DOI: 10.1002/anie.201202948

Water Chemistry

Mononuclear Water Oxidation Catalysts

Dennis G. H. Hetterscheid and Joost N. H. Reek*

coordination chemistry · homogeneous catalysis · redox chemistry · water chemistry · water splitting

***R**ecently, several mononuclear water oxidation catalysts have been reported, a breakthrough considering the dogma that at least two metal sites were required to oxidize water efficiently. In this Review various mononuclear catalysts which have been reported in the last five years are reviewed, as well as their implementation in prototype devices that allow dioxygen formation to be coupled to dihydrogen production will be discussed.*

1. Introduction

Global climate change and exhaustion of natural resources are among the most important problems that scientists need to solve within the next decades. Moving away from fossil fuels would require incorporation of solar energy into the energy infrastructure as this is the only source of renewable energy which can be harvested in sufficient amounts to sustain the world's population.[1] Yet, solar radiation reaching the earth varies considerably over time and with location. In addition, for several applications fuels will be needed, as electric alternatives imply major changes in technology that require time or simply are impossible. Therefore the efficient conversion of solar radiation into a form of chemical energy (e.g. H_2) is a key issue. One could achieve such an energy conversion by splitting water upon irradiation of light, thus resulting in the formation of O_2 and H_2. To do this efficiently, robust water oxidation catalysts are required to produce oxygen efficiently, that is, with high rates using only a small overpotential.

Initially most attention has been focused on multinuclear complexes based on natural systems, with the rationale that these are better able to cycle through a wide range of oxidation states under strongly oxidative conditions compared to mononuclear catalysts. Consequently several manganese, ruthenium, and cobalt clusters have been reported for water oxidation.[2] Dinuclear complexes have also received some attention, with ruthenium systems in particular giving interesting results.[2] In 2005, the first mononuclear water oxidation catalyst was presented,[3] and it broke the dogma that at least two metal sites are required for catalytic water oxidation. This initial report was followed by a plethora of examples, which includes manganese, iron, cobalt, iridium, and ruthenium catalysts. Some of these systems have been shown to be very active and can even compete with the oxygen-evolving center of photosystem II[4] in terms of turnover frequency. Consequently, this class of water oxidation catalysts may be of great importance for future solar energy to fuel conversion technologies.

Herein we provide an overview of mononuclear water oxidation catalysts which have been reported recently, without the intention of being comprehensive. Catalysts based on various metals will be described, and examples as to where these catalysts are implemented into devices will be presented.

[*] Dr. D. G. H. Hetterscheid, Prof. Dr. J. N. H. Reek
Van 't Hoff Institute for Molecular Sciences, University of Amsterdam
Sciencepark 904, 1098 XH, Amsterdam (The Netherlands)
E-mail: d.g.h.hetterscheid@uva.nl
Homepage: http://www.science.uva.nl/research/imc/HomKat/

2. Catalyst and Catalytic Activity

2.1. Manganese Complexes

To the best of our knowledge, manganese corroles are the only mononuclear systems that are catalytically active in water oxidation (Figure 1).[5] Water oxidation catalysis was carried out electrochemically and the formation of dioxygen was detected with an oxygen electrode.

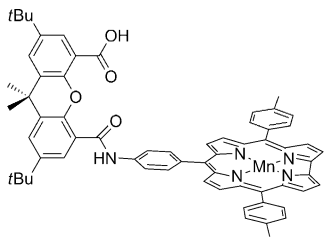


Figure 1. A manganese corrole complex that is catalytically active in water oxidation catalysis.

2.2. Ruthenium Complexes

A large number of mononuclear ruthenium water oxidation catalysts has been published in the last couple of years. A representative selection of catalysts, including the most important ones, is reviewed below.

2.2.1. Polypyridyl Ligands

In 2005, $[Ru(bpn)(MePy)_2(OH_2)]^{2+}$ (Py = pyridine) was reported as the first well-defined mononuclear ruthenium catalyst that was catalytically active in water oxidation.[3,6] Several structural variations have been reported since,[7] and in addition to nitrogen donors, stable carbene ligands[8] were used successfully (see Figure 2 for some examples but note that this is not a comprehensive list). The complex $[Ru(tpy)(bpy)(OH_2)]^{2+}$ is not the most active or robust catalyst known to date, but it is noteworthy as it has been thoroughly studied by several research groups.[9]

Catalyst activities could be increased upon substituting the tpy ligand with electron-withdrawing groups. Ligand variations influence the pK_a values and the oxidation potentials of the complexes. This change in oxidation potential has a direct effect on the rates of the elementary steps of the catalytic cycle and thus also on the catalytic performance of these species. The complex $[Ru(Mebimpy)(bpy)(OH_2)]^{2+}$ is the fastest catalyst of this family, with an observed turnover frequency of $0.057\ s^{-1}$. For these systems water oxidation typically occurs through a pathway wherein nucleophilic attack of water on a high-valent metal oxide species occurs (Scheme 1).

