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研究課題名(和文) Compartmentalization of catalysts into metal-organic polyhedra gel for cascade reactions  
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研究成果の概要(和文)：The project lies in the use of MOPs to (i) isolate multiple catalytic species; (ii) control their spatial organization during gel formation and (iii) use the mesoporosity created by the gel networks as diffusion channels.

#### 研究成果の学術的意義や社会的意義

The developed system will be used as bifunctional membrane offering extra free hierarchical porosity for optimal reaction-diffusion and perform one-pot multi-steps catalysis. This work could lead to high impact journals publication and presentation in international conferences.

研究成果の概要(英文)：As porous molecular solids, MOPs present improved prospects for materials processing. They have been used as templates to accommodate and control properties of various guests. However, the joint use of (i) the intrinsic cage porosity with the extrinsic porosity of MOP-assembled structure and (ii) the compartmentalized catalytic sites into a MOP-based gel for tandem catalytic applications has never been described. The originality of the project lies in the use of MOPs to (i) isolate multiple catalytic species; (ii) control their spatial organization during gel formation and (iii) use the mesoporosity created by the gel networks as diffusion channels for reactants to create a bifunctional catalytic porous membrane for continuous reactions. The work will demonstrate new applications for porous molecules not only in the field of catalysis but also for selective sensing and chiral separation.

研究分野：Supramolecular Chemistry

キーワード：Porous material supramolecular system metal organic cages host-guest system metal nanoparticles

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## 1 . 研究開始当初の背景

Orthogonal tandem catalysis involves multiple catalytic processes occurring consecutively in the same reaction vessel and is used for industrially relevant transformations such as conversion of CO<sub>2</sub> into gasoline fuel. To avoid migration and sintering of catalysts leading to loss of catalytic activity, their controllable integration into one single structure is primordial. The catalytic activity can be preserved when forming heterogeneous binary materials, which may consist of for example, metal-metal oxides interfaces or metal nanoparticles (MNPs) with core-shell architecture. The performance of these systems depends strongly on the spatial configuration of each component and their inter-compatibility. Indeed fabrication of heterostructure with positional control of the components can be quite challenging. As an alternative, tandem reactions mediated by two separated metals are more attractive and flexible for the realization of two or more fundamentally different transformations by using the specificity of each metal. However, this strategy has remained largely unexploited due to incompatibility issues between transition metals or reagents.

## 2 . 研究の目的

The project will use metal-organic polyhedra (MOPs) to synthesize continuous binary material. MOPs will be used as containers for different catalytic species. By assembling MOPs into porous gels, hierarchical porosity is created offering optimal reaction-diffusion for one-pot multi-step catalysis. This project will allow isolation and spatial organization of multicatalyst into a continuous system without the necessity to control the composition at interfaces. These hybrid systems will eliminate the need for purification between steps, favor stabilization of reactive intermediate species, and thus allow different chemical transformations to be carried out in a single vessel with continuous flow.

## 3 . 研究の方法

The aims of this proposal are to (i) synthesize MOPs with specific cage sizes and functionalities as host for catalytic guests; (ii) compartmentalize the different catalyst@MOP through solution processing before their assembly into colloidal gel; and (iii) to perform tandem catalytic reactions.

The first step is the synthesis of individual MOP. One class of MOP will provide catalytic activity through Lewis acid sites of the metal nodes of the MOP as found in rhodium-based MOP for example. The 2<sup>nd</sup> type (Cat. 2) will use MOPs to host catalytically active metal nanoparticles (MNPs). This requires the design of porous solid cage with specific size and functionality to stabilize the catalysts inside the structure.

The next objective will be the spatial organization of binary MOPs into porous gels. Varying the composition of this new system along one dimension will allow us to spatially isolate and organize multicatalyst species. This will be achieved by layering a solution of Cat. 1 over a solution of Cat. 2 to create density gradient on the final solution. The host-guest system can be further processed in a controlled fashion as “monomer” for supramolecular polymerization and form three-dimensionally interconnected colloidal porous gel.

