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Jeffrey Miles Tan

Cobalt-substituted Polyoxometalates as Viable Water Oxidation Catalysts

By

Jeffrey Miles Tan
Master of Science
Chemistry

Craig L. Hill, Ph.D.
Advisor

Tianquan Lian, Ph.D.
Committee Member

Cora E. MacBeth, Ph.D.
Committee Member

Accepted:

Lisa A. Tedesco, Ph.D.
Dean of the Graduate School

Date

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An abstract of a thesis submitted to the Faculty of the Graduate School of Emory University in partial fulfillment of the requirements for the degree of Master of Science

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Abstract

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The cobalt-substituted polyoxometalate $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ was studied and evaluated for catalytic water oxidation activity. It was found to have such activity and preliminary experiments have revealed that the complex is functional in a photochemical water oxidation system. The pH dependence of catalytic activity was also explored. The hydrolytic stability of the cluster was studied using UV-Visible and ^{31}P NMR spectroscopy. This represents the second example of a polyoxometalate-based water oxidation catalyst.

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Introduction

Solar Energy and the Energy Crisis

Recently, mankind's need for a clean and renewable source of energy has been brought to the forefront of the world's attention. As such, harnessing solar energy efficiently has become the focus of various research efforts. One approach to accomplishing this is to use a light harvesting compound or material to capture light energy from the sun and subsequently channel it to a molecule that can store this energy. This results in the creation of a fuel. Ideally, the source of this fuel would be abundant, inexpensive and at the same time, carbon-neutral and harmless to the environment.

Of the many candidates for this role, water is the most attractive. Energy can be stored in by converting water into O_2 and H_2. The subsequent recombination of H_2 and O_2 in a fuel cell yields energy with water as a by-product. It is therefore apparent that using water as a fuel source is carbon-neutral. The abundance and affordability of water is clearly evident.[1]

Harvesting Solar Energy and the Use of Water as a Fuel Precursor

The oldest and most abundant example of solar energy harvesting occurs in plants. The photosynthetic cycle begins with light striking a light harvesting complex in Photosystem II. This leaves the complex in a charge-separated excited state, wherein an electron is promoted to a higher energy orbital. Water oxidation catalyzed by an oxygen evolving complex (OEC) replenishes the hole derived from the charge-separated excited state. This process causes the release of four equivalents of H^+ per water molecule. Some of these protons are used in a proton gradient, which the plant employs to store energy by synthesizing adenosine triphosphate (ATP). The high energy electrons move along an electron transport chain and are eventually used to reduce the rest of the protons from the water oxidation process into NADPH molecules, which is another way for the plant to store energy. The molecules ATP and NADPH, which constitute high energy “fuels” that are vital for plant function, are thus synthesized from the more stable precursors AMP and $NADP^+$ respectively, with the help of sunlight.[2]

Numerous light harvesting, water-based fuel producing systems have been developed artificially. As mentioned before, conversion of water into O_2 and H_2 results in storage of energy. To accomplish this, water must first be oxidized to O_2 and H^+. Hydrogen gas can then be created by subsequent reduction of H^+. Ideally this is modeled by the scheme below:[3]

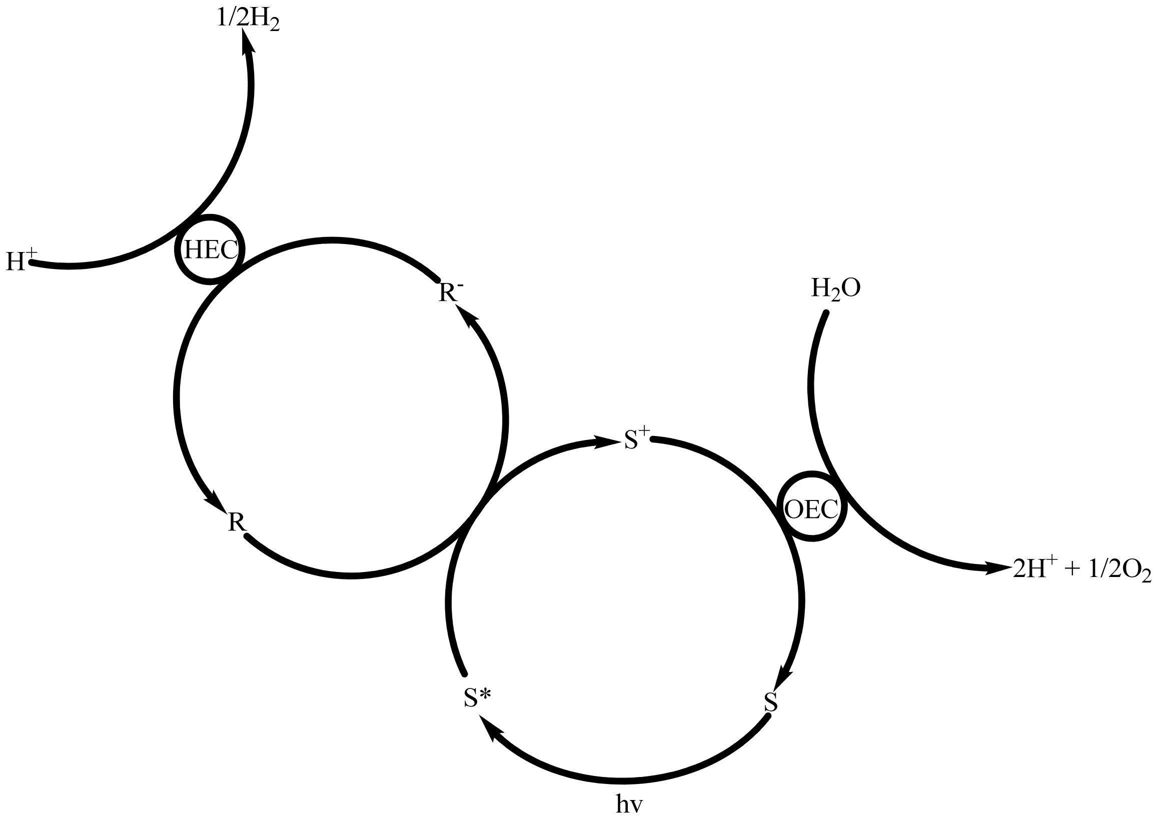

Figure 1. Artificial photosynthetic system (S = dye, HEC = hydrogen evolution catalyst, R = electron relay, OEC = oxygen evolving catalyst).[3]

In such a system, light excites an electron in a photosensitizing, or light harvesting, molecule S to a higher orbital so that the short-lived charge-separated excited state S* forms. This state is very highly energetic and reduces an electron relay R to its reduced form R^-. With the help of a hydrogen evolving catalyst (HEC) protons are reduced to form H_2. Now the dye S is in its oxidized form S^+, which can oxidize water into protons and O_2 gas with the help of an oxygen evolving catalyst (OEC). However, in practice these schemes require that the HEC and OEC be spatially separated to avoid back reactions, such as recombination of S^+ and the reduced relay R^- to form S and R. To be better able to study either water oxidation or hydrogen evolution individually, separate half-cell systems have been developed, using sacrificial oxidants and sacrificial reductants respectively, to avoid favorable back reactions.[3]

In the half-cell depicted below, equivalents of H^+ produced are reduced to H_2:

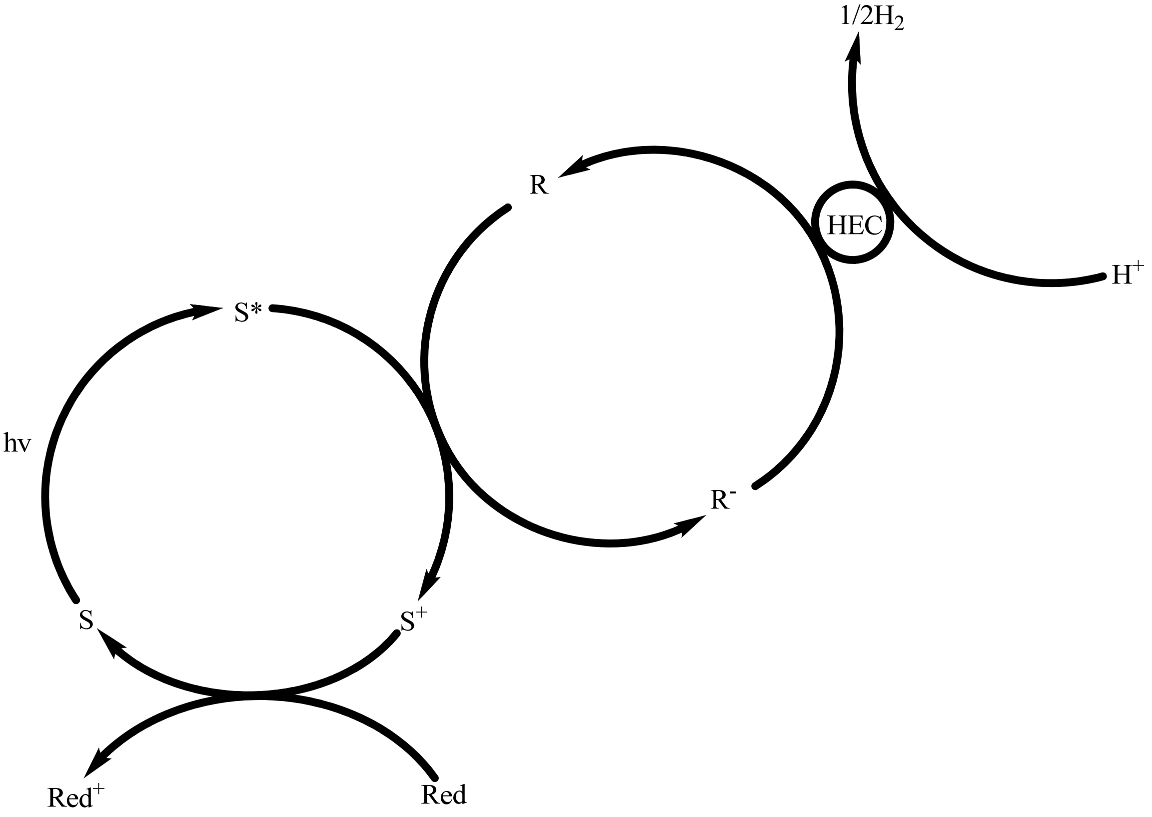

Figure 2. Artificial catalytic hydrogen gas evolution system (S = dye, Red = sacrificial reductant, HEC = hydrogen evolution catalyst, R = electron relay).[3]