2.2.2. Anionic Ligands

The dicationic catalysts described above typically operate with a large overpotential. A significant decrease of the overpotential for catalytic water oxidation can be obtained by the use of anionic ligands instead.[10] This ligand type results in complexes having a more electron-rich metal center and thus lower oxidation potentials. Since the overpotential for catalytic water oxidation at pH 7 is sufficiently low, $[Ru^{III}(bpy)_3]^{3+}$ can also be used effectively as an oxidant in a photocatalytic manner (Figure 3).[11] The complex $[Ru(bda)(isoq)_2]^0$, where isoquinoline (isoq) was used as an axial ligand instead of 4-methylpyridine, shows an extremely

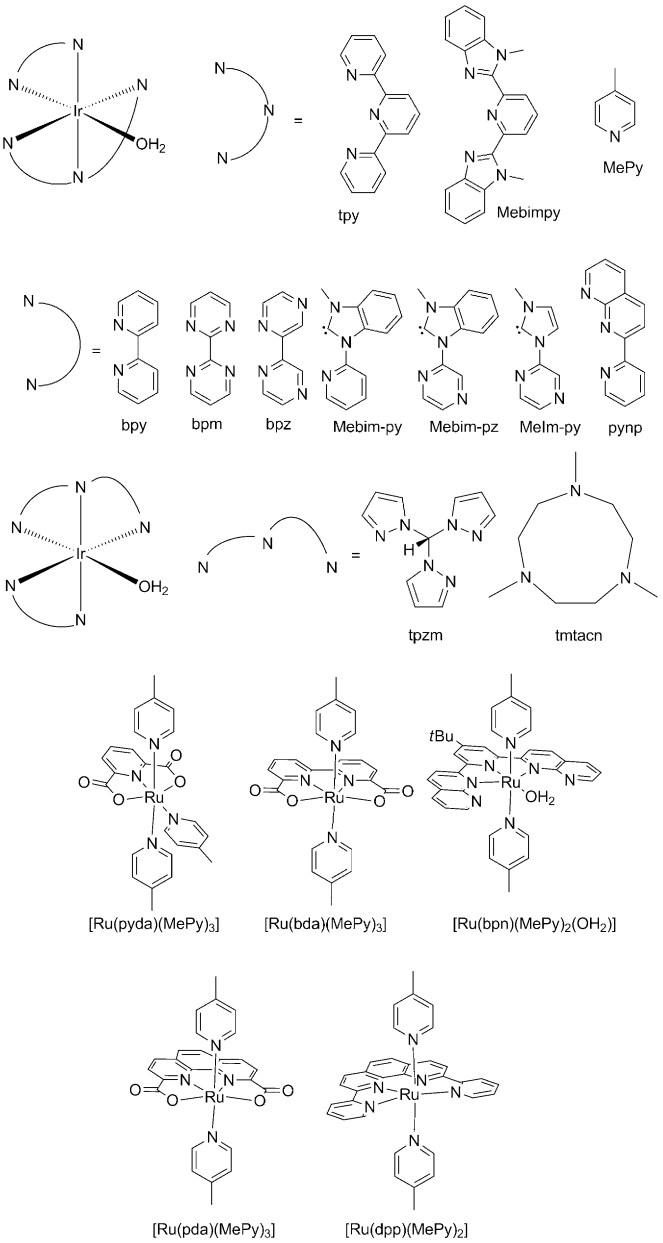
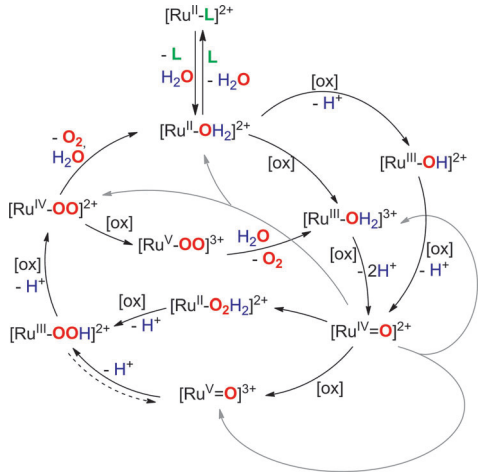


Figure 2. Chemical structures of selected ligands and ruthenium catalysts.

Dennis Hetterscheid obtained his PhD at the Radboud University of Nijmegen under the supervision of Dr. Bas de Bruin. He then moved to the Massachusetts Institute of Technology with a Rubicon fellowship where he worked in the lab of Prof. Richard Schrock. Currently, he works at the University of Amsterdam in the group of Prof. Joost Reek with an independent VENI research grant, where his research is focused on catalytic water oxidation.

Joost Reek completed his PhD with Prof Nolte 1996, and after post-doctoral studies with Prof. M. J. Crossley he began a lecture position at the University of Amsterdam with Prof. Piet Van Leeuwen. In 2006 he was appointed as a full professor at the University of Amsterdam. His research focuses on various topics related to supramolecular chemistry and transition-metal catalysis, with applications in asymmetric catalysis, conversion of biorenewables, and catalysis for green energy applications.



Scheme 1. Combined mechanism of water oxidation mediated by $[Ru(OH_2)(tpy)(bpy)]^{2+}$ and some of its analogs.[9]

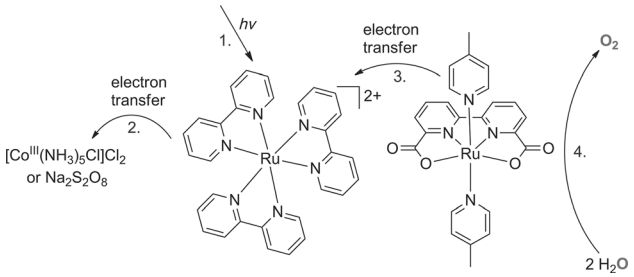
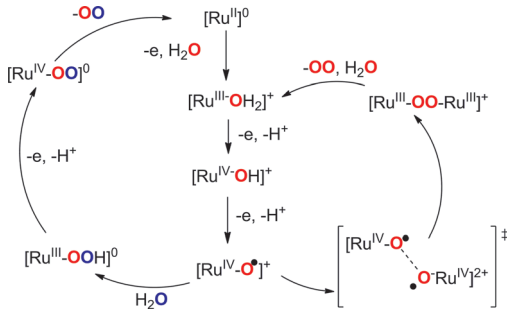


Figure 3. Sequential redox reactions of light-driven water oxidation using a $[Ru^{II}(bpy)_3]^{2+}$ photosensitizer. The photosensitizer is excited upon irradiation with visible light and expels an electron (1), which is picked up by an electron scavenger (2). The remaining oxidized $[Ru^{III}(bpy)_3]^{3+}$ in turn acts as an oxidant for the catalytic water oxidation reaction (3 and 4), thereby regenerating $[Ru(bpy)_3]^{2+}$.

high turnover frequency of 300 s^{-1}, which compares to that of the oxygen-evolving center of photosystem II (100–400 s^{-1}).[12] In contrast to the dicationic systems described earlier, these neutral systems may also react through a bimolecular pathway, and the preferred pathway depends upon subtle ligand variations (Scheme 2).[13]



Scheme 2. Competing pathways in case of $[Ru(pda)(MePy)_2(=O)]$ and $[Ru(bda)(MePy)_2(=O)]$.

