Report of overseas dispatch by Materials Education program for the future leaders in Research, Industry and Technology

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Doctor course student of Nishihara lab, department of chemistry, school of science

Yohei Hattori

Background

I stayed at laboratory of Prof. Dr. Guido Clever in the University of Göttingen (George-August-Universität Göttingen) and studied for two and half months. The University of Göttingen is a historic university established in 1734, and known for many famous people. Names seen in textbooks of chemistry such as Debye, Langmuir, Nernst have studied or taught at the University of Göttingen. Prof. Clever is researching about supramolecular chemistry, such as self-assembled molecular cage and DNA nano-architecture, and reported a lot of important results as he is young. He knows much about Japan since he was in Shionoya lab, the University of Tokyo from 2007 to 2010, and attends recent academic conferences in Japan.

I have studied at Nishihara lab since fourth year of undergraduate school, done research about redox and complexation reaction of dinuclear copper complex in master course, and researched about photochemistry of fluorescent radical and its coordination compounds. Area of coordination chemistry is the same, but the size of complex and aim are different from supramolecular chemistry. Supramolecular chemistry is one of the most attracting area recently, and I was very interested in its methodology of research and direction of development. Thus, I wanted dispatch to Clever lab, and was kindly accepted.

Picture 1. Buildings of chemistry department

Contents of research

Molecular cages, which can incorporate with specific guest molecules, are expected to be applied for separation of harmful material, catalytic reactions, and drug delivery. In Clever lab, molecular cages formed by coordination of 4 banana-shaped ligands to 2 palladium metal ions have been developed. These cages have simple structures and can incorporate various functional parts at center of banana-shaped ligands. To date, photo- and redox-active cages were reported (M. Han, R. Michel, B. He, Y.-S. Chen, D. Stalke, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2013**, *52*, 1319-1323. M. Frank, J. Hey, I. Balcioglu, Y.-S. Chen, D. Stalke, T. Suenobu, S. Fukuzumi, H. Frauendorf, G. H. Clever, *Angew. Chem. Int. Ed.* **2013**, *52*, 10102-10106.).

I researched about electrochemistry of various cages in Clever lab. (1) I studied about

electrochemical response of photo-responsive DTE cage. It was known that some DTE derivatives show isomerization from closed-ring isomer to open-ring isomer by oxidation. A banana-shaped ligand containing DTE part showed oxidation of closed-ring isomer, however it did not show isomerization to open-ring isomer and decomposed. It is thought that molecular parts added to DTE to form complex is weak to oxidation. (2) Electrochemical measurements of host-guest complex with oxidation-active guests were done and loss of oxidation activity of the guest molecules were found. Protection of the guest from electrochemical reaction prove that the guest stays inside the cage with high affinity. (3) Reduction potentials of ligands containing reduction-active parts were compared. Changing of the reduction potentials by substitution was studied. Molecular cages showed irreversible reduction as is often seen in other self-assembled cages. It is probably because of difficulty of stable structure at various oxidation states due to limitation of the shape of the self-assembled complexes. (4) Changing of reduction properties of reduction-active molecular cage by formation of host-guest complex was observed. The research was started from finding appropriate guest molecule, that has a large complexation constant. An anionic guest molecule which show relatively slow exchange was found by NMR titration experiments. The guest molecule was expected to change reduction property of the cage, because they would change density distribution of negative charge in the cationic molecular cage. Electrochemical measurements by titrating guest displayed change and shift of the reduction peaks. This result is interpreted that reduction of the cage became more difficult by guest anion inside the cage.

Life in Germany

When I arrived to Germany, I noticed that German people care a lot about safety. There were hammer to break window in emergency in ICE, and there were much more fire extinguishers on passages of research institute of the university than in Japan. I had to learn how to use them first. Many metal and glass doors on passages are thought to be for fire prevention.

Picture 2. Members of Clever lab

Members of the lab mainly spoke Germany, however I had no trouble since they spoke English for me when it is needed. Because they spoke clear English, it was easier for me to talk with them than to talk with native English speakers. Since, people in shops or town usually also can speak English, I had no big trouble when I went shopping or sightseeing. I felt that poor English is weak point of Japanese. On the other hand, I could also learn some communication without language, and importance of basic greetings, numbers, and information by letters such as signs on streets or trains. I got chance to think about globalization, which is often talked imaginarily in Japan. Some measurements, such as mass

spectrometry were done by technicians. It has merits and demerits since work is efficient but sometimes fast measurements or measurements by myself are desirable.

Balance of work and life seemed to be thought to be more important than in Japan. Core time of the lab was from 9 to 18 o'clock, and it seemed that there are few people after 20. Cafeteria was open only for lunch. I thought, it was inconvenient but healthy and attentive.

In spite of relatively short working time and numbers of members, Clever lab publishes papers in fast pace in one of the most competitive area. This is thought to be because of clear and sophisticated design of molecules, aims and ideas. Explanation of research by the members were also clear and they understand their characteristic points of molecules well.

Conclusion and acknowledgement

Although it was a short term, by working on new theme and subject, I could obtain new knowledge and skills, such as self-assembled complexes, treating of Host-Guest systems, and electrospectroscopy. By be accustomed to new environment, culture, and communication without mother language, I got some toughness and confidence in international activities. I could also review my research from another view point, and want to improve my future research.

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