

Fluorescent Decay Times of Molecular Butterflies

This summer, I have been given a fantastic opportunity; as I am writing this, I am in the final week of my internship at Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. This laboratory traces its roots to the construction of the atomic bomb during World War II, and today it is still among the foremost centers of nuclear science in the United States, including fusion science. However, nuclear science is not exclusively the work that ORNL headlines; for example, the second-fastest computer in the world, Titan, is housed here. The entire place is a bustling hub, seeking knowledge and exchanging information, driven by some of the foremost scientists in the world. I found this out rather quickly when I first arrived; my spectroscopic research for the summer was conducted in collaboration with Dr. Yingzhong Ma, best described by his co-workers as an "international legend" in his field.

For ten weeks I have been studying a pyrazolate-bridged platinum binuclear complex recently synthesized by researchers at Florida State University, BF₂PtPZ. It is structurally comprised of two symmetric, cyclometallating ligand "wings" and a pyrazolate "backbone" which bridges the wings and gives the compound a butterfly-like appearance. For this reason the compound is called a "molecular butterfly." In addition to the compound's appearance, BF₂PtPZ shares another similarity to its namesake: depending upon the electronic excited-state energy of the compound, its wings' position can vary between "folded" and "unfolded" much in the same way a real butterfly can flap its wings to take flight. This structural difference between

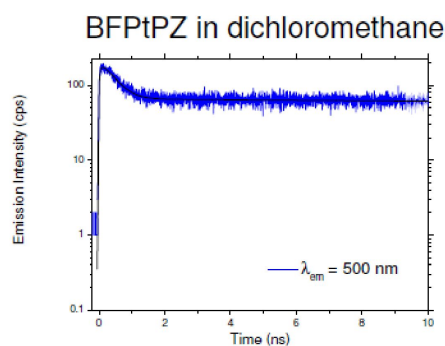
the two states is the result of a photoinduced structural change (PSC) which causes the central platinum (Pt) atoms to shorten the distance between themselves at a triplet excited-state with higher energy and relax that distance at the state with lower energy. This structural difference between these two states also results in different spectral characteristics of phosphorescent emission from these triplet-states upon optical excitation. With the wings folded (i.e. at the shorter Pt-Pt distance), the compound emits a photon from its lower-lying excited state at a red wavelength; when unfolded, however, (i.e. at the longer Pt-Pt distance), the wings emit photons at a blue/green wavelength from the higher-lying triplet state.

As this is a very recently synthesized compound, spectroscopic characterization is needed in great detail to better understand the complex PSC process and its associated timescales, and, to simplify, my work involved collecting the time-resolved emission data. I helped align and calibrate the equipment used in preparation of our experiments, and my day-to-day responsibilities included preparing chemical solutions of our samples, running photon-counting measurements, and maintaining records of the experimental data we obtained. Additionally, I used curve-fitting software to examine the data and determine the timescales of the excited-state relaxation process devoid of the background interference from our instrument response. I examined the wavelength dependence of time-resolved emission of this compound and the effect of sample temperature on the time-resolved emission kinetics. For example, at an emission wavelength of 500 nanometers, I obtained decay curves similar to

08/08/2016

Davis Easley- 3

the one below, which initiates with the faster decay with lifetime of approximately 280 picoseconds and a much long-lived subsequent decay.

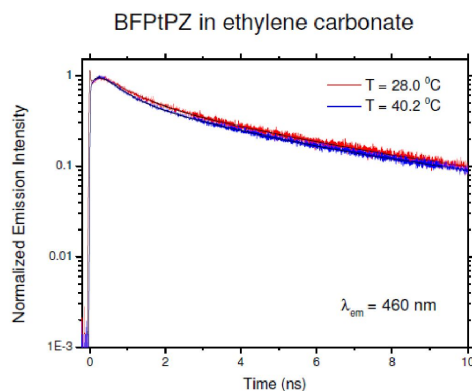
Figure 1¹

We were able to detect small but noticeable differences between the decays of BFPtPZ for a temperature change as small as 12 degrees Celsius, demonstrated in the graph below. This observed change arises from the distinct molecular conformations at these temperatures. This has never been measured before.

Figure 2²

¹ Figure 1: Time-resolved emission kinetics for BFPtPZ dissolved in dichloromethane probed at 500 nm upon an excitation at 350 nm.

² Figure 2: Time-resolved emission kinetics for BFPtPZ dissolved in ethylene carbonate probed at 460 nm for two different sample temperatures as noted.



By doing this research, I was able to explore some cutting-edge laboratory techniques, using equipment beyond what I would be able to find at Sewanee. I was able to learn new topics in optics that are above what is normally taught in an undergraduate classroom, better preparing myself for graduate school. Furthermore, this work has prepared me for my courses in quantum chemistry and optics this coming fall semester, and it has given me new insight and understanding of the techniques I have been using in my on-going undergraduate research at Sewanee for the past year.

In addition to my immediate work as a spectroscopic research intern, I was able to do many other things to positively benefit my future career as a scientific researcher. Weekly seminars, where facility employees could present hour-long talks about their research to co-workers, were readily available in a variety of topics, and I did my best to attend every one I could. These gave me a good overview of the other opportunities for research offered at Oak Ridge and ideas for courses I might be interested in taking during my final two years at Sewanee. Additionally, I was able to get in touch with researchers in these different disciplines

and tour their laboratories, seeing their work first hand; I received a lot of insight into my career goals and reaffirmed that scientific research is exactly what I want to be doing for the rest of my life. I hope to work here someday, and I am very grateful to have been able to get this head start on my career. ³

³ I would like to thank the Sewanee physics department, Dr. Benjamin Lawrie, and Dr. Yingzhong Ma for helping to arrange this opportunity, as well as give a special thanks to Sewanee's Career & Leadership Development office and their sponsors for funding me. Y.Z.M. was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. We thank Prof. Biwu Ma and his students of Florida State University for synthesis of the BFpTPZ molecules and discussion about sample handling procedure.