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## The Electronic Structure of Photosystem II

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## SUMMARY

The main objective of this Thesis is to investigate how photosynthetic organisms transform the energy of sunlight into electrochemical energy by means of the charge separation (CS) process, one of the key processes in photosynthetic energy conversion. The CS process occurs in the photosystem II reaction center (PSII RC), a pigment-protein complex embedded in the photosynthetic membrane of oxygen evolving organisms (cyanobacteria, algae and higher plants). The photosynthetic membrane network located inside a cellular organelle, the chloroplast, holds the whole photosynthetic machinery which is composed of many different pigment-protein complexes with different functions.

Light from the sun is collected and transferred to the photochemically active RC by light-harvesting complexes, the so-called antennas. Once the sunlight excitation energy reaches the RC, a series of energy and electron transfer reactions among the chromophores in the RC (six chlorophylls, two pheophytins and two  $\beta$ -carotenes) and two electron acceptors (quinones) convert the sunlight energy into a charge separated state. This charge separated state, in turn, creates an electrochemical gradient across the photosynthetic membrane which ultimately powers the photosynthetic organism.

The CS process in PSII RC has been extensively studied since the first biochemical isolation of the PSII RC was achieved in 1987 by Nanba and Satoh. Despite the apparent simplicity of the isolated RC, the spectral congestion in the RC (the chlorophylls and pheophytins absorb at approximately the same energy) complicates the interpretation of the spectroscopic data and has led to a long and extensive debate in the literature regarding the mechanism and time scale of CS. In chapter 2 we present a detailed transient absorption study aimed to investigate the molecular mechanisms of CS. The design of the experiment provides the required data which after the application of global and target analysis leads us to demonstrate that CS can occur via two different pathways with participation from different sets of chromophores at every stage of the process. Each RC complex reaches a common final charge separated state following one of the two pathways depending on protein configuration. This result highlights the role of the protein in controlling the CS dynamics in the PSII RC.

In chapter 3 we further verify the idea of the two pathways by the physical modeling of the transient absorption kinetics using the modified Redfield-generalized Förster theory.

In chapter 4 we present an unexpected observation in the experimental data of chapter 2. Until this point, generally only the chlorophylls and pheophytins were considered to participate in the energy transfer reactions within the RC. Even so, we observe a perturbation in the energy of the two  $\beta$ -carotenes present in the RC when the peripheral chlorophylls, the so-called Chls<sub>z</sub>, are in the excited state. This observation suggests that the electronic states of the Chls<sub>z</sub> and the  $\beta$ -carotenes are mixed. The Chls<sub>z</sub> are located at opposing sides at the periphery of the complex (at  $\approx 25$  Å from the central chromophores which are separated by  $\approx 10$  Å from each other) and transfer excitation energy to the center of the complex in  $\approx 20$  ps ( $1$  ps =  $10^{-9}$  s). However, if the energy transfer time is calculated theoretically, much longer energy transfer times are obtained (up to 100 ps). The fact that the  $\beta$ -carotenes are not included in the theoretical calculations and the presence of their electronic mixing with the Chls<sub>z</sub>, lead us to hypothesize the involvement of the  $\beta$ -carotenes in accelerating the energy transfer process between the Chls<sub>z</sub> and the chromophores in the center of the complex.

In chapter 5 we have assessed the properties of the electronic states which initiate CS by a combined approach: Stark spectroscopy (a extremely sensitive technique to the movement of charge associated with an electronic transition) applied to site-directed mutants (where the exchange of a single amino acid modifies the pigment-protein interactions of the naturally occurring organism, the so-called wild-type). The comparison of the Stark spectra of the wild-type PSII complex with eight different site-directed mutants allows us to demonstrate that the electronic states which initiate CS are collective excited states (excitons) mixed with charge transfer (CT) states. The CT character of these mixed states promotes ultrafast and efficient CS in the PSII RC. This work, in line with chapter 2, provides further evidence for the presence of two CS pathways and for the capacity of the protein to fine-tune the energy of the exciton and CT states and the degree of mixing between them which ultimately controls the CS dynamics.

In chapter 6 we examine the pigment-protein interactions directly by applying light-induced Fourier transform infrared (FTIR) difference spectroscopy. The comparison of several PSII preparations with different antenna size indicates that the vibrational properties of the RC complex are independent of the total size of the PSII complex, and do not change during the isolation procedure. The comparison of the wild-type RC with two site-directed mutants allows us to identify the specific pigment-protein interactions which may control the selection of a specific CS pathway in each RC.

In chapter 7 we move to the study of a different pigment-protein complex, a peripheral light-harvesting complex of photosystem I, Lhca4. A distinctive characteristic of this complex is the presence of red chlorophylls, which absorption and emission energy is much lower than for the typical antenna chlorophylls. Using Stark spectroscopy we have demonstrated that the low energy of the red chlorophylls in Lhca4 originates from the mixing of the lowest energy state with a CT state.

Overall, this Thesis deals with the study of the electronic structure and energy dynamics in photosynthetic pigment-protein complexes. Our main objective is to gain insight into the design principles which lead to their high efficiency in converting solar energy into electrochemical energy. The understanding of these design principles is very important in the present time, with vital issues as the energetic crisis and the climate change in front of us. Therefore, we need to find alternative strategies to the fossil fuels in order to fulfil our energetic demands with a clean energy source. Therefore, we hope the work presented in this Thesis contributes to the efforts of the scientific community for achieving the efficient and clean utilization of our largest energy source: the Sun.