In this example, the photosensitizer S is transformed into a charge-separated excited state S*. This is then quenched by the relay, R, which is converted into its reduced form R^-. With the help of a catalyst, the reduced form of the relay reduces a proton. The oxidized form of the dye, S^+, is restored to its original form by oxidation of a sacrificial reductant (Red), thus completing the catalytic cycle. In this case, an excess of reductant is added to avoid recombination of S^+ and R^-.[3]

A representative scheme for the water oxidation half cell is shown below:

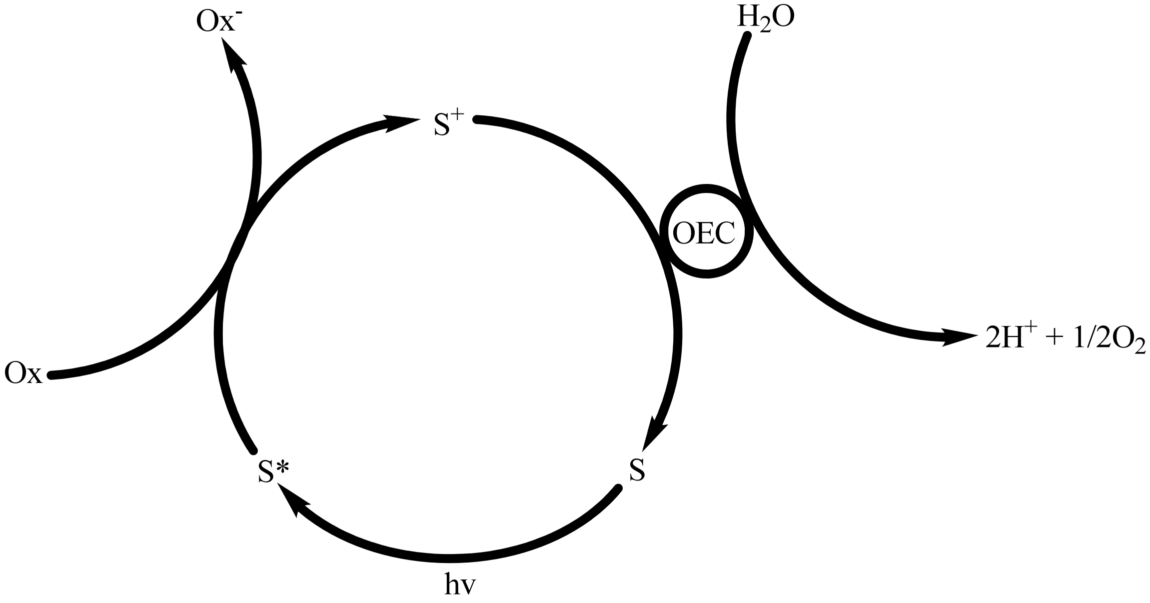

Figure 3. Artificial catalytic water oxidation system (S = dye, Ox = sacrificial oxidant, OEC = water oxidation catalyst).[3]

Once again, in this system a photosensitizing (or light harvesting) complex S absorbs light and transforms into a charge separated excited state S*. The excited electron, now in a higher energy orbital, is quenched by a sacrificial oxidant Ox. Thus, the dye forms the oxidant S^+ which subsequently oxidizes water with the help of a catalyst (OEC) to complete a catalytic cycle.[3]

Attacking the Water Oxidation Problem

A major hindrance to the success of such artificial systems is the difficulty involved in oxidizing water efficiently. Water oxidation is a four electron process and can be summarized by the following half reaction:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (1.23\ V)$$

Aside from the thermodynamic difficulty involved in the process, a catalyst is needed. Therefore, the nature and properties of the water oxidation catalyst are key determinants to the efficiency of the overall process.

There are currently a host of known water oxidation catalysts. An important example is that utilized by plants. The OEC in plants is believed to be a Mn_4-oxo cluster and numerous studies have been undertaken to elucidate its structure.[2] Artificial catalysts that have been developed include both nonmolecular heterogeneous materials and molecular homogeneous compounds. Each subarea has its advantages and disadvantages. If an efficient artificial light harvesting, clean fuel producing apparatus is to be realized, then it is vital that a viable water oxidation catalyst be developed.

For decades, various materials have been known to be good water oxidation catalysts. Among these are MnO_4^-,[4] and noble metal oxides, such as PtO_2, IrO_2 and RuO_2,[3] which have been shown to oxidize water with stoichiometric oxidants such as Ce(IV), $Ru(bpy_3)^{3+}$ and $Fe(bpy)_3^{3+}$. Hydroxides of Fe and Co[5] were also found to be effective catalysts in water oxidation systems with $Ru(bpy)_3^{3+}$ as the stoichiometric oxidant. A closely related catalyst was reported by Sutin et al. in 1984. Sutin's system utilized $Ru(bpy)^{3+}$ as the stoichiometric oxidant and aqueous Co^{2+} as the water oxidation catalyst. The *in situ* formation of cobalt hydroxides as precatalysts from aqueous Co^{2+} ions is implicated in Sutin's work, which can be considered a confirmation of the earlier finding by Shafirovich et al.[6]

Over the years, many water-soluble molecules were found to be able to catalyze the chemical oxidation of water. The first such catalyst was that reported by Meyer et al.

in 1982. This complex, $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)\ (bpy)_2]^{4+}$ (popularly known as the "blue dimer") was reported to be able to catalyze water oxidation using Ce(IV) as a stoichiometric oxidant.[7] Numerous structurally similar diruthenium complexes have been prepared and found to be catalytically active since Meyer's revolutionary result. In 1986, Kaneko et al. reported that the complex $[(bpy)_2(NO_2)Ru^{III}ORu^{III}(NO_2)(bpy)_2]^{2+}$ was also capable of catalyzing water oxidation by Ce(IV).[8] One year later, the same group reported a water oxidation system using the complex $[(NH_3)_5Ru^{III}ORu^{IV}(NH_3)_4ORu^{III}(NH_3)_5]^{6+}$ as a precatalyst.[9] In this case, Ce(IV) was used as the stoichiometric oxidant as well.

The so-called "blue dimer" has since become one of the most studied water oxidation catalysts in literature. Its history, as such, highlights the importance of developing molecular water oxidation catalysts, since most studies on the mechanism of water oxidation utilize solution-based techniques. Such an approach is only viable when applied to purely homogeneous systems whose components are robust over an extended period of time. Therefore, the next logical step in the development of such catalysts is to search for candidates that are molecular and at the same time, oxidatively stable. This approach necessitates the minimization of oxidizable organic structures in potential catalysts.

Polyoxometalates

Polyoxometalates (POM's) are a unique class of compounds. Composed primarily of M-O-M (M = Nb, Ta, V, W, Mo) bonds, where the metals M are in high oxidation states (either d^0 or d^1 configuration), POM's have been known for well over a century.

The very interesting properties of polyoxometalates have made them the subject of more than one hundred years of study and exploration by numerous research groups.[10]

One technically significant property of POM’s is their versatility with respect to solubility. Being negatively charged compounds, their solubility varies depending on the nature of the counteractions with which they are paired. For example, most POM’s are isolated as alkali metal salts that are soluble in water. This, however, does not preclude the option of dissolving POM’s in organic solvents. Cation exchange procedures with cations such as tetrabutylammonium that contain organic groups yield POM’s that are soluble in organic solvents such as acetonitrile. This procedure has been used by numerous research groups internationally.[10]

POM’s are also very robust with respect to oxidation. Since almost all the metals M in unfunctionalized POM structures possess d^0 configurations, it is very difficult to oxidize them. This property is a major advantage that POM’s have over compounds with any sort of organic structure, as it ensures the stability of POM species under conditions that are too oxidatively harsh for organic structures. This is a major reason why POM’s are attractive and viable oxidation catalysts.

Polyoxometalates are also very tunable structurally. Over the years, countless polyoxometalates substituted with transition metals (other than Nb, Ta, V, W and Mo) have been reported. Many of these substituted POM’s have since then been demonstrated to possess varying noteworthy catalytic properties. In addition, a range of structural motifs have been reported. This gives POM’s a very rich structural and functional chemistry because these different structures enable the incorporation of different numbers of main group and transition metals into the otherwise unfunctionalized cluster networks.

Polyoxometalates as Water Oxidation Catalysts

When subjected to targeted functionalization, POM's can become unusually attractive candidates as potential catalysts for water oxidation, not for the reasons mentioned above, but also because of the structural similarities between some POM's and known water oxidation catalysts. Specifically, all the previously mentioned water oxidation catalysts, such as Meyer's blue dimer and the various catalytically active heterogeneous metal oxide based materials, contain M-O-M (M = metal) units, a moiety that recurs in water oxidation catalysts as well as in POM structures. Therefore, it would not be surprising if POM's containing the right redox-active functional metals exhibit catalytic water oxidation activity.

Indeed in 2008, our group and that of Bonchio et al. independently developed the water soluble ruthenium-substituted POM $\{[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 25H_2O\}^{10-}$ (**1**) and demonstrated that it evolved O_2 from water in the presence of strong oxidants.[11,12] Complex **1** was shown to be stable over a wide range of pH values. Indeed, the system utilized by Bonchio et al. used Ce(IV) as a stoichiometric oxidant at low pH our group used $Ru(bpy)^{3+}$ in neutral pH. Studies have also shown that **1** is oxidatively stable despite the severely oxidizing conditions used by both research groups.

Despite these key findings by our group and that of Bonchio, the development of a stable molecular catalyst utilizing cheap materials remains elusive. This has sparked interest in exploring polyoxometalates as water oxidation catalysts in our group. In light of findings by Sutin et al. and Shafirovich et al., the next logical step was to explore Co-substituted polyoxometalates as oxygen evolving catalysts. This work reports preliminary studies that indicate the polyoxometalate $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22H_2O$ (**2**) is a viable water oxidation catalyst.

Experimental

Materials. All materials and chemicals used were reagent grade unless otherwise indicated.

Infrared (IR) Spectra. A Nicolet FT-IR 6700 spectrometer was used to take all infrared (IR) spectra. All samples prepared for IR spectra were KBr pellets.