2.2.3. Inorganic Ligands

The inorganic complexes $[Ru^{III}(SiW_{11}O_{39})(OH_2)]^{5-}$ and $[Ru^{III}(GeW_{11}O_{39})(OH_2)]^{5-}$ are also active in water oxidation.[14] Despite their lack of organic ligands, which are susceptible towards oxidative decomposition, the turnover numbers were low (50).

2.3. Iridium Complexes

Since the discovery of the first homogenous, iridium water oxidation catalyst in 2008,[15] the number of reported iridium catalysts active in water oxidation has been rapidly increasing. In addition to homogeneous iridium catalysts, iridium oxo nanoparticles[16] and heterogeneous iridium oxide[17] have also been reported to catalyze water oxidation very efficiently. Moreover it has been reported that molecular iridium complexes can easily degrade to iridium nanoparticles.[18]

2.3.1. The $[Ir(ppy)_2(OH_2)_2]^+$ Complex

Treatment of $[Ir(ppy)_2(OH_2)_2]OTf$ (Tf = trifluoromethanesulfonyl), the first molecular iridium water oxidation catalyst, with ceric ammonium nitrate (CAN) leads to formation of dioxygen (Figure 4).[15] Although the catalytic activity of this complex was fairly low, turnover numbers were reported to exceed one thousand.

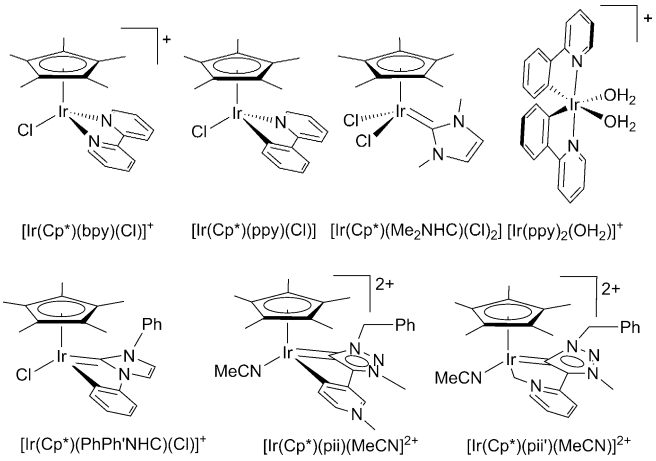


Figure 4. Chemical structure of selected homogeneous iridium water oxidation catalysts.

2.3.2. Pentamethylcyclopentadienyl Ligands

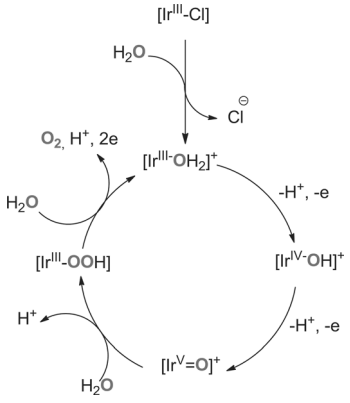
[IrCp*] complexes (Cp* = pentamethylcyclopentadienyl) proved to be a very suitable structural element for iridium-based water oxidation catalysts, and several related complexes have been reported (Figure 4). The complexes [Ir(Cp*)(ppy)(Cl)] and [Ir(Cp*)(bpy)(Cl)]Cl were shown to be very potent catalysts for water oxidation upon oxidation with CAN (Table 1), and were shown to catalyze water oxidation through a mechanism similar to that of the bipyridyl

Table 1: Catalytic performance of selected water oxidation catalysts in the presence of CAN.

Catalyst	TOF [s^{-1}]	TON	Catalyst [μM][a]	CAN [mM][a]	Ref.
$[Ru(Mebimpy)(bpz)(OH_2)]^{2+}$	0.18	–	51	1.5	[9b]
$[Ru(pyda)(MePy)_3]$	0.23	550	–	–	[11a]
$[Ru(tpy)(MePy)_2(OH_2)](ClO_4)_2$	0.092	450	67	320	[10a]
$[Ru(dpt)(MeCN)_4]^{2+}$	1.1	19	1000	100	[7b]
$[Ru(pda)(MePy)_2]$	0.10	310	–	–	[10c]
$[Ru(bda)(MePy)_2]$	4.5	1200	–	–	[10c]
$[Ru(bda)(isoq)_2]$	300	8360	216	480	[12]
$[Ir(ppy)_2(OH_2)_2]OTf$	0.005	2500	0.5	150	[15]
$[Ir(Cp^*)(bpy)Cl]Cl$	0.24	320	5.0	78	[19]
$[Ir(Cp^*)(ppy)Cl]$	0.17	1500	5.0	78	[19]
$[Ir(Cp^*)(OH_2)_3](NO_3)_2$	0.26	1250	5.3	2	[23]
$[Ir(Cp^*)(Ph_2NHC)Cl]$	0.13	–	4.5	78	[21a]
$[Ir(Cp^*)(pii)(MeCN)]^{2+}$	0.09	10000	0.2	10	[21b]
$[Ir(Cp^*)(pii')(MeCN)]^{2+}$	0.04	8350	0.2	10	[21b]
$[Ir(Cp^*)(Me_2NHC)(OH)_2]$	0.34	2000	1.0	90	[22]
$[Fe(mcp)(OTf)_2]$	0.23	360	12.5	125	[28]
$[Fe(TAML)(OH_2)]$	1.3	16	–	0.15	[27]

