and in aggregates, which are widely used to mimic the quenching state in vivo. The experiments indentify several quenching sites in the aggregates.

888-Pos

Effect of Antenna-Depletion in Photosystem II on Excitation Energy Transfer in Arabidopsis thaliana

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The role of individual photosynthetic antenna complexes of Photosystem II (PSII) both in membrane organization and excitation energy transfer have been investigated. thylakoid membranes from wild-type (WT) Arabidopsis thaliana, and three mutants lacking light-harvesting complexes CP24, CP26 or CP29, respectively, were studied by picosecond-fluorescence spectroscopy. By using different excitation/detection wavelength combinations it was possible for the first time to separate PSII and PSII fluorescence kinetics. The sub-100 ps component, previously ascribed entirely to PSII, turns out to be partly due to PSI. Moreover, the migration time of excitations from antenna to PSII reaction center (RC) was determined for the first time for thylakoid membranes. It is four times longer than for PSII-only membranes, due to additional antenna complexes, which are less well connected to the RC. The results in the absence of CP29 and, especially, of CP24 show that a large fraction of the light-harvesting complexes becomes badly connected to the RCs. Interestingly, the excited-state lifetimes of the “disconnected” light-harvesting complexes appear to be substantially quenched.

891-Pos

Spectroscopic Determination of HOMO and LUMO Energies of Retinal in Bacteriorhodopsin for Solar Cell Applications

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Bacteriorhodopsin (bR) is a potential sensitizer for bio-sensitized solar cells (Fig. 1). In this study, the energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of retinal in bR are investigated using X-ray Photoemission Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS), and Ultraviolet Photoemission Spectroscopy (UPS). With the combination of XPS, XAS and UPS methods, the absolute energies of the HOMO and LUMO can be determined for comparison to the valence and conduction band energies of the biosensitized semiconductor. The HOMO-LUMO gap of retinal was spectroscopically determined to be 2.49 eV. For comparison, we also test the feasibility of DFT calculations in determining the HOMO-LUMO gap of free retinal. Using the GGA 98 G basis set, the calculated HOMO-LUMO gap was 2.69 eV. The results shows that the DFT method overestimates the experimentally found band gap; consequently, higher level calculations are required.

892-Pos

Photosynthetic Antenna Systems: The Place Where Light Interfaces with Biology

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All photosynthetic organisms contain a light-gathering antenna system, which functions to collect light and transfer energy to the reaction center complex where electron transfer reactions take place. Our work centers on the antenna complexes found in green photosynthetic bacteria, which include chlorosomes, the Fenna-Matthews-Olson (FMO) antenna protein and integral-membrane antenna and reaction center complexes. All of these complexes are involved in the light-energy collection process in these organisms, which are adapted for life in very low light intensities. Chlorosomes are ellipsoidal structures attached to the cytoplasmic side of the inner cell membrane. These antenna complexes provide a very large absorption cross section for light capture. Evidence is overwhelming that the chlorosome represents a very different type of antenna from that found in any other photosynthetic system yet studied. Chlorosomes do not contain traditional pigment-proteins, in which the pigments bind to specific sites on proteins. These systems are of interest from both a basic science perspective of what is the structure of this unique class of photosynthetic antennas and how they work so efficiently, as well as more applied aspects in which the principles of self organization and extraordinary pigment properties that characterize these systems are used in a bio-mimetic approach to devise artificial light-energy capture systems. Recent work involves studies on the structure of the FMO antenna complex and the architecture of the membrane that includes the chlorosome, FMO protein and reaction center. Additional work involves using chlorosomes as part of bio-hybrid systems in which the biological complex feeds energy to an inorganic semiconductor substrate such as titanium dioxide.