Artificial Photosynthesis: From Nanosecond Electron Transfer to Catalytic Water Oxidation

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CONSPECTUS

Human society faces a fundamental challenge as energy consumption is projected to increase due to population and economic growth as fossil fuel resources decrease. Therefore the transition to alternative and sustainable energy sources is of the utmost importance. The conversion of solar energy into chemical energy, by splitting H_2O to generate molecular O_2 and H_2, could contribute to solving the global energy problem. Developing such a system will require the combination of several complicated processes, such as light-harvesting, charge separation, electron transfer, H_2O oxidation, and reduction of the generated protons. The primary processes of charge separation and catalysis, which occur in the natural photosynthetic machinery, provide us with an excellent blueprint for the design of such systems.

This Account describes our efforts to construct supramolecular assemblies capable of carrying out photoinduced electron transfer and to develop artificial water oxidation catalysts (WOCs). Early work in our group focused on linking a ruthenium chromophore to a manganese-based oxidation catalyst. When we incorporated a tyrosine unit into these supramolecular assemblies, we could observe fast intramolecular electron transfer from the manganese centers, via the tyrosine moiety, to the photooxidized ruthenium center, which clearly resembles the processes occurring in the natural system. Although we demonstrated multi-electron transfer in our artificial systems, the bottleneck proved to be the stability of the WOCs. Researchers have developed a number of WOCs, but the majority can only catalyze H_2O oxidation in the presence of strong oxidants such as Ce^{IV}, which is difficult to generate photochemically. By contrast, illumination of ruthenium(II) photosensitizers in the presence of a sacrificial acceptor generates $[Ru(bpy)_3]^{3+}$-type oxidants. Their oxidation potentials are significantly lower than that of Ce^{IV}, but our group recently showed that incorporating negatively charged groups into the ligand backbone could decrease the oxidation potential of the catalysts and, at the same time, decrease the potential for H_2O oxidation. This permitted us to develop both ruthenium- and manganese-based WOCs that can operate under neutral conditions, driven by the mild oxidant $[Ru(bpy)_3]^{3+}$.

Many hurdles to the development of viable systems for the production of solar fuels remain. However, the combination of important features from the natural photosynthetic machinery and novel artificial components adds insights into the complicated catalytic processes that are involved in splitting H_2O.
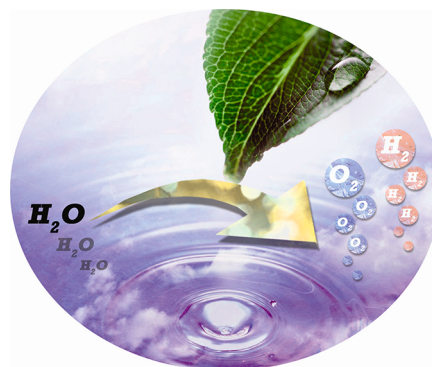
The supply and production of clean and sustainable carbon-neutral energy will unquestionably be the 21st century's most demanding scientific challenge. One attractive option that holds sufficient potential to feed this process on a global scale would be to use the energy derived from sunlight to split H_2O into O_2 and couple it with the production of solar fuels, such as H_2. Here, Nature provides us with an excellent example of how this can be achieved, thus making it attractive to mimic the basic principles of natural photosynthesis for the sustainable production of renewable solar fuels.[1-4]

Photosynthesis: Nature's Masterpiece

About 2 billion years ago, Nature developed an extraordinary process for storing solar energy, by converting H_2O and CO_2 into carbohydrates and other valuable chemical feedstocks, such as ATP. To accomplish this demanding task, it is important to efficiently combine several complex features: light-harvesting by a chromophore, charge separation, electron transfer (ET), oxidation of H_2O, and finally reduction of the generated protons.[5]

Light-Induced Charge Separation. The first step in the multistep process of photoinduced splitting of H_2O is the

absorption of a photon by chlorophyll and other light-absorbing pigments. They efficiently transfer the captured energy to the reaction center of photosystem (PS) II, P_{680}, resulting in an excited state (P_{680}*). From the excited state of P_{680}, ET occurs to a pheophytin molecule, whereby the electron is passed along a transport chain to finally end up in PS I for the reduction of $NADP^+$ and production of "H_2" in the form of NADPH. However, the primary charge-separated state that is created is short lived and would recombine without this series of ET processes. The key to efficient harnessing of the absorbed sunlight is to create a charge-separated state where the electrons and electron holes are sufficiently separated from each other. The oxidized form of P_{680}, $P_{680}^{\bullet+}$, is a strong oxidant with an oxidation potential of ca. $+1.2$ V versus the normal hydrogen electrode (NHE). Regeneration of the P_{680} reaction center is accomplished by the abstraction of an electron from the oxygen evolving complex (OEC) via a redox-active tyrosine moiety (Tyr$_z$).[1−5]

The Oxygen Evolving Complex: The H_2O Splitting Site. The electrons that are used to convert CO_2 into valuable building blocks are ultimately derived from H_2O. At the heart of PS II, resides the so-called OEC, which is responsible for catalyzing the four-electron oxidation of H_2O. After four consecutive electron abstractions from the OEC, two molecules of H_2O are converted into one molecule of O_2 and four protons. The elaborate core of the OEC consists of a tetranuclear manganese complex with a calcium atom in close proximity (Mn_4Ca).[6] It is surrounded by amino acids, which are essential for stabilizing the OEC by charge neutralization and promoting proton-coupled electron transfer (PCET).