[a] Catalyst and CAN concentrations are those for the conditions under which the highest turnover frequency (TOF) was recorded. These are not necessarily the conditions under which the maximum turnover number (TON) was recorded. dpt = 3, 4-di(2-pyridyl)-1,2,5-thiadiazole.

ruthenium complexes (Scheme 3).[19] Related complexes with Cp instead of Cp* ligands (Cp = cyclopentadienyl) showed somewhat lower catalytic activity, but proved to be more



Scheme 3. Proposed mechanism for iridium-catalyzed water oxidation.[19]

robust towards catalyst deactivation,[19] which in the case of Cp* is probably initiated by oxidation of the Cp* methyl groups.[20] N-heterocyclic carbenes (NHCs) and irregular carbenes have also been shown to act as good ligands[21] even in a monodentate fashion.[22] Besides the Cp* moiety, additional ligands are not required to obtain an active species. $[Ir(Cp^*)(OH_2)_3]^{2+}$ [23] shows catalytic activity, although relative catalyst activity does increase with catalyst concentration.[19]

In contrast, clear first-order rate constants are observed for $[Ir(Cp^*)(Me_2NHC)(OH)_2]$, $[Ir(Cp^*)(ppy)(Cl)]$, and $[Ir(Cp^*)(bpy)(Cl)]Cl$ (Figure 4), thus suggesting a different active species. Therefore ligand loss from these systems to produce the same active species as $[Ir(Cp^*)(OH_2)_3]^{2+}$ does not occur.[19,22] Electrochemical oxidation of $[\{IrCp^*Cl_2\}_2]$, $[Ir(Cp^*(OH_2)_3]SO_4$, and $[\{IrCp^*\}_2(\mu\text{-}OH)_3]OH$ in aqueous solutions results in deposition of a blue iridium oxide layer on the electrode.[17] Formation of this blue layer of iridium oxide is observed for the [Cp*Ir] species which have three vacant sites. This requirement for three vacant sites to produce iridium oxide does not mean that other complexes are by definition molecular because these may form nanoparticles which do not precipitate on the electrode.

2.3.3. Nanoparticles?

Several other iridium precursors such as $IrCl_3$,[19,24] $K_2[IrCl_6]$,[19] and $[Ir(acac)_3]$[24] (acac = acetylacetonato) have shown catalytic activity for water oxidation. It is most likely in these cases that the actual catalytic species are iridium oxo nanoparticles rather than a well-defined molecular catalyst. In line with this, broken rate orders with respect to CAN and the catalyst were found, and for diluted systems longer incubation times were observed, which points to formation of nanoparticles. The presence of such species has been established in the case of $IrCl_3$.[24] $[Ir(ppy)_2(OH_2)_2]OTf$, $[Ir(Cp^*)(ppy)(Cl)]$, $[Ir(Cp^*)(Me_2NHC)(OH)_2]$, $[Ir(Cp^*)(pii)(MeCN)]^{2+}$, and $[Ir(Cp^*)(pii')(MeCN)]^{2+}$ (Figure 4) were also shown to quickly decompose in the presence of CAN, as illustrated by TEM measurements or signals in the UV/vis of the dark-blue mixtures which were determined to be the formation of the nanoparticles.[18] However, in most cases the catalytic activity was ascribed to a molecular species for kinetic reasons. Nevertheless, one should be very careful with the interpretation of these data as more and more evidence has been gathered to show that several mononuclear complexes form catalytically active metal oxides[18,25] and it would be best to move away from CAN as the chemical oxidant, especially since CAN does not always behave as an innocent one-electron oxidant.[26]

2.4. Iron Complexes

The complex $[Fe(TAML)(OH_2)]$ is an efficient water oxidation catalyst with a very high initial catalyst activity (Figure 5).[27] The maximum observed turnover frequency of 1.3 s^{-1} is impressive. However, the catalyst degrades rapidly and an turnover number of only 16 has been reported. Higher turnover numbers were obtained for complexes having

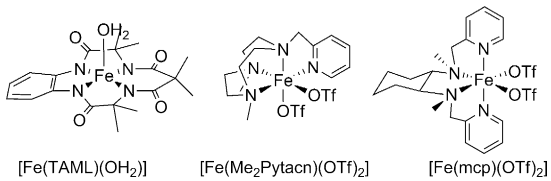


Figure 5. Chemical structure of selected homogeneous iron complexes used for chemical water oxidation.

tetradentate nitrogen ligands, which allow the iron center to have two *cis* vacant sites.[28] Turnover numbers between 40 and 360 were obtained. Similar catalysts having either *trans* vacant sites or only one vacant site were not active (Figure 5 and Table 1).

