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Mechanism of Water Oxidation by Fe(TPA) Analogues Using Sodium Periodate

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Solar fuels are one of the most promising means for storing and transporting energy derived from sunlight. In order to generate solar fuels, two chemical reactions are required: the reduction of a feedstock to the fuel, and the oxidation of an electron source. Only water is a sufficiently abundant electron source to provide for production of solar fuels on a global scale. Unfortunately, oxidation of water to form dioxygen gas has a very large kinetic barrier requires an efficient catalyst in order to be commercially viable. Thus, significant research has been conducted in the past fifteen years to develop robust and efficient water oxidation catalysts.

While many catalysts for water oxidation have been developed in recent years, the majority depend on second or third row transition metals, which are not sufficiently abundant to meet global need. For this reason recent attention has been on the development of base metal water oxidation catalysts. Fillol and Costas have recently reported a family of N4 non-heme iron based water oxidation catalysts which may be driven with either cerium(IV) or sodium periodate (Fillol *Nat. Chem.* **3** 807 (2011)). The mechanism of water oxidation by these complexes is not yet well characterized, however. As such, we have investigated the mechanism of these catalysts using sodium periodate in an attempt to better understand their properties. We find that when driven with sodium periodate these catalysts are homogeneous in nature, and by measuring the kinetic isotope effect we have been able to identify the rate determining step to be oxidation of Fe(III) to Fe(V). Additionally the visible spectra show that the Fe(IV) oxidation state is not involved in the catalytic cycle when periodate is used as the oxidant.