DOI: 10.1002/anie.200802659

Artificial Photosynthesis

Molecular Catalysts that Oxidize Water to Dioxygen

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artificial photosynthesis · heterogeneous catalysis · homogeneous catalysis · oxidation · sustainable chemistry

During the past four years we have witnessed a revolution in the field of water-oxidation catalysis, in which well-defined molecules are opening up entirely new possibilities for the design of more rugged and efficient catalysts. This revolution has been stimulated by two factors: the urgent need for clean and renewable fuel and the intrinsic human desire to mimic nature's reactions, in this case the oxygen-evolving complex (OEC) of the photosystem II (PSII). Herein we give a short general overview of the established basis for the oxidation of water to dioxygen as well as presenting the new developments in the field. Furthermore, we describe the new avenues these developments are opening up with regard to catalyst design and performance, together with the new questions they pose, especially from a mechanistic perspective. Finally the challenges the field is facing are also discussed.

1. Introduction

Recently the journal *Inorganic Chemistry* devoted one of its "Forums" to the topic of "Making Oxygen".[1] At the moment this is a very hot topic because of the recent discoveries about the PSII structure and its functioning at a molecular level and also because of its implications for new solar-energy conversion schemes. Actually for the solar-energy conversion schemes a good catalyst capable of oxidizing water to dioxygen and its assembly into a cell for the photo-production of hydrogen is seen as one of the most promising sustainable solutions, not only for our present demands, but also to be able to maintain our lifestyle in the near future.

Potential schemes for the use of sunlight to split water into H_2 and O_2, that is the photo-production of H_2 and O_2, have been recurrently presented but to date have never been put into practice. A recent example has been offered by Aukaloo and co-workers[2] and is shown in Figure 1. This device is based on a modification of the so-called Grätzel cell,[3] where instead of simply generating a photocurrent, the cell is modified to use the electron flow to prepare a storable chemical fuel, in this particular case molecular hydrogen. The cell is made out of two compartments physically separated by a proton exchange membrane and is made basically of three components. The

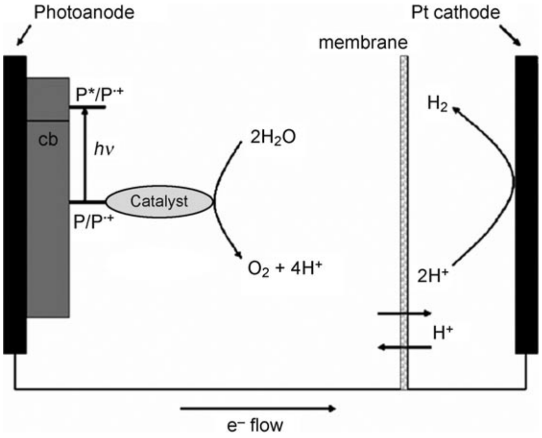

Figure 1. Schematic drawing of a water-splitting photochemical cell with three components: a light-harvesting device attached to a semiconductor photoanode; a water-oxidation catalyst; and a Pt cathode where hydrogen is evolved. For details see text. Reprinted with permission from reference [2].

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first component is the light-harvesting antenna, the photosensitizer P (typically a $[Ru(bpy)_3]^{2+}$ type of complex; bpy = 2,2′-bipyridine), that upon irradiation generates an excited state that in turn transfers an electron to the conduction band of a TiO_2 photoanode semiconductor (TiO_2(cb), cb = conduction band). A very important feature of this Grätzel cell is that upon excitation by light the electron transfer (ET) from the bpy-based excited state into the TiO_2(cb) surface takes place at the pico- to femtosecond time scale and the quantum yield of charge injection exceeds 90 %. These two processes are depicted in Equations (1) and (2) where TiO_2^-(cb) represents the conduction band of the TiO_2 containing a transferred electron.

$$4\,[Ru^{II}(bpy)_3]^{2+} + 4h\nu \rightarrow 4\,[Ru^{III}(bpy^-)(bpy)_2]^{2+} \tag{1}$$

$$4\,[Ru^{III}(bpy^-)(bpy)_2]^{2+} + 4\,TiO_2(cb) \rightarrow 4\,TiO_2{}^-(cb) + 4\,[Ru^{III}(bpy)_3]^{3+} \tag{2}$$

The reaction is indicated four times for stoichiometric reasons (see below). Then the TiO_2 photoanode sends electrons to the second component, which is a Pt cathode where the reduction takes place as indicated in Equations (3)–(5) and that ends up making molecular hydrogen in the right compartment of the cell (Figure 1).

$$4\,TiO_2{}^-(cb) + 4\,Pt \rightarrow 4\,TiO_2(cb) + 4\,Pt^- \tag{3}$$

$$4\,Pt^- + 4\,H^+ \rightarrow 4\,Pt + 4\,H^{\bullet} \tag{4}$$

$$4\,H^{\bullet} \rightarrow 2\,H_2 \tag{5}$$

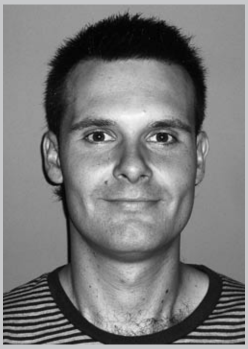
The third component contains the water-oxidation catalyst, in this case represented by $[\{Ru^{II}(H_2O)\}_2]^{n+}$, that is, a diruthenium diaqua complex similar to the ones that will be described later (see Sections 2–4) and whose auxiliary ligands are not shown. The oxidized photosensitizer $[Ru^{III}(bpy)_3]^{3+}$, is now used to oxidize the water-oxidation catalyst to its higher oxidation states that end up making dioxygen in the left compartment of the device (see Figure 1), as illustrated in Equations (6) and (7). Overall Equations (1)–(7) correspond to water splitting by visible light [Eq. (8)].

$$4\,[Ru^{III}(bpy)_3]^{3+} + [\{Ru^{II}(H_2O)\}_2]^{n+} \rightarrow 4\,[Ru^{II}(bpy)_3]^{2+} + [\{Ru^{IV}(O)\}_2]^{n+} + 4\,H^+ \tag{6}$$

$$[\{Ru^{IV}(O)\}_2]^{n+} + 2\,H_2O \rightarrow [\{Ru^{II}(H_2O)\}_2]^{n+} + O_2 \tag{7}$$

$$2\,H_2O + 4h\nu \rightarrow O_2 + 2\,H_2 \tag{8}$$

The water-oxidation catalyst is currently recognized as the bottleneck for the development of devices such as the one described and thus constitutes a very important and urgent



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Montse Rodríguez received her PhD from the Universitat de Girona under the direction of Prof. Antoni Llobet and Dr. M. Corbella (2000). She fulfilled a postdoctoral stay in the Laboratoire de Chimie de Coordination (Toulouse) with Prof. Bernard Meunier and she became full lecturer at Universitat de Girona in 2005. Her research interests are based on the use of transition-metal complexes as catalysts for water oxidation and also for enantioselective organic oxidations, both in homogeneous and heterogeneous phase.