2.5. Cobalt Complexes

Although heterogeneous cobalt catalysts are very successful,[29] mononuclear cobalt catalysts have hardly been reported. This is partly due to the facile catalyst degradation as the ligand opposite the Co=O bond is very weakly coordinated. Ligand decoordination can be prevented by using a pentadentate pyridine ligand (Figure 6).[30] In the

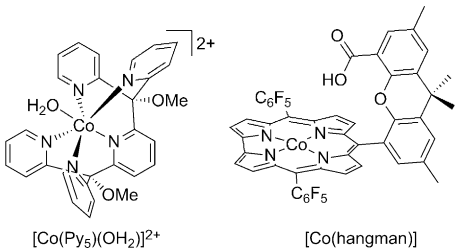


Figure 6. Chemical structure of homogeneous cobalt water oxidation catalysts used for water oxidation.

resulting geometry the pyridine opposite the aqua ligand is tightly bound to the complex because of the rigidity of the ligand and coordination of the other four pyridines to cobalt. Consequently, the complex is stable upon oxidation and able to shuttle between the Co^{II}, Co^{III}, and Co^{IV} oxidation states required for catalytic activity. Water oxidation activity was established by electrochemistry experiments.[30] The observed turnover frequency for this system was found to be 79 s^{-1}, which is substantially higher than most other catalysts. However, very similar cyclic voltammograms were observed in the case of $[Co(OH_2)_6]^{2+}$,[31] and several other cobalt complexes decomposed readily to nanoparticles.[32] Cobalt corroles, for example [Co(hangman)], are also catalytically active both in water oxidation[33] as well as in dioxygen reduction.[34] In case of water oxidation, the presence of a nearby base is a requirement for activity.

3. Prototype Water Splitting Devices

Aside from catalyst optimization, several additional challenges need to be solved before solar energy to fuel conversion devices are at the level of practical use. The first question to be answered is: Will the water oxidation catalyst still work when implemented into devices in which the half reaction for O_2 formation and H_2 production are coupled.

3.1. Electrochemical Cells

Efficient water splitting can be achieved by immobilization of the catalyst onto an electrode. In combination with a proton reduction catalyst, typically a platinum wire, electrolysis of water may occur at relatively mild reaction conditions. The complex $[Ru(Mebimpy)\{bpy(PO_3H_2)_2\}(Cl)]^+$ was immobilized on fluorine-doped SnO_2 (FTO), Sn^{IV}-doped In_2O_3 (ITO), and on optically transparent films of TiO_2 nanoparticles on FTO (Figure 7a).[35] It was illustrated by

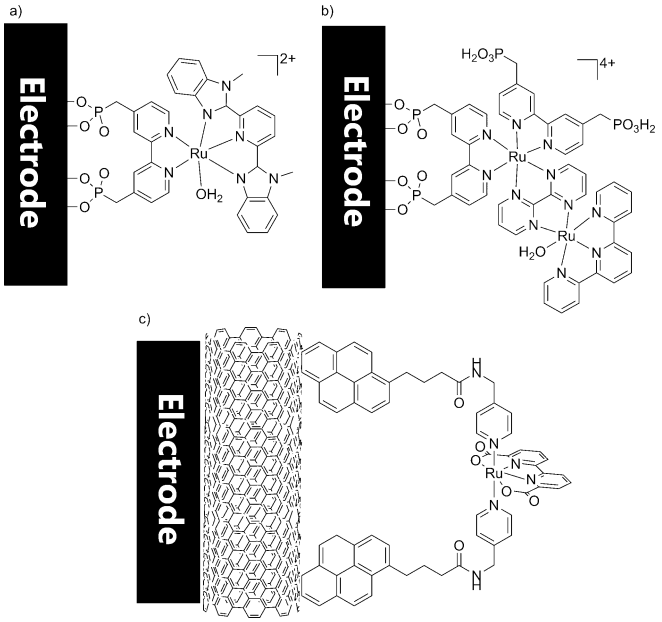


Figure 7. Structure-immobilized $[Ru(Mebimpy)\{bpy(PO_3H_2)_2\}(OH_2)]^{2+}$ (a), [Ru(tpy)(bmp)] redox mediator complex (b), and ITO | MWCNT | $[Ru(dpa)(Py\text{-}pyrene)_2]$ (c).

electrochemical experiments that the ruthenium catalysts retained their catalytic properties upon attachment to the surface. Excellent rates were reported for a system that contained a redox mediator between the catalyst complex and the electrode (Figure 7b). Turnover numbers are above 28000, still without any sign of catalyst deactivation (Table 2).[36] A turnover frequency of approximately 1 s^{-1} was found for the catalyst on the electrode, and is significantly faster compared to the catalyst in solution (TOF = 0.06 s^{-1}) when oxidized with CAN (Table 1).

In another device, the complex $[Ru(bda)(Py\text{-}pyrene)_2]$ was attached to deposited multiwalled carbon nanotubes (MWCNTs) on ITO glass (Figure 7c).[37] The redox potentials of the immobilized catalyst are similar to that of the catalyst in solution.[11] Also, for the immobilized system high rates are observed at relatively low overpotential. The results are summarized in Table 2, and show that these heterogenized architectures display great catalyst activities and have increased robustness compared to homogeneous analogues which have been driven by CAN.

Table 2: Prototype electrochemical cells.

Catalyst assembly	Current density [$\mu A\,cm^{-2}$]	Γ [$mol\,cm^{-2}$]	TOF [s^{-1}]	TON	pH	E [V vs NHE]
ITO | MWCNT | [Ru(bda)(Py-pyrene)$_2$]	220	1.8×10^{-9}	0.3	11000	7.0	1.4
ITO | redox mediator assembly with tpy	6.7	7×10^{-10}	0.3	8900	1.0	1.8
ITO | redox mediator assembly with Mebimpy		3×10^{-10}	0.6	28000	1.0	1.8
ITO | redox mediator assembly with Mebimpy	1.5	5.7×10^{-10}	0.007	70	1.0	1.5
FTO | TiO_2 | redox mediator assembly with tpy	83	8.5×10^{-8}	0.0027	82	1.0	1.8

3.2. Photoanodes for Light-Driven Water Splitting

Ultimately, devices should run in the absence of external potential, wherein the water oxidation reaction is fully driven by light using photosensitizers to produce the charge separation. In 2008 the first example in which iridium oxo nanoparticles were used as the active water oxidation catalyst was published (Table 3).[38] It was also demonstrated that deposition of the [Ir(Cp*)(ppy-COOH)(Cl)] water oxidation catalyst onto TiO_2 nanoparticles, together with a high-potential zinc porphyrin as the chromophore, results in a working photoanode (Figure 8).[39] Visible light is absorbed by the zinc porphyrin, which expels an electron into the conduction band of TiO_2, thus resulting in the formation of oxidized zinc porphyrin complexes at the surface of the TiO_2 nanoparticles. Oxidation of the iridium water oxidation catalysts takes place by the photooxidized zinc porphyrin. Upon irradiation of the system with visible light and with a small bias voltage of 300 mV, a photocurrent of about 30 $\mu A\,cm^{-2}$ is generated.

