

## Spectroscopic Characterization of the Water Oxidation Intermediates in the Blue Dimer Ru-based Catalysts for Artificial Photosynthesis

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Utilization of sunlight requires solar capture, light-to-energy conversion and storage. One effective way to store energy is to convert it into chemical energy by fuel-forming reactions, such as water splitting into hydrogen and oxygen. Ruthenium complexes are among few molecular-defined catalysts capable of water splitting. Insight into the mechanism of their action will help to design future robust and economically feasible catalyst for light-to-energy conversion.

The blue dimer,  $\text{cis-cis}(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}^{\text{III}}\text{ORu}^{\text{III}}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$  is the first designed molecule to function as a water oxidation catalyst as it meets the stoichiometric requirements for water oxidation by utilizing proton-coupled electron-transfer reactions (PCET) in which both electrons and protons are transferred [1]. We characterized structures and electronic configurations of intermediates of water oxidation by the “blue dimer.” The intermediates of water oxidation were prepared chemically by oxidation of Ru-complexes with defined number of Ce(IV) equivalents and freeze-quenched at controlled times. Changes in the oxidation state of the Ru atom were detected by XANES at Ru K-edges. We demonstrate that K-edges are very sensitive to changes in Ru oxidation state for Blue Dimer  $[3,3]^{4+}$ ,  $[3,4]^{4+}$ , and  $[4,5]^{4+}$  thus allowing a clear assignment of Ru oxidation state in intermediates. EXAFS at Ru K-edge demonstrated clear structural changes in the oxidation states. We detected considerable changes in distances for Ru-N and Ru-O interactions as well as changes in the angle of Ru-O-Ru fragment in higher intermediates of the blue dimer molecule.

[1] Feng Liu, Javier J. Concepcion, Jonah W. Jurss, Thomas Cardolaccia, Joseph L. Templeton, Thomas J. Meyer, “Mechanisms of Water Oxidation from the Blue Dimer to Photosystem II”, *Inorg. Chem.* 2008, 47, 1727-1752