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

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

Herbert van Amerongen[1], Bart van Oort[1], Marieke Alberts[1], Silvia de Bianchi[2], Luca Dall 'Osto[2], Roberto Bassi[2], Gediminas Trinkunas[3], Roberta Croce[4].
[1]Wageningen University, Wageningen, Netherlands, [2]University of Verona, Verona, Italy, [3]Institute of Physics, Vilnius, Lithuania, [4]University of Groningen, Groningen, Netherlands.

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 PSI and PSII fluorescence kinetics. The sub-100 ps component, previously ascribed entirely to PSI, turns out to be partly due to PSII. 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 CP26 are very similar to those of WT, demonstrating that the PSII organization is not disturbed. However, the kinetics 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.

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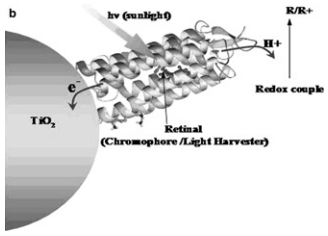
Spectroscopic Determination of HOMO and LUMO Energies of Retinal in Bacteriorhodopsin for Solar Cell Applications

Gau Xingyu[1], **Surya N. Viswanathan**[2], Chih-Wei Chang[2,3], Bernardo Barbiellini[2], David E. Budil[2], Venkatesan Renugopalakrishnan[2,3].
[1]National University of Singapore, Singapore, Singapore, [2]Northeastern University, Boston, MA, USA, [3]Children's Hospital, Harvard Medical School, Boston, MA, USA.

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 G-311G 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.



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Photosynthetic Antenna Systems: The Place Where Light Interfaces with Biology

Robert E. Blankenship.
Washington Univ. In St. Louis, St. Louis, MO, USA.

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.

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Investigating The CP29 Photosynthetic Light Harvesting Complex with 2D Electronic Spectroscopy

Naomi S. Ginsberg[1,2], Jeffrey A. Davis[3], Matteo Ballottari[4], Yuan-Chung Cheng[5], Roberto Bassi[4], Graham R. Fleming[1,2].
[1]Lawrence Berkeley National Laboratory, Berkeley, CA, USA, [2]Univeristy of California at Berkeley, Berkeley, CA, USA, [3]Swinburne University of Technology, Melbourne, Australia, [4]University of Verona, Verona, Italy, [5]National Taiwan University, Taipei, Taiwan.

Though chlorophyll-binding protein CP29, a light harvesting complex in photosystem II of green plants, is proposed to play a role in the regulation of potentially-damaging excess chlorophyll excitations in the supercomplex, little is known about its spatial structure and its relation to excitation energy transfer dynamics and photoprotective action. In vivo, the presence of carotenoid pigment zeaxanthin is correlated with the quenching of excess chlorophyll excitations. Although the mechanism of quenching is still unknown, it is evident that CP29 exchanges carotenoid pigments depending on illumination conditions–in low light, the complex binds violaxanthin, while in high light zeaxanthin is bound.

We probe the chlorophyll Qy band of isolated CP29, binding either violaxanthin or zeaxanthin, using conventional and polarization-sensitive two-dimensional electronic spectroscopy (2DES) in order to better characterize electronic and spatial structure. 2DES resolves both excitation and emission energy of the molecular complexes being studied, providing a picture of the correlations between multiple excited states and revealing the presence of states that may go undetected by other spectroscopies. It also provides a direct map of excitation energy transfer processes within the complex by identifying signals from correlated donor and acceptor energies. Polarization-dependent studies provide clues in particular about chromophore configuration. We furthermore investigate whether the binding of zeaxanthin alters the excitation energy landscape and the resulting dynamics of CP29 to potentially modulate the quenching of excess excitations.

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The Ligand Environment of the S_2 State of Photosystem Ii: A Study of the Hyperfine Interactions of the Tetranuclear Manganese Cluster by 2D Hyscore Spectroscopy.‡

K.V. Lakshmi, Sergey Milikisiyants, Ruchira Chatterjee, Amanda M. Weyers, Ashley Meenaghan, Andrew Schwendeman, Christopher Coates.
Rensselaer Polytechnic Institute, Troy, NY, USA.

The solar water-splitting protein complex, photosystem II (PSII), catalyzes the light-driven oxidation of water to dioxygen in Nature. The four-electron water oxidation reaction occurs at the tetranuclear manganese-calcium-oxo (Mn_4Ca-oxo) cluster that is present in the oxygen-evolving complex (OEC) of PSII. The mechanism of light-driven water oxidation has been a subject of intense interest and the OEC of PSII has been studied extensively by structural methods. While the recent X-ray crystal structures, single crystal EXAFS and EPR spectroscopy investigations provide a model for the geometry of the catalytic Mn_4Ca-oxo cluster, there is limited knowledge of the protein environment that surrounds the catalytic site. It is suggested that the binding and activation of the substrate water molecules at the Mn_4Ca-oxo cluster in the OEC of PSII are facilitated by key amino acid residues that could be ligated to the catalytic cluster. In this study, we demonstrate the application of two-dimensional (2D) hyperfine sublevel correlation spectroscopy to determine the magnetic couplings of the S_2 state of PSII. We utilize 2D difference spectroscopy to facilitate unambiguous assignments of the spectral features arising from the substrate molecules and surrounding amino acid residues in the S_2 state of PSII. The results presented here, for the first time, identify previously unknown ligands to the catalytic