SABBATICAL LEAVE REPORT

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Spring 2015

For my Spring 2015 sabbatical leave, I took the opportunity to relocate to Wichita, Kansas so that I could spend extended time doing library and laboratory research at Wichita State University. During my stay at Wichita State University, I was hosted by Dr. Paul Rillema of the Chemistry Department who had invited me to work in his research laboratory. My report will be organized according to the three goals I established for my sabbatical in my sabbatical application prospectus.

Goal 1: Gain knowledge and experience in using electrochemical and photochemical techniques to study the structure and reactivity of transition metal complexes.

The first goal of my sabbatical was to gain expertise in two experimental techniques in which I had no previous experience. The first technique that I wanted to learn was an electrochemical method known as cyclic voltammetry. This technique was being actively used in the Rillema research group. So, after mastering the technique, I was able to apply it to the research project I was collaborating on with Dr. Rillema.

The second technique that I had hoped to learn was photochemistry—how to initiate a light-driven chemical reaction and then analyze the products. In this case, I had to make an adjustment to my goal. Neither the research project on which I worked nor any of the other active Rillema research projects involved photochemistry. So, any learning and work that I any did on this technique would just involve "playing around" time and would not be producing results with publication potential. Therefore, I elected to devote my time to learning another technique—time-correlated single-photon counting (TCSPC) to measure fluorescence lifetimes. This technique was needed for the research project on which I was collaborating and so it enabled me to achieve my second sabbatical goal: producing research with publication potential.

For both cyclic voltammetry and TCSPC, I was successfully able to master the techniques well enough to obtain publication quality data. In fact, by the end of the spring, I had a better theoretical understanding of the techniques than the "expert" graduate student who initially trained me.

Outcomes

1) Professional expertise in cyclic voltammetry.
2) Professional expertise in time-correlated single-photon counting (TCSPC) measurement of fluorescence lifetimes.

Summary Evaluation

In terms of learning cyclic voltammetry, my sabbatical was a success. In this case, there was a perfect overlap between my goal for developing technical expertise for my future research and my goal for producing publication quality research in the Rillema lab. By the end of the spring, I was able to collect high quality data and have a great understanding of the theoretical principles of the technique. The FHSU chemistry department has an instrument capable of

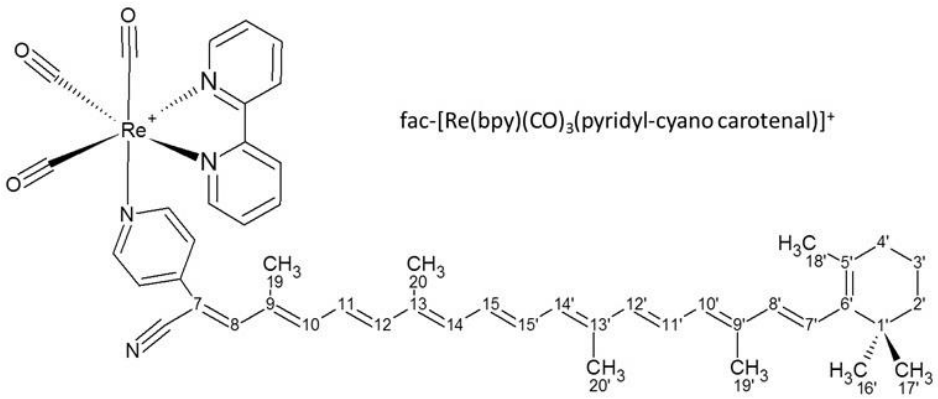
performing cyclic voltammetry and I have complete confidence that I can employ this technique effectively in both teaching and research.

With regards to photochemistry, "the best-laid plans of mice and men often go awry". Dr. Rillema has extensive experience in photochemistry and the Rillema group did have the instrumentation to do this technique. But in this case, there was no overlap between my desire to develop expertise in this area and the research focus of the Rillema group during the time of my sabbatical visit.

Gaining expertise in time-correlated single-photon counting (TCSPC) measurement of fluorescence lifetimes was an unexpected bonus of my sabbatical. I had the opportunity to collect data and gain expertise on an expensive, cutting edge research instrument. It was challenging and fun to learn how to utilize the instrument to measure the nanoseconds between when a photon excites our target molecule and when a lower energy photon was released by the excited molecule.

Goal 2: Engage in laboratory research which has a strong potential for publication in a peer-reviewed journal with an impact factor of 1.0 or greater.

My research collaboration with the Rillema group at Wichita State University consisted of characterizing a series of rhenium complexes using cyclic voltammetry, absorbance spectroscopy, fluorescence spectroscopy, and fluorescence lifetime measurements. A total of four compounds were studied. Unfortunately, in the process of analyzing the spectra, it was determined that three of the compounds were either impure or had decomposed during storage. The rhenium complex shown below was the only one to be studied with high purity. For this complex, high quality spectral data was obtained.



The motivation for synthesizing this compound was to develop more efficient substrates for solar energy conversion. The rhenium (Re) metal center is capable of converting light into electrical energy within a dye-sensitized solar cell. One limitation of this particular complex (absent the carotene side chain) is that it absorbs only UV light and thus does not utilize most of the solar spectrum. The ligand with the very long side chain is a carotene derivative. In nature, carotenoid compounds act as "light harvesting attennas" for the chlorophyll in photosystems I and II of plants. The carotenoid absorbs light in a wavelength region not absorbed by chlorophyll. After absorbing light, the carotenoid transfers its energy to the chlorophyll center where it is ultimately converted into chemical energy. In an analogous fashion, it was hoped that the carotene ligand in the above compound would act as a light antenna to absorb light energy in the visible region and transfer this energy to the rhenium center where it could be converted to

electrical energy. This would enable the compound to absorb a broader spectrum of light and boost its solar conversion efficiency. Unfortunately for solar energy applications, my studies did not find any evidence of energy conversion from the carotene ligand to the rhenium center.

