

Report for MERIT Long-Term Overseas Dispatch

Graduate School of Frontier Sciences, Department of Advanced Materials Science

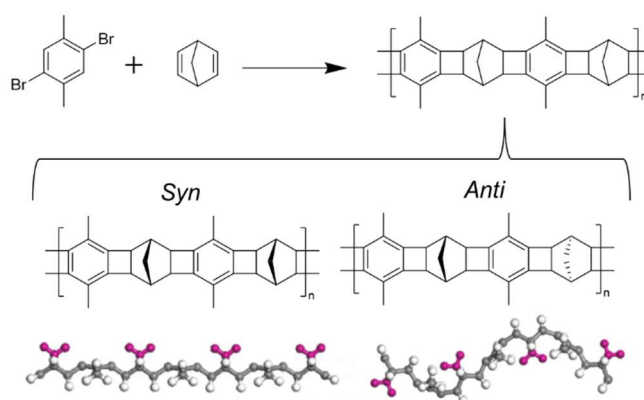
Uemura Lab. D2, Nagi Mizutani

Destination : Xia Lab (Department of Chemistry, Stanford University)
Period : 1.3.2023~3.29.2023
Theme : Shape control of CANAL ladder polymer using MOF

1. Research

The Catalytic Arene-Norbornene Annulation (CANAL) polymerization method developed at the Xia Lab, Stanford University, is a catalytic cyclization of dibromo arenes and norbornadienes to obtain ladder polymers. In this reaction, different shapes of CANAL ladder polymers are obtained depending on the direction of norbornene addition, which is difficult to control (Figure 1).

The shape of CANAL ladder polymer is thought to affect its performance as a gas separation membrane, such as permeability and selectivity. Therefore, in this overseas dispatch, I conducted collaborative research to control the shape of CANAL ladder polymers by using Metal – Organic Framework (MOF) and to elucidate the effects of the



shape on the physical properties and performance as separation membranes.

First, I learned the CANAL reaction, and then I investigated two approaches to control the shape of CANAL ladder polymers. One is to perform the CANAL reaction in the nanopores of MOF. By conducting the CANAL reaction in spatially restricted pores, I aimed to control the shape of the ladder polymer chain. However, not only was the CANAL reaction inhibited by the MOF, but the structure of the MOF was also destroyed during the reaction. Therefore, upon discussion with Dr. Xia, I switched to the second approach, in which the CANAL reaction is performed under normal conditions and then introduced into the MOF for shape-based separation. Model compounds were synthesized and insertion speeds of CANAL compounds were measured.

I will continue to work with Dr. Xia on this topic in Japan.

2. Life at Stanford University

Stanford University is located in the Bay Area of California. Near the campus, many well-known IT

companies such as Apple, Meta, and Google have their headquarters, and the area, also known as Silicon Valley, was surprisingly rural and relaxing. At the campus, there were so many beautifully buildings and lushly green, complete with hiking trails and golf courses, making it look like a tropical resort. Stanford was very safe place and I never felt unsafe even when I walked outside after sunset.



Figure 2. A view of the campus. The Hoover Tower in the back is a well-known symbol of Stanford University and is visited by many tourists.

There were no core hours in the Xia Lab, and each student adopted the lifestyle that worked best for him or her: some were always doing experiments, some came in late in the morning, and some went home early to enjoy their personal lives. Xia Lab seminars were held once a week, where the person in charge would give a presentation on the progress of his/her research or on his/her area of interest, and the discussions were held in an open atmosphere over food and drink. The students were very professional and independent, and I was impressed by the way that they confidently responded when they were asked for their opinions by professors and proposed many new themes.

3. Life in the Bay Area

Although the Bay Area is known for its mild, dry, and pleasant climate, my visit there was "the worst three months of weather in history (by Dr. Xia). It rained and winded on some days, and I experienced three power outages in the short period of three months. Even so, the days were more comfortable than in Japan, and when I woke up in the morning and basked in the sun, I was able to quickly turn my mind off any hardships and spend my time with a positive and relaxed mindset. On weekends, I was able to spend my time actively going to San Francisco to visit sightseeing spots such as the Golden Gate Bridge, Golden Gate Park, and Alcatraz Island, as well as watching NBA games. In addition, since I stayed in a shared house, I was able to communicate with people from various countries who visited the Bay Area for research and internships, which was a very valuable experience.

4. Acknowledgements

I would like to thank Dr. Yan Xia for accepting me as a visiting scholar, his hospitality and guidance, I also thank the members of Xia Lab for not only their research guidance and discussions, but also for their daily close contact. I would like to express my sincere gratitude to my supervisor Prof. Takashi Uemura for his encouragement to study abroad, Dr. Nobuhiko Hosono for his advice and research discussions, and Ms. Kathleen Ann Kieffer and Ms. Kayako Honjo for their generous support about my stay in Stanford. I acknowledge the Japan Society for the Promotion of Science (JSPS) and the University of Tokyo Go Global Scholarship 2022 for financial support during the stay.