

## MERIT Report for Long-Term Overseas Dispatch

Department of Chemistry and Biotechnology, School of Engineering  
MERIT 5th, 3rd-Year Doctor Course Student Michihisa Ueda

**Period:** September 1st 2019 ~ November 30th 2019

**Host Institute:** Hecht Group, Department of Chemistry, Humboldt Universität zu Berlin

### Summary

From September 1st to November 30th 2019, I stayed in the Hecht research group at Humboldt Universität zu Berlin and conducted an overseas collaborating research about photo-responsive supramolecular assemblies. The Hecht group is one of the top research groups in the field of photochemistry and they have developed novel photochromic molecules with multi-stimuli responsiveness by the arts of synthetic chemistry. This overseas research aimed to develop a new kind of supramolecular architecture that responds to multi-wavelength photoirradiation by combining their knowledge of photochemistry and my knowledge of supramolecular chemistry. The visiting and staying fees were supported by JSPS overseas challenge program for young researchers and an overseas research fellowship from Yoshida foundation for science and technology.

### Research

After the first discovery of photochromism of tetracene molecules in 1867, lots of photochromic molecules have been developed to date. Recently, a new class of photochromic molecules that possess plural photochromic moieties intramolecularly was developed and they exhibit unique photochromism such as multi-step photochromism or wavelength-selective photochromism by multi-wavelength light. I focused on this wavelength-selective photochromism by combining different photochromic moieties. By incorporating this system into supramolecular assemblies, "complex spatiotemporal light control of supramolecular assemblies" could be achieved. The biggest problem to realize is that a molecular pair with almost no overlapping absorption bands is very limited. Then, I decided to focus on the N,N'-substituted indigo derivatives that were investigated by the Hecht group in 2017. The molecules can be isomerized by red-light irradiation and have a wide absorption window in the ultraviolet region. In this research, I tried to develop a supramolecular monomer based on the N,N'-substituted indigo and incorporation into supramolecular assemblies with other photochromic molecules that respond to ultraviolet light irradiation.

I initially planned to synthesize a di-cationized indigo derivative as I thought to utilize salt-bridge interaction for a supramolecular co-assembly. However, the synthesis of di-cationic indigos was totally tough because of its low reactivity and stability, and eventually, I could not synthesize it. Then, I discussed with professor Hecht and the other group members who know indigo derivatives well and reconsidered the synthetic scheme again and again. Finally, I tried to make di-azido indigo that can be derivatized by click-reactions and successfully synthesized and isolated it. I measured ultraviolet-visible absorption spectra and its change upon irradiation, and I found that the obtained molecule showed a wide absorption window around 350 - 500 nm and also exhibited fast photochromism by 660 nm red-light irradiation. This suggested that this newly synthesized indigo is possibly photo-isomerizable orthogonal to other ultraviolet light-responsive photochromic molecules. Also, this molecule can be derivatized to ones with a wide variety of functions by utilizing click reactions of its azido moiety. We are planning to continue this work as a collaborating work and achieve the initial goal; development of "complex spatiotemporal light control of supramolecular assemblies".

### **Acknowledgement**

I would like to acknowledge Prof. Stefan Hecht who kindly accept my stay and helped me a lot even during a busy time due to lab move to Aachen. Also, I am thankful to Dr. Björn Kobin, Dr. Kosuke Nakashima, Mr. Jan Boelkes, Mr. Kevin Broi, Ms. Anna Jasny and other Hecht group members for their kind and warm support on my experiments and the research discussion. I would like to sincerely thank Prof. Takuzo Aida for allowing me to join the valuable opportunity of this overseas research project. I appreciate the financial support of Japan Society for the Promotion of Science (overseas challenge program for young researchers) and Yoshida foundation for science and technology (overseas research fellowship). Finally, I thank MERIT program for accepting my application to this long-term overseas dispatch.