Isabel Romero received her PhD from Universitat Autònoma de Barcelona in 1995. After several years of postdoctoral work in Grenoble (France) she currently holds a position of Professor Titular of Inorganic Chemistry at the Universitat de Girona. Her present research interests are related to transition-metal chemistry, the application of coordination compounds in homogeneous and heterogeneous catalysis, and bioinorganic chemistry.

Lluis Escriche was born in Manresa, Spain, in 1957. He received BS and PhD degrees in chemistry from the Universitat Autònoma de Barcelona in 1982 and 1988, respectively. Since 1990 he has been associate professor of Inorganic Chemistry at this university. His current research interests are the synthesis of coordination complexes with potential abilities as catalyst in different oxidation processes.

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theme to be solved.[4] The topic is so appealing that lately many groups have started to work in this field and as a result very important contributions have recently appeared. The objective of the present Minireview is to give an overview of the key elements described before 2008, and to describe and discuss the new aspects of recent contributions that are reshaping the way we think about this field.

There are a few manganese complexes[5] that have been reported to oxidize water to dioxygen with a very small turnover number (TN), however, they are not free of controversy since in most cases the oxidants used are peroxide or peroxide derivatives, such as oxone or *t*BuOOH. For these oxidants there is an intrinsic difficulty in distinguishing between simple peroxide disproportion and real $4H^+,4e^-$ water oxidation as it happens in the OEC-PSII. Furthermore, most of the manganese complexes do not work with $1e^-$ outer-sphere electron transfer (OSET) oxidants, such as Ce^{IV}, or with potentiostatic methods. In contrast, a number of Ru and Ir complexes have been shown to excel in catalyzing the oxidation of water to dioxygen and thus are the focus of this Minireview.

2. Description of the Water-Oxidation Processes at a Molecular Level

Nature takes advantage of proton-coupled electron transfer (PCET) in a variety of enzymatic processes, for example, those involving vitamin B_{12}, cytochromes P_{450}, and lipoxygenases.[6] Another important example of PCET is the activation of PSII toward water oxidation. Oxidative quenching of a chlorophyll excited state P_{680}* by a bound Q_A plastoquinone generates the ^-Q_A–$P_{680}{}^+$ complex in which there is charge separation. This step is followed by fast electron transfer (ET; on the μs to ns timescale), from Tyr161 (Tyrosine-161) to $P_{680}{}^+$ which are separated by approximately 10 Å, to give the neutral species P_{680} and the tyrosine radical TyrO$^\bullet$ together with a released proton. This process becomes energetically favored thanks to a proximal histidine residue, His190, that picks up the released proton. Thus this process is an example of multiple-site coupled electron proton transfer (MS-EPT) [Eqs. (9) and (10)].[7] The process shown in Equation (10) is

$$Q_A - P_{680} \xrightarrow{h\nu} Q_A - P_{680}{}^* \rightarrow {}^-Q_A - P_{680}{}^+ \qquad (9)$$

$$[{}^-Q_A - P_{680}{}^+ + \mathrm{TyrOH} + \mathrm{His}] \rightarrow [{}^-Q_A - P_{680} + \mathrm{TyrO}^\bullet + \mathrm{H\text{-}His}^+] \qquad (10)$$

thermodynamically favored by $\Delta G^\circ = -8.4\ \mathrm{kcal\,mol^{-1}}$. It is important to realize that stepwise processes where first the proton and then the electron are transferred (PT–ET) or vice versa (ET–PT) incur serious energy penalties of 6.0 and 1.8 kcal mol^{-1} respectively.[7b]

In the following step, the TyrO$^\bullet$ radical species oxidizes the OEC tetranuclear manganese complex through a series of electron and proton transfer processes, finally releasing dioxygen; this sequence of redox reactions is known as the Kok cycle and is the subject of intense research.[8] Thus the tetranuclear manganese complex acts as a water-oxidation catalyst, in a photochemically induced reaction that occurs in the dark.

The water oxidation reaction is a thermodynamically demanding reaction since $E^0 = 1.23$ V (vs. standard hydrogen electrode) at pH 0. It is an example of PCET as shown in Equation (11). This reaction is of enormous molecular com-

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (11)$$

plexity from a mechanistic perspective, since formally it involves the removal of four protons and four electrons from two water molecules, together with the formation of an oxygen–oxygen bond, and therefore an important reaction to be modeled. Recently substantial efforts have been directed at elucidating the OEC-PSII structure and the mechanisms of the water oxidation that takes place at it.[9–13] These efforts can provide fundamental information required to generate low-molecular-weight structural and functional models.

Most of the ruthenium complexes described that are capable of oxidizing water to dioxygen are based on, or are precursors of, the so-called Ru−OH_2/Ru=O system discovered by Meyer's group about three decades ago.[14] The capacity of ruthenium aqua polypyridyl complexes to lose protons and electrons and easily reach higher oxidation states[15] is exemplified in Equation (12) with L_5 = polypyri-

$$[L_5Ru^{II}-OH_2] \underset{+H^+ +e^-}{\overset{-H^+ -e^-}{\rightleftharpoons}} [L_5Ru^{III}-OH] \underset{+H^+ +e^-}{\overset{-H^+ -e^-}{\rightleftharpoons}} [L_5Ru^{IV}=O] \qquad (12)$$

dylic ligand. The higher oxidation states are accessible within a narrow potential range mainly because of the σ–π-donation character of the oxo group. In addition, the simultaneous loss of protons and electrons precludes an otherwise highly destabilized scenario with highly charged species. Thus PCET again provides energetically reasonable reaction pathways that avoid high-energy intermediates. For instance, for the comproportionation reaction of $[LRu^{II}-OH_2]$ and $[LRu^{IV}=O]$ to give two molecules of $[LRu^{III}-OH]$ ($L = (bpy)_2(py)$), the energy penalty for a stepwise process is more than 12.6 kcal mol^{-1} for ET–PT and more than 13.6 kcal mol^{-1} for PT–ET, whereas the concerted pathway is exothermic by −2.5 kcal mol^{-1}. Furthermore the energy of activation for the concerted process is 10.1 kcal mol^{-1} and is lower than the thermodynamic value of any of the stepwise pathways.[16]