A similar photoanode was prepared by using [Ru(bda)-(MePy)$_2$] as a catalyst and [Ru{bpy(PO$_3$H$_2$)$_2$}(bpy)$_2$] as a chromophore.[40] A film of TiO_2 was covered with [Ru{bpy-(PO$_3$H$_2$)$_2$}(bpy)$_2$] and placed on FTO conducting glass (Figure 9). The anode was layered with a film of neutralized nafion containing the [Ru(bda)(MePy)$_2$] catalyst. When the photoanode was connected to a platinum electrode as the reduction catalyst, both hydrogen and oxygen could be detected upon irradiation of the device. Also, for this system a bias voltage of 325 mV was applied to achieve water splitting.

The heterogenized [Ir(Cp*)(ppy-COOH)(Cl)] and [Ru(bpy)$_2${bpy(PO$_3$H$_2$)$_2$}] systems show similar catalytic activities compared to the recently reported systems based on heterogeneous iridium oxide[38] and manganese oxide (Table 3).[41] Interestingly, the device based on the manganese oxide cluster did not require a bias voltage to oxidize water. It is interesting to note that mononuclear water oxidation catalysts can compete with the heterogeneous catalysts.

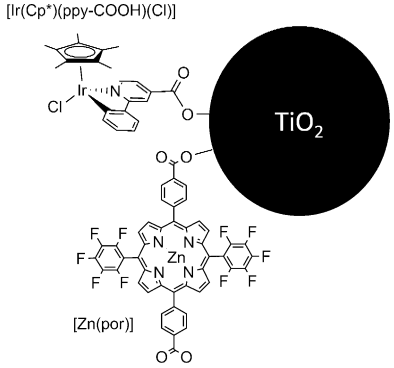


Figure 8. The porphyrin chromophore and iridium water oxidation catalysts as components of a photoanode of a light-driven water oxidation device.

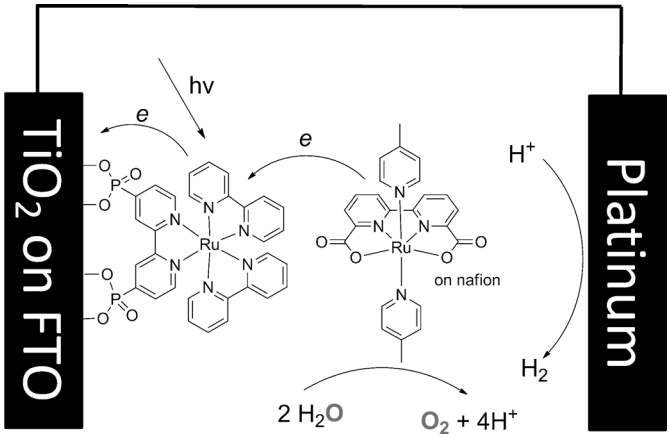


Figure 9. A Photoelectrochemical cell, consisting of an anode based on a [Ru{bpy(PO$_3$H$_2$)$_2$}(bpy)$_2$]-sensitized TiO_2 film attached to an FTO conducting glass coated with a Nafion film penetrated with [Ru(bda)-(MePy)$_2$], a Pt cathode, and an aqueous electrolyte, for light-driven water splitting.

Table 3: Prototype photoanodic cells.

Catalyst assembly	Cut off wavelength [nm]	Light intensity [$mW\,cm^{-2}$]	Current density [$\mu A\,cm^{-2}$]	Bias potential [mV]
FTO | TiO_2 | $[Ru(bpy)_3]^{2+}$ | Ir_xO_y	450	7.8	12.7	325
FTO | TiO_2 | [Zn(por)] | [Ir(Cp*)(Cl)(ppy-COOH)]	400	200	30	300
FTO | TiO_2 | $[Ru(bpy)_2\{bpy(PO_3H_2\}_2]^{2+}$ | [Ru(MePy)$_2${bpy(PO$_3$H$_2$)$_2$}]	400	100	50	325
FTO | TiO_2 | $[Ru(bpy)_2\{bpy\text{-}(COOH)_2\}]^{2+}$ | Mn_xO_y	250	100	25	0

Having said that, the best device reported so far was achieved by using a heterogeneous cobalt catalyst for water oxidation, albeit in for a very different device architecture using ITO, triple-junction amorphous silicon, and a complementary NiMoZn hydrogenase catalyst.[42]

4. Summary and Outlook

In the last couple of years many mononuclear water oxidation catalysts have been reported. Although the first catalysts of this type were recently discovered, initial results illustrate the huge potential of these systems. In terms of catalytic activities and turnover numbers these mononuclear complexes easily compete with, or even outcompete molecular catalysts which are composed of more than one metal site. Catalytic activity can be tuned by subtle variations of the ligand system and have led to catalyst activities that compare well to those of the oxygen-evolving center of photosystem II. Whereas the robustness of many catalysts is at least questionable under CAN conditions, initial results, wherein catalysts are immobilized in electrochemical cells, illustrate excellent turnover numbers without significant loss of catalyst activity. Moreover, the catalytic activities of these immobilized architectures are typically largely improved compared to their fully solvated equivalents.

