Studies of Molecular Excitons formed by Porphyrin Dimers in Lipid Bilayer Vesicles using Two-Dimensional Electronic Coherence Spectroscopy

GEOFFREY LOTT, Department of Physics, University of Oregon, ANDREW MARCUS, Department of Chemistry, University of Oregon, Eugene, OR 97403 — When a macromolecular complex is labeled with two or more closely spaced fluorescent chromophores, resonant dipolar coupling can give rise to delocalized exciton states whose energies and transition strengths are sensitive to site conformation. We study the exciton structure of dimers of Magnesium tetraphenylporphyrin (MgTPP), which self-assemble within phospholipid bilayer vesicles. As the concentration of membrane-bound MgTPP is increased, low-lying vibronic features of the linear absorption spectrum are observed to broaden and develop blue-shifted shoulders. We apply a fluorescence-detected phase-modulation approach to two-dimensional electronic coherence spectroscopy (2D-ECS) to measure the 2D electronic spectrum of the exciton-coupled dimers. The 2D spectra exhibit clearly resolved diagonal and off-diagonal features associated with the exciton splitting, whose shapes and relative amplitudes evolve on femtosecond time scales.

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