figure 2A). MOP-enzyme composites can be obtained in in water at pH 7 and without additive, by simple mixing of MOP and enzyme solution. Thanks to these extremely mild conditions, and to the porosity of MOP that guarantee an easy access of substrates toward enzymes active sites, the composite retained a high catalytic activity, while also bringing the advantages of supported catalysis. Furthermore, in the specific case of cytochrome c (**CytC**), the immobilization resulted in a 44-fold improvement of catalytic activity, due to multiple interactions between enzymes and the highly ionic environment (Figure 2B). As of today, these results have been submitted and are currently under review. In future article, the system will be expanded to add more versatility, as well as by selecting specific target enzymes for device application.

Assembly of ionic MOPs offers thus a very generalist platform for the preparation of new functional materials with high performances, enabled notably by the ubiquitous character of ionic species in chemistry.

5. 主な発表論文等

〔雑誌論文〕 計1件（うち査読付論文 1件/うち国際共著 1件/うちオープンアクセス 0件）

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| 1. 著者名 Le Ouay Benjamin, Yoshino Haruka, Sasaki Kenta, Ohtsubo Yuta, Ohtani Ryo, Ohba Masaaki | 4. 巻 57 |
| 2. 論文標題 Crystalline assembly of metal-organic polyhedra driven by ionic interactions with polyoxometalates | 5. 発行年 2021年 |
| 3. 雑誌名 Chemical Communications | 6. 最初と最後の頁 5187-5190 |
| 掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1CC01185E | 査読の有無 有 |
| オープンアクセス オープンアクセスではない、又はオープンアクセスが困難 | 国際共著 該当する |

〔学会発表〕 計5件（うち招待講演 1件/うち国際学会 1件）

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| 1. 発表者名 Le Ouay Benjamin |
| 2. 発表標題 Crystalline assembly of cationic metal-organic polyhedra with polyoxometalates |
| 3. 学会等名 The 71st meeting of the Japanese Society of Coordination Chemistry |
| 4. 発表年 2021年～2022年 |

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| 2. 発表標題 Charge-driven assembly of metal-organic polyhedra with polyoxometalates |
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| 2. 発表標題 Zr Coordination Cages Isomerism and Assembly with Polyoxometalates |
| 3. 学会等名 The 101st meeting of the Chemical Society of Japan |
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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

| 氏名 (ローマ字氏名) (研究者番号) | 所属研究機関・部局・職 (機関番号) | 備考 |
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

| 共同研究相手国 | 相手方研究機関 |
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