Artificial Photosynthesis

The photoinduced splitting of H_2O requires interfacing several fundamental but challenging photophysical steps with complicated chemical transformations. During the last four decades great efforts have been devoted to develop systems that are capable of mimicking the basic principles of Nature for conversion of solar energy into chemical energy. The key components in an artificial system for H_2O splitting are a light-absorbing photosensitizer, a water oxidation catalyst (WOC), that is, a catalyst that refills the holes that are created, and a reduction catalyst that converts the generated electrons and protons to solar fuels. The essential feature in realizing artificial photosynthesis is the coupling of the one-photon−one-electron charge separation events to the four-electron oxidation of H_2O.[1]

Coupling Light Sensitization to Electron Transfer. In the late 1990s, we initiated a project dedicated to developing

man-made systems that mimicked the basic principles of the reaction center in PS II. It was decided to synthesize simple model systems where a [Ru(bpy)$_3$]$^{2+}$-type photosensitizer (bpy = 2,2′-bipyridine) was covalently coupled to a redox-active moiety containing manganese or tyrosine. It was anticipated that upon illumination of the [Ru(bpy)$_3$]$^{2+}$ moiety, the excited state of ruthenium(II) would deliver an electron to the external acceptor to yield ruthenium(III). The generated hole would subsequently be refilled by an intramolecular ET from the incorporated redox-active moiety. The [Ru(bpy)$_3$]$^{2+}$-type complexes were chosen because they have been studied for several decades as a result of their long-lived excited state lifetimes, high chemical and thermal stability, and easy functionalization.[7]

Our first attempts in achieving this focused on linking a mononuclear manganese complex to a ruthenium photosensitizer. Our approach resulted in the synthesis of the heterobimetallic assemblies **1**−**8** (Figure 1).[8,9] Flash photolysis experiments of complex **1** and the corresponding complex without the manganese center, in the presence of an external electron acceptor (methyl viologen, MV^{2+}), confirmed that ET occurred from the excited ruthenium center to MV^{2+} to generate [Ru(bpy)$_3$]$^{3+}$ and MV$^{\bullet+}$. Regeneration of [Ru(bpy)$_3$]$^{2+}$ proved to be 1 order of magnitude faster for **1** than for the complex lacking the manganese, supporting that intramolecular ET takes place to give a manganese(III) species. The process displayed first-order kinetics with a rate constant of 1.8×10^5 s^{-1}.

Additional proof that the manganese(II) moiety in **1** is able to reduce the photogenerated [Ru(bpy)$_3$]$^{3+}$ species was afforded by electron paramagnetic resonance (EPR). Since both manganese(II), with $S = 5/2$, and [Ru(bpy)$_3$]$^{3+}$ are EPR active, ET from the manganese(II) moiety should drastically alter the EPR spectra. Mixing equimolar amounts of [Ru(bpy)$_3$]$^{3+}$ (chemically generated) and **1** resulted in the disappearance of the characteristic peaks for the starting compounds, highlighting that [Ru(bpy)$_3$]$^{3+}$ is capable of oxidizing manganese(II) to manganese(III). This work demonstrated for the first time that coupled ruthenium−manganese systems can undergo intramolecular ET to the photooxidized ruthenium(III) center in the presence of an external electron acceptor, thereby mimicking the concept of Nature.

Additional work focused on investigating the different parameters that influenced the efficiency and rates of the excited state quenching and the intramolecular ET between the manganese moiety and the photogenerated ruthenium(III).[10] The recovery of ruthenium(II) was found to be
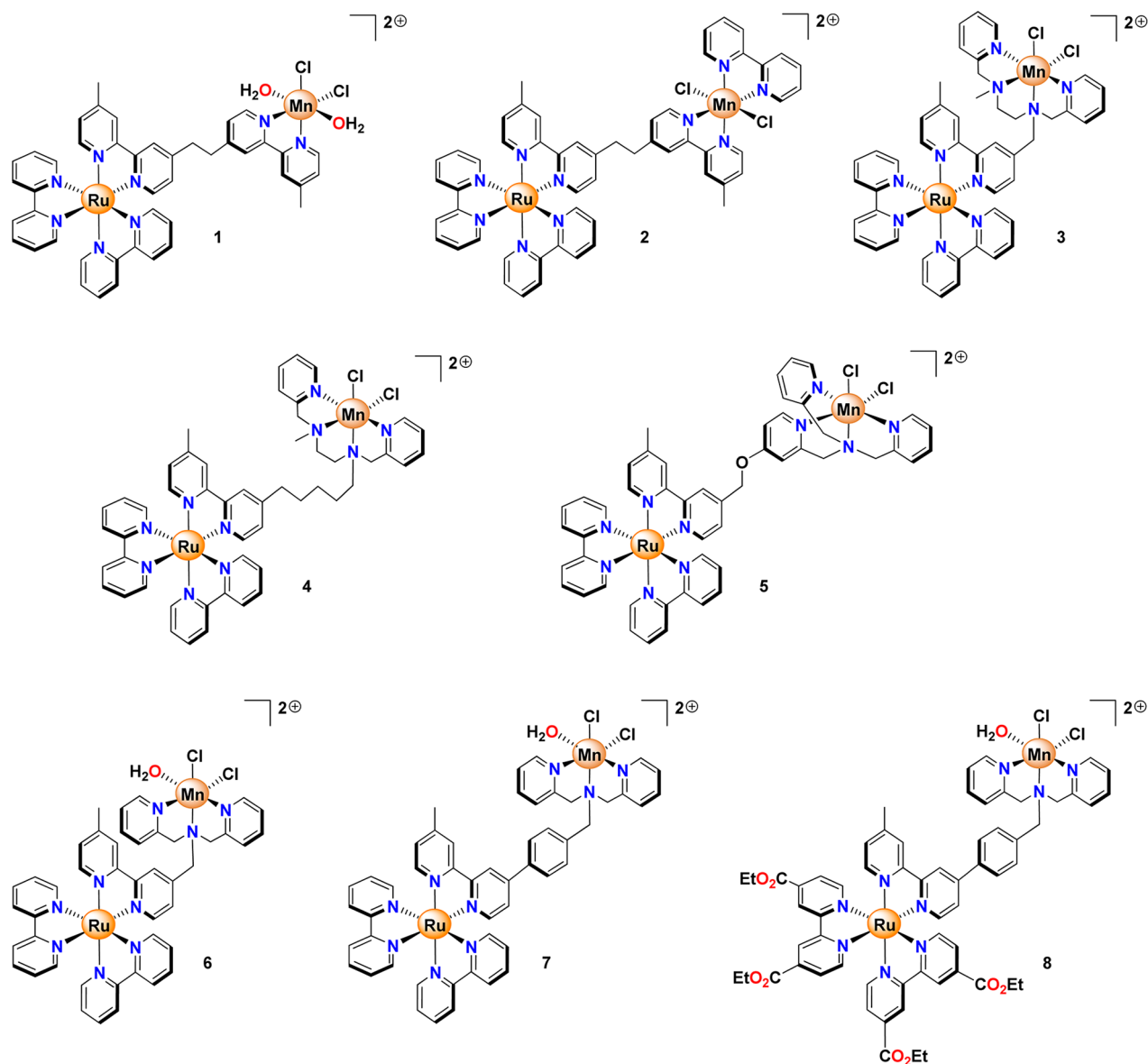
FIGURE 1. Molecular structures of the coupled ruthenium–manganese complexes **1**–**8**.