A large amount of literature has emerged related to these types of systems, mainly because of the rich oxidative properties of the Ru^{IV}=O species. Reaction mechanisms for the oxidation of several substrates by Ru^{IV}=O have been established and catalytic oxidation systems described.[17] The Ru−OH_2/Ru=O system provides low-energy oxidation pathways for a $2H^+,2e^-$ loss; it follows that the design of a complex containing two Ru−OH_2 groups with the adequate redox potentials should be able to provide low-energy pathways for the $4H^+,4e^-$ loss required for the oxidation of water to O_2 [Eq. (11)]. Finally, to be able to make oxygen, another inevitable requirement is naturally the formation of an oxygen–oxygen bond.

3. Meyer's Pioneering Work

3.1. The Blue Dimer

In 1982 Meyer's group[18a] reported the synthesis, structure, and electrochemical properties of a dinuclear complex *cis,cis*-$[(bpy)_2(H_2O)Ru(\mu\text{-}O)Ru(H_2O)(bpy)_2]^{4+}$ (**1**; Scheme 1 shows all the ligands reported in this Review). This complex is commonly known as the "blue dimer" ($\lambda_{max} = 637$ nm; $\varepsilon = 21100$ at pH 1.0).[18] This dimer contains two Ru^{III}–OH_2 groups, the two ruthenium centers are bridged by a dianionic oxide ligand, and the rest of the available positions for an octahedral type of coordination are occupied by bpy ligands (Figure 2). It is also important to note that the aqua ligands are *cis* with regard to the oxide bridging ligand and their relative torsion angle is 65.7°.

A thorough thermodynamic picture of the zones of stability of the different oxidation states of the blue dimer is offered by its Pourbaix diagram (also known as a potential/pH diagram, a Pourbaix diagram maps out stable (equilibrium) phases of an aqueous electrochemical system). In lower oxidation states, such as III,II, this complex undergoes reductive cleavage of the Ru–O–Ru bond within the cyclic voltammetry time scale, leading to the corresponding mononuclear complexes; a behavior typical for this type of oxide-bridged compounds.[21] As this is a chemically irreversible process the thermodynamic redox potential can not be easily obtained and is thus not shown in the Pourbaix diagram.

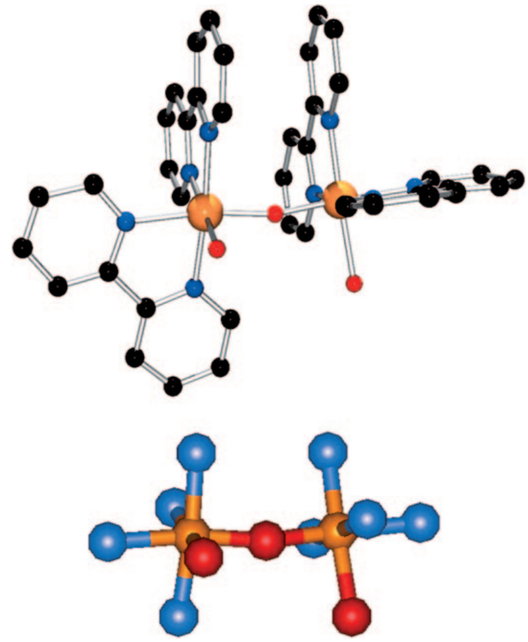
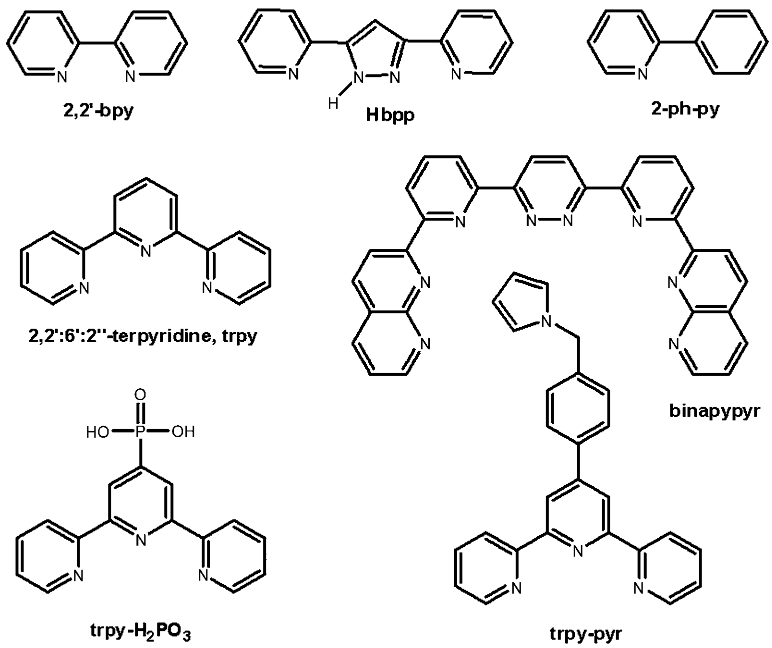


Figure 2. Top: POV-Ray drawing of the X-ray structure of the "blue dimer" **1**. Bottom: Drawing showing only the atoms constituting the first coordination sphere of the ruthenium centers. Orange Ru, blue N, red O, black C; all hydrogen atoms have been removed for clarity.

At pH 1.0, where most of the catalytic water-oxidation reactions are carried out, the blue dimer shows two redox processes. One at $E^{0\prime} = 0.79$ V that involves the removal of one electron from the III,III (that is Ru^{III}–O–Ru^{III}) to give the III,IV oxidation state. The second one involves the removal of three electrons from III,IV to give V,V with $E^{0\prime} = 1.22$ V. Overall the potential $E^{0\prime}$ for the four-electron process V,V to III,III has the value 1.12 V, that is, it is 180 mV above the thermodynamic value for the oxidation of water to dioxygen at pH 1.0 ($E^{0\prime} = 0.94$ V, see Table 1).

In the presence of excess Ce^{IV}, the blue dimer is capable of oxidizing water to dioxygen yielding at least TN = 13.2.[22] It is assumed that one of the major handicaps for this catalytic cycle is the coordination of anions (anation) that deactivates the process. The slow step in this process is the oxidation of



Scheme 1. The N ligands reported in this Review.

