

Abstract Submitted
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Conformation of self-assembled porphyrin dimers in liposome vesicles by phase-modulation 2D fluorescence spectroscopy

ALEJANDRO PERDOMO-ORTIZ, Department of Chemistry and Chemical Biology, Harvard University, GEOFFREY A. LOTT, JAMES K. UTTERBACK, Department of Physics, Oregon Center for Optics, University of Oregon, JULIA R. WIDOM, Department of Chemistry, Oregon Center for Optics, Institute of Molecular Biology, University of Oregon, ALÁN ASPURU-GUZIĆ, Department of Chemistry and Chemical Biology, Harvard University, ANDREW H. MARCUS, Department of Chemistry, Oregon Center for Optics, Institute of Molecular Biology, University of Oregon — By applying a phase-modulation fluorescence approach to 2D electronic spectroscopy (PM-2D FS), we studied the conformation-dependent exciton coupling of a porphyrin dimer embedded in a phospholipid bilayer membrane. Our measurements specify the relative angle and separation between interacting electronic transition dipole moments and thus provide a detailed characterization of dimer conformation. PM-2D FS produces 2D spectra with distinct optical features, similar to those obtained using 2D photon-echo spectroscopy. Specifically, we studied magnesium meso tetraphenylporphyrin dimers, which form in the amphiphilic regions of 1,2-distearoyl-sn-glycero-3-phosphocholine liposomes. Comparison between experimental and simulated spectra show that although a wide range of dimer conformations can be inferred by either the linear absorption spectrum or the 2D spectrum alone, consideration of both types of spectra constrain the possible structures to a “T-shaped” geometry. These experiments establish the PM-2D FS method as an effective approach to elucidate chromophore dimer conformation.

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