independent of the concentration of complexes **1**–**8**, establishing that the ET occurs intramolecularly. This work showed that the quenching rate constant decreased exponentially with the metal-to-metal distance for complexes **1**–**8**. More importantly, it demonstrated that it is possible to increase the excited state lifetime with unchanged metal-to-metal distance by tuning the ligand environment. Although complexes **4**, **7**, and **8** all have approximately the same metal-to-metal distance, the excited state lifetime of **7** is significantly shortened. This dramatic difference can be ascribed to the fact that the excited state in **7** is delocalized over the phenyl ring that is linking the ruthenium and manganese moieties together, bringing the excited state closer to the manganese moiety and shortening the lifetime.

The introduction of electron-withdrawing substituents on the bpy ligands made it possible to localize the excited state on these ligands and thus increase the distance to the manganese moiety. This is clearly demonstrated by the dramatic differences in excited state lifetimes of **7** (23 ns) and **8** (1200 ns). Furthermore, it was established that the ET rate was not only dependent on the metal-to-metal distance and that variations in reorganization energy and electronic coupling were also important.

As observed from our initial work, having a too short distance between the ruthenium- and manganese centers resulted in undesirable quenching of the excited photosensitizer. It was thought that introducing a spacer between the ruthenium chromophore and the manganese moiety would
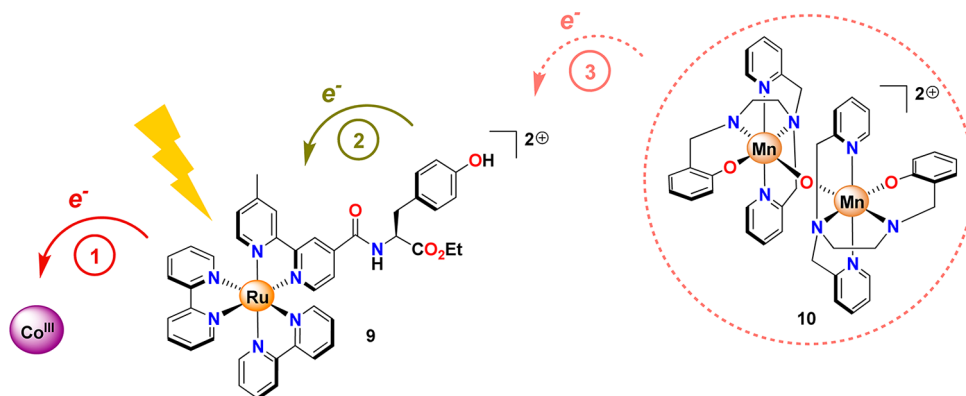
FIGURE 2. Light-induced electron transfer in an artificial triad consisting of the ruthenium−tyrosine assembly **9** and the Mn$_2^{III,III}$ complex **10**.

be favorable. This modification should preferably not quench the excited state of the photosensitizer and the reorganization energy should be lower than for the manganese moiety, allowing for faster ET. In Nature, a redox-active tyrosine unit (Tyr$_z$) is involved in the ET between P$_{680}$ and the OEC. We therefore prepared a supramolecular assembly consisting of a tyrosine unit linked to a ruthenium(II) photosensitizer (Figure 2).[11]

When the tyrosine containing compound **9** was studied by time-resolved emission spectroscopy, in the absence of any electron acceptors, negligible quenching was observed by the tyrosine unit. However, addition of one of the electron acceptors, MV^{2+} or pentaamminechlorocobalt(III) chloride ([Co(NH$_3$)$_5$Cl]$^+$, Co^{III}), resulted in a decreased emission lifetime. With transient absorption spectroscopy, the electron transfer was followed for compound **9** and a reference compound, lacking the tyrosine unit. The reference compound exhibited similar behavior as [Ru(bpy)$_3$]$^{2+}$. A deviating result was observed with the tyrosine containing compound **9**, which displayed an increased rate for the ruthenium(II) recovery. This effect suggested that intramolecular ET from tyrosine to photogenerated ruthenium(III) occurred in **9**, regenerating ruthenium(II) and forming a tyrosyl radical. Further support for this tyrosine−ruthenium ET was afforded by EPR measurements, in which an EPR signal at $g = 2.0045$ was generated and ascribed to a tyrosyl radical. To prove that ET indeed took place intramolecularly, the ET for the separate components (i.e., tyrosine and [Ru(bpy)$_3$]$^{2+}$) was studied. This demonstrated that the tyrosine enhanced the ruthenium(II) recovery but to a lower extent compared with the coupled system **9**.

The intriguing results derived with compound **9** led us to test whether a suitable manganese complex could be photooxidized by **9**.[12] Our expectation was that the photogenerated tyrosyl radical would possess enough oxidizing power

to oxidize the external manganese complex in a controlled fashion, to allow for efficient ET to occur. If successful, this biomimetic approach would mimic several important aspects in the natural photosynthetic machinery. The Mn$_2^{III,III}$ complex **10** would be an excellent candidate, because the one-electron oxidation product, the mixed-valence Mn$_2^{III,IV}$, is stable and EPR-active. Combined flash photolysis and EPR measurements of a reaction mixture containing **9**, manganese complex **10**, and an electron acceptor (MV^{2+} or Co^{III}), resulted in the 16-multiline signal characteristic of a mixed-valence Mn$_2^{III,IV}$ species. Solutions lacking either **9** or the manganese complex did not result in any observable 16-multiline signal, verifying that the Mn$_2^{III,IV}$ is generated from light-dependent reactions. Transient EPR measurements in the absence of **10** revealed that the photogenerated ruthenium(III) center was reduced via intramolecular ET from the tyrosine moiety (*vide supra*). However, addition of manganese complex **10** resulted in a faster decay of the tyrosyl radical, establishing that manganese complex **10** mediates ET to it. The promising findings with this system were significant steps toward realizing ruthenium−manganese-based systems for artificial photosynthesis.