Outcomes

1) Obtained publication quality absorbance spectra, steady-state fluorescence spectra, and TCSPC fluorescence lifetime data for the *fac*-[$Re(CO)_3$(bipyridyl)(all-*trans*-7'-cyano-7'-pyridyl-7'-apo-β-carotenal)] complex.

Summary Evaluation

I made substantial progress towards my goal of obtaining publication quality data. By the end of the spring semester, I had results which my collaborator Paul Rillema thought were ready to write up for publication. At this point, the spring semester was over and I had to move back to Hays due to financial limitations. Unfortunately, during the summer I tried to be ambitious and immediately begin making progress on my third goal of establishing a home-grown undergraduate research program. I thought I would be able to kill two birds with one stone. I thought after devoting June to training Kelci Glover (an undergraduate student) to work on my research project, I could devote most of July to writing up my Wichita State research. Instead, training Kelci, planning experiments, and supervising Kelci's research took more time and energy on my part than expected. But since Kelci had committed to spending her summer to do research with me, I felt obligated to give her first priority. At present, Kelci and I are in the process of preparing our summer research for presentation. In October once Kelci's poster presentation has been prepared, I will switch my focus and give my highest research priority to writing up my Wichita State results.

Goal 3: Initiate a sustained program of research investigation that could be continued at Fort Hays State University with the collaboration of undergraduate students.

In addition to my laboratory collaboration with Dr. Paul Rillema, I also engaged in extensive literature research in my own specialization. The sabbatical enabled me to catch up on new developments in the literature and engage deep thinking about future research directions. Several tentative ideas that I had were developed into a full-fledged program of research in which undergraduates can participate. In brief, my research is focused on the study of iron-binding molecules secreted by microbes known as siderophores. Specifically, I am interested in the role of ternary complexes in the chemical reactions associated with the release of iron from the siderophore complex. Ternary complexes are molecular combinations formed from three components: iron, siderophore, and a competing iron binding molecule. Ternary complex formation is hypothesized to enhance the iron exchange process between the siderophore and an iron transport molecule or receptor site within the organism. My research goals are to form ternary complexes with model siderophore molecules and quantitatively measure: (1) the stability of the ternary complexes; and (2) the reduction potential of the ternary complexes. For more detailed information about my research plans, refer to Attachments A and B.

Using my newly developed ideas as a basis, I then wrote grant proposals for two FHSU internal grant programs. The first proposal was an application to the FHSU Faculty Summer Research and Creative Activity Grant (see Attachment A). This proposal was not funded. The second proposal was for an FHSU Chemistry Department grant, the Werth Summer

Undergraduate Research Award (see Attachment B). This proposal was funded and enabled me to recruit Kelci Glover (a rising senior chemistry student) to work on my research and pay her a stipend. Over the summer, Kelci and I worked full time on research doing a variety of preliminary studies and one in-depth study. The results of the in-depth study will be presented by Kelci as a poster presentation at the 2015 Midwest Regional Meeting of the American Chemical Society to be held on October 21-24 in St. Joseph, Missouri. See Attachment C for a copy of the abstract which has been accepted for the program of the meeting.

Outcomes

1) Grant Proposal: *Measurement of the Stability and Reduction Potentials of Ternary Iron-Siderophore Complexes*. Edwin G. Olmstead, Jr., FHSU Faculty Summer Research and Creative Activity Grant FY15, submitted but not funded, $3,785. See Attachment A.

2) Grant Proposal: *Measurement of the Formation Constants and Redox Potentials of Model Siderophore Ternary Complexes*. Edwin G. Olmstead, Jr. and Kelci Glover (student); FHSU Chemistry Department Werth Summer Undergraduate Research Award 2015, submitted and funded, $3,900. See Attachment B.

3) Poster Presentation: *Equilibrium studies of the iron exchange reaction of ferrioxamine B with 8-hydroxyquinoline-5-sulfonate.* Kelci Glover (presenter) and Edwin G. Olmstead, Jr., 2015 Midwest Regional Meeting of the American Chemical Society, St. Joseph, MO, October 21-24, 2015, accepted and to be presented. See Attachment C.

Summary Evaluation

In my opinion, I achieved a great amount of success on this goal. Prior to going on sabbatical, I felt like my research activities had no momentum. The sabbatical enabled me to revisit a research topic that I had not actively engaged in since 2005 and develop a new program of research that was suitable for undergraduate student involvement. The process of applying for funding helped me focus my thinking on concrete and achievable goals. The receipt of the Werth Summer Undergraduate Research Award enabled me to immediately begin work on the research in the summer following my sabbatical while the ideas were still fresh in my head. Kelci's participation is a demonstration that undergraduate students can be successfully incorporated in my research. The acceptance of our poster at the regional meeting of American Chemical Society is a professional validation of the quality of my research ideas. Taken together, I feel like I have achieved a promising start and a great amount of momentum towards producing publication quality research at FHSU with undergraduate student collaboration.

Acknowledgements

To Fort Hays State University, I thank you for the funds to support my sabbatical. To the FHSU Chemistry Department, I thank you for a Werth Summer Undergraduate Research Award which enabled me to employ Kelci Glover and immediately put my sabbatical research ideas into action. To my department colleagues, I thank you for carrying a heavier load of responsibilities created by my absence.