The Bernard[*] Research Group:
Effective, Tunable Ir Catalysts for the Visible-Light Induced Water Splitting in the Search for Efficient Solar Energy Sources

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Today's global energy demand rests at levels higher than at any other point in history, and levels are only expected to increase for the foreseeable future. Unfortunately, associated with this high energy demand are equally high emissions of greenhouse gases contributing to global climate change. In order to satiate the desire for energy in a sustainable manner, new forms of energy are required, and among the most promising is artificial photosynthesis for the direct conversion of solar to chemical energy in the form of hydrogen storage and fuel.

The main method utilized in artificial photosynthetic energy systems is the conversion of water into its higher energy parent materials, H_2 and O_2, storing the energy produced for later use. However, water splitting is a thermodynamically uphill process by $\Delta G \approx 237$ with a minimum of 1.23 eV per electron.[1] To simplify the processes, water photolysis can be reduced to its independent oxidative and reductive half-reactions, in which two hydrogen ions and two electrons are used to produce H_2 in the reduction reaction and two waters generate O_2, $4H^+$, and $4\ e^-$ in the oxidative reaction. While the reduction half-reaction has gained significant progress in research, the oxidative half-reaction remains elusive due to the complexity of mediating the four highly energetic charge transfers and producing only the desired oxygen gas despite the harshly oxidative environment created during the reaction.[2] The Bernhard group has focused on this last process and developed a water oxidizing catalyst (WOC) based on a cyclometalated iridium complex that shows significant advantages over previously developed WOC compounds.

The compound, shown in Figure 1 below, has been extensively studied for its catalytic properties for the homogeneous oxidation of water. Among these properties are rate studies based on the evolution of oxygen due to variation of concentration and ligand structure, substitution on the phenylpyridine to explore electrochemical tunability, stability of the catalyst in catalytic cycle endurance, and also comparisons of electrochemical tunability to density functional theory calculations.

The Bernhard group has found that the iridium complex is an effective and exciting new WOC, and has many features promote it over previous WOC generations. First, the iridium complex can be generated from a straightforward, economical synthesis due to its fairly simple structure. Second, the cyclometalating ligand makes the iridium complex exceptionally robust, with more than 2800 turnovers in the catalytic cycle. Third, the complex eliminates the need for mixed solvent systems due to its water soluble nature, even over a wide range of pH levels. Finally, the electronic structure of the compound can be precisely controlled through modification of the cyclometalated ligands, without significantly altering the catalytic functionality. This last property allows for the tuning of the HOMO energy by more than 500 mV, and thus the ability to the compound's oxidative potential.[1,2]

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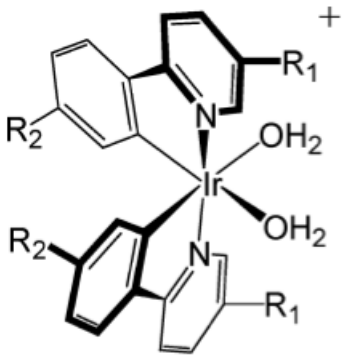

1 $R_1 = H$, $R_2 = H$
2 $R_1 = CH_3$, $R_2 = H$
3 $R_1 = CH_3$, $R_2 = Ph$
4 $R_1 = CH_3$, $R_2 = F$
5 $R_1 = CH_3$, $R_2 = Cl$

Figure 1: Structure of the described oxidation catalyst, $[Ir(5\text{-}R_1, 4'\text{-}R_2,2\text{-phenylpyridine})_2(OH_2)_2]^+$.[2]

References:

[1] Cline, E. D.; Bernard, S. *Chimia* **2009**, *63*, 709-713. DOI: 10.2533/chimia.2009.709

[2] McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. *J. Am. Chem. Soc.* **2008**, *130*, 210. DOI: 10.1021/ja074478f