Based on the collected data from our synthesized model systems, a dinuclear manganese(II,II) complex was connected to a ruthenium photosensitizer through an amide link to generate the trinuclear supramolecular assembly **11** (Figure 3).[13,14] Emission lifetime measurements confirmed that the manganese centers in **11** had a profound influence on the quenching of the ruthenium excited state. From flash photolysis experiments of **11**, it could be seen that the generated ruthenium(III) species was not reduced by recombination of ruthenium(III) and MV$^{•+}$. The recovery of the ruthenium(II) was essentially complete in less than 100 ns, and instead intramolecular ET from the dinuclear manganese moiety had occurred. The ET events were found to be
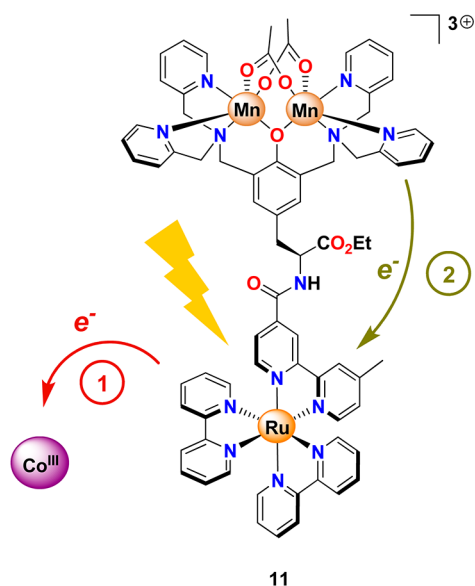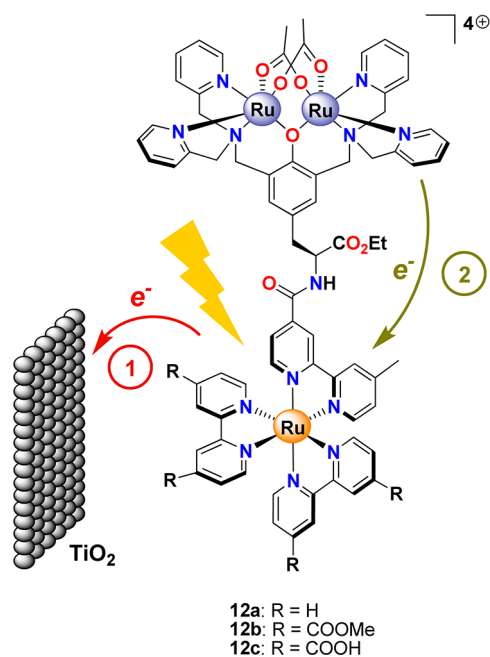
FIGURE 3. The coupled Ru−Mn$_2$ system **11**, where the Mn$_2^{II,II}$ unit is capable of mediating three consecutive electron transfers to the photogenerated Ru^{III} to generate Mn$_2^{III,IV}$.

FIGURE 4. Coupled Ru−Ru$_2$ systems for photoinduced electron transfer.

limited by the initial quenching of the MV^{2+}, indicating that the rate constant for the intramolecular ET from the manganese moiety to the generated ruthenium(III) is greater than $1 \times 10^7 \ s^{-1}$. This is an enhancement by 2 orders of magnitudes compared with other ruthenium−manganese dyads with comparable ruthenium−manganese distances (∼16 Å).

In related studies, Wieghardt and co-workers presented a trinuclear manganese complex coupled to an array of six [Ru(bpy)$_3$]$^{2+}$-type photosensitizers, where it was shown that after excitation and transfer of an electron to an acceptor, the Mn$_3^{II}$ cluster was oxidized to Mn$_2^{II}$Mn^{III}.[15]

Charge separation with single electronic transitions is relatively easy to accomplish, but additional hurdles appear when carrying out multi-electron transfer. The excited ruthenium(II) is a strong reductant and has the possibility of being oxidatively quenched by any intermediate with a higher redox potential. Therefore, absorption of the next photon by the ruthenium chromophore increases the driving force for the oxidized manganese complex to become reduced by ET from the excited state of the ruthenium(II) chromophore. This is a nonproductive and energy wasting reaction that obviously cannot be avoided by manipulating the redox potentials. Instead, it has to be resolved by rendering the backward reaction slow compared with the forward ET from the ruthenium(II) excited state.

The question now was whether we could extract several electrons from the manganese moiety, allowing for multi-step oxidations. To answer this question, flash photolysis

and EPR measurements were combined. When **11** was subjected to several flashes (in aqueous solutions), EPR showed that the manganese centers in **11** were oxidized three steps to generate the Mn$_2^{III,IV}$ species. Electrochemical measurements showed that the presence of H$_2$O had a profound effect on the redox chemistry of the dinuclear manganese moiety in **11**. The addition of H$_2$O alters the cyclic voltammogram of **11** where the most significant alteration is lowering of the Mn$_2^{III,IV}$/Mn$_2^{III,III}$ redox potential. It is assumed that when the Mn$_2^{III,III}$ state is reached, ligand exchange occurs in the presence of H$_2$O. Replacement of the acetate ligands by aqua ligands enables the complex to access the Mn$_2^{III,IV}$ state by allowing for PCET. This reduces the overall charge of the complex and allows for the generation of the Mn$_2^{III,III}$ state by the photochemically generated ruthenium(III), a key element for performing multi-electron transfer and catalysis.

