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2-Dimensional Fluorescence Spectroscopy: Determining the Temperature-Dependent Conformations of Porphyrin Dimers and Nucleic Acids¹ JULIA WIDOM, University of Oregon, ALEJANDRO PERDOMO-ORTIZ, ALAN ASPURU-GUZIK, Harvard University, ANDREW MARCUS, University of Oregon — I will describe spectroscopic studies on a covalently-linked zinc tetraphenylporphyrin dimer embedded in a phospholipid bilayer membrane. Using phase-modulation 2-Dimensional Fluorescence Spectroscopy (2D FS, a fluorescence-detected version of 2D electronic spectroscopy) along with linear absorption and fluorescence spectroscopy, it was found that the dimer adopts two predominant conformations in the membrane, and that the relative populations of these two states change as a function of temperature. Simultaneously fitting the linear absorption spectrum and the 2D FS spectra at four different excitation wavelengths revealed a wealth of information about these two states, including their relative populations, relative fluorescence quantum yields, the strength of the exciton coupling present in each state, and the approximate angles between the electronic transition dipole moments of the two porphyrins. Ongoing analysis focuses on elucidating the relaxation and energy transfer dynamics of this system through the population time dependence of the 2D spectra. Finally, I will present preliminary results from experiments in which 2D FS was performed with ultraviolet excitation to study the conformations of DNA constructs labeled with a fluorescent analogue of guanine.

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