Table 1: Thermodynamics of water oxidation.

Redox couple	$E^{0\prime[a]}$ [V]	
	pH 1.0	pH 7.0
$OH + 1H^+ + 1e^- \rightarrow H_2O$	2.5	2.15
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.48	1.13
$HO_2 + 3H^+ + 3e^- \rightarrow 2H_2O$	1.37	1.02
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0.94	0.58

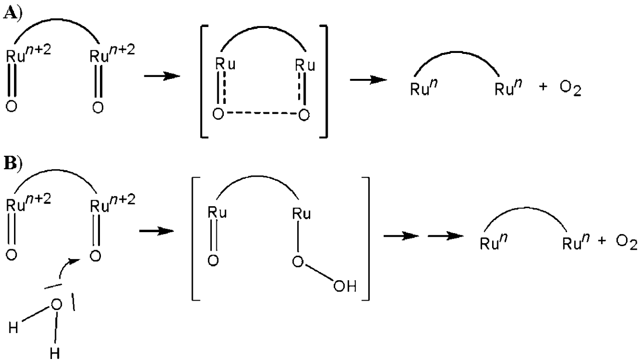
[a] Versus sodium saturated calomel electrode.

the Ru^{IV}–O–Ru^{III} species to the higher oxidation states responsible for oxygen evolution.

A number of blue-dimer analogues have been reported based on the Ru–O–Ru framework and using different polypyridylic type of ligands.[23] Their redox and catalytic properties are described in a recent Review[24] and thus will not be further discussed herein.

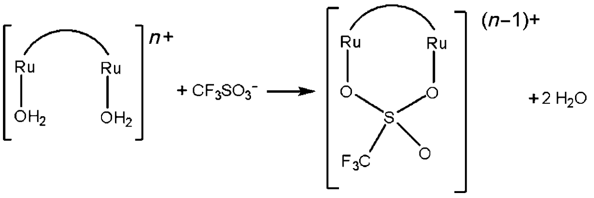
3.2. Reaction Mechanisms

A few mechanistic studies have been carried out with the ^{18}O-labeled blue dimer and solvent, with rather controversial results. While Meyer's group found a ratio of $^{18}O^{18}O/^{18}O^{16}O/^{16}O^{16}O$ of 0.13/0.64/0.23[25] for the evolved dioxygen, Hurst's group found a ratio of traces/0.40/0.60[26] and thus the interpretation of the mechanisms is rather different. While the presence of $^{18}O^{18}O$ allows intramolecular interactions, such as the one shown in Scheme 2A, to be invoked, or a bimolecular Ru–O···O–Ru interaction, its absence clearly denies both possibilities. The significant amount of $^{18}O^{16}O$ in both experiments strongly advocates an intermolecular type of mechanism with solvent water forming a hydroperoxide intermediate that evolves to oxygen (Scheme 2B). Finally the presence of $^{16}O^{16}O$ in both cases indicates a certain degree of exchange during the reaction cycle, involvement of first coordination expansion, and/or formation of oxygen with no involvement of the Ru^V=O groups.



Scheme 2. Potential mechanistic pathways for the formation of O_2, involving the ruthenium centers of the blue dimer.

The elucidation of the reaction mechanisms for this process is intrinsically difficult given the number of species present in the reaction cycle which involves species in different oxidation states (including thermodynamically metastable species) with different degrees of protonation; this is further complicated by the difficulty of handling the samples under a strictly oxygen-free atmosphere, by the limited solubility of the catalyst in water, and by anation [Eq. (13)], in which weakly coordinating anions, such as triflate, can coordinate in a chelating fashion and thus compete with water for the first coordination sphere of the ruthenium centers.



(13)

DFT calculations have also been carried out to shed some light on the potential reaction mechanisms involved in the formation of oxygen.[27] However, at the levels of theory used the reliability of the results is rather low given: 1) the open-shell nature of all ruthenium oxidation states involved, 2) the inherent difficulty in correctly evaluating electron correlation and spin coupling of metal centers, and 3) the cycling among different oxidations states during the catalytic cycle.[28]

4. Ruthenium Complexes without Oxide Bridges

4.1. The 3,5-Bis(2-pyridyl)pyrazole (Hbpp) System

A new synthetic approach for the design of $4e^-$ water oxidation catalysts was taken by our group.[29] To improve the stability of the blue-dimer type of complexes we envisioned the replacement of the oxide bridging ligand by a more robust and rigid chelating bridging ligand, to avoid the known reductive cleavage deactivation pathways of the oxide bridge as well as to avoid the potential *cis–trans* isomerization of the bis oxo-group active sites that is known to happen in *cis*-$[Ru^{VI}(bpy)_2(O)_2]^{2+}$.[24] Furthermore the design of the new bridging ligands had to bear in mind the relative disposition of the active sites of the complex, the two aqua/oxo groups, and thus had to allow a certain control of preorganization but also a certain degree of flexibility. Thus geometrically the bridging ligand had to: 1) place the two aqua/oxo groups sufficiently far apart that an oxide bridge, Ru–O–Ru, could not be formed and 2) place the two aqua groups sufficiently close together so that they could have a significant through-space intramolecular interaction. If all these requirements were met then upon reaching higher oxidation states the corresponding Ru=O groups would be properly oriented and situated so that they could reductively couple to generate oxygen. To meet all these requirements the synthetic chemistry related to the dinucleating bridging ligand Hbpp (see Scheme 1) was chosen.[30] In combination with the tridentate meridional 2,2′:6:2″-terpyridine (trpy) ligand the corresponding *in*,*in*-diaqua (see red atoms in Figure 3) complex *in*,*in*-$[Ru_2(\mu\text{-}bpp)(trpy)_2(H_2O)_2]^{3+}$ (**2**) could be prepared (Figure 3).

