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Fast Water Oxidation Using Iron

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Abstract: Photolysis of water, a long-studied strategy for storing solar energy, involves two half-reactions: the reduction of protons to dihydrogen and the oxidation of water to dioxygen. Proton reduction is well-understood, with catalysts achieving quantum yields of 34% when driven by visible light. Water oxidation, on the other hand, is much less advanced, typically involving expensive metal centers and rarely working in conjunction with a photochemically powered system. Before further progress can be made in the field of water splitting, significant developments in the catalysis of oxygen evolution are needed. Herein we present an iron-centered tetraamido macrocyclic ligand (Fe-TAML) that efficiently catalyzes the oxidative conversion of water to dioxygen. When the catalyst is combined in unbuffered solution with ceric ammonium nitrate, its turnover frequency exceeds 1.3 s^{-1}. Real-time UV−vis and oxygen monitoring of the active complex give insights into the reaction and decay kinetics.

The ability to drive energetically uphill, homogeneous chemistry using radiative energy, particularly with the visible wavelengths prevalent in sunlight, has long been pursued in chemical research for both pure and applied goals.[1] Achieving the practical photoconversion of water into dihydrogen and dioxygen is a core challenge that is currently hindered by the relative performance of the available catalysts for the two half-reactions. At its best, homogeneous photocatalytic water reduction to dihydrogen proceeds with a 34% quantum yield and a respectable catalyst lifetime.[2] However, homogeneous water oxidation (WO) to form dioxygen has yet to be driven by visible light alone, proceeding only in the presence of strong chemical oxidants.[3] Furthermore, chemically driven homogeneous WO catalysis suffers from both low turnover frequencies (TOFs) and small turnover numbers (TONs).[4] These limitations have sparked widespread interest in the design and discovery of faster WO catalysts, preferably having low molecular mass and composed of biologically innocuous, inexpensive elements.[5−7]

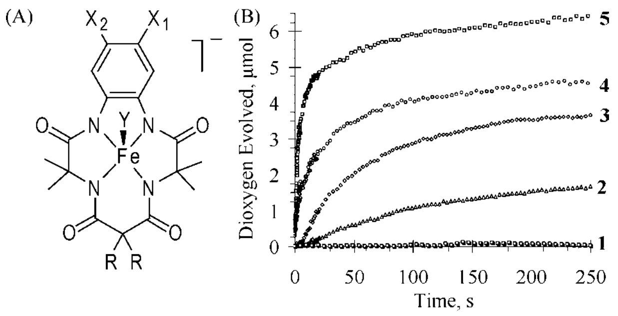

Figure 1. (A) Fe^{III}-TAMLs used for WO: **1**, $X_1 = X_2 = H$, $R = CH_3$; **2**, $X_1 = X_2 = H$, $R = (CH_2)_2$; **3**, $X_1 = X_2 = H$, $R = F$; **4**, $X_1 = NO_2$, $X_2 = H$, $R = F$; **5**, $X_1 = X_2 = Cl$, $R = F$. $Y = H_2O$. (B) Plots of O_2 evolution with time from **1**−**5** (0.6 μmol) upon addition of ceric ammonium nitrate (145.7 μmol) in unbuffered water (total volume 0.8 mL).

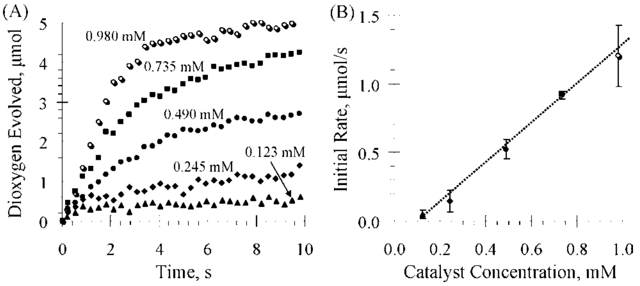

Figure 2. (A) Plots of O_2 evolution with time for different [**5**] upon addition of $(NH_4)_2Ce(NO_3)_6$ (145.7 μmol) in water (0.8 mL); the theoretical O_2 yield was 36.4 μmol. (B) Initial rates of WO plotted against [**5**].

