

Report on MERIT Long-term Overseas Dispatch

Graduate School of Engineering, Department of Applied Chemistry

Uemura Lab. D1, Yuto Osugi

Destination : Institut Catala de Nanociencia i Nanotecnologia (ICN2)

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Research Topic : **Self-Expansion of Metal-Organic Frameworks (MOFs) and Covalent-Organic Frameworks (COFs) to Create Uniformly Cross-Linked Polymer Networks**

Research background

Regularity of network structure in polymer gels strongly influences their mechanical properties. Although various approaches have been explored to improve the network regularity, preparation of polymer gel with crystalline-level uniformity remains difficult. To address this challenge, we designed an approach that employs metal–organic frameworks (MOFs) and covalent–organic frameworks (COFs), crystalline compounds formed by self-assembly of small molecules, as precursors to directly transform their organic ligands into polymeric linkers. During this research stay, we worked on developing a self-expansion approach (*Angew. Chem. Int. Ed.*, **2024**, 63, e202404155., Fig.1) of MOFs using ring-openable ligands, affording uniformly cross-linked polymeric materials.

Before the research stay, I succeeded in synthesizing self-expandable MOFs that contain ring-openable ligand by C=C bond cleavage. Following this, we tried to optimize the ozonolysis conditions for the MOF; however, further improvements were required for the reaction to preserve their morphology. In addition, in the COFs case, although the ligand synthesis had been completed, the synthesis of the corresponding COFs had not yet been achieved at that time.

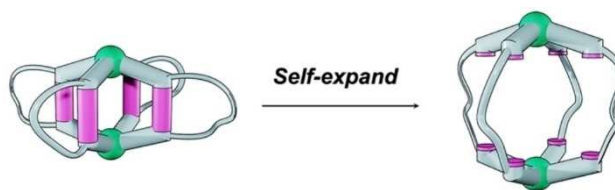


Fig. 1. The concept image of self-expansion. This process involves ring-opening reaction of ligands.

Objective

Prof. Daniel Maspoch Group has been developing “Clip-off Chemistry” (*Angew. Chem. Int. Ed.* **2022**, 61, 4, e202111228), which inspired the idea of ring-openable ligands. They have performed ozonolysis on MOF single crystals while maintaining their single crystal manner (*J. Am. Chem. Soc.* **2018**, 140, 6, 2028). In addition, the group possesses expertise in the synthesis of COFs containing ligands with C=C bonds (*Science* **2025**, 388, 6753, 1318). Therefore, in this collaborative research, we aimed to work together on the ring-opening (self-expanding) reactions of self-expandable MOFs that had been synthesized in Japan, as well as on the synthesis of COFs using ring-openable ligands, in order to achieve the self-expansion of both MOFs and COFs.

Methods

For the MOF study, I brought the synthesized ligand to Maspoch group and carried out experiments on MOF synthesis

and the optimization of ozonolysis conditions. To analyze the structures of the expanded MOFs, I attempted detailed evaluations of their network structures and uniformity using techniques such as powder X-ray diffraction, single-crystal X-ray diffraction, and X-ray absorption fine structure analysis. For the COF study, I brought the synthesized ligand as well and conducted a screening of suitable synthesis conditions for COF formation.

Results and Discussion

Regarding the ozonolysis of MOFs, we achieved significant improvements by controlling the reaction parameters such as temperature and ozone flow rate, as well as by revising the reaction setup itself. We also reexamined the synthetic procedure for the MOF and developed a more efficient method to grow larger crystals. The enlarged crystal size made it easier to analyze the properties of the ozonized networks. These results clearly demonstrate the benefit of close collaboration with researchers experienced in this field.

On the other hand, the synthesis of COFs proved to be extremely challenging. Although various synthetic conditions were explored, the optimization of synthetic conditions has not yet been achieved. Nevertheless, some reaction conditions yielded samples showing crystalline diffraction peaks, which provides a promising starting point for further studies. Based on these findings, we plan to continue the collaboration and further investigate COF synthesis in Japan.

Research life in Spain

The Catalan Institute of Nanoscience and Nanotechnology (ICN2), where I stayed for this research, is located on the campus of the Universitat Autònoma de Barcelona (UAB) in Barcelona, Catalonia, Spain. Because of this setting, the research environment differed in several ways from that of my home university. ICN2 collaborates closely with UAB, hosting its doctoral students and sharing research facilities.

Maspoch group consists of about 30 members, mainly postdoctoral researchers at ICN2 and Ph.D. students from UAB. As a first-year doctoral student, I was the youngest member of the group. This created a distinctly different atmosphere from that of my laboratory in Japan.

The experimental laboratory was located in a UAB building, while measurement instruments were shared between UAB and ICN2. Many of these instruments were managed by dedicated technical staff and were jointly used by several research groups. Although I often had to walk several minutes each time I conducted measurements, I experienced no major difficulties in using the instruments, as the technical staff can speak English and communication went smoothly.

Everyone in the Maspoch group was highly fluent in English, and I fortunately had no serious communication barriers. The members were very kind and frequently talked with me, which helped me adapt quickly to the group. However, expressing my own thoughts precisely in English was often difficult, and I strongly realized the importance of language skills. Even so, through gestures, visual aids, and mutual effort, I was able to carry out experiments and communicate effectively. This experience has been a valuable opportunity for personal and professional growth.

Barcelona, where I stayed, had a very comfortable climate. Even during the summer, the air was dry, and it was not excessively hot, with little rainfall and daylight lasting until around 9 p.m. In addition, the food culture was rich and diverse. I was quite satisfied living on local ingredients, including rice. Meals at restaurants were about 1.5 to 2 times more expensive than in Japan, so I usually cooked for myself. When I prepared Spanish dishes and brought them as lunch to the lab, my colleagues joked that I was being “more Spanish than the Spaniards,” which became one of my fondest memories from the stay.



Fig. 2. Paella I cooked in Spain

The people of Barcelona were very warm and welcoming. When I entered shops and greeted them cheerfully with “Hola!”, I was welcomed despite being from another country. As a large international city, English was also widely understood in many situations. Linguistically, in addition to Spanish, Catalan is also commonly used, and it was frequent to see signs and documents written in three languages. The cityscape, originally designed by



Fig. 3. Buildings and sceneries around Barcelona

Antoni Gaudí, retains its distinctive aesthetic charm even today, creating streets elegant. Moreover, Barcelona is rich in nature, surrounded by both the sea and the hills, and I grew deeply fond of it during my stay (Fig. 3).

During weekends and holidays, I took the opportunity to travel to various parts of Europe. I was deeply impressed by how dramatically languages, cityscapes, and food cultures change from one country to another. Through these experiences, I realized that, regardless of the country, a smile, kindness, and the willingness to communicate are what truly matter.

Acknowledgements

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