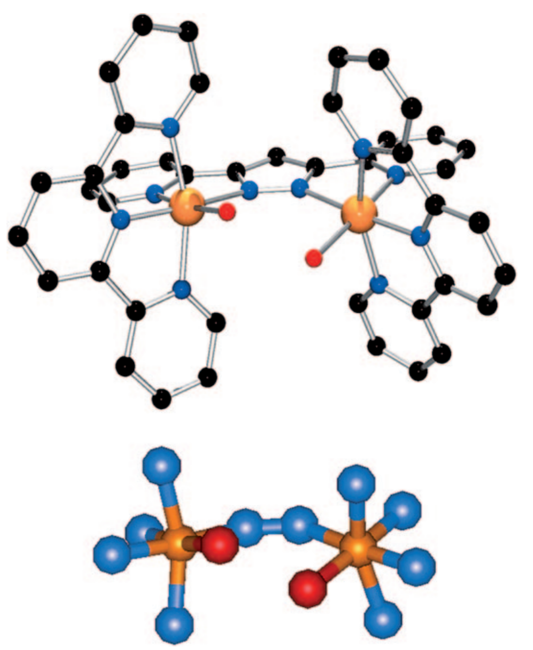
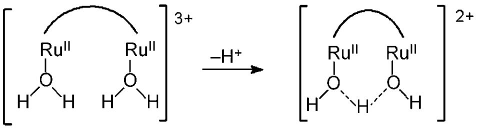


Figure 3. Top: POV-Ray drawing of the calculated structure of **2** (semi-empirical calculations at the ZINDO[19] level performed using the CAChe program package[20]). Bottom: Drawing showing only the atoms constituting the first coordination sphere of the ruthenium centers. Orange Ru, blue N, red O, black C; all hydrogen atoms have been removed for clarity.

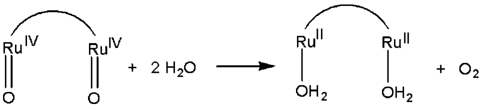
The interaction between the two aqua groups in **2** (oxidation state II) is clearly seen in the four orders of magnitude increase in acidity over the corresponding mononuclear complex, owing to the formation of a very stable $\{H_3O_2\}^-$ entity as shown in Equation (14). Furthermore, this interaction between the two active groups manifests itself in the fluxional behavior of the molecule at room temperature, which is detected by NMR spectroscopy: the C_2 symmetry enantiomers of the molecule interconvert very quickly into each other.[31]



(14)

The electronic coupling between the metal centers is also demonstrated by their redox potentials which are entirely different from those of their mononuclear counterparts. The Pourbaix diagram of **2** is significantly different from that of the blue dimer, mainly because of the absence of the oxide ligand linking the ruthenium centers. In the blue dimer, the highest oxidation state that can be reached is Ru^VRu^V which is responsible for the formation of O_2, whereas in **2** the highest oxidation state that can be reached is $Ru^{IV}Ru^{IV}$. On the other hand for **2**, both $Ru^{II}Ru^{II}$ and $Ru^{II}Ru^{III}$ oxidation states are stable whereas for the blue dimer oxidation states lower than $Ru^{III}Ru^{III}$ (see Section 3.1) cause the cleavage of the oxide bridge. Complex **2**, in the presence of an excess of Ce^{IV}, generates dioxygen very rapidly, giving $TN = 18$ although under optimized conditions a TN close to 200 can be obtained.[24] Initially Ce^{IV} is used to oxidize **2** to its $Ru^{IV}Ru^{IV}$ oxidation state followed by a slower process involving the formation of dioxygen, with an initial pseudo-first-order rate constant of $1.4 \times 10^{-2}\,s^{-1}$ [Eqs. (15) and (16)].

$$\{Ru^{II}(H_2O)Ru^{II}(H_2O)\} + 4\,Ce^{IV} \rightarrow \\ \{Ru^{IV}(O)Ru^{IV}(O)\} + 4\,H^+ + 4\,Ce^{III} \tag{15}$$



(16)

The exceptional performance of complex **2** is attributed to a) a favorable disposition of the Ru=O groups that are rigidly facing each other; b) the absence of the oxide bridge, thereby avoiding decomposition by reductive cleavage and by the strong thermodynamic driving force to *trans*-dioxo formation; and c) a lower degree of the competing anation side reaction, because the overall charge of the active complex is lower as are the ruthenium oxidation states.

4.2. The Binapypyr System

Following a similar strategy to that adopted for the Hbpp system (Section 4.1), Thummel and co-workers prepared an octadentate (that acts as a hexadentate) dinucleating neutral ligand (binapypyr; see Scheme 1) that contains two naphthyridyl groups coupled to a bispyridylpyridazine unit.[32] This ligand together with four monosubstituted pyridine ligands coordinates two ruthenium centers to generate the corresponding μ-Cl complex *trans,trans*-$[Ru_2(\mu\text{-}Cl)(\mu\text{-binapypyr})(4\text{-}Me\text{-}py)_4]^{3+}$ (**3**). The preliminary X-ray structure of **3** has been reported and the calculated structure of the corresponding *in,in*-diaqua complex is shown in Figure 4.[32] This diaqua complex has not been characterized or isolated, but might be formed when **3** is dissolved in a 1.0 M solution of triflic acid or when the initial Ru^{II}–Cl–Ru^{II} complex is oxidized. Addition of Ce^{IV} to the triflic acid solution generates a spectacular amount of dioxygen, giving turnover number of 538 with an efficiency of 23.6% with regard to the Ce^{IV} oxidant (The values presented are measured by GC with a thermal conductivity detector (TCD) and are much more reliable than those obtained with the electrochemically based method previously published.[33])

In this case all ligands bonding to the metal center of the aqua complex are neutral and therefore should generate a rather different thermodynamic scenario than that obtained with **1** and/or **2**. It is thus very important to study the electrochemical properties of this series of complexes so as to try to understand the pathways by which they perform the oxidation of water.

Thummel et al.[32] have also described a family of mononuclear complexes using monochelating ligands that also contain two naphthyridyl groups. These complexes are also capable of oxidizing water to dioxygen. Further, a series of

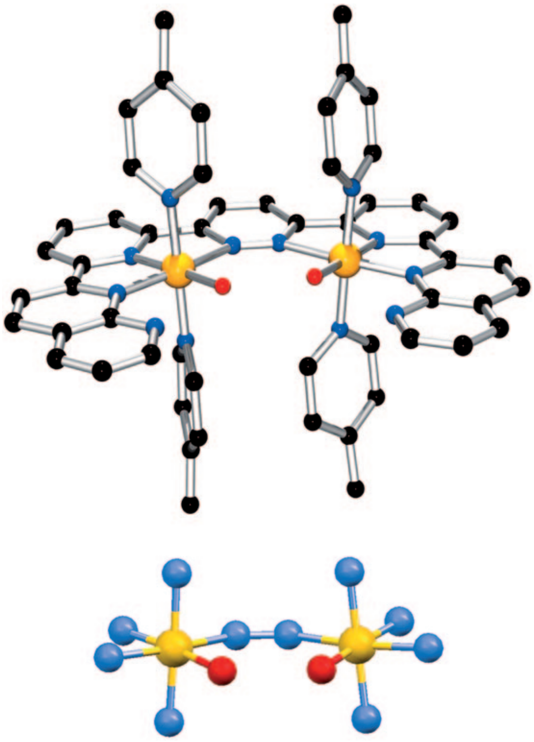


Figure 4. Top: POV-Ray drawing of the calculated structure of the *in,in*-diaqua complex corresponding to **3** (semiempirical calculations at the ZINDO[19] level performed using the CAChe program package[20]). Bottom: Drawing showing only the atoms constituting the first coordination sphere of the ruthenium centers. Orange Ru, blue N, red O, black C; all hydrogen atoms have been removed for clarity.