Cascade or tandem reactions are consecutive series of catalytic reactions. The advantage of using bifunctional gel membrane is that the mesoscopic organization of the cage molecules will prevent aggregation and deactivation of the different catalysts. The composite system could be a powerful platform for cascade catalysis because it can combine the coordinately unsaturated metal nodes of the MOP which is a Rh-Rh paddlewheel with accessible labile axial site, (Catalyst 1) with the metal nanoparticles previously encapsulated inside the MOP cages (Catalyst 2). As an example, the reaction of epoxidation is known to be catalyzed by Au MNPs while the transformation of epoxide to cyclic carbonate is catalyzed by Rh paddlewheels. Therefore, the direct alkene to cyclic carbonate conversion will be studied. Acid/base incompatible catalyst can also be investigated. Each catalytic system can be investigated individually in order to assess their performances for the specified reaction before to perform tandem catalysis on the bifunctional membrane.

#### 4 . 研究成果

OHRhMOP was selected for its cage size (~2 nm) and window opening of 6.6 and 3.8 Å for the square and triangular windows respectively. A direct impregnation method was first tested by adding OHRMOP with HAuCl<sub>4</sub> into a MeOH solution under vigorous stirring for 2 hours at room temperature. The green solution was then reacted with NaBH<sub>4</sub> for 2 more hours in order to reduce the metal precursor into Au<sup>0</sup> and a violet solution was obtained (Au<sup>0</sup>@OHRhMOP<sub>as synth</sub>). The violet powder obtained after removing the MeOH and washing the sample with water (Au<sup>0</sup>@OHRhMOP<sub>washed</sub>) was first characterized by UV-vis spectroscopy. Deconvolution of the absorption band in the visible range shows the presence of two bands at 527 and 572 nm which are different from the pristine OHRhMOP which has a single absorption band ( $\lambda_{\max} = 590$  nm). This difference is attributed to the modification of the coordination environment around the Rh-Rh center leading to a shift of  $\lambda_{\max}$  towards lower wavelength at a value similar to the one of OHRhMOP fully coordinated by imidazole type linker ( $\lambda_{\max} = 548$  nm). The contribution at 527 nm could be attributed to the presence of Au<sup>0</sup> nanoparticles (NP), in concordance to Au NPs embedded within triazine based covalent organic polymer networks ( $\lambda_{\max} = 545$  nm). DLS analysis of the as synthesized sample shows a size of 3.6 nm close to expected size cage. However, the washed sample couldn't be solubilized again in MeOH once dried as shown by the particle size of 8.7 nm, thus limiting the possibility of further assembly of the cages. Scanning electron microscopy coupled to EDX of Au<sup>0</sup>@OHRhMOP<sub>washed</sub> showed a homogeneous distribution of Au<sup>0</sup> over the sample and a ratio of Rh: Au of 5:1. Transmission electron microscopy (TEM) analysis of the sample showed an averaged size of Au particles of  $9.7 \pm 6.0$  nm, which is close to the DLS value obtained for the washed sample but higher to the as synthesized one. It is hypothesized that the washing and drying process lead to the aggregation of the Au<sup>0</sup>@OHRhMOP or that the NP are not present within the host cage.

A two phases liquid-liquid approach was tested, which required the transfer of Au ion from an aqueous phase to an organic phase containing the cage using tetraoctylammoniumbromide (TOAB), followed by the reduction of the ion to Au<sup>0</sup> with NaBH<sub>4</sub>. Powder X-Ray diffraction pattern (PXRD) of the washed and dried sample showed three peaks in the 30-80° 2 $\theta$  range attributed to Au<sup>0</sup> according to literature. The Debye-Scherrer equation applied to those peaks allowed to determine a NP with size of 1.9 nm below to the cage size of 2.7 nm observed on the as synthesized samples by DLS. SEM analysis showed a homogeneous distribution of Au over the sample with a ratio of 12 Rh for 1 Au. Analysis of the TEM images of the sample showed particles size around  $1.3 \pm 0.4$  nm. The similar size of Au NP obtained by the different techniques let us hypothesize that Au NP have been synthesized within the MOP host cage. Similar results were obtained with Pd using the same approach.

Nevertheless, further test on assembling the host@guest systems using a reported method developed by our group remained unsuccessful.