Synthesis of K-2. The K^+ salt (**K-2**) of the POM **2** was synthesized according to a previously published method.[13] The identity of the sample is confirmed by IR spectroscopy and comparison of its UV-Visible spectrum to that reported by Finke et al.[15]

Synthesis of α,β-$K_6P_2W_{18}O_{62}$ (3). The complex was prepared according to a previously published method. The identity of the product is confirmed by IR spectroscopy.[14]

Synthesis of α-$K_6P_2W_{18}O_{62}$ (4). This POM was synthesized from **3** by the method employed by Finke et al.[14] The identity and isomeric purity of the POM were established by IR spectroscopy and ^{31}P NMR spectroscopy.

Synthesis of α-$Na_{12}P_2W_{15}O_{62}$ (5). The complex was synthesized from **4** according to the method reported by Finke et al.[14] and the identity confirmed by IR spectroscopy.

Synthesis of $Na_{16}[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]$ (6). This POM was prepared according to the method of Finke et al.[14] by using **5** as a precursor. Its identity is confirmed by IR spectroscopy.

Synthesis of $Na_9(A\text{-}\alpha\text{-}PW_9O_{34})\cdot 7H_2O$ (7). This POM was prepared according to a literature method[15] and characterized by IR spectroscopy.

Synthesis of $K_{12}(Co_3H_2O)_3(PW_9O_{68})$ (8). This complex was prepared according to a literature method[16] and characterized by IR spectroscopy and UV-Vis spectroscopy.

Synthesis of K-Na-Li-2. A sample of crude non-crystalline **8** is dissolved in a minimal amount of 1M LiCl, until the solution no longer becomes clearer. The solution is then filtered and allowed to evaporate under ambient air for 5-7 days, after which a small amount of crystals grew (<5% yield). Along with the crystals appeared a purple precipitate. The identity of the crystalline sample is confirmed by IR spectroscopy and x-ray crystallography.

Synthesis of $Ru(bpy)_3(ClO_4)_3$. The perchlorate salt of $Ru(bpy)_3^{3+}$ was synthesized according to published methods.[17]

Oxidation of water by $Ru(bpy)_3(ClO_4)_3$ (performed by co-worker Qiushi Yin). POM's **2**, **6**, and **8** were screened for catalytic water oxidation activity via "dark reactions" where $Ru(bpy)_3^{3+}$ is used as the stoichiometric oxidant. In a typical dark reaction, a sample of $Ru(bpy)_3(ClO_4)_3$ is dissolved in water. In a separate vessel, a sample of the candidate POM is dissolved in 0.05 mM sodium phosphate buffer along with a certain amount of 2,2'-bipyridyl. Both solutions are purged with argon gas. The catalyst solution is then rapidly transferred to the $Ru(bpy)_3(ClO_4)_3$ solution by a 18-gauge cannula. The pressure for transferring the solution is provided by pumping a large pressure of argon gas into the catalyst solution while it is in contact with the cannula, which serves as a bridge between the $Ru(bpy)_3(ClO_4)_3$ solution and the catalyst solution. Yields of O_2 are determined by analyzing samples of gas from the headspace using a 250 μL Hamilton gas-tight syringe and then injecting these into a Hewlett-Packard 5890 gas chromatograph fitted with a thermal conductivity detector (TCD).

Photochemical oxidation of water. In a typical photochemical experiment, $Na_2S_2O_8$, **K-2** and $Ru(bpy)_3Cl_2 \cdot 6H_2O$, are dissolved in sodium phosphate buffer and placed in a roundbottom flask and vigorously stirred. The vessel is then capped with a rubber stopper, bubbled with argon gas for a few minutes, placed in a beaker full of water and illuminated with a 150 W Hamamatsu Xenon lamp. The light from this lamp is focused onto a 450-550 nm cutoff filter to match the absorption spectrum of $Ru(bpy)_3^{2+}$. Yields of O_2 are determined by methods previously described for the dark reaction.

Examining post-catalysis degradation of $Ru(bpy)_3^{2+}$. The degree to which the $Ru(bpy)_3^{2+}$ was degraded was examined by adding an excess of ascorbic acid to the post catalytic solution to fully reduce the $Ru(bpy)_3^{3+}$ and make sure none of it is in its oxidized form. This solution was then examined by UV-Visible spectroscopy. The protocol is applied to all catalytic trials. All post catalysis solutions were diluted 10-fold prior to this treatment.

UV-Visible and ^{31}P NMR studies for 2. These were performed by monitoring the change in the UV-Vis absorptions of 2 mM samples of **K-2** in aqueous buffered solutions. To determine pH stability, this experimental procedure was performed using multiple solutions at different pH values. In addition, ^{31}P NMR spectra were collected for the various samples. All ^{31}P NMR spectra were obtained using a Varian INOVA 400

(400 MHz) NMR spectrometer. All UV-Visible spectra were taken using an Agilent 8453 spectrometer in a quartz cell with a 1 cm path length.

Results and Discussion

Catalytic dark reaction trials. Since the objective of these experiments was to screen for catalytic water oxidation activity, the method selected was one that simulates the water oxidation step in **Figure 3**. This is an approach used by various research groups, and the net reaction in this method is:

$$4\text{Ru(bpy)}_3{}^{3+} + 2\text{H}_2\text{O} \overset{\text{cat}}{\rightarrow} 4\text{H}^+ + \text{O}_2 + 4\text{Ru(bpy)}_3{}^{2+}$$

As a starting point, we also decided that ideally, our studies would be performed close to or at neutral pH. This was based on our knowledge of the work of Sutin et al., which indicated that Co^{2+} was active at pH 6.5-9.0.

The candidate POM's were selected based on a number of different criteria. First, the POM's chosen were determined to be stable at our catalytic conditions. The properties, such as pH stability, of the POM's **6** and **8**, for example, have been studied extensively.[16,18,19] Second, it was determined that POM's with multiple cobalt centers were more promising candidates as water oxidation catalysts than monosubstituted ones. This is because we felt that multi-cobalt POM's are closer analogs to the known metal oxide and hydroxide catalysts, which are essentially networks of metal-oxo bonds. Furthermore, since water oxidation is a multi-electron process, we believed that POM's with multiple redox-active metal centers would be more likely to function as water oxidation catalysts. Lastly, we only screened POM's that were likely to be stable under our reaction conditions. Specifically, since POM stability is largely determined by pH, the POM's screened were all determined to be stable at pH 6 to pH 7. For example, the POM **6** is known to be stable from pH 1 to pH 6, while **2** can be synthesized in aqueous pH 6 or pH 7 medium.

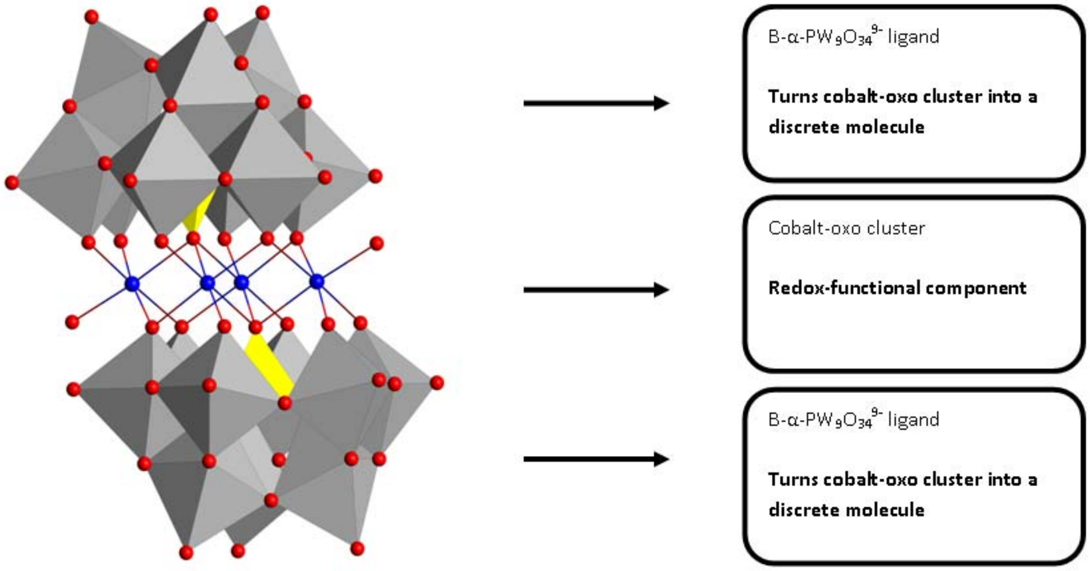

Figure 4. POM's as molecular metal oxide water oxidation catalysts.

The dark reaction trials revealed that of the cobalt substituted POM's screened, only the salts of **2** are active water oxidation catalysts. Furthermore, studies suggest that optimum yields occur at pH 8 when **2** is used as a water oxidation catalyst under dark conditions. We were able to recover the catalyst by precipitation with Ru(bpy)$_3^{2+}$ ions and its IR spectrum remains the same after being corrected for the peaks of Ru(bpy)$_3^{2+}$. This suggests that **2** is stable under oxidative conditions at pH 8. Significantly, we also determined that adding approximately 5 equivalents of 2,2'-bipyridyl to the system removes the catalytic activity of aqueous Co^{2+} ions. Using this method, we were able to confirm our hypothesis that **2** is indeed either a precatalyst or the active catalytic species in our system. These findings form the basis of our assumption that **2** will also be stable in a photochemical system.