mononuclear complexes containing different ligand has been reported to oxidize water to dioxygen,[34] however, in general, they are in need of a thorough electrochemical characterization and their performances are inferior with regard to the dinuclear complexes described above. The mononuclear complexes are probably precursors of a more complex species, for instance oxide-bridged dimers, which are the real catalysts. Finally there is a dinuclear ruthenium complex which contains an anthracene bridging unit with two trpy moieties and also a quinone ligand, that is reported to electrochemically oxidize water to dioxygen, although it suffers from the drawback of requiring the application of a nearly 1 V overpotential over a period of 40 h.[35]

5. The First Iridium Complexes

Very recently Bernhard et al. have prepared a series of iridium organometallic complexes with general formula *cis*-$[Ir^{III}(L)_2(H_2O)_2]^+$ [L = 2-(2-pyridyl)phenylate anion (2-ph-py (**4**; Figure 5; see Scheme 1 for the ligand) and related ligands][36] which are reported to efficiently catalyze the oxidation of water to dioxygen using Ce^{IV} as oxidant. The TNs reported are impressive and are on the order of 2500 with efficiencies on the order of 66% with regard to the Ce^{IV} oxidant. The system however takes a long time to reach completion, around one week, whereas the ruthenium systems described previously are finished in less than one hour. A comparative performance of all the catalysts with regard to initial rates of oxygen formation is presented in Table 2 and will be discussed in Section 8.

Figure 5. POV-Ray drawing of the calculated structure of **4** (semiempirical calculations at the ZINDO[19] level performed using the CAChe program package[20]). Yellow Ir, blue N, red O, black C; all hydrogen atoms have been removed for clarity.

These iridium complexes are structural analogues of *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ reported by Dobson and Meyer a few years ago.[37] In sharp contrast to the iridium complexes, the ruthenium complex does not oxidize water to dioxygen because it deactivates through *trans* isomerization owing to the instability of the *cis*-dioxo group. Furthermore the treatment of *cis*-$[Ru(bpy)_2Cl_2]$ with excess Ag^I generates the blue dimer through the oxidation of the Ru^{II} complex.

While this series of iridium complexes includes the first relatively well structurally characterized non-ruthenium complexes that oxidize water to dioxygen, their spectroscopic and electrochemical characterization needs to be studied in more detail. In particular, the characterization of their corresponding higher oxidation states should be performed together with a thorough kinetic analysis, in order to be able to address the important questions that these complexes have raised. The most important being what are the active species in the catalytic cycle? The typical oxidation states for iridium complexes are III and IV; oxidation states higher than IV are very unusual.[38] Given the $4e^-,4H^+$ nature of the oxidation of water to dioxygen, if the complex remained mononuclear it would reach oxidation state VII, which seems very unlikely. Another possibility would be the formation of an oxide-bridged dimer structurally analogous to that of the ruthenium blue dimer, which would form upon the oxidation of Ir^{III}, generating $Ir^{IV}{-}O{-}Ir^{IV}$ that would need the two iridium centers to cycle between oxidation states IV and VI or alternately III and V. The anionic phenylate ligands, together with the dianionic oxide bridging ligand, might be sufficiently electron-donating to stabilize these higher oxidation states. Other options might be the formation of a trimer or higher oligomers, if no direct intramolecular oxygen–oxygen coupling were needed, where the iridium aqua moieties would be situated at the extremes and the rest of the iridium centers would act as electron-transfer shuttles.

Even though iridium is an expensive transition metal and the rates of water oxidation by these iridium complexes are much lower than those of the ruthenium complexes, this research is certainly an important contribution since it clearly shows that the careful choice of appropriate ligands might enlarge the range of transition metals capable of performing this difficult task. Furthermore, the careful study of the mechanism might bring new insights that are urgently needed in this field.

6. A New Ruthenium Polyoxometalate Complex

A very important breakthrough in this chemistry is the polyoxometalate complex $[Ru^{IV}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ (**5**, Figure 6) that has also been shown to oxidize water to dioxygen and that has been reported independently and nearly simultaneously by two groups.[39] The structure consists of an adamantane unit $\{Ru_4O_6\}$ in which all the metal centers alternate with O atoms. The oxygen atoms can be regarded as occupying the vertexes of an octahedron and the metal atoms those of a tetrahedron. The γ-$SiW_{10}O_{36}$ units act as tetradentate bridging ligands between two ruthenium centers and finally each ruthenium center completes its octahedral coordination with a terminal aqua ligand.

The performance of this complex is impressive. With a ratio **5**:Ce^{IV} of 1:400 in 0.1 M triflic acid, it generates an amount of dioxygen corresponding to TN = 385, which represents an efficiency of 90 %, while the reaction is completed in about 2 h.

The interest in this complex lies in the following aspects: first there are no organic ligands that can be oxidized and thus from this point of view it may not suffer intermolecular catalyst–catalyst deactivation pathways, even though the geometry and stability might change as a function of oxidation state and pH value, as has been described for related ruthenium complexes.[40] Secondly, all the ruthenium aqua complexes are in the oxidation state IV and thus potentially the $4H^+,4e^-$ pathway can take place at two ruthenium sites, either adjacent or non-adjacent, thus cycling from oxidation states $(IV)_4$ to $(IV)_2(VI)_2$ or if all the ruthenium atoms participate then the cycling would be to $(V)_4$. Irrespective of this, if the main structure is maintained in the different oxidation states then there cannot be an intramolecular pathway for the formation of an oxygen–oxygen bond. Thus O_2 must be formed by an intermolecular pathway involving nucleophilic attack of solvent water or by a bimolecular interaction of two polyoxometalate complexes. A thorough kinetic analysis is needed to elucidate the mechanism involved. Furthermore, an investigation of the electrochemistry and spectroscopy as a function of oxidation state is again highly desired, as it was the case in the iridium complex (Section 5), to be able to fully characterize this system.

