

Report of G-COE Internship Program

Graduate School of Science, Department of Chemistry, Kubo Lab

D1 Inokuchi Daisuke

Term: July/1, 2009–September/26, 2009

Stay: Eugene, Oregon, U.S.A, University of Oregon, Haley Lab.

I stayed at Eugene City in state of Oregon in this summer. The Eugene City is a peaceful city, and therefore people living in this city make me feel so calm. University of Oregon is located in such a



Figure 1. Gate of University of Oregon

city. I studied in Haley laboratory in University of Oregon for 3 months. Professor Haley is so famous in our research field. I was so glad to be able to study as a member of Haley laboratory. He has been researching the correlation between structure of organic molecules and their properties. Especially, his research interests are creation of novel functional fluorochromes and investigation of their physical properties.

My purpose of this internship was to get accustomed to English conversation during

long term staying at overseas. I hoped that research works surrounding by native speakers of English would give me an opportunity to strengthen my ability in English conversation.

My theme given by Professor Haley was creation of redox active fluorescent dyes. I accepted his suggestion of changing from dithiol to disulfide, and attempted to synthesize the fluorescent dye including two thiol groups in the molecule. Generally, the oxidation from dithiol to disulfide progresses easily. Therefore, we expected that different fluorescence color or decrease of luminescence intensity would be observed by changing from dithiol to disulfide, when such dye is added to the solution including oxidizing or reducing agent. I had studied toward development of such fluorescent dye from this viewpoint. Former person tried to synthesize such dye, but he got disulfide derivative instead of desired compound. Namely, the dithiol derivative would be oxidized easily in the air. Accordingly, my concrete research theme was to isolate both pure samples of a dithiol and disulfide derivative, and to measure both UV-Vis and fluorescence spectra of these samples. I thought that it is necessary to be difficult to form disulfide bond by introduction of substituent on α -carbon to isolate stably a dithiol derivative. So, I designed a dithiol derivative introducing four methyl groups on α -carbon by referring literature, and attempted to synthesize it. However, I could not obtain a dithiol derivative. It was found by NMR spectrum that substances like

polymers were obtained. I found that a dithiol derivative which I designed was easier to form intermolecular disulfide bond than intramolecular one by oxidation. From this result, I could suggest two ideas as a reason why a dithiol derivative could not be obtained. These were possibility that a dithiol derivative is polymerized during workup or that it is polymerized in situ. Therefore, I had to investigate reaction condition. When deprotection of a precursor protected with acetyl group was performed with K_2CO_3 , thiolate anion would exist mainly in the reaction mixture. I could think the existence of dissolved oxygen in the solvent as a reason why substances like polymers were obtained, because it was generally known that thiolate ion is easily oxidized in the air. Thus, to remove the influence of dissolved oxygen, deprotection was performed under nitrogen bubbling. As expected, a targeted dithiol derivative could be isolated stably. And I confirmed the molecular shape by X-ray crystal structure analysis. And I was also able to synthesize a disulfide derivative by treatment of excess iodine and triethylamine to a dithiol derivative. When fluorescence spectra of these compounds were measured, I found that fluorescence intensity of a disulfide derivative was much lower than that of a dithiol derivative. I could further



Figure 2. With all members of Haley Lab.

(Center: Professor Haley, Right: Me)

synthesize two compounds possessing different substituent. Thus, I got very good results for 3 months. And I got also very precious experiences in this summer.

Finally, I appreciate to G-COE internship program that gave such a chance to me. I also appreciate to all member of Kubo laboratory. I also appreciate to Professor Haley and all members of Haley laboratory who accepted me pleasantly.