Confirmation of the identity of K-2 and $K_8Na_6Li_2[Co_4(PW_9O_{34})_2]\cdot xH_2O$ (K-Na-Li-2). K-2 was characterized by IR and UV-Visible spectroscopy. They match previously reported spectra by Finke et al.[14] and Knoth et al.[16] The IR and UV-Visible spectra are shown below:

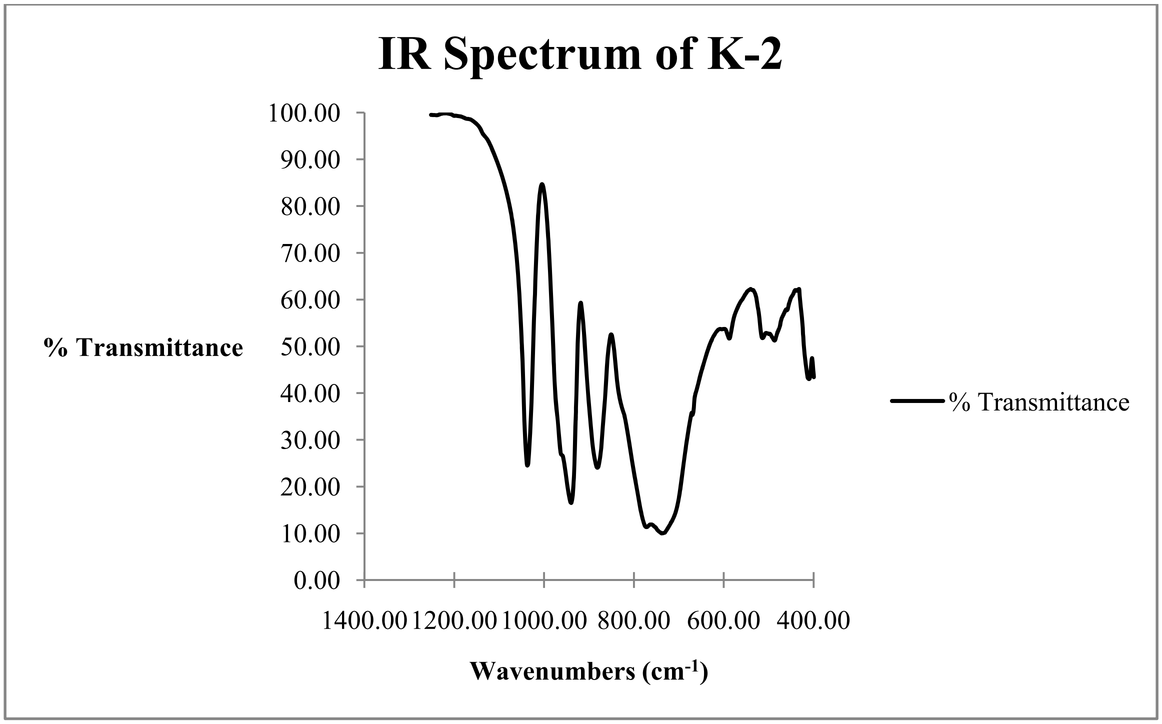

Figure 5. IR spectrum of **K-2**. It matches that reported by Finke et al.[14]

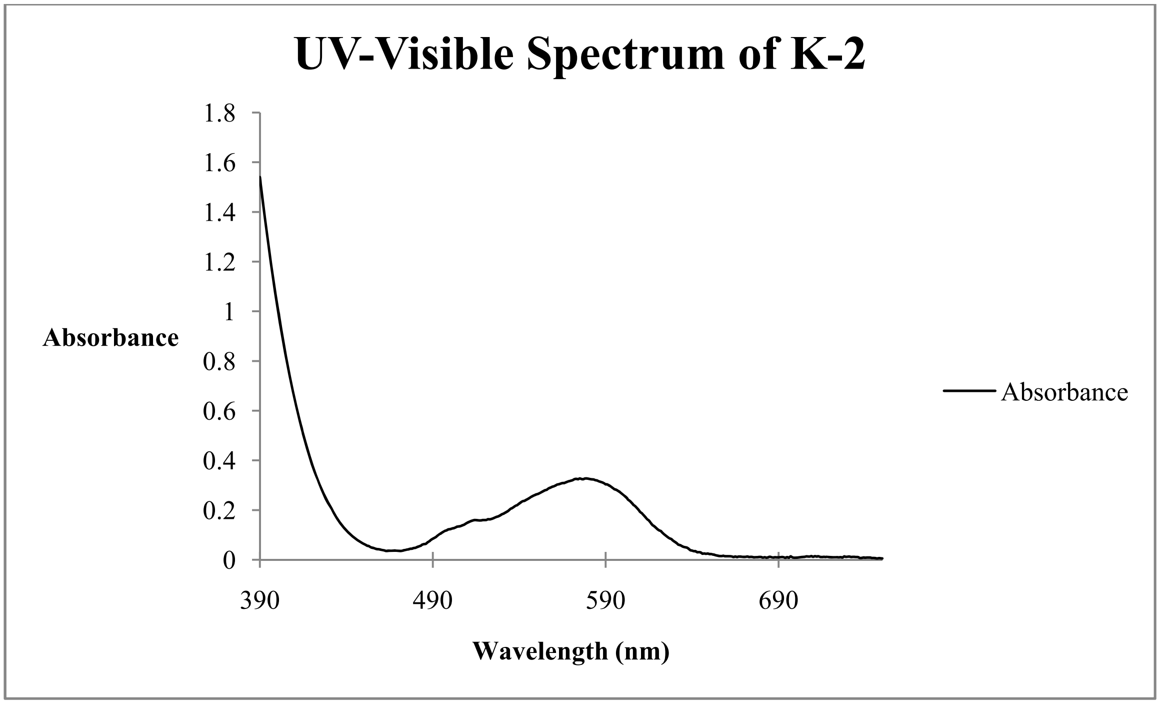

Figure 6. The UV-Visible spectrum of **K-2**. It matches that reported by Knoth et al.[16]

A crystal structure was obtained for **K-Na-Li-2**. The X-ray crystal structure for this is shown below:

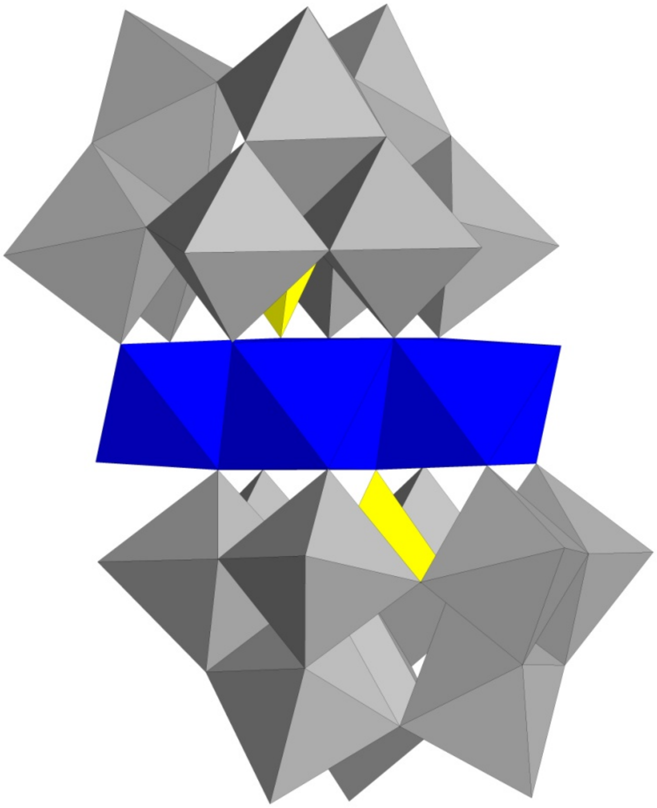

Figure 7. Structure for **K-Na-Li-2**. Gray octahedra = WO_6, Yellow tetrahedra = PO_4, Blue octahedra = CoO_6.

Stability studies for 2. One of the themes of this work is the unequivocal establishment of the stability of the catalytic or precatalytic compound **2**. In POM chemistry, hydrolytic stability is always a concern and is often pH dependent. Therefore, studies under different pH's were conducted for **K-2**. UV-Visible spectra were collected and the intensity of the peak absorbances were monitored over a 5-hour period. The results are shown below:

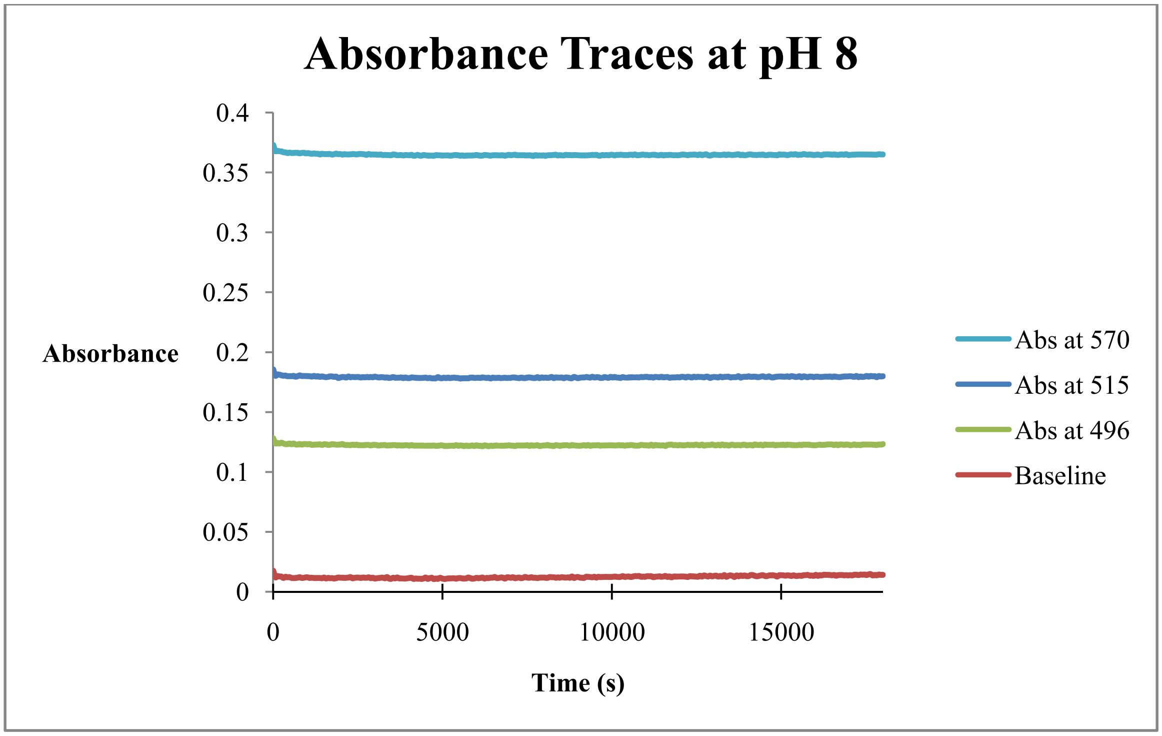

Figure 8. UV-Visible study of **2** at pH 8. Conditions: 2 mM **2** in 50 mM Na_2HPO_4/NaH_2PO_4 (pH 8) buffer.