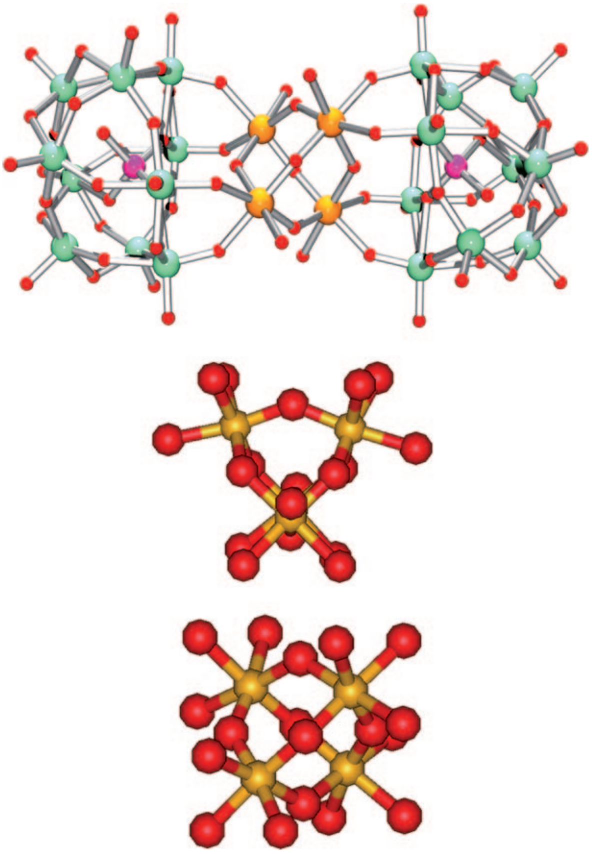


Figure 6. Top: POV-Ray drawing of the X-ray structure of **5**. Bottom: Two perspectives of the atoms constituting the first coordination sphere of the ruthenium centers. Orange Ru, red O, pink Si, green W; all hydrogen atoms have been removed for clarity.

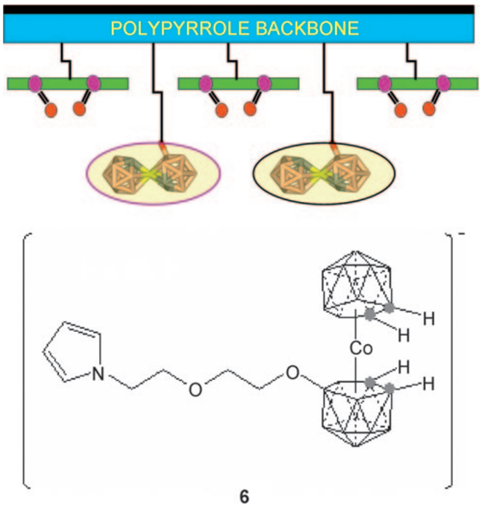
7. An Efficient Molecular Heterogeneous System

Besides the intrinsic advantages of heterogeneous catalysis versus homogeneous catalysis, the anchoring of a molecular water-oxidation catalyst into a solid support is of interest mainly for two reasons: one is that the reduced translational mobility can furnish a deeper insight into the potential deactivation pathways and secondly to demonstrate the viability of a water-oxidation catalyst in the solid state. This development would allow the catalyst to be incorporated into complex devices for solar-energy harvesting based on water splitting.[3] From a practical point of view, the availability of these solid-state materials would greatly facilitate the handling and assembling of devices based on energy-conversion schemes such as the one shown in Figure 1.

An attempt to heterogenize the blue dimer **1** into nafion polymer films was carried out by Kaneko et al.[41] by simple cationic exchange. Addition of Ce^{IV} generated dioxygen but with a much lower efficiency than with the same catalysts in the homogeneous phase. Another example of a water-oxidation catalyst immobilization into a solid support has been reported recently by the group of Meyer et al.[42] In this case a blue dimer derivative containing a trpy ligand functionalized with a phosphonate group (trpy-H_2PO_3; see Scheme 1), $[Ru_2(\mu\text{-}O)(trpy\text{-}H_2PO_3)_2(H_2O)_4]^{4+}$, has been anchored onto solid-oxide conductive surfaces, ITO (Sn^{IV}-doped In_2O_3) and FTO (fluorine-doped tin oxide). In the homogeneous phase this trpy-Ru complex generates nearly 1 TN and anchored in solid surfaces reaches a maximum value of 3 TN.[42]

A very convenient method to anchor redox-active metal complexes into conducting solid supports is by anodic electropolymerization of N-substituted pyrrols.[43] We have recently used this strategy utilizing the modified trpy ligand 4′-(*para*-pyrrolylmethylphenyl)-2,2′:6′,2′′-terpyridine (trpy-pyr; see Scheme 1) to synthesize a derivative of complex **2**, anchored into conducting solid surfaces.[44] Under sufficiently anodic potentials the pyrrol group of trpy-pyr polymerizes generating a material that remains firmly attached at the surface of the electrode (complex **2′**). The surfaces used are vitreous carbon sponges (VCS) and FTO. The performance of **2′** is dramatically improved with regard to that of **2**, a result of the minimization of catalyst–catalyst interactions.

To further separate the catalytically active species from each other in the solid support, co-polymers with robust non-active redox species that act as a diluting agent were prepared.[44] For this purpose the N-substituted pyrrolic anionic carborane complex **6** (Figure 7) was used because it has been described that it inhibits polypyrrole backbone oxidation[45] that in our particular case would also be detrimental. The copolymerization of **2** with **6** in an FTO electrode generates a new material, FTO/poly-(**2**-co-**6**), that is capable of oxidizing water to dioxygen giving TN = 250[44] which constitutes the best TN reported in heterogeneous phase using a chemical oxidant. This work demonstrates the feasibility of building a solid-state device for the oxidation of water into dioxygen, which can be integrated by a modular assembly into a larger device for the photo-production of H_2. This modular approach is a step forward in this field.



6

Figure 7. Schematic drawing of the copolymeric material FTO/poly-(**2**-co-**6**) (pink Ru, red O, green ancillary ligands) and formula of the anionic monomer **6**.