Iron(III)−tetraamido macrocyclic ligand catalysts (Fe^{III}-TAMLs) rapidly activate both dioxygen and peroxides.[8] At nanomolar to low micromolar concentrations, Fe^{III}-TAMLs activate hydrogen peroxide in water to mimic peroxidase-like processes at enzymatic rates and can be used to destroy numerous water contaminants.[9] In noncoordinating solvents, Fe^{III}-TAMLs split dioxygen to form a μ-oxo−diiron(IV) complex,[10] and this species in water participates in a pH-dependent equilibrium with a monomeric Fe(IV)−oxo species.[11] In organic solvents at −60 °C, peracids oxidize an Fe^{III}-TAML quantitatively to an Fe(V)−oxo complex.[12] Cyclic voltammetric studies of either Fe(V)−oxo or Fe(IV)−oxo species under a variety of conditions have revealed an irreversible Fe(V)−oxo/Fe(IV)−oxo couple.[11] Thus, Fe-TAML−oxo complexes exhibit a diverse and highly reactive chemistry suggesting the possibility that Fe^{III}-TAMLs might catalyze the formation of dioxygen from water under oxidizing conditions.

Complexes **1**−**5** (Figure 1) were investigated for WO by mixing them with excess ceric ammonium nitrate (CAN) in water at pH 0.7 (generated from CAN) with pressure monitoring and GC analysis as previously described.[13] No activity was observed with **1**, the least acid-stable and oxidatively reactive Fe^{III}-TAML in the **1**−**5** series.[8] Likewise, no O_2 evolution occurred with the controls Fe_2O_3, $Fe(acac)_3$, $[Fe(bipy)_3](NO_3)_2$, and $Fe(NO_3)_3 \cdot 9H_2O$, either alone or in combination with the TAML starting material fragments α-aminoisobutyric acid, diethyl difluoromalonate, and 1,2-dichloro-4,5-phenylenediamine.

In contrast, fast O_2 liberation was observed with **2**−**5** at varying rates, apparently correlating with the addition of electron-withdrawing substituents to the ligand. Figure 2 shows that the O_2 evolution rate for **5** is first-order in [**5**]. The measured TOF was $>1.3\ s^{-1}$, which compares well to the best previously reported WO rates involving first-row transition metals and is sufficiently large that it could be limited by the kinetics of bubble formation and release (visible to the eye). Elizarova and co-workers[6] reported similar to slightly higher TONs and TOFs using various first-row transition metal (including iron) tetrapyrrole complexes. However, as with the Fe^{III}-TAMLs reported here, no fast-acting, first-row homogeneous catalyst has sustained its high performance for more than a

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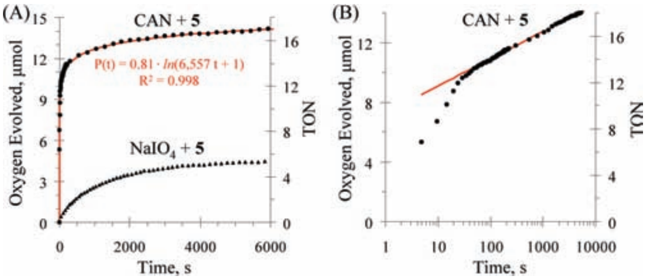

Figure 3. (A) Black points are measured oxygen evolution obtained from combining 0.78 μmol of **5** with 145.7 μmol of cerium(IV) in a total volume of 0.8 mL of unbuffered water (the theoretical O_2 yield was 36.4 μmol). Plotted in red is the logarithmic best-fit regression function. (B) The same data are plotted vs logarithmic time, highlighting a mechanistic progression that is manifested 20 s after the reaction's initiation.

