The Quantum Design of Photosynthesis

In photosynthesis sunlight is absorbed by the photosynthetic pigments, chlorophyll and carotenoid and the resulting excited state is stored as chemical energy. This energy conversion under optimal conditions occurs with a remarkable efficiency that scientists hope to mimic in bio-inspired solar energy converting devices, based on abundant elements. Two ultrafast (femtoseconds-picoseconds, $10^{-15}$-$10^{-12}$ sec) processes are at the basis of the success of photosynthesis: excitation energy transfer in a light-harvesting antenna followed by charge separation in the photosynthetic reaction center. In plants pigments involved in light-harvesting antenna and charge separation are bound to specialized proteins that are organized in a membrane, the thylakoid membrane. Plants make do with two reaction centers that operate in series, Photosystem 1 and Photosystem 2, the former is sufficiently reducing to reduce CO$_2$, the latter has the capacity to extract the necessary electrons from water and produce molecular oxygen. Upon absorption of light collective excitations (excitons) are formed that are delocalized over a number of pigments that move extremely rapidly through the light-harvesting antenna to the reaction center in such a way that the quantum coherence is maintained even during the final charge separation. Two-dimensional (2D) electronic spectroscopy is an ultrafast laser technique that allows a visualization of how these coherences are involved in the primary processes of energy and charge transfer. Based on quantitative modeling we identify the exciton-vibrational coherences observed in 2D photon echo of the photosystem II reaction center (PSII-RC). We find that the vibrations resonant with the exciton splittings can modify the delocalization of the exciton states and produce additional states, thus promoting directed energy transfer and allowing a switch between the two charge separation pathways. We conclude that the coincidence of the frequencies of the most intense vibrations with the splittings within the manifold of exciton and charge-transfer states in the PSII-RC is not occurring by chance, but reflects a fundamental principle of how energy conversion in photosynthesis was optimized.

For a recent review of this work see:

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