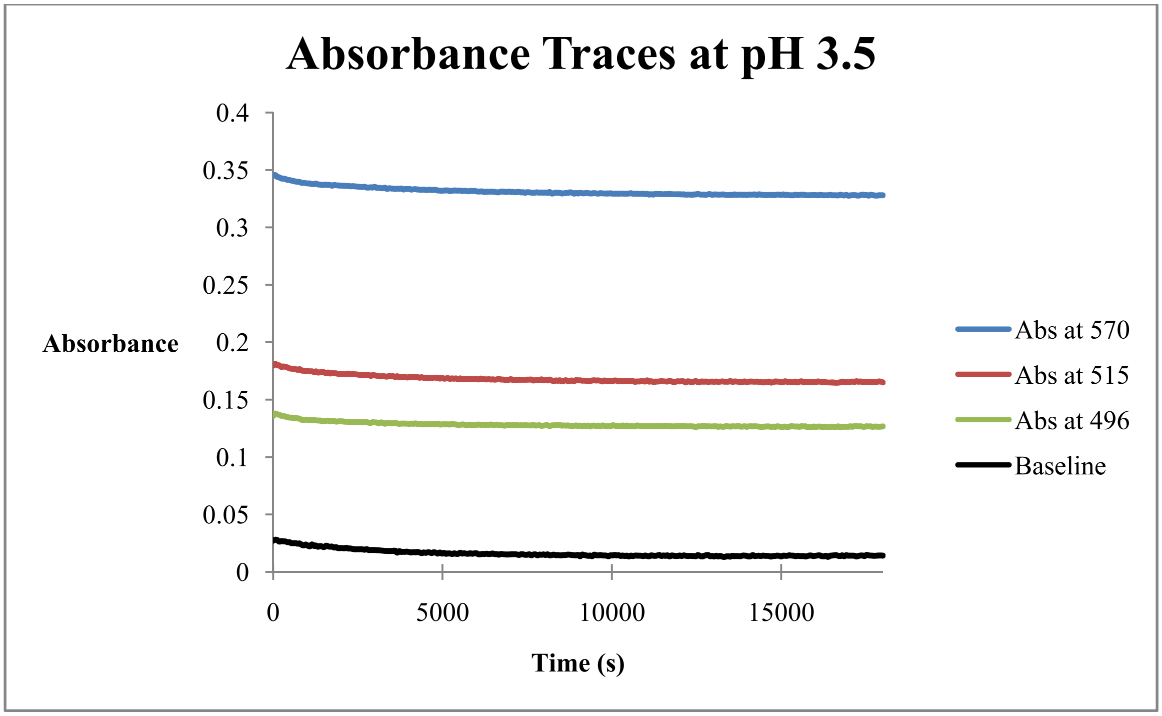

Figure 9. UV-Visible study of **2** at pH 3.5. Conditions: 2 mM **2** in 50 mM $NaOOCCH_3/HOOCCH_3$ (pH 3.5) buffer.

Over 5 hours, there is no significant change in the shape or the absorbance intensities of the UV-Visible absorption spectrum of **2** from pH 3.5 to 8. This is a line of evidence that indicates that there is no isomerization or decomposition of **2** caused by hydrolysis at the said pH range.

The ^{31}P NMR spectra of a solution of **K-2** at its natural pH (ca. 7) was taken. Only one phosphorus peak was seen at 1875 ppm. This is to be expected since **K-2** contains two phosphorus atoms that are chemical shift equivalent. Solutions at pH 3.5 acetate buffer and pH 8 borate buffer aged over at least 10 hours show only one peak at the 1894 and 1870 ppm region respectively. These peaks were assigned as the peak for

K-2. The lack of extraneous peaks suggests that there is no significant decomposition or isomerization due to hydrolysis of **2** at these pH's.

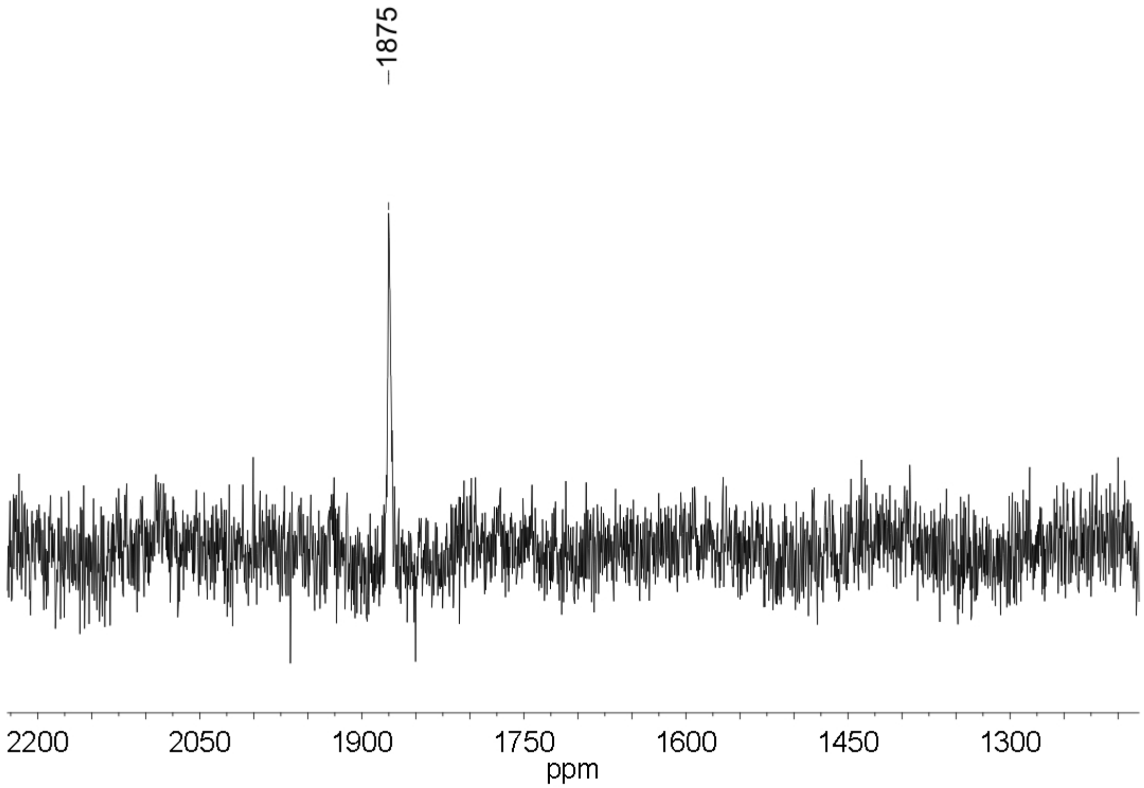

Figure 10. ^{31}P NMR of **K-2** at its natural pH (ca. 7.0) from 2225-1175 ppm. The peak at 1875 is assigned to the two phosphorus atoms in **K-2**, which are equivalent by symmetry.

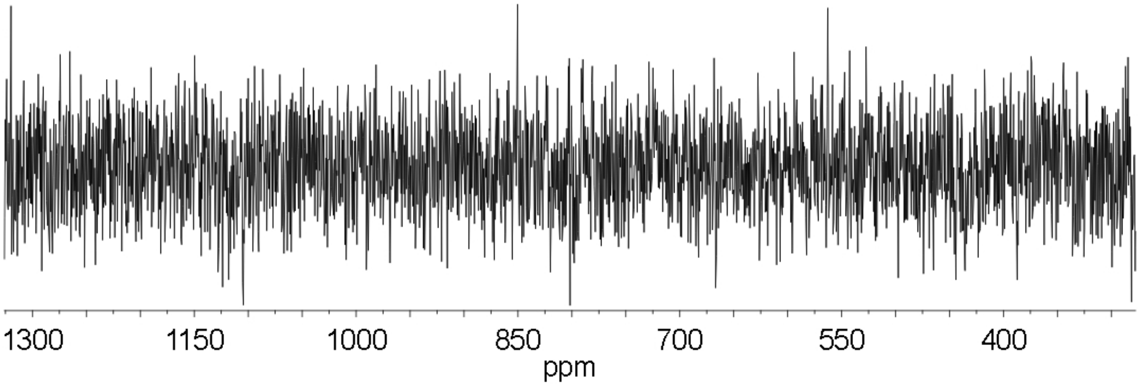

Figure 11. ^{31}P NMR of **K-2** at its natural pH (ca. 7.0) from 1375-350 ppm. There is no peak seen in this region.

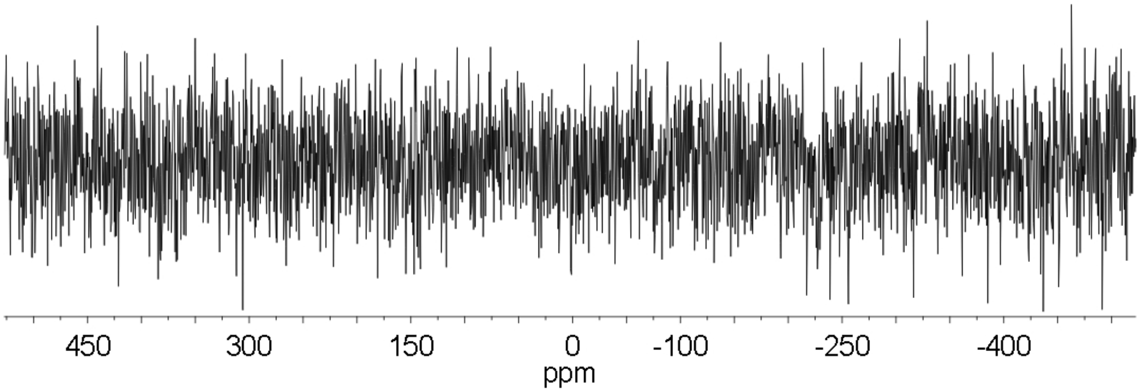

Figure 12. ^{31}P NMR of **K-2** at its natural pH (ca. 7.0) from 525 to -525 ppm. No peak is seen in this region.

