Studies of Natural and Artificial Photosynthesis

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Mechanistic investigations of the water-splitting reaction are fundamentally informed by structural studies of the oxygen-evolving complex (OEC) of photosystem II (PSII) and biomimetic catalytic complexes. Many physical techniques have provided important insights into the OEC structure and function, including X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy as well as mass spectrometry (MS), electron paramagnetic resonance (EPR) spectroscopy, and Fourier transform infrared spectroscopy applied in conjunction with mutagenesis studies. However, experimental studies have yet to yield consensus as to the nature of the reaction mechanism responsible for oxygen evolution. Computational modeling studies, including density functional (DFT) theory combined with quantum mechanics/molecular mechanics (QM/MM) hybrid methods for explicitly including the influence of the surrounding protein provide powerful modeling tools to explore reaction mechanisms for the fully ligated OEC within PSII and examine whether they are maximally consistent with experimental data. The computational models are useful for rationalizing spectroscopic and crystallographic results and for building a complete structure-based mechanism of water-splitting as described by the intermediate oxidation states of oxomanganese complexes. This talk summarizes our recent advances in studies of water oxidation catalyzed by the OEC of PSII and biomimetic catalysts for artificial photosynthesis.