One key bottleneck of the prototype for direct solar energy to fuel conversion devices is the relatively short lifetime of charge separation (h^+) compared to the turnover frequency of the water oxidation catalysts (i.e., h^+ reacts faster through electron back transfer rather than with the water oxidation catalyst). Consequently, turnovers in direct-light-driven devices are still low and a bias potential is often required. To circumvent this problem water oxidation catalysts which are directly linked in a well-defined manner to the semiconductor/photosensitizer are necessary, thus allowing efficient electron transport from the catalyst to h^+. Typically mononuclear catalysts contain relatively simple ligands which can easily be substituted with appropriate linkers for attachment to various supports, whereas substitution of the ligand system of dinuclear catalysts often requires more synthetic effort and immobilization of heterogenous systems in a well-defined manner is far from straightforward. Hence, mononuclear systems may be the way to go in direct solar energy to fuel conversion applications.

This work was supported by the Netherlands' Organization for Scientific Research (NWO-CW, VENI grant 700.59.410).

Received: April 17, 2012
Published online: August 31, 2012

[1] a) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15279; b) D. G. H. Hetterscheid, J. I. Van der Vlugt, B. De Bruin, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, 8324; *Angew. Chem. Int. Ed.* **2009**, *48*, 8178; c) N. D. McDaniel, S. Bernhard, *Dalton Trans.* **2010**, *39*, 10021.

[2] For examples of water oxidation catalysts comprising more than one metal center, see: a) H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, *ChemCatChem* **2010**, *2*, 724; b) X. Sala, I. Romero, M. Rodriguez, L. Escriche, A. Llobet, *Angew. Chem.* **2009**, *121*, 2882; *Angew. Chem. Int. Ed.* **2009**, *48*, 2842; c) L. Duan, L. Tong, Y. Xu, L. Sun, *Energy Environ. Sci.* **2011**, *4*, 3296, and references therein.

[3] R. Zong, R. P. Thummel, *J. Am. Chem. Soc.* **2005**, *127*, 12802.

[4] Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **2011**, *473*, 55; J. Yano, J. Kern, K. Sauer, M. J. Latimer, Y. Pushkar, J. Biesiadka, B. Loll, W. Saenger, J. Messinger, A. Zouni, V. K. Yachandra, *Science* **2006**, *314*, 821; J. Barber, *Inorg. Chem.* **2008**, *47*, 1700.

[5] Y. Gao, J. Liu, M. Wang, Y. Na, B. Åkermark, L. Sun, *Tetrahedron* **2007**, *63*, 1987.

[6] H.-W. Tseng, R. Zong, J. T. Muckerman, R. Thummel, *Inorg. Chem.* **2008**, *47*, 11763.

[7] See for example: a) N. Kaveevivitchai, R. Zong, H. W. Tseng, R. Chitta, R. P. Thummel, *Inorg. Chem.* **2012**, *51*, 2930; b) L. Bernet, R. Lalrempuia, W. Ghattas, H. Mueller-Bunz, L. Vigara, A. Llobet, M. Albrecht, *Chem. Commun.* **2011**, *47*, 8058; c) B. Radaram, J. A. Ivie, W. M. Singh, R. M. Grudzien, J. H. Reibenspies, C. E. Webster, X. Zhao, *Inorg. Chem.* **2011**, *50*, 10564; d) D. E. Polyansky, J. T. Muckerman, J. Rochford, R. Zong, R. P. Thummel, E. Fujita, *J. Am. Chem. Soc.* **2011**, *133*, 14649; e) X. Sala, M. Z. Ertem, L. Vigara, T. K. Todorova, W. Chen, R. C. Rocha, F. Aquilante, C. J. Cramer, L. Gagliardi, A. Llobet, *Angew. Chem.* **2010**, *122*, 7911; *Angew. Chem. Int. Ed.* **2010**, *49*, 7745; f) M. Yoshida, S. Masaoka, K. Sakai, *Chem. Lett.* **2009**, *38*, 702.

[8] Z. Chen, J. J. Concepcion, T. J. Meyer, *Dalton Trans.* **2011**, *40*, 3789.

[9] a) J. J. Concepcion, J. W. Jurss, J. L. Templeton, T. J. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 16462; b) J. J. Concepcion, J. W. Jurss, M. R. Norris, Z. Chen, J. L. Templeton, T. J. Meyer, *Inorg. Chem.* **2010**, *49*, 1277; c) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, C. P. Berlinguette, *J. Am. Chem. Soc.* **2010**, *132*, 16094; d) J. J. Concepcion, M.-K. Tsai, J. T. Muckerman, T. J. Meyer, *J. Am. Chem. Soc.* **2010**, *132*, 1545; e) D. J. Wasylenko, C. ganesamoorthy, B. D. Koivisto, M. A. Henderson, C. P. Berlinguette, *Inorg. Chem.* **2010**, *49*, 2202; f) M. Yagi, S. Tajima, M. Komi, H. Yamazaki, *Dalton Trans.* **2011**, *40*, 3802; g) T. F. Hughes, R. A. Friesner, *J. Phys. Chem. B* **2011**, *115*, 9280; h) Z. Chen, J. J. Concepcion, X. Hu, W. Yang, P. G. Hoertz, T. J. Meyer, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 7225.

[10] a) L. Duan, Y. Xu, L. Tong, L. Sun, *ChemSusChem* **2011**, *4*, 238; b) L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **2009**, *131*, 10397; c) L. Tong, L. Duan, Y. Xu, T. Privalov, L. Sun, *Angew. Chem.* **2011**, *123*, 465; *Angew. Chem. Int. Ed.* **2011**, *50*, 445.