In parallel to the NP synthesis as guest within MOP, the study on the formation of colloidal gel from MOP published by the group in Nature Communication was deepened. I applied the technique of dynamic light scattering (DLS) for the *in-situ* study of the formation of our systems. Indeed, physical models have been developed to follow the supramolecular assembly of colloidal particles in gel over time, using time-resolved light scattering techniques (static, dynamic and low-angle). This made it possible to understand the mechanism of formation of colloidal gel in order to better control certain properties such as:

- (1) the possibility of designing a gradient of mechanical properties and porosity on several length scales (*Chem. Sci.* **2019**, 10, 10833)

I was able to show that the detailed evaluation of the hierarchical self-assembly process of MOPs is an essential step to then create continuous gradients of porosities and mechanical properties within colloidal gels (Figure 8b). First, I was able to determine the link between the resulting macroscopic architecture of gel formation using time-resolved dynamic light scattering (TRDLS) techniques, and the effect on the mechanical properties of gels. The TRDLS technique can be used to better understand (i) the dynamics of self-assembly near the gelation threshold (tg); (ii) the gelation mechanism; and (iii) the final architecture of the MOP-based supramolecular gel. To do this, I synthesized cuboctahedral cages which form during the coordination between isophthalate ligands and "paddle wheel" type di-rhodium precursors. These cages soluble in organic solvents can assemble into a hierarchical structure in the presence of ditopic N-donor ligands. Indeed, the latter can coordinate on the labile

metallic sites on the surface of the cages, which initiates a supramolecular polymerization reaction during which the cages connect via the ditopic ligand in order to form colloidal particles. After reaching a critical concentration, these colloids aggregate to form a porous colloidal network which extends over the entire volume of the solution and traps the solvent molecules by capillary force, thus creating a gel. This mechanism was demonstrated by the analysis and processing of TR-DLS data that I also performed (Figure 1a). The mechanical properties of the gels were determined by rheology in collaboration with the Kyoto Institute of Technology. The gels were then transformed into an aerogel after drying the gel by supercritical CO<sub>2</sub>. From these aerogels, it is possible (i) to obtain the composition and the degrees of crosslinking of the system after digestion and <sup>1</sup>H NMR analysis in solution, (ii) to observe the architecture of the aerogel by SEM, and (iii) measure porous properties (micro and meso) by N<sub>2</sub> sorption. Finally, I was able to show that the application of centrifugal force only at the beginning of colloidal aggregation leads to the formation of a density gradient of colloidal networks, which induces a gradual change in mechanical properties.

- (2) to have a spatio-temporal control of the supramolecular polymerization which makes it possible to adjust the architectures, the mechanical properties and the shape of soft porous materials (*J. Am. Chem. Soc.* **2021**, 143, 3562).

From this research, I was able to show first, that a weak acid can be used to induce the supramolecular polymerization reaction of monomeric MOP units (Figure 9a). Indeed, the modification of the concentration of trifluoroacetic acid (TFA) in the MOP solution allows a temporal control of the kinetics of the reaction. From the characterization techniques (TRDLS, SEM, NMR), it was concluded that increasing the concentration of TFA leads to a faster polymerization reaction due to an increased number of vacant coordination sites on the MOPs, resulting in faster colloid nucleation and growth. Moreover, the decrease in the number of ditopic ligand by MOP with the increase in the concentration of TFA leads to fewer nuclei formed and therefore to an increase in the size of the colloidal particles. On the other hand, the macroscopic behavior of the gel is the result of the denser network, which is explained by the larger colloidal particles and the reduced volume of gel leading to the formation of more fragile gels. Then, the irradiation of a MOP solution containing a PAG