Continued work addressed linking a dinuclear ruthenium unit to a ruthenium chromophore, which resulted in assemblies **12a−c** (Figure 4).[16] Surprisingly, quenching of the [Ru(bpy)$_3$]$^{2+}$ chromophore excited state was very efficient. Even attachment of carboxyl groups to the chromophore, which had proven to be efficient with the corresponding manganese dyads, failed, and the lifetime remained short. However, attaching dyads **12b** and **12c** to nanostructured TiO$_2$ allowed for charge separation thanks to the extremely fast electron injection from the excited ruthenium(II) state into the conduction band of TiO$_2$. Recently, several
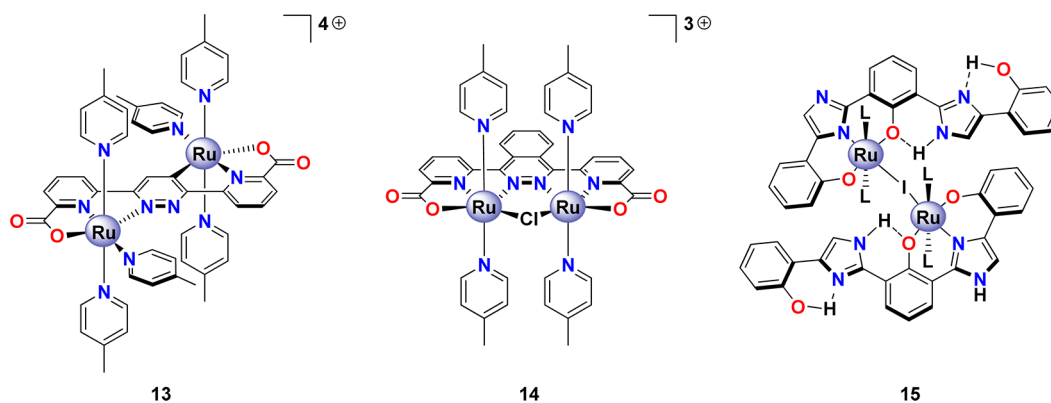
FIGURE 5. Molecular structures of complexes **13**–**15**.

examples have appeared where a ruthenium photosensitizer has been coupled to a ruthenium WOC and subsequently attached to an electrode, which splits H_2O photo(electro)-chemically.[17,18]

Water Oxidation Catalysis

The four-electron oxidation of H_2O manages to connect single-electron chemistry with multi-electron catalysis. One way of facilitating this complicated task would be to involve PCET. PCET is of fundamental importance in many biological and chemical process, and involves the coupling of electron transfer to proton transfer, which has a profound effect in the natural H_2O oxidation. PCET permits the total charge of a chemical species to remain unchanged, whereas just single-electron transfers without the loss of a proton leads to charge build-up and high-energy intermediates. Coupling electron transfer to proton transfer may open a route for the accumulation of multiple redox equivalents at single metal centers and influence reaction pathways and energetics of a chemical reaction.[19]

Introducing Negatively Charged Groups into the Ligand Backbones of Water Oxidation Catalysts. Most of the developed WOCs suffer from a serious drawback; in order for the oxidations to be thermodynamically favorable, they need to be driven by a strong oxidant, such as ceric ammonium nitrate (Ce^{IV}). Since Ce^{IV} cannot be photochemically regenerated from Ce^{III}, its use in large scale applications is questionable. An appealing and more viable approach would be to drive H_2O oxidation with $[Ru(bpy)_3]^{3+}$ that can be photogenerated from the corresponding $[Ru(bpy)_3]^{2+}$-type complex.

This could be accomplished by lowering the catalyst redox potentials by the introduction of anionic functionalities (i.e., substituents that have the possibility to be deprotonated) into the ligand frameworks of WOCs. Our

group has previously shown that negatively charged groups in the ligand backbones decreased the redox potentials of the corresponding metal complexes.[20,21] Replacing the benzylic amines in these complexes by more robust functional groups, in combination with phenolic and carboxylic groups, would hopefully favor proton-coupled events and result in active WOCs with low redox potentials. This led to the development of complexes **13**–**15** (Figure 5),[22−25] which were all active WOCs and had significantly decreased redox potentials compared with earlier WOCs based upon neutral polypyridyl ligands.

Molecularly Defined Single-Site Ruthenium Water Oxidation Catalysts: Simple and Efficient. Based on the efficiency of complex **15**, it was envisioned that the two molecularly defined single-site ruthenium complexes **16** and **17** housing two benzimidazole-based meridionally coordinating ligands were promising ligand backbones and could favor proton-coupled events (Figure 6).[26] In order to assess the catalytic activity, real-time mass spectrometry (MS) measurements were used to detect the evolved gaseous products during catalysis. To our delight both complexes were active WOCs, when either pregenerated or photogenerated $[Ru(bpy)_3]^{3+}$-type complexes were used as oxidant. In the chemical oxidations, it was revealed that complex **16** generated a high turnover number (TON) and a high turnover frequency (TOF).

Electrochemical measurements showed that the redox potentials of both complexes were significantly lowered compared with other ruthenium WOCs housing neutral ligands, together with an electrocatalytic wave for H_2O oxidation starting at 1.24 V vs NHE (at pH 7). Support for a ligand exchange process in which a picoline is exchanged by a solvent H_2O molecule, to generate the important ruthenium–aqua species, was obtained from UV–vis spectrophotometric titration, along with high-resolution MS experiments. We could also
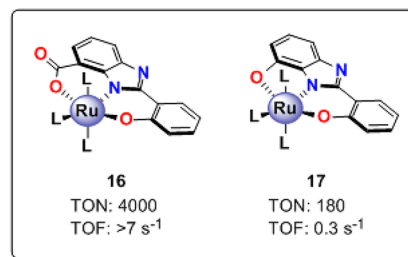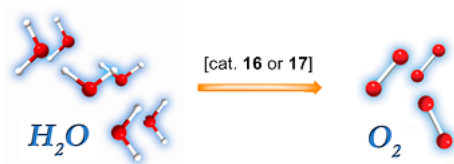
FIGURE 6. Water oxidation catalysis by the single-site ruthenium complexes **16** and **17**. L = 4-picoline.
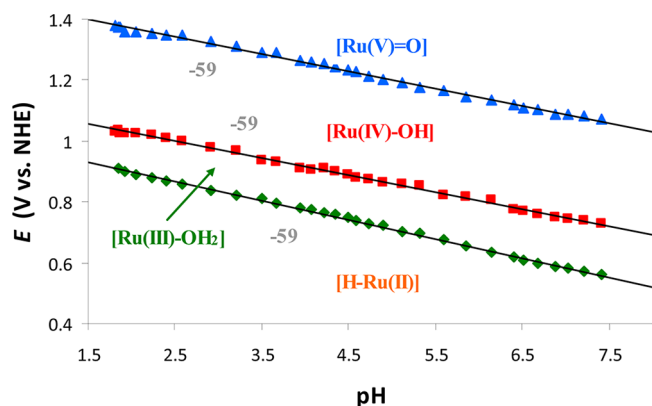

