Understanding the mechanism of substrate delivery and binding in the oxygen-evolving complex of photosystem II

K. V. Lakshmi,[1] V. Kalendra,[1] G. Banerjee,[2] I. Ghosh,[2] K. Reiss,[2] K. Yang,[2] V. S. Batista[2] and G. W. Brudvig[2]

[1]Department of Chemistry and Chemical Biology and The Baruch '60 Center for Biochemical Solar Energy Research, Rensselaer Polytechnic Institute, Troy, NY 12180, USA (Lakshk@rpi.edu)
[2]Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT 06511, USA

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The solar water-splitting protein complex, photosystem II (PSII), catalyzes one of the most energetically demanding reactions in Nature by using light energy to drive a catalyst capable of oxidizing water. The water oxidation reaction is catalyzed by the Mn_4Ca-oxo cluster in the oxygen-evolving complex (OEC) which cycles through five light-driven S-state intermediates (S_0-S_4) as it accumulates charge equivalents to split water. However, a detailed mechanism of the reaction remains elusive as it requires knowledge of the binding of substrate water in the higher S-state intermediates of the OEC. In particular, the binding of substrate in the S_2 to S_3 state transition of the OEC that leads to O-O bond formation is poorly understood because of the inability of conventional methods to probe water molecules. We are using two-dimensional (2D) hyperfine sublevel correlation spectroscopy and density functional theory methods to determine the binding of water in the S state intermediates of the OEC. In this presentation, we will describe ongoing studies that employ small molecule analogs and site-directed mutagenesis of PSII to elucidate the mechanism of the delivery and binding of substrate at the Mn_4Ca-oxo cluster in the S_2 and S_3 states. These studies have important implications on the mechanistic models for water oxidation in PSII.

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