Computational Structural Studies of the Oxygen-Evolving Complex of Photosystem II

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The oxygen-evolving complex (OEC) of photosystem II contains four manganese ions and a single calcium ion, and catalyzes the electrochemical half-reaction (1).

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \quad (1)$$

We have developed a hypothesis for the mechanism of the OEC that is largely consistent with the biochemical and spectroscopic studies of ourselves and others, as well as with the recent crystallographic model of the site by Ferreira *et al.*[1,2] This latter work has provided the best image of the OEC yet available, modeling the site in a Mn_3CaO_4–Mn arrangement, but limitations in resolution and the possibility of radiation damage mean that efforts are required to complete and validate the structure. Here we computationally test and extend this crystallographic model of the OEC[2] using molecular mechanics (MM), quantum mechanics (QM) and finally QM/MM at the ONIOM (UHF B3LYP/lacv3p*:AMBER) level of theory.

Our QM/MM computational structure of the OEC in the S_1 state (proposed Mn oxidation states IV, IV, III and III) incorporates surrounding amino-acid residues within 15 Å of the OEC cluster and is consistent both with our mechanistic hypothesis[1] and with the crystal structure of Ferreira *et al*.[2] The only qualitative difference in the protein coordination of the cluster from that seen in the crystal structure is seen at D1-Glu333, whose sidechain in our model bridges bidentally between two manganese ions. The coordination of the five metal ions is elsewhere completed in a chemically plausible manner by the addition of several water molecules and a single chloride ion, whose locations and implied roles are consistent with experimental data. Our calculated Mn-Mn distances (2.74 Å, 2.75 Å and some longer distances) are close to those obtained by EXAFS. The single manganese ion attached to the outside of the Mn_3CaO_4 cuboidal cluster is aligned with the calcium ion so that a pair of their respective ligand waters are well positioned for reaction in the O–O bond forming step, which occurs upon attainment of the S_4 oxidation state in our mechanism.

[1]McEvoy and Brudvig, Phys. Chem. Chem. Phys. **6** (2004), 4754-4763

[2]Ferreira *et al.*, Science **303** (2004), 1831-1838