

## II.G.8 Heterogeneous Water Oxidation Catalysis With Molecular Catalysts

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### Objectives

- **Development of fast, efficient and robust molecular water oxidation catalysts:** Design, synthesis and characterization of molecular water oxidation catalysts capable of carrying up this reaction with high turnover frequencies (fast) at low overpotentials (efficient) and with high turnover numbers (robust).
- **Deep understanding of the mechanism(s) of water oxidation:** Mechanistic studies using a combination of experimental techniques and DFT calculations to gain insight into the interplay of thermodynamics and kinetics in water oxidation catalysis.
- **Development of stable anchoring groups/heterogenization:** Incorporation of anchoring groups on molecular water oxidation catalysts for attachment to planar and high surface area electrodes. Evaluation of catalytic activity in a true device configuration.

### Technical Barriers

- The development of efficient water oxidation catalysts is one of the limiting factors in solar fuels production via artificial photosynthesis.
- Water oxidation is a complex process involving multi-electron, multi-proton steps. Isolation/characterization of intermediates is difficult due to the harsh conditions used to study this reaction. Progress has been made but a better mechanistic understanding is needed, especially on metal oxide surfaces in a true device configuration.
- Available/known anchoring groups from dye-sensitized solar cells are usually stable in organic solvents but not in aqueous solutions under water oxidation conditions.

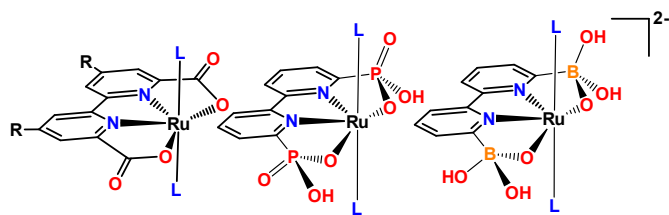
### Abstract

Water oxidation to oxygen in nature's photosynthesis is the source of most of the energy we use today. It is also anticipated to be the source of most of the energy we use in the future through artificial photosynthesis. For the latter, one of the main challenges is the development of efficient and robust water oxidation catalysts. We are developing new water oxidation catalysts and performing detailed mechanistic studies using a combination of experimental and theoretical tools. In addition, we are combining studies with catalysts in solution using sacrificial oxidants and electrochemical techniques with studies of "heterogeneous" catalysis with the catalysts anchored to planar and high surface area electrodes. We have discovered significant differences in both catalytic activity and mechanistic details between solution and surface studies. Furthermore, there are also significant differences between catalytic behavior in planar and high surface area electrodes. These results emphasized the need to study water oxidation catalysis under true device configuration conditions.

### Progress Report

We have developed a series of catalysts that can efficiently oxidize water to oxygen, Figure 1. These catalysts seem to follow catalytic cycles involving seven coordinate intermediates, although different mechanisms are operative for the different families of catalysts. We have also developed anchoring groups that are appropriate for these catalyst's structural motifs.

We have used a combination of experimental techniques and DFT calculations to understand how these catalysts oxidize water. One of the most powerful tools to study water oxidation catalysis is electrochemistry. We have



**FIGURE 1.** Representative structures of catalysts

used this technique to generate intermediates that have been characterized by X-ray crystallography. In addition, combining surface anchoring to metal oxide electrodes with rotating ring-disc electrode techniques has allowed us to study water oxidation catalysis in a true device configuration. These experiments provide all the required information regarding catalytic activity but in addition they also provide mechanistic insight.

We have employed high surface area transparent conductive metal oxide electrodes to perform spectroelectrochemistry of surface-bound water oxidation catalysts. We have been able to identify key intermediates in the water oxidation cycle using this technique by comparison with calculated absorption spectra from time-dependent DFT calculations.

### Future Directions

We are currently developing new catalysts based on the gained knowledge from previous experiments and DFT calculations. We are also developing new approaches for “surface synthesis” of highly efficient molecular water oxidation catalysts with long-term surface stability. These approaches also take into account the combination of catalysts and chromophores for incorporation into solar cells for light-driven water splitting.