few seconds, thereby precluding practical applications. Hull et al.[14] have reported iridium catalysts that liberate O_2 rapidly for hours, setting a standard for catalyst designers working with first-row metals. As shown in Figure 3, **5** with CAN does produce oxygen over the course of hours. The behavior is biphasic, with rapid O_2 release in the first 20 s followed by a slower, steady logarithmic evolution, which the technique employed here can easily and accurately monitor.[13] In future work, the origins of this biphasic behavior will be studied. Evolution of O_2 by **5** was also detected using $NaIO_4$ as the oxidant, although it is unclear whether the mechanism is the same as with CAN; the kinetic trace is depicted in Figure 3.

Unlike CAN, $NaIO_4$ is transparent in the visible spectrum and does not produce strongly acidic media, allowing for UV−vis examination of **5** under O_2-evolving and other pertinent conditions. Both oxidative and hydrolytic inactivation pathways can limit the catalytic performance of Fe-TAMLs.[8] The data in Figure 4 show that **5** with $NaIO_4$ at pH 5.5 produces over 100 s a UV−vis spectrum that is characteristic of an $Fe^{IV}-O-Fe^{IV}$ dimer.[10−12] Dioxygen is liberated from this solution slowly (Figure 3). In HNO_3 at pH 0.7, **5** is essentially stable over 1500 s, in agreement with previous studies.[8] However, upon exposure to $NaIO_4$ at pH 0.7, a decay process ensues that is first-order in [**5**] for at least five half-lives with $k_{obs} = 2.2 \times 10^{-3}$ s^{-1}. In contrast to **5**/CAN at pH 0.7, O_2 is not released from this **5**/IO_4^- medium during the 1500 s decay process—the entire spectrum is bleached. The IO_4^- data may indicate that the oxidized states of **5** are more sensitive to acid hydrolysis than the starting ferric state.

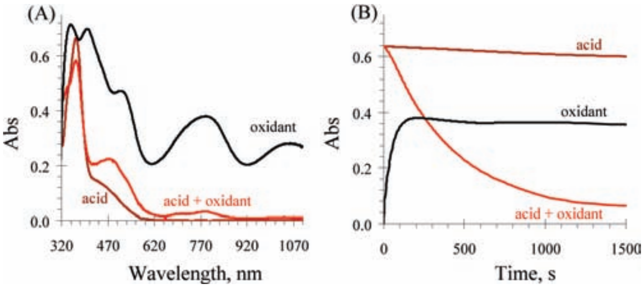

Figure 4. (A) UV−vis spectra for **5** (0.77 mM) under conditions of excess $NaIO_4$ at pH 5.5 (black, oxidant), pH 0.7 (brown, acid), and excess $NaIO_4$ at pH 0.7 (red, acid + oxidant). (B) Plots of absorbance vs time for each set of conditions in (a): 790 nm (black), 360 nm (brown), 367 nm (red). Colors have been chosen to mimic the actual colors of the solutions.

In summary, many of the well-characterized peroxide- and dioxygen-activating Fe-TAMLs[8] catalyze the production of dioxygen by chemical oxidants. At pH 0.7, one of five tested Fe-TAMLs, **5**, activates ceric ammonium nitrate to liberate oxygen from water at a rate that is among the highest in the literature; **2**−**4** are also active. Notably, Fe-TAMLs have low molecular weights (~500 g/mol) and are based on iron, the safest and most abundant transition metal, which helps to set this research on an affordable trajectory for large-scale conversion of solar to chemical energy. Equally important, Fe-TAMLs are very soluble in water and have low molar extinction coefficients in the visible spectrum, qualities that could be very helpful in attaining unimpeded photon harvesting in a future photosynthetic process. It is well-established that synthetic modification of TAMLs allows the electronic properties of derivative complexes to be widely tuned.[8] Studies are underway to improve the usefulness of Fe-TAMLs for water splitting.

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