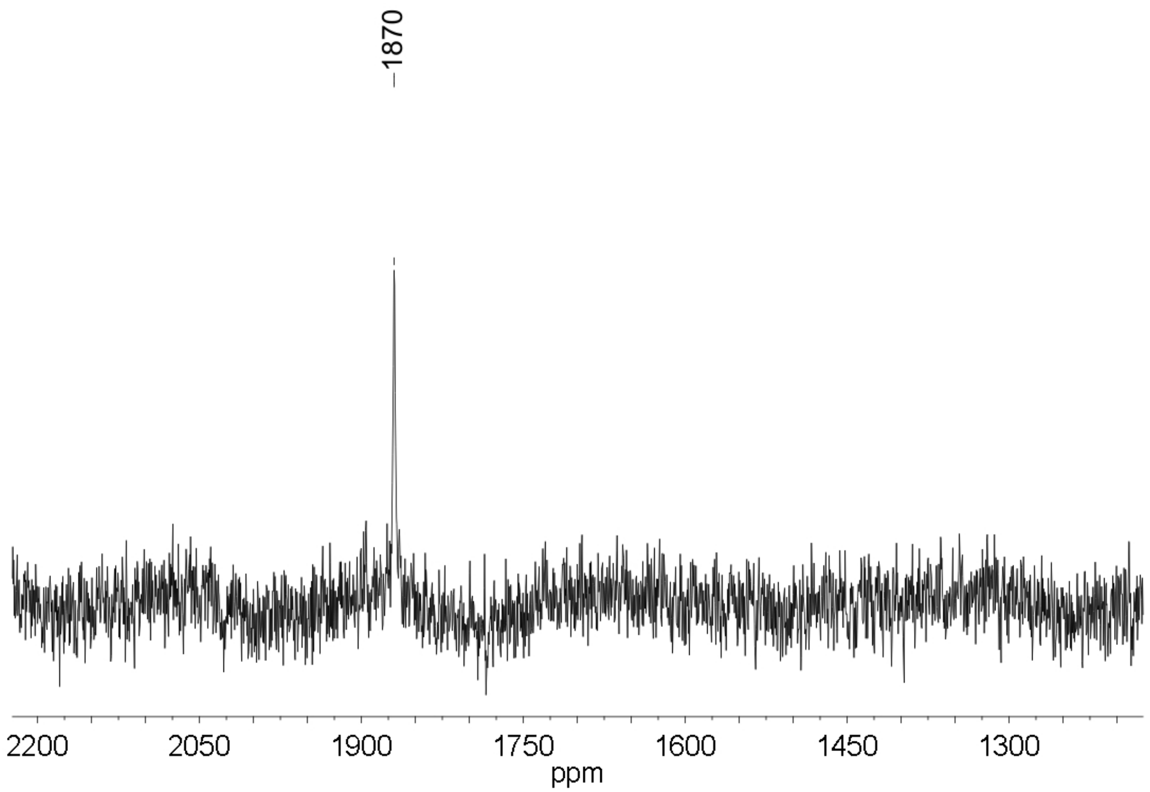

Figure 13. ^{31}P NMR of **K-2** at pH 8 (in borate buffer) from 2225-1175 ppm. The peak at 1870 is assigned to the two phosphorus atoms in **K-2**, which equivalent by symmetry.

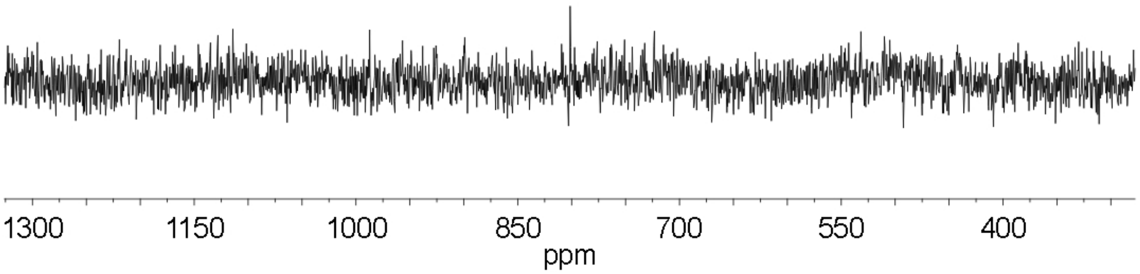

Figure 14. ^{31}P NMR of **K-2** at pH 8 (in borate buffer) from 1325-375 ppm. No peak is seen in this region except the one in the center of the window. This peak was determined to be an artifact and is either changed or removed when scans are taken in a different window.

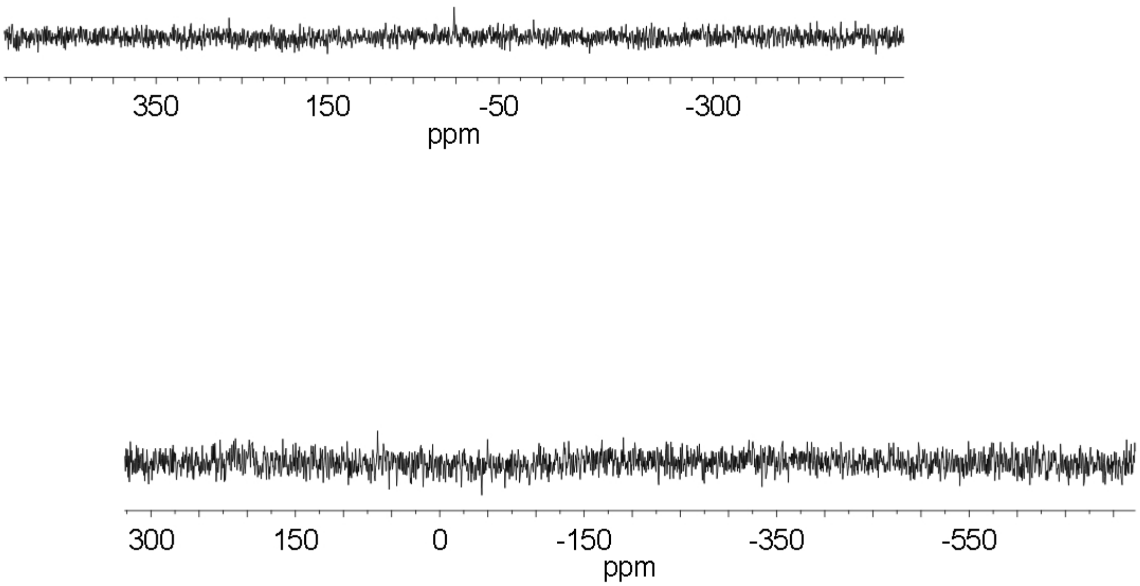

Figure 15. Top: ^{31}P NMR of **K-2** at pH 8 (in borate buffer) from 525 to -525 ppm. No peak is seen in this spectrum outside of the artifact seen in the middle of the top window. Bottom: Spectrum taken in order to prove that the peak in the top spectrum is merely an artifact that appears as a result of limitations in the NMR instrument.

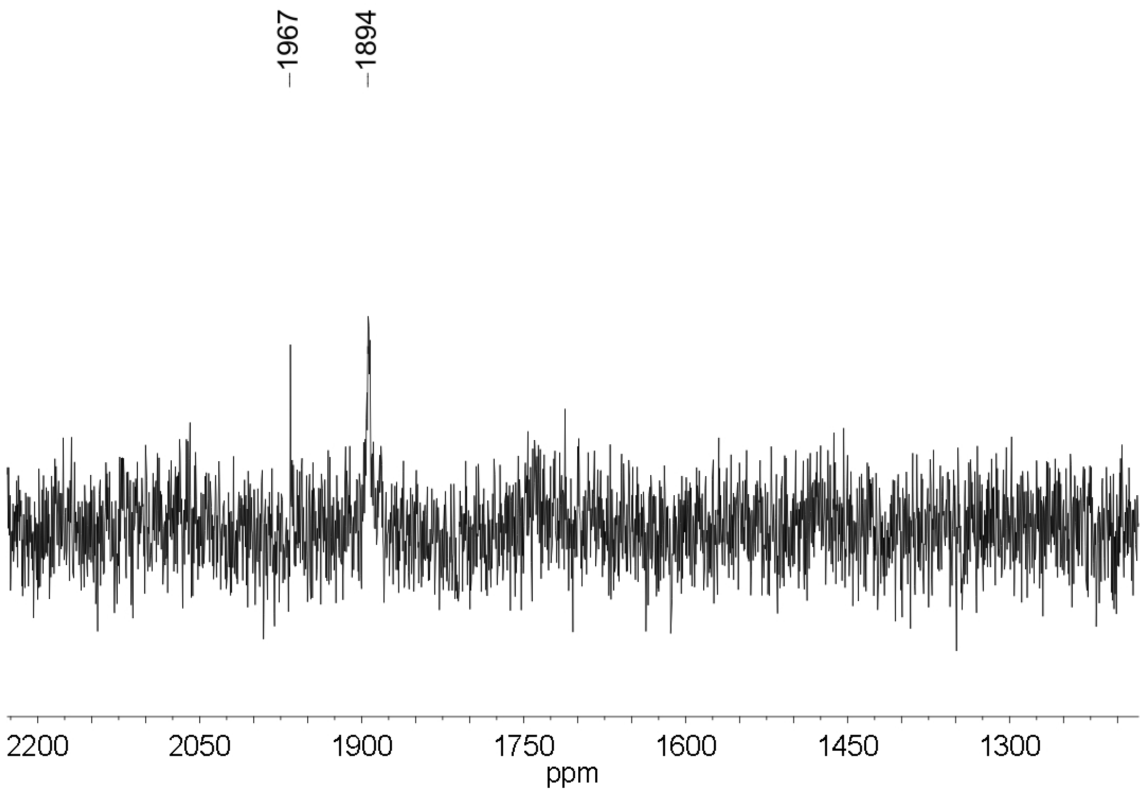

Figure 16. ^{31}P NMR of **K-2** at pH 3.5 (in acetate buffer) from 2225 to 1175 ppm. No peak is seen in this spectrum outside of the artifact seen at 1967. We know this is an artifact and not an actual peak because the same sample taken in a different window does not show this peak

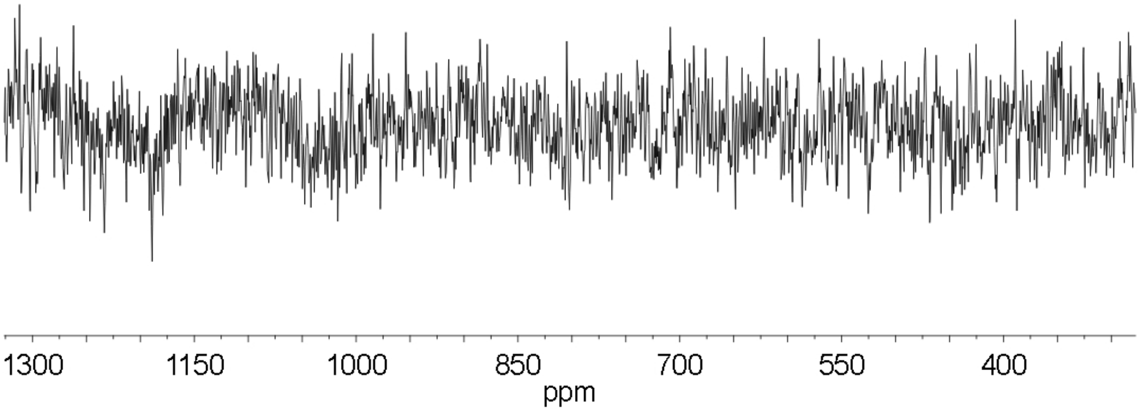

Figure 17. ^{31}P NMR of **K-2** at pH 3.5 (in acetate buffer) from 1325 to 275 ppm. No peak is seen in this spectrum.