8. Summary and Conclusions

During the past four years, water-oxidation catalysis has experienced an enormous advancement based on well-defined molecules that are capable of performing this reaction in a very efficient manner. At the beginning the reaction was restricted to ruthenium complexes, now there is a new series of complexes based on iridium that can also perform this oxidation. This clearly opens up the door to other transition metals, provided they contain the right ligands, that is ligands that are not oxidized, which remain bound to the metal center during catalytic turnover, and also meet the stringent thermodynamic demands. For the case of ruthenium complexes with organic ligands it is interesting to see the wide diversity of polypyridylic ligands used as well as the different oxidations states. A key aspect of the dinuclear ruthenium complexes is the bridging ligand[46] used because it determines the degree of electronic coupling between the metal centers and also can control the relative disposition of the active ruthenium-aqua groups. This feature has strong implications with regard to the available oxidation states and also with regard to the potential mechanistic pathways at work. Thus, with neutral and mono-anionic ligands as in complexes **3** and **2**, respectively, it its assumed that the ruthenium centers cycle between oxidation states II,II and IV,IV whereas with the oxide dianionic ligand it cycles between III,III and V,V. Furthermore, from a mechanistic perspective the spatial arrangement of the two ruthenium-aqua groups in **2** and **3** is ideal for a potential intramolecular pathway if it were energetically available. The new Ru-polyoxometalate complex **5** is radically different from the previous ones in that the ruthenium centers are only bound to oxygen atoms (oxide and hydroxide ligands). The large amount of electron density donated by the oxide/hydroxide ligands to the ruthenium centers allows stabilization of oxidation state IV. Thus, in this case, it is assumed that the metal centers cycle between oxidation states $(IV)_4$ and $(V)_4$. This feature is also interesting because if the main polyoxometalate structure is maintained in the catalytic cycle then the intramolecular mechanism cannot take place. Therefore it can be inferred that water-splitting catalysts do not necessarily need to have the two metal centers in close proximity, but actually they could be in remote positions provided they are adequately electronically coupled. This coupling is required so that electron shuttling can occur to the ruthenium active site where the oxygen–oxygen–metal bond is formed, its subsequent oxidation produces the dioxygen.

Finally it is also important to have efficient catalysts that can work in a heterogeneous manner. This development is required to aid mechanistic studies but also from an engineering point of view, as it would enable the construction of a solid-state device that can be integrated, by a modular assembly, into a larger device for the photo-production of H_2.

Table 2 lists the kinetic data of the complexes described herein together with that of the OEC-PSII. An initial rate constant, k_i, is presented assuming a first-order behavior with regard to [cat.] and [Ce^{IV}], which does not always need to be the case, but it might be helpful to contrast performances. Another parameter that can be useful for comparison purposes is the initial turnover frequency TOF_i. It is interesting to note that all values for the synthetic complexes range from 0.05 to 22, whereas TOF_i for the OEC-PSII is close to five-orders of magnitude higher. It is also interesting to note that the fastest homogeneous system is **2** where the two oxo groups are facing each other in the higher oxidation states prior to oxygen generation, thus indicating a potentially faster

Table 2: Kinetic data related to the complexes studied in the present work.[a]

Catalyst	[Cat.] [mM]	[Ce^{IV}] [mM]	[Ce^{IV}]/[Cat.]	V [mL]	T [°C]	μmol h^{-1}	nmol s^{-1}	$k_i \times 10^{5}$[b]	TOF$_i$[c]	Ref.
1	0.20	620	3100.0	5.00	25.0	18.0	5.0	4.03	5.00	[41]
2	1.05	263	250.5	2.00	25.0	97.9	27.2	9.85	12.95	[29][d]
3	65.60	328	5.0	3.05	20.0	33.3	9.3	0.04	0.05	[32][d]
4	0.15	172	1178.1	10.00	25.0	19.8	5.5	21.90	3.77	[36][d]
5	0.15	1009	6726.7	10.00	20.0	50.0	13.9	9.18	9.27	[39a][d]
FTO/Poly(**2**-co-**6**)	2.5×10^{-4}	0.90	3600	2.00	25.0	0.04	0.011	4888	22.0	[44]
OEC-PSII									10^{6}	[9b]

[a] All complexes in 0.1 M triflic acid, except the Ir complex that is at pH 1.7 through the Ce^{IV} ($(NH_4)_2[Ce(NO_3)_6]$). [b] $k_i = \upsilon_i/([Ru][Ce^{IV}])$ in mol s M^{-1} M^{-2}. [c] TOF$_i$ in mol O_2 per mol Ru per 1000 s. [d] Data taken from the reported linear behavior with regard to [Cat.].

intra- than intermolecular mechanism based on water nucleophilic attack. Finally, the fastest synthetic process is the one where an analogue of complex **2** is supported in a conductive solid support, a result that demonstrates the importance of the surrounding environment in encapsulated catalysts.

As a general conclusion, the interplay between electronic coupling, geometry, nature of the active species, and nature of the transition metal are the key factors that determine the performance of the catalysts and thus have to be taken into consideration. The field at the moment is facing two difficult but fascinating challenges. The first is to deepen our knowledge and understanding with regard to the reaction mechanisms involved in the catalytic water oxidation, and this necessarily demands the characterization of reaction intermediates. This is a difficult task, but in the present case is made even more difficult because the reactions are performed in water, and therefore the range of temperatures at which the reactions can be carried out is very narrow. The second grand challenge it to achieve reaction rates of oxidation close to that of the OEC-PSII. At the moment nature is ahead by five-orders of magnitude and therefore there is still a long way to go. Taking into account that similar reactions carried out by first-row transition metals are faster than those of second- or third-row transition metals and that the OEC-PSII is made of a tetranuclear Mn complex it seems clear that this challenge will most likely be overcome by complexes of first-row metals.

9. Addendum

After submission of this Minireview a new contribution to the field appeared by Kanan and Nocera[47] using Co^{II} and phosphate as a water-oxidation catalyst. The TN in this case is only 5.2 and the TOF is two-orders of magnitude smaller than that of the best ruthenium complex described herein. However the contribution is of interest because cobalt is a relatively cheap and abundant transition metal.

Support form SOLAR-H2 (EU 212508), ACS (PRF 46819-AC3), MEC (CTQ2007-67918 and 60476) and from the Consolider Ingenio 2010 (CSD2006-0003) are gratefully acknowledged. X.S. thanks the Spanish MICINN for a Torres Quevedo grant.

Received: June 5, 2008

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