[11] a) L. Duan, Y. Xu, M. Gorlov, L. Tong, S. Andersson, L. Sun, *Chem. Eur. J.* **2010**, *16*, 4659; b) L. Duan, Y. Xu, P. Zhang, M. Wang, L. Sun, *Inorg. Chem.* **2010**, *49*, 209.

[12] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **2012**, *4*, 418.

[13] a) Y. Gao, T. Åkermark, J. Liu, L. Sun, B. Åkermark, *J. Am. Chem. Soc.* **2009**, *131*, 8726; b) T. Privalov, L. Sun, B. Åkermark, J. Liu, Y. Gao, M. Wang, *Inorg. Chem.* **2007**, *46*, 7075; c) Y. Xu, A. Fischer, L. Duan, L. Tong, E. Gabrielsson, B. Akermark, L. Sun, *Angew. Chem.* **2010**, *122*, 9118; *Angew. Chem. Int. Ed.* **2010**, *49*, 8934.

[14] M. Murakami, D. Hong, T. Suenobu, S. Yamaguchi, T. Ogura, S. Fukuzumi, *J. Am. Chem. Soc.* **2011**, *133*, 11605.

[15] N. D. McDaniel, F. J. Coughlin, L. L. Tinker, S. Bernhard, *J. Am. Chem. Soc.* **2008**, *130*, 210.

[16] a) T. Nakagawa, C. A. Beasley, R. W. Murray, *J. Phys. Chem. C* **2009**, *113*, 12958; b) T. Nakagawa, N. S. Bjorge, R. W. Murray, *J. Am. Chem. Soc.* **2009**, *131*, 15578; c) Y. Zhao, E. A. Hernandez-

Pagan, N. M. Vargas-Barbosa, J. L. Dysart, T. E. Mallouk, *J. Phys. Chem. Lett.* **2011**, *2*, 402; Y. Zhao, N. M. Vargas-Barbosa, E. A. Hernandez-Pagan, T. E. Mallouk, *Small* **2011**, *7*, 2087.

[17] a) J. D. Blakemore, N. D. Schley, G. W. Olack, C. D. Incarvito, G. W. Brudvig, R. H. Crabtree, *Chem. Sci.* **2011**, *2*, 94; b) N. D. Schley, J. D. Blakemore, N. K. Subbaiyan, C. D. Incarvito, F. D'Souza, R. H. Crabtree, G. W. Brudvig, *J. Am. Chem. Soc.* **2011**, *133*, 10473.

[18] a) D. B. Grotjahn, D. B. Brown, J. K. Martin, D. C. Marelius, M.-C. Abadjian, H. N. Tran, G. Kalyuzhny, K. S. Vecchio, Z. G. Specht, S. A. Cortes-Llamas, V. Miranda-Soto, C. Van Niekerk, C. E. Moore, A. L. Rheingold, *J. Am. Chem. Soc.* **2011**, *133*, 19024; b) D. Hong, M. Murakami, Y. Yamada, S. Fukuzumi, *Energy Environ. Sci.* **2012**, *5*, 5708; c) R. H. Crabtree, *Chem. Rev.* **2012**, *112*, 1536.

[19] a) J. D. Blakemore, N. D. Schley, D. Balcells, J. F. Hull, G. W. Olack, C. Incarvito, O. Eisenstein, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* **2010**, *132*, 16017; b) J. F. Hull, D. Balcells, J. D. Blakemore, C. D. Incarvito, O. Eisenstein, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* **2009**, *131*, 8730.

[20] a) C. Zuccaccia, G. Bellachioma, S. Bolano, L. Rocchigiani, A. Savini, A. Macchioni, *Eur. J. Inorg. Chem.* **2012**, 1462; b) A. Savini, P. Belanzoni, G. Bellachioma, C. Zuccaccia, D. Zuccaccia, A. Macchioni, *Green Chem.* **2011**, *13*, 3360.

[21] a) T. P. Brewster, J. D. Blakemore, N. D. Schley, C. D. Incarvito, N. Hazari, G. W. Brudvig, R. H. Crabtree, *Organometallics* **2011**, *30*, 965; b) R. Lalrempuia, N. D. McDaniel, H. Muller-Bunz, S. Bernhard, M. Albrecht, *Angew. Chem.* **2010**, *122*, 9959; *Angew. Chem. Int. Ed.* **2010**, *49*, 9765.

[22] D. G. H. Hetterscheid, J. N. H. Reek, *Chem. Commun.* **2011**, *47*, 2712.

[23] A. Savini, G. Bellachioma, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, A. Macchioni, *Chem. Commun.* **2010**, *46*, 9218.

[24] N. Marquet, F. Gartner, S. Losse, M.-M. Pohl, H. Junge, M. Beller, *ChemSusChem* **2011**, *4*, 1598.

[25] B. Limburg, E. Bouwman, S. Bonnet, *Coord. Chem. Rev.* **2012**, *256*, 1451.

[26] a) M. Yoshida, S. Masaoka, J. Abe, K. Sakai, *Chem. Asian J.* **2010**, *5*, 2369; b) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, C. P. Berlinguette, *Inorg. Chem.* **2011**, *50*, 3662.

[27] W. C. Ellis, N. D. McDaniel, S. Bernhard, T. J. Collins, *J. Am. Chem. Soc.* **2010**, *132*, 10990.

[28] J. L. Fillol, Z. Codola, I. Garcia-Bosch, L. Gomez, J. J. Pla, M. Costas, *Nat. Chem.* **2011**, *3*, 807.

[29] M. W. Kanan, D. G. Nocera, *Science* **2008**, *321*, 1072.

[30] D. J. Wasylenko, C. Ganesamoorthy, J. Borau-Garcia, C. P. Berlinguette, *Chem. Commun.* **2011**, *47*, 4249.

