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Controlling Structure and Energy Transfer in Liposome Ordered Porphyrin Aggregates by Fluorescence-Detected 2D Electronic Spectroscopy

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Excited state dynamics of biological and artificial chromophore arrays are often studied using femtosecond laser spectroscopy. In principle, two-dimensional electronic coherence spectroscopy (2D-ECS) can probe the conformation-dependent electronic couplings, and the directional flow of photo-induced excitation energy from chromophore antennas to charge generating reaction centers. In most room temperature biological systems (e.g. cellular membranes), electronic couplings are difficult to observe in real time because i) the electronic interactions are generally weak in comparison to energetic disorder, ii) the structural heterogeneity of biological samples leads to the dispersion of phase coherent optical signals, and iii) artificial bio-membrane systems are highly susceptible to photo-degradation.

I will discuss a new high signal-to-noise (S/N) approach to 2D-ECS that employs phase-modulation of high repetition sequences of low energy laser pulses, and amplifies weak nonlinear fluorescence signals from membrane-ordered phorphyrin aggregates. The principles of the phase-modulation technique are described in [1]. These fluorescence based measurements uniquely detect nonlinear optical coherence pathways that reduce spectral congestion, and thus achieve superior spectral resolution to established four-wave mixing techniques.

Specifically, I will present results for magnesium meso tetraphenylporphyrin dimers, which form in room temperature lipid bilayer vesicles. At intermediate concentration, the linear absorption line shape of the lowest electronic transition broadens asymmetrically, suggesting the formation of electronically interacting aggregates. The measured 2D spectra exhibit well resolved features of an exciton-coupled dimer of two-level molecules, with time-dependence indicating apparent uphill energy transfer on sub-100 fs time scales. Comparison between data

and theoretically simulated spectra indicate that a herring bone structure is the predominant dimer morphology.

The advantages of the fluorescence-detected 2D-ECS approach make it ideally suited to study excited state dynamics in artificial membrane systems, which may serve as model platforms to examine the influence of electric dipole coupling strength, molecular orientation, solvent environment, and conformational transitions. The high S/N ability of the approach might be combined with micro-fluidic technologies to enable measurements on very small numbers of membrane-bound chromophore arrays as they pass one at a time through the excitation spot. Further extensions could involve implementation at shorter wavelengths, and synchronization of 2D-ECS signals with x-ray sources to obtain atomic scale resolution of photo-initiated energy flow.

1. P. F. Tekavec, G. A. Lott, and A. H. Marcus, "Fluorescence-detected two-dimensional electronic coherence spectroscopy by acousto-optic phase modulation," *J. Chem. Phys.* **127**, 214307 (2007).