Photosystem II structure: Successes and challenges

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The elucidation of the atomic resolution structure of an enzyme is critical for understanding its mechanism of catalysis. This could not be more true for Photosystem II (PSII), the water splitting enzyme of oxygenic photosynthesis. In the mid-1990s our understanding of PSII structure was limited to the analogy between its D1 and D2 proteins and the L- and M-subunits of the reaction centre of purple photosynthetic bacteria (1, 2) although EXAFS and EPR studies were giving some hints of the organisation of the Mn-cluster(3, 4). This changed with the application of electron microscopy by 1998 (5-8) and by 2001 crystallography, both electron and X-ray, had provided low resolution structures of the dimeric PSII complex isolated from plants (spinach) (9) and cyanobacteria (*Thermosynechococcus elongates*)(10). Since then a slightly more detailed model of PSII from *T. vulcanus* was published (11) followed a fully refined X-ray diffraction model of the *T. elongates* PSII at 3.5A (12) and 3.0A/2.9A (13,14). Therefore we now have a good understanding of the positioning of all the protein subunits of cyanobacterial PSII with all the transmembrane helices assigned. Moreover, we also have the assignment of all the major cofactors and their protein environments coupled with information about the location of lipids and detergent molecules within the membrane spanning portion of the dimeric complex.

The challenge now is to improve the resolution of the model so as to tidy-up the modeling of protein side chains, cofactors, pigments and lipids and determine the positioning of water molecules, especially in the region of the water splitting site.

However, the biggest challenge is to provide a confident model of the four Mn ion/Ca ion cluster (Mn_4Ca-cluster) which catalyses the water oxidation reaction, a challenge hampered by radiation induced reduction of high valency Mn (15, 16). Despite this apparent problem the information already gleamed for the structure of the Mn_4Ca-cluster is having impact in formulating reaction mechanisms for water splitting and dioxygen formation as well as for the construction of artificial photochemical/electrochemical systems which can mimic the catalytic properties of PSII.

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