

Abstract Submitted
for the MAR12 Meeting of
The American Physical Society

Spectroscopic Characterization of the Water Oxidation Intermediates in the Blue Dimer Ru-Based Catalyst for Artificial Photosynthesis¹

DOOSHAYE MOONSHIRAM, YULIA PUSHKAR, Purdue University, JONAH JURSS, JAVIER CONCEPCION, THOMAS MEYER, University of North Carolina at Chapel Hill, TAISIYA ZAKHAROVA, IGOR ALPEROVICH, Purdue University — 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. Mechanistic insights about such catalysts can be acquired by spectroscopic analysis of short-lived intermediates of catalytic water oxidation. Use of techniques such as EPR and X-ray absorption spectroscopy (XAS) are used to determine electronic requirements of catalytic water oxidation. About 30 years ago Meyer and coworkers reported first ruthenium-based catalyst for water oxidation, the “blue dimer”. We performed EPR studies and characterized structures and electronic configurations of intermediates of water oxidation by the “blue dimer”. Intermediates were prepared chemically by oxidation of Ru-complexes with defined number of Ce (IV) equivalents and freeze-quenched at controlled times. Changes in oxidation state of Ru atom were detected by XANES at Ru K-edges. K-edges are sensitive to changes in Ru oxidation state for Blue Dimer $[3,3]^{4+}$, $[3,4]^{4+}$, $[3,4]^{4+}$ and $[4,5]^{3+}$ allowing a clear assignment of Ru oxidation state in intermediates. EXAFS demonstrated structural changes.

¹DOE

Dooshaye Moonshiram
Purdue University

Date submitted: 23 Nov 2011

Electronic form version 1.4