FIGURE 7. Pourbaix diagram of complex **16** (where H−Ru(II) corresponds to the ruthenium(II) complex with the protonated imidazole). Adapted with permission from ref 26. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

observe the high-valent Ru^V=O intermediate by MS, regarded as the key intermediate in H_2O oxidation.[27] Finally, the Pourbaix diagram (potential/pH diagrams) for complex **16** was constructed since this type of diagram is a valuable tool and points out possible stable (oxidation) states of a system. The Nernst equation reveals that the potential for a one-electron−one-proton redox reaction will change by -59 mV per pH unit and for a two-electron−one-proton redox reaction this change will be -29 mV per pH unit. This distinguishes redox processes that are proton-coupled from nonproton-coupled, that is, only processes associated with the loss of one or more protons will display a pH-dependent behavior. The Pourbaix diagram of complex **16** showed that all three redox couples, Ru^{III}/Ru^{II}, Ru^{IV}/Ru^{III}, and Ru^V/Ru^{IV}, were pH-dependent with slopes of -59 mV per pH unit (Figure 7). This suggests that the imidazole unit is involved in the redox processes and can participate as a proton mediator.

The amide bond is one of the most, if not the most, essential bonds occurring in biological systems. It represents the fundamental backbone in peptides, enzymes, and a vast array of natural products. Although transition metal complexes containing amines (-NR$_3$) or amides (-NR$_2$) are well explored, complexes containing *N*-amidato (deprotonated

amide) ligands are still relatively exotic. An important feature of *N*-amidato ligands is that they display strong σ-donor ability from the coordinated nitrogen(s). This stabilizes the metal center and allows access to high oxidation states. It was envisioned that a tailored catalyst design based upon the tetradentate ligand H$_2$bpb (H$_2$bpb = *N,N'*-1,2-phenylene-bis(2-pyridine-carboxamide) would afford active ruthenium WOCs.[28] This tetradentate ligand contains two sites with dissociable protons, and the readily accessible ligand scaffold offers an easily modified environment. This is an important factor for the tuning of future WOCs and in the construction of integrated supramolecular assemblies for overall H$_2$O splitting.

Complex **18** was found to be capable of driving H_2O oxidation with [Ru(bpy)$_3$]$^{3+}$ as chemical oxidant. Under the highly oxidizing conditions required to carry out the oxidation of H_2O, the WOCs decompose or deactivate after a certain period of time. This is a serious and general issue encountered with WOCs and insight into the deactivation pathways is necessary if more efficient WOCs are to be developed. Examining the reaction mixtures after O$_2$ evolution had ceased showed the appearance of a peak at *m/z* 462.9985, corresponding to [Ru(bpb)(CO)(H$_2$O) (**19**) − H$^+$]$^-$ (Figure 8). During H_2O oxidation, CO and CO$_2$ are usually observed due to decomposition of the organic components, arising either from the catalyst itself or from the [Ru(bpy)$_3$]$^{3+}$ oxidant. This constitutes the source of CO and explains the conversion of complex **18** into **19**. These results imply that the generated complex **19** is not active in H_2O oxidation and to affirm this, **19** was synthesized separately. Several attempts were performed to utilize complex **19** for H_2O oxidation, but none produced detectable amounts of O$_2$.

To elucidate the fundamental difference in reactivity between complexes **18** and **19**, the Pourbaix diagrams were constructed (Figure 9). The Pourbaix diagram for **18** revealed that H_2O coordinates to the low-valent ruthenium(II) center as a seventh ligand, due to the large bite angle (115°) offered by the ligand. A key feature observed from these
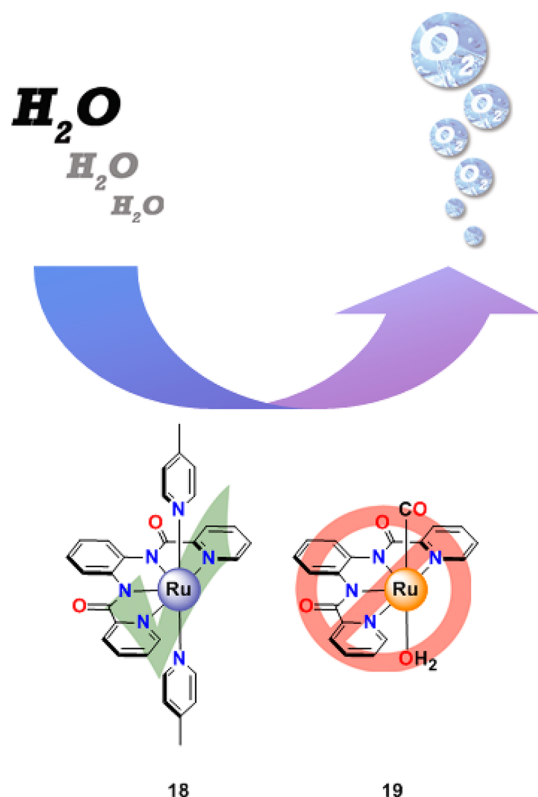
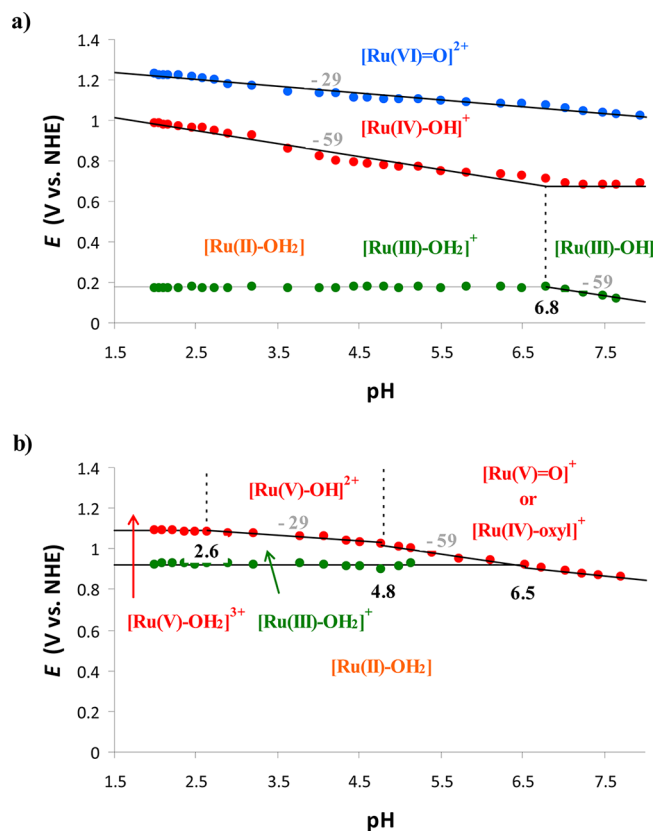**FIGURE 8.** Structures of the active ruthenium-based WOC **18** and the inactive complex **19**.

