

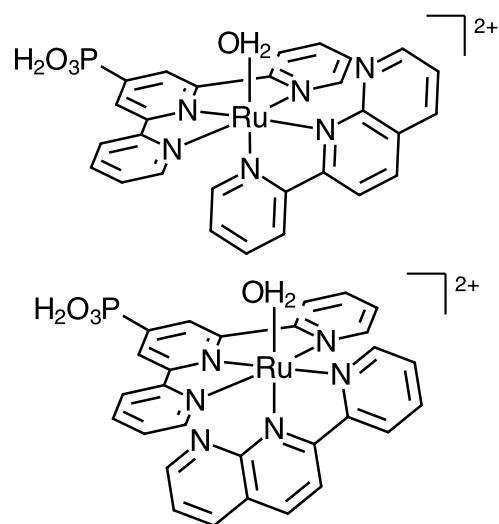
Water Oxidation by Mononuclear Ru(II) Catalysts  
Functionalized onto Metal Oxide Surfaces

Diane K. Zhong, Shengliang Zhao, Dmitry E. Polyansky,  
Jonathan F. Hull, Etsuko Fujita\*  
Chemistry Department, Brookhaven National Laboratory  
Upton, NY 11973-5000

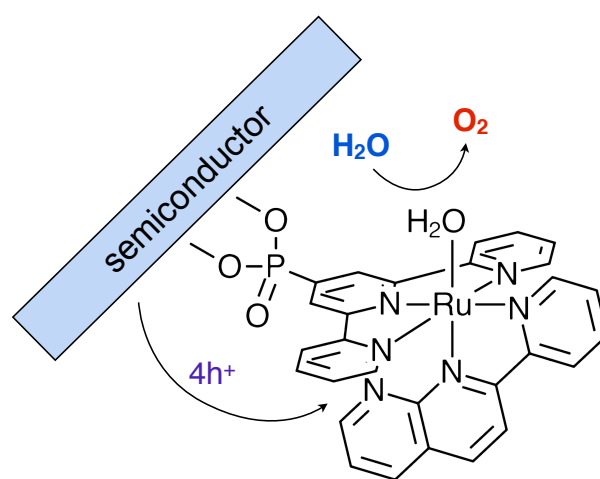
Inspired by Nature's photosynthesis, photoelectrochemical water splitting is an attractive approach to storing the abundant energy of sunlight in the form of chemical bonds. Recently, composite catalyst/semiconductor photoelectrodes have shown improved efficiencies for water splitting by allowing the tasks of photon absorption, charge separation, and redox catalysis to be separated and individually optimized. This strategy presents new challenges in understanding interfacial charge transfer and catalytic reactions at electrode surfaces. To address these challenges, we will focus on photoelectrochemical studies of a mononuclear ruthenium water oxidation catalyst recently developed by our group. The catalyst  $[\text{Ru}(\text{tpy})(\text{pynap})(\text{OH}_2)]^{2+}$  (tpy = 2,2',6',2''-terpyridine, pynap = 2-(pyrid-2'-yl)-1,8-naphthyridine) oxidizes water with turnover numbers of 3200 and an initial rate of  $1.8 \times 10^{-2} \text{ s}^{-1}$ . Two isomers, proximal and distal, were isolated and show distinctly different electrochemical properties. Only the d isomer is catalytic towards water oxidation, but it isomerizes to the p isomer under photo-irradiation. By attaching a phosphonate group onto the terpyridine ligand (see Figures 1 and 2), the catalyst can be anchored onto metal oxide surfaces, including light absorbing semiconductors, for increased stability of the catalyst, and electrochemical and mechanistic studies. Here, we present electrochemical and photoelectrochemical experiments, Pourbaix diagrams, pH dependence behavior, and spectroelectrochemical characteristics of phosphonated  $[\text{Ru}(\text{tpy})(\text{pynap})(\text{OH}_2)]^{2+}$  catalysts attached onto FTO, ITO and  $\text{WO}_3$  surfaces. The results are compared to known electrochemical and mechanistic properties of the bare catalyst. Overall, phosphonating and immobilizing the catalysts do not significantly alter its redox chemistry, suggesting ruthenium oxidation pathways are similar with or without surface attachment. Challenges with catalyst loading and anchoring stability limit long-term mechanistic studies of these composite photoelectrodes. These investigations may have important implications in the functionalization of semiconductor surfaces with redox catalysts and the general design of composite PEC cells for improved PEC water splitting efficiencies.

#### ACKNOWLEDGMENTS

The work at Brookhaven National Laboratory (BNL) is funded under contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Geosciences, & Biosciences, Office of Basic Energy Sciences.



**Figure 1.** proximal- $[\text{Ru}(\text{H}_2\text{PO}_3\text{-tpy})(\text{pynap})\text{OH}_2]^{2+}$  (top) and distal- $[\text{Ru}(\text{H}_2\text{PO}_3\text{-tpy})(\text{pynap})\text{OH}_2]^{2+}$  (bottom)



**Figure 2.** distal- $[\text{Ru}(\text{H}_2\text{PO}_3\text{-tpy})(\text{pynap})\text{OH}_2]^{2+}$  anchored onto a semiconductor surface for water oxidation.