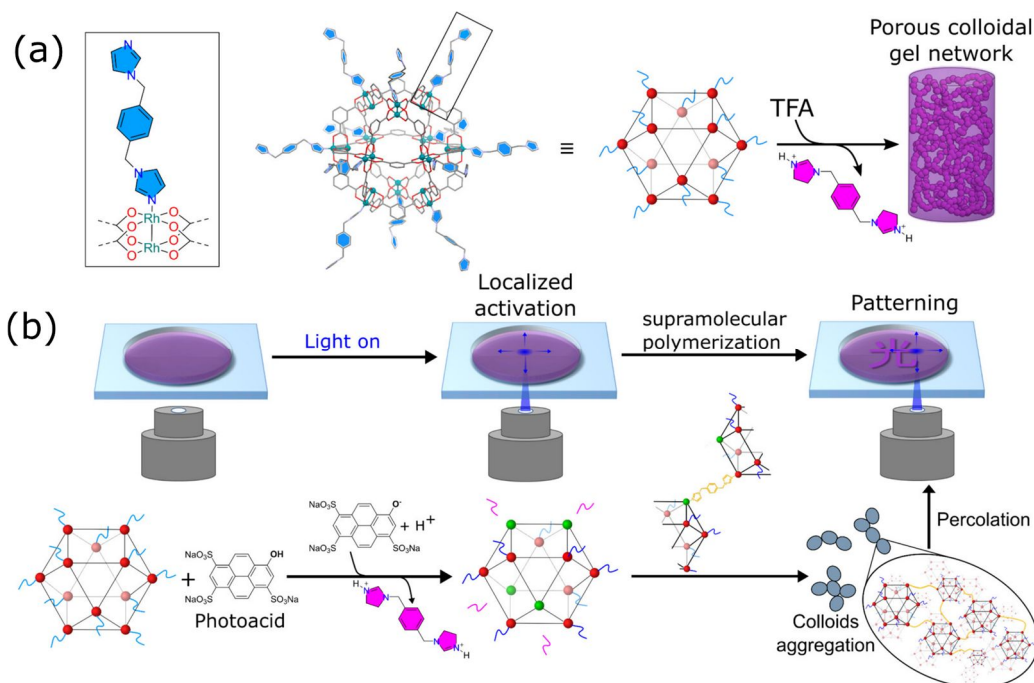


Figure 1. Strategy for achieving temporal and spatio-temporal control. (a) Schematic view of the molecular structure of the kinetically trapped MOP, where the 12 metal nodes of the cage are coordinated by six molecules in a monodentate fashion. The addition of trifluoroacetic acid (TFA) triggers the supramolecular polymerization reaction and the formation of the porous colloidal gel network. (b) Schematic representation of the light shaping experiment using confocal laser scanning microscopy. The corresponding supramolecular polymerization reaction when irradiating the solution containing pyranine as a photoacid. The use of TFA or pyranine leads, in both cases, to the protonation of six molecules and the creation of labile metal sites (green), which initiate self-assembly among neighboring MOPs through ditopic coordination (orange).

(pyranine) can spatially modulate the local acid concentration and thus remotely trigger the process of self-assembly and the structuring of the solution into a gel of desired shape. (Figure 1b). Indeed, in situ irradiation of the MOP solution and a photoacid, followed by TRDLS, shows a decrease in the time required for gel formation compared to a non-irradiated system. Moreover, once the conditions have been optimized, it is even possible to control the shape of the gel using a confocal laser scanning microscope. This spatio-temporal control of assembly could allow the integration of MOP-based soft matter into devices for applications such as sensing, separation, and catalysis, as observed for MOFs. This control on the spatial organization of the MOP cages within the porous gel is a promising basis for the realization of a hierarchical multicatalyst system for tandem catalytic reactions.

More recently, via a collaboration with a catalytic research team in France (IRCELYON), the catalytic efficiency of dirhodium paddlewheels heterogenized within MOP (Rh-MOP) and their three-dimensional assembled supramolecular structures (aerogel) was demonstrated for the selective photoreduction of CO<sub>2</sub> into formic acid (*J. Am. Chem. Soc.* **2022**, 144, 3626). Surprisingly, the catalytic activity per Rh atom is higher in the supramolecular structures than in its molecular sub-unit Rh-MOP or in the Rh-metal-organic framework (Rh-MOF) and yields turnover frequencies of up to 60 h<sup>-1</sup> and production rates of approx. 76 mmole formic acid per gram of the catalyst per hour, unprecedented in heterogeneous photocatalysis. The enhanced catalytic activity is investigated by X-ray photoelectron spectroscopy and electrochemical characterization, showing that self-assembly into supramolecular polymers increases the electron density on the active site, making the overall reaction thermodynamically more favorable. The catalyst can be recycled without loss of activity and with no change of its molecular structure as shown by pair distribution function analysis. These results demonstrate the high potential of MOP as catalysts for the photoreduction of CO<sub>2</sub> and open a new perspective for the electronic design of discrete molecular architectures with accessible metal sites for the production of solar fuels.

## 5. 主な発表論文等

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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

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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