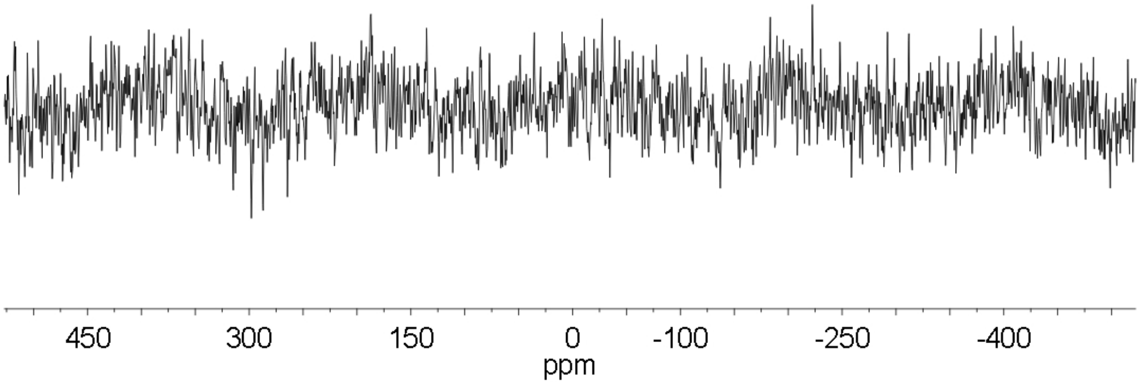

Figure 18. ^{31}P NMR of **K-2** at pH 3.5 (in acetate buffer) from 525 to -525 ppm. No peak is seen in this spectrum.

Light-driven oxidation of water. The system used for the photo-oxidation of water follows the scheme below:

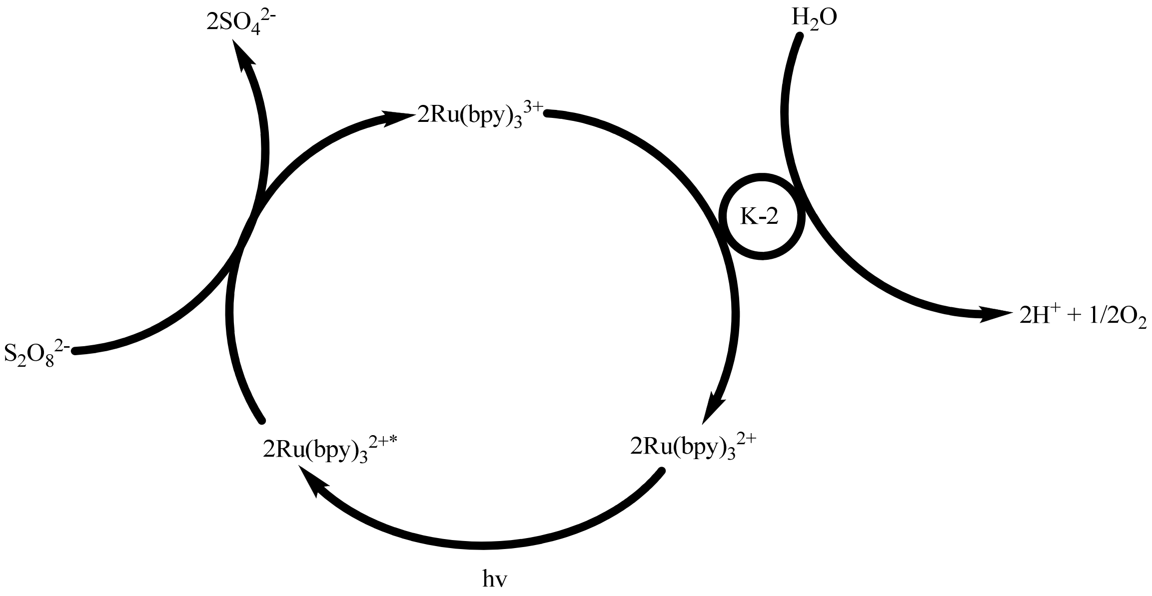

Figure 19. Catalytic water oxidation half-cell used in this work.

In such a half-cell the dye molecule, $Ru(bpy)_3^{2+}$, absorbs light, forming an excited state. This excited state is a strong oxidizing agent and is quenched by the persulfate molecules to form $Ru(bpy)_3^{3+}$, the oxidized form of the dye. This species is a strong enough oxidant to oxidize water and does so with the help of a catalyst, in this case the POM, **K-2**. The dye is then returned to its original form and a new catalytic cycle begins. The overall net reaction therefore is:

$$S_2O_8^{2-} + H_2O \xrightarrow{\text{K-2}} 2H^+ + \frac{1}{2}O_2$$

Optimization data and yield versus time graphs are shown below for the photochemical trials:

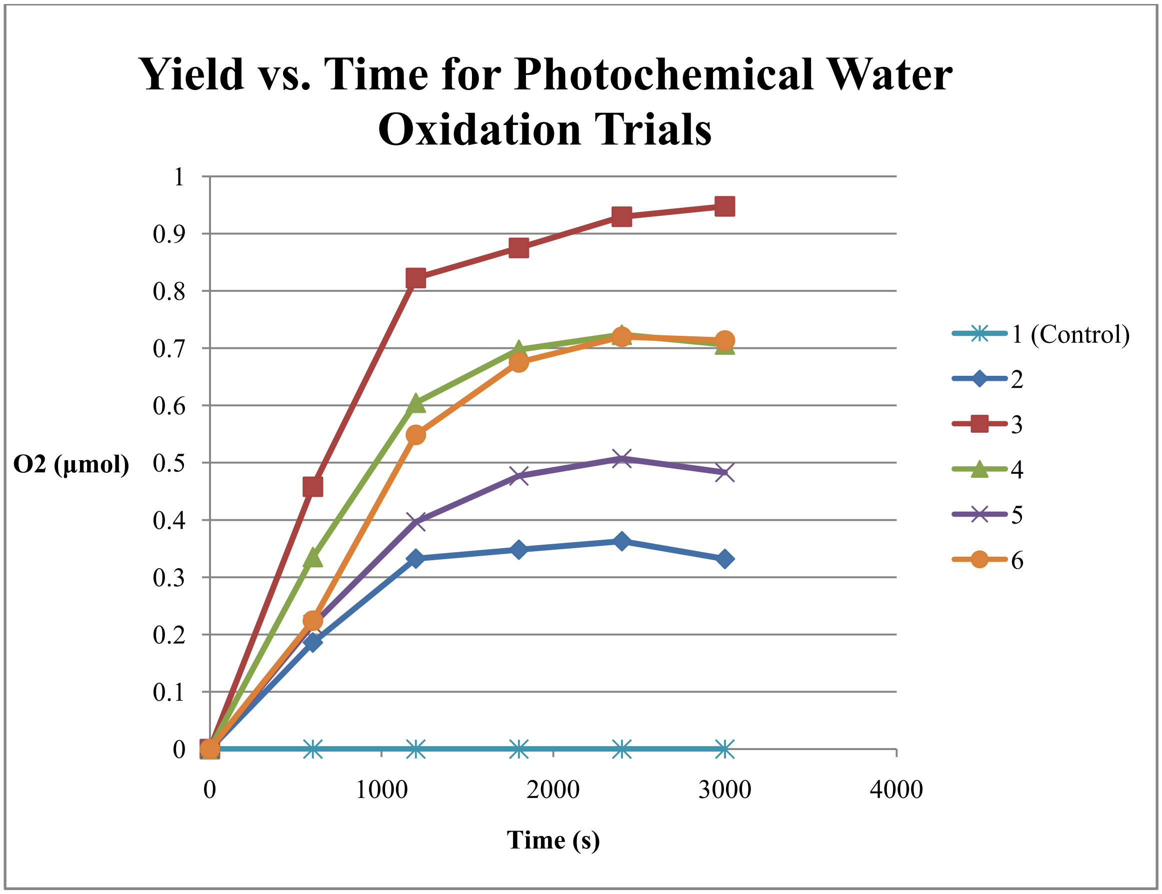

Figure 20. Yield vs. time graphs for photochemical water oxidation trials.

Yields for Photochemical Water Oxidation Trials

	$Ru(bpy)_3^{2+}$ (mM)	K-2 (µM)	Na_2HPO_4/NaH_2PO_4 buffer (mM)	$Na_2S_2O_8$ (mM)	O_2 (µmol) (after 50 mins)	TON (after 50 mins)
1	0.5	0	15	5	0	0
2	0.5	1.25	15	5	0.33	33.2
3	0.5	5	15	5	0.95	23.69
4	0.5	2.5	15	5	0.71	35.32
5	0.5	2.5	30	5	0.48	24.16
6	1	2.5	15	5	0.71	35.69

Table 1. Optimization data for photochemical water oxidation trials. Final volume: 8 mL.

A few observations and conclusions can be made based on the above data. First, it is evident that the addition of **2** has positive effect on the efficiency of the system.

Specifically, there is no appreciable production of O_2 gas without the POM, as can be seen in the control trial. This is a strong indicator that **K-2** serves as a catalyst or precatalyst in the system.

Second, increasing buffer concentration has an adverse effect on the efficiency of the system. This may seem counterintuitive if the pH effect is considered, since it is known from our studies in the dark system that the activity of **K-2** decreases as the pH decreases from 8. An investigation by Bard et al.[20] can be invoked to explain this phenomenon. In 1984, Bard's group revealed an alternative reaction pathway wherein the initial excitation and photooxidation events occur after the pre-formation of the ion pair complex ($Ru(bpy)_3^{2+} \cdot S_2O_8^{2-}$). This sequence is unimolecular and the rate is likely faster than that of the conventional bimolecular pathway wherein a free $Ru(bpy)_3^{2+*}$ collides with a $S_2O_8^{2-}$ atom. Increasing the buffer concentration increases the ionic strength of solution, which can conceivably cause the separation of the ion pair complex. Therefore it would not be unreasonable to argue that this is the reason for the negative effect of a higher buffer concentration on the efficiency of the system.