FIGURE 9. Pourbaix diagrams of (a) complex **18** and (b) complex **19** in the range $1.5 < pH < 8.0$ (pK_a values are denoted by the vertical dashed lines). Reprinted with permission from ref 28. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

electrochemical measurements is that catalytic H_2O oxidation occurs after the $Ru^{IV} \rightarrow Ru^{VI}$ oxidation, suggesting that the Ru^{VI} oxidation state initiates O_2 evolution. This is exceptional and differs from a majority of reported single-site ruthenium-based WOCs, in which the catalysts usually reach the ruthenium(V) state, which has enough power to mediate H_2O oxidation. Several attempts to detect this high-valent Ru^{VI} species by MS were made without any success, probably due to the high reactivity of this ruthenium species. The Pourbaix diagram for the CO-containing complex **19** shows that the complex only reaches the ruthenium(V) state. The observed diverse catalytic activity toward H_2O oxidation for the two ruthenium complexes might be ascribed to the fact that it is essential for the catalyst to reach the ruthenium(VI) state, in order to enable H_2O oxidation.

Manganese-Based Water Oxidation Catalysts. Special attention has been devoted to developing catalysts based upon earth-abundant metals, in particular manganese, due to its low cost and biomimetic nature. Although a variety of molecular manganese complexes have been prepared to mimic the structural motif of the natural system,[29,30] only a handful of them have been reported to evolve O_2.[31−33]

Early work in our laboratories focused on systems based on corroles, which are naturally occurring macrocyclic ligands and known to stabilize the coordinated metal centers in high-valent oxidation states. We therefore decided to synthesize the mono- and bis-manganese corroles **20** and **21** (Figure 10).[34] In **21**, the two corrole units are situated in a face-to-face manner, which keeps the two metal centers in a close and rigid environment that is beneficial in stabilizing the metals in high-valent states. The xanthene moiety was employed as the bridge between the two corrole moieties since it offered more flexibility compared with the often employed aryl bridge. In the monocorrole complex **20**, the xanthene unit could participate by coordinating an aqua ligand to the metal center through hydrogen bonding.

Electrochemical measurements of the two corrole complexes verified that high-valent oxidation states could be reached at relatively low potentials. The bis-corrole complex **21** also showed that there existed an intramolecular interaction between the two manganese centers. These intriguing properties encouraged us to examine the possibility of mediating H_2O oxidation with the developed
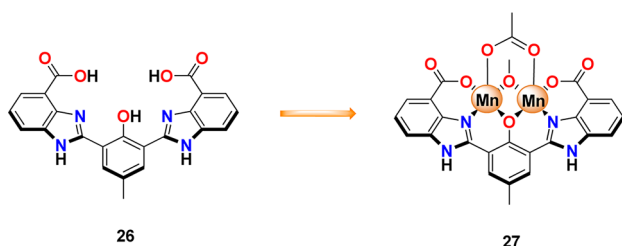
FIGURE 10. Molecular structures of manganese-based water oxidation catalysts.

SCHEME 1. Plausible Mechanistic Cycle for O_2 Evolution by Manganese Corrole Complex **22**

manganese corrole complexes. The catalytic activities of the two complexes were studied by electrochemistry. Upon scanning to anodic potentials ($E > 0.8$ V vs. Ag/Ag$^+$), a reduction peak appeared at -1.29 V for both complexes, which could be assigned to the reduction of O_2. This study proved that manganese complexes could be used for H_2O oxidation and that the formation of high-valent manganese at low redox potentials could be the key feature in the developed complexes.

Density functional theory (DFT) calculations suggested that O_2 formation from complexes **20** and **21** occurred via nucleophilic addition of H_2O (or OH$^-$) to a Mn^V=O intermediate.[35] To obtain experimental evidence for this

mechanism, it was decided to prepare the related manganese corrole complex **22** which had the possibility of forming a stable Mn^V=O species.[36] The addition of the oxidant *t*-BuOOH generated the Mn^V=O, and the subsequent addition of (*n*-Bu)$_4$NOH triggered rapid O_2 evolution, as verified by real-time MS measurements. The catalytic intermediates responsible for the O_2 formation could be observed by the combined use of electronic absorption spectra and high-resolution MS. The assumed mechanism by which H_2O is oxidized is depicted in Scheme 1 and begins with generation of the high-valent Mn^V=O species **23**. This is subsequently attacked by hydroxide to afford a manganese(III)-hydroperoxy intermediate (**24**). Further oxidation results in the

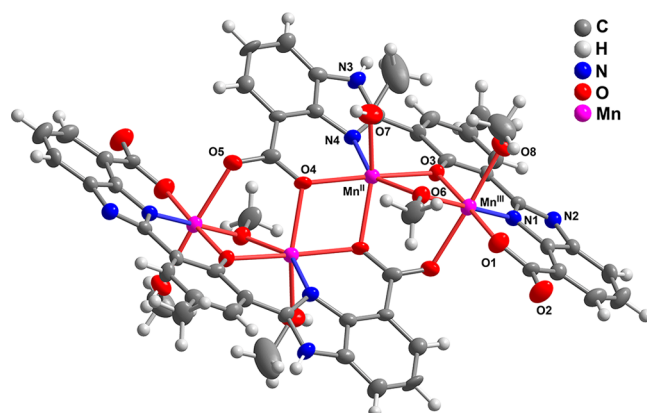**FIGURE 11.** Molecular structures of ligand **26** and the dinuclear $Mn_2^{II,III}$ complex **27**.

FIGURE 12. Crystal structure of the tetranuclear manganese complex generated from complex **27**, with ellipsoids displayed at 50% probability level. Adapted with permission from ref 37. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Mn^{IV}-hydroperoxy, which after loss of a proton gave intermediate **25**. Intermediate **25** may disproportionate with liberation of O_2 or be further oxidized to the Mn^V state, from which O_2 is released to regenerate the starting complex **22**. This work proved that nucleophilic attack of hydroxide on a $Mn^V=O$ intermediate is a viable mechanism for the generation of O_2 from H_2O.

As previously described, the manganese moiety in **11** was capable of delivering three electrons to the photogenerated ruthenium(III) center. A fourth ET would certainly have produced a species with enough power to oxidize H_2O to O_2, but instead probably resulted in decomposition of the dinuclear manganese moiety due to the labile benzylic amines in the ligand. By replacing the benzylic amines with more robust functional groups, we aimed to increase the stability of the ligand and the corresponding manganese complex. It was projected that ligand **26** would accommodate all the necessary features to generate a proper environment for manganese that would result in an active WOC; replacing the benzylic amines with imidazoles would generate a more oxidatively stable ligand and the inclusion of carboxylate functions would promote the lowering of the redox potential of the complex. With ligand **26**, the dinuclear manganese(II,III) complex **27** was obtained (Figure 11), which in the solid state shows a tetranuclear manganese core (Figure 12), resembling the active site of the OEC.[37]

The catalytic activity was first assessed with the mild chemical oxidant $[Ru(bpy)_3]^{3+}$ ($E° = 1.26$ V vs. NHE). When a deoxygenated buffered aqueous solution containing the dinuclear complex **27** was added to the single-electron oxidant, O_2 evolution was immediately detected. After approximately 1 h, the O_2 evolution had ceased, giving a TON of ∼25 and an initial TOF of ∼0.027 s^{-1}. It was also of interest to test whether complex **27** displayed activity in photodriven H_2O oxidation under neutral conditions. The photocatalytic setup consisted of $[Ru(bpy)_3](PF_6)_2$ or $[Ru(bpy)_2(deeb)](PF_6)_2$ (deeb = diethyl 2,2′-bipyridine-4,4′-dicarboxylate) as photosensitizers and persulfate as electron

acceptor. However, with $[Ru(bpy)_3](PF_6)_2$ as photosensitizer only a single turnover could be achieved. Replacing $[Ru(bpy)_3](PF_6)_2$, with $[Ru(bpy)_2(deeb)](PF_6)_2$, which generates a higher oxidation potential and a higher thermodynamic driving force, allowed for four catalytic turnovers.

With several of the previously reported manganese-based WOCs, inconclusive evidence exists regarding the source of the oxygens in the generated O_2. To ensure that both oxygen atoms in the generated O_2 originate from H_2O, experiments were conducted with ^{18}O-labeled H_2O ($^{18}OH_2$). The ratio of $^{16,18}O_2/^{16,16}O_2$ was found to be in agreement with the theoretical value when both oxygen atoms are derived from H_2O, confirming that H_2O is the source of the evolved O_2. Although extensive effort has been dedicated into developing manganese-based complexes capable of mediating the four-electron oxidation of H_2O, this has generally resulted in decomposition of the complexes or formation of heterogeneous manganese oxides as the active catalysts (for in depth discussions, see refs 38 and 39). Our study revealed that the ligand environment afforded by ligand **26** provided a stabilizing surrounding for the manganese centers to allow for catalytic H_2O oxidation by use of the mild single-electron oxidant $[Ru(bpy)_3]^{3+}$, both chemically and photochemically generated. This seems to be the first example of a homogeneous manganese-based catalyst capable of promoting catalytic H_2O oxidation with one-electron oxidants, although the involvement of active metal nanoparticles cannot be ruled out.[38,39]

Conclusions and Future Prospects

The conversion of H_2O into solar fuels holds enormous potential, and here Nature provides us with an excellent

example of how to achieve this. Mimicking the photosynthetic machinery constitutes a central scientific challenge in the route toward a carbon-neutral energy economy and is a prime example of research that requires interplay among numerous different disciplines. The development of more efficient WOCs is highly important for future solar fuel conversion processes and is currently considered to be the bottleneck.

Our intensified efforts in developing new WOCs have resulted in several biomimetically inspired catalysts, both manganese- and ruthenium-based, capable of mediating the oxidation of H_2O, operating under benign conditions. There still exist several difficulties to be overcome before a viable artificial system for production of solar fuels can be realized. But every small finding that is made brings us one step forward toward a sustainable energy future.

BIOGRAPHICAL INFORMATION

Markus D. Kärkäs received his Ph.D. degree in 2013 in organic chemistry at Stockholm University. As a graduate student, Markus carried out research with Professor Björn Åkermark on the development and mechanistic insight of artificial water oxidation catalysts.

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FOOTNOTES

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The authors declare no competing financial interest.

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