Chapter 19

Photosystem II: Structural Elements, the First 3D Crystal Structure and Functional Implications

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Summary

In the first part of this chapter structural elements of Photosystem II (PS II) and their functional behavior which have been elucidated primarily through special spectroscopic techniques are described. A transmembrane charge separation was identified as the primary act of light-energy conversion. The chlorophyll-containing P680 complex was discovered as the electron donor of PS II at the luminal side of the membrane while the bound plastoquinone Q0 was discovered as the first stable electron acceptor and localized at the stromal side of the membrane. This membrane-spanning chlorophyll/quinone couple represents the PS II reaction center (RC)

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that drives water oxidation. This couple also provides a model for the RC of Photosystem I (PS I) and of other photosystems which drive different redox reactions. Two intermediate chlorin molecules located between the chlorophyll/quinone couple were found to function in the path of fast electron transfer from P680 across the membrane to Qₐ, while a pool of plastoquinones was found to function in a transmembrane path for electrons from reduced Qₐ to PS I and for protons from the stroma to the membrane lumen. Primary electron donors located at the membrane base of PS II and PS I were found to be organized as chlorophyll pairs. Electron microscopy identified PS II as a dimer and PS I as a trimer. Based on the sequence homologies between PS II, PS I and the bacterial RC, predictions were made on the helical structure of the PS II complex. The preceding results served as the essential basis for the analysis and interpretation of the 3D crystal structures of PS I and PS II. In the second part of this chapter, the first PS II crystals capable of water oxidation are described. Based on the X-ray structure analysis of these crystals at 3.6 – 3.8 Å resolution, the framework of PS II, the architecture of the antenna system, the electron transfer chain, and the manganese cluster are discussed. The manganese environment is considered in terms of the more recent structure at 3.2 Å resolution. In the third part, functional events are described, especially changes in manganese valences, deprotonations, and the water states which were followed spectroscopically during the quaternary cycling of the water-oxidizing complex and which are summarized in a functional model. Finally, the implication of the high oxidation potential of the PS II RC is discussed as well as the functional cooperation between the dimeric electron donor P680, the monomeric electron donor chlorophyll D1 and the pheophytin D1 within the electron transfer chain.

I. Introduction

The very basis of life on our planet is oxygenic photosynthesis, which absorbs light energy of the sun and converts it into biochemical energy that is used to release oxygen from water into the biosphere. This process is driven by the cooperation of two different light-activated, pigment/protein complexes, Photosystem I (PS I) and Photosystem II (PS II), working in series within the functional membranes of plants, algae and cyanobacteria. In PS II the oxidation of water results in the release of O₂, protons and electrons. The electrons are trapped by a specially bound plastoquinone Q₂, forming the first stable reductant. Subsequently, the electrons from PS II are transferred via intermediates energetically further up to a state sufficient to reduce NADP⁺ to NADPH in PS I. This process is coupled with the formation of a proton gradient across the membrane that drives the formation of ATP. With NADPH and ATP, absorbed CO₂ is reduced to energy-rich carbohydrates.

The reactive components of this ‘light driven engine of life’ are present in relatively low concentrations; changes during their reaction, e.g., if allowed optically, are mostly very short-lived and buried in noise. A major breakthrough was made in the 1960s with the introduction of repetitive light-pulse spectroscopy (Witt, 1967; Rüppel and Witt, 1969). With this method the signal/noise ratio of the measurements was increased 100-fold, whereby the time resolution could be extended to the ns range. The optical difference spectra observed with this technique during the turnover of photosynthesis gave evidence regarding the nature of the chemical and physical constituents of the photosystems and their reaction sequences. In this way, more than ten components and their behavior, were elucidated at the Max-Volmer-Institute: the dimeric chlorophyll (Chl) a complex P700; the Chl a complex P680; the specially bound plastoquinone Qₐ; the pool of plastoquinones; the catalytic manganese cluster; the redox-active tyrosine; Chl and carotenoid triplet states; and localized and delocalized electrochromic changes which indicate various electric events (for overviews, see Witt, 1971, 1979, 1996; Ks, 2001; for a historical personal perspective, see Witt, 2004). These spectroscopic results have been, together with the X-ray structure analysis, the basis for the characterization of the RCs of PS II and PS I.

Abbreviations: BCHL – bacteriochlorophyll; BPho – bacteriopheophytin; BRC – purple bacterial reaction center; Car – carotene; Chl – chlorophyll; CP43/47 – subunits of the PS II inner antenna system; Cyt – cytochrome; D1/D2 – subunits of the PS II reaction center; ENDOR – electron nuclear double resonance; EPR – electron paramagnetic resonance; ETC – electron transfer chain; EXAFS – extended X-ray absorption fine structure; P680/P700 – primary electron donors of PS II/PS I, respectively; Pₐ/D₁ – Chl coordinated by D1/D2 histidines 198/197, respectively; Pheo – pheophytin; PS I/PS II – Photosystem I/Photosystem II; Q – plastoquinone of the pool; Qₐ – stable primary plastoquinone acceptor of PS II; Qₐ – secondary plastoquinone acceptor of PS II; RC – reaction center; Sₙ – states of the water oxidizing complex n = 0,1,2,3,4; TMH – transmembrane α-helix; WOC – water-oxidizing complex; Y₂/Yₐ – redox-active tyrosines 161/160 of the D1/D2 subunits, respectively; Y₂ – notation for (Y₂ ... H His190)