Third, it is clear from observation that when the POM and $Ru(bpy)_3^{2+}$ ions are in the same system, they are mutually insoluble. This is to be expected since both are large polyanions that have a low charge density. This behavior was also observed in similar studies with **1** conducted by our group.[21] Such a problem will very likely complicate the kinetics and adversely affect the overall efficiency of the system.

Fourth, the *in situ* generation of oxidative $Ru(bpy)_3^{3+}$ is clearly too fast for rapid quenching by the catalyst. This is inferred from the fact that the reaction solution turns green upon illumination, indicating the formation of $Ru(bpy)_3^{3+}$, even in the presence of the POM catalyst. The presence of an excessive amount of $Ru(bpy)_3^{3+}$ in a high pH aqueous system under oxidative conditions for extended periods of time is very likely to cause the oxidative degradation of the $Ru(bpy)_3^{2+}$ ion, inevitably leading to inefficiency in the system. As a matter of fact, it has been shown that the water oxidation steps in the system of Sutin et al. simultaneously with oxidative degradation of the 2,2'-bipyridyl ligands on the $Ru(bpy)_3^{2+}$ molecule.[6] This has been observed in this work as well, by UV-Visible spectroscopy.

On self-assembling catalysts. Recently, Nocera et al. reported a water oxidation catalyst based on cobalt and phosphate ions in aqueous medium.[22,23] He also subsequently reported the discovery of analogs with borate and methylphosphate as the anions.[24] These discoveries are considered noteworthy for good reason, which is the fact that Nocera et al. have been able to regenerate these catalysts *in situ*. In other words, the catalysts utilized by Nocera are self-repairing.

We believe that in the POM **2**, a similar claim of a self-assembling catalyst can be made. Discovered first by Weakley et al.,[25] **2** was first prepared by heating the requisite WO_4^{2-}, Co^{2+} and HPO_4^{2-} in the proper stoichiometric ratios in aqueous medium at pH 7. This implies that at this pH, the thermodynamic product of the mixture of precursors is **2**. Since then, two different preparations have yielded the same product. In this work, we also believe that we have isolated **2** by decomposing **8** in aqueous medium at room temperature. In other words, this catalyst has its own way of self-assembling under the proper conditions.

Conclusions

We believe that we have demonstrated that **2** is a POM-based molecular water oxidation catalyst that is oxidatively stable and robust. While not the first POM found to catalyze water oxidation, this is the first POM based on cheap metals (Co, W) that has been found to have such catalytic activity. Furthermore, preliminary studies have shown that this POM is stable with respect to hydrolysis from pH 3.5 to pH 8 and also stable oxidatively at pH 8. Furthermore, **2** is in its own right, a self-assembling complex, as indicated by the various ways that it has been prepared.[14,16]

We have also been able to observe catalytic turnovers of O_2 under a photochemical system involving only visible light. Problems with this system include decomposition of the photosensitizer molecule and lack of solubility of the POM in the presence of $Ru(bpy)_3^{2+}$.

Future Directions

Especially in this day and age, work in the field of artificial photosynthesis is important and water oxidation is a major hurdle to overcome. Therefore, it is worth the time investment to study such mechanisms, in an attempt to be able to more rationally design catalysts and systems that are more efficient than those known today. Such a task is made considerably easier when a molecular water oxidation catalyst is available. We believe therefore, that the recent discovery of **2**, being cheap and easily prepared, stable, molecular and water soluble, will greatly aid the efforts of many laboratories and research groups, including ours who will now attempt to elucidate the detailed mechanism of water oxidation by this POM-based system.

Furthermore, the long-established structural tunability of POM's opens the possibility for the development of more inexpensive POM water oxidation catalysts other than **2** that exhibit a larger range of activity and robustness than this multi-cobalt prototype. Also, it is known that organic ligands can also be attached to POM's, facilitating the creation of multi-functional nanomaterials capable of visible light-based artificial photosynthesis.

1. Lewis, N. S.; Nocera, D.G., Powering the planet: Chemical challenges in solar energy utilization. *Proc. Nac. Acad. Sci.* **2006**, *103*, 15729-15735.
2. Barber, J.; Photosynthetic energy conversion: natural and artificial. *Chem. Soc. Rev.*, **2009**, *38*, 185-196.
3. Serpone, N.; Pelizzetti, E.; Gratzel, M., Photosensitization of semiconductors with transition metal complexes – a route to the photoassisted cleavage of water. *Coord. Chem. Rev.,* **1985**, *64*, 225-245.
4. Shafirovich, V. Y.; Shilov, A. E. Catalytic oxidation of water with the participation of manganese compounds in neutral and slightly acid media. *Kinetika i Kataliz*, **1979**, *20*, 1156-1162.
5. Shafirovich, V. Y.; Khannanov, N. K.; Strelets, V. V., Chemical and light-induced catalytic water oxidation. *Nouv. J. de Chimie*, **1980**, *4*, 81-84.
6. Ghosh, P. K.; Brunschwig, B. S.; Chou, M.; Creutz, C.; Sutin, N., Thermal and light-induced reduction of $Ru(bpy)_3^{3+}$ in aqueous solution. *J. Am. Chem. Soc.*, **1984**, *106*, 4772-4783.
7. Gersten, S. W.; Samuels, G. J.; Meyer, T. J., Catalytic oxidation of water by an oxo-bridged ruthenium dimer. *J. Am. Chem. Soc.*, **1982**, *104*, 4029-4030.
8. Ramaraj, R.; Kira, A.; Kaneko, M., Electrochemistry and stability studies of oxo-bridged dinuclear ruthenium (III) complexes for water oxidation. *J. Chem. Soc., Faraday Trans. 1*, **1986**, *82*, 3515-3524.
9. Ramaraj, R.; Kira, A.; Kaneka, M., Oxygen evolution by water oxidation with polynuclear ruthenium complexes. *J. Chem. Soc., Faraday Trans. 1*, **1987**, *83*, 1539-1551.

10. Pope, M. T.; Heteropoly and Isopoly Oxometalates. Springer-Verlag, Berlin, Heidelberg, 1983.
11. Sartorel, A.; Carraro, M.; Bagno, A.; Scorrano, G; Bonchio, M., Polyoxometalate embedding of a tetraruthenium(IV)-oxo-core by template-directed metalation of [γ-$SiW_{10}O_{36}]^{8-}$: A total inorganic oxygen-evolving catalyst. *J. Am. Chem. Soc.*, **2008**, *130*, 5006-5007.
12. Geletii, Y. V.; Botar, B.; Kogerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L., An all-inorganic, stable, and highly active tetraruthenium homogeneous catalyst for water oxidation. *Angew. Chem. Int. Ed.* **2008**, *47*, 3896-3899.
13. Evans, H. T.; Tourne, C. M.; Tourne, G. F.; Weakley, T. J. R., X-ray crystallographic and tungsten-183 nuclear magnetic resonance structural studies of the $[M_4(H_2O)_2(XW_9O_{34})_2]^{10-}$ heteropolyanions (M = Co(II) or Zn, X = P or As). *J. Chem. Soc., Dalton Trans.*, **1986**, *12*, 2699-2705.
14. Finke, R. G.; Droege, M. W.; Domaille, P. J., Trivacant heteropolytungstate derivatives. 3. Rational syntheses, characterization, two-dimensional ^{183}W NMR and properties of $P_2W_{18}M_4(H_2O)_2O_{68}{}^{10-}$ and $P_4W_{30}M_4(H_2O)_2O_{112}{}^{16-}$ (M = Co, Cu, Zn). *Inorg. Chem.*, **1987**, *26*, 3886-3896.
15. Domaille, P. J., *Inorg. Synth.*, **1990**, *27*, 96-104.
16. Knoth, W. H.; Domaille, P. J.; Farlee, R. D., Anions of the type $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ and $[H_2OCo]_3W_{18}P_2O_{68}{}^{12-}$. A reinvestigation of "B,*β*-$W_9PO_{34}{}^{9-}$." *Organometallics*, **1985**, *4*, 62-68.
17. Geletii, Y. V.; Botar, B.; Kogerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L., An all-inorganic, stable, and highly active tetraruthenium homogeneous catalyst for

water oxidation. *Angew. Chem. Int. Ed.* **2008**, *47*, 3896-3899, *Supporting Information*.

18. Ruhlmann, L.; Costa-Coquelard, C.; Canny, J.; Thouvenot, R., Mixed-metal Dawson sandwich complexes: synthesis, spectroscopic characterization and electrochemical behavior of $Na_{16}[M^{II}Co_3(H_2O)_2(P_2W_{15}O_{56})_2]$ (M = Mn, Co, Ni, Zn and Cd), *Eur. J. Inorg. Chem.* **2007**, *11*, 1493-1500.
19. Ruhlmann, L.; Nadjo, L.; Canny, J.; Contant, R.; Thouvenot, R., Di- and tetranuclear Dawson-derived sandwich complexes: synthesis, spectroscopic analysis and electrochemical behavior. *Eur. J. Inorg. Chem.* **2002**, *4*, 975-986.
20. White, H. S.; Becker, W. G.; Bard, A. J., Photochemistry of the Tris(2,2'-bipyridine)ruthenium (II) – peroxydisulfate system in aqueous and mixed acetonitrile-water solutions. Evidence for a long-lived photoexcited ion pair. *J. Phys. Chem.*, **1984**, *88*, 1840-1846.
21. Geletii, Y. V. et al., unpublished results
22. Kanan, M. W.; Nocera, D. G., In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+}. *Science*, **2008**, *321*, (5892), 1072-1075.
23. Lutterman, D. A.; Surendranath, Y.; Nocera, D. G., *J. Am. Chem. Soc.*, **2009**, *131*, 3838-3839.
24. Surendranath, Y.; Dinca, M.; Nocera, D. G., Eletrolyte-dependent electrosynthesis and activity of cobalt-based water oxidation catalysts. *J. Am. Chem. Soc.*, **2009**, *131*, 2615-2620.

25. Weakley, T. J. R.; Evans, H. T. Jr.; Showell, J. S.; Tourne, G. F.; Tourne, C. M., 18-tungstotetracobalto(II)diphosphate and related anions. Novel structural class of heteropolyanions. *J. Chem. Soc., Chem. Commun.*, **1973**, *4*, 139-140.