Ultrafast spectroscopy and the analysis of art pigment degradation and solar energy harvesting complex photoprodusts

M. Cather Simpson
University of Auckland, New Zealand

Abstract

Many fundamental chemical and physical processes occur very rapidly, over femtoseconds (10^{-15} s) to nanoseconds (10^{-9} s). The ‘choices’ molecules make as they undergo these fast processes have significant consequences on macroscopic timescales, from milliseconds to hundreds of years. We explore these fast processes and longer-term consequences to better understand and predict the photolability of art pigments, the efficiency of self-assembled solar energy harvesting complexes, and to analyze the photoprodusts of both. Ultrafast pump-probe laser spectroscopic methods probe these dynamics directly in photoexcited molecules, and provide evidence for the electronic and nuclear evolution of the system as it ‘chooses’ whether to undergo electron or proton transfer, photoisomerisation, bond-breaking or forming, or simply return unchanged to the ground state. Anthraquinone-based dyes and pigments have been used for ~4000 years, and are well known for their photo-fugitive qualities. Recently, we began explorations of the ultrafast transient UV/Vis absorption spectra of two related red lake chromophores, purpurin and alizarin, with 9,10-anthroquinoid core structures that differ by a single hydroxyl group. The results are consistent with the hypothesis that more rapid photodynamics leads to greater overall photostability in these systems. We have also applied ultrafast transient UV/Vis and NIR spectroscopy to a new class of self-assembled porphyrin-fullerene complexes, in order to explore structural correlations with the lifetime of the charge-separated state and better inform synthetic chemistry approaches to maximizing this important parameter. These studies, in their early stage, indicate the potential of these systems for solar energy harvesting applications.

Biography

Associate Professor Cather Simpson earned a Ph.D. in Medical Sciences with a Howard Hughes Predoctoral Fellowship. After a Department of Energy Distinguished Postdoctoral Fellowship at Sandia National Labs, she joined the Chemistry Department at Case Western Reserve University, where she earned tenure and promotion in 2005. In 2007, she moved to the University of Auckland, where she holds appointments in Chemistry and Physics, and is founding Director of a multiuser laser facility called The Photon Factory, that opened in 2010. Her team of ~25 physics, chemistry, and engineering researchers perform fundamental research in the photodynamics of molecules, targeted research to advance ultrafast laser micromachining and fabrication, and industry-facing research with over a dozen companies and research institutes. A spin-off company is commercializing a novel approach to cell sorting. She has published over 50 papers and was recently awarded a Callaghan Commercialisation Fellowship and a University of Auckland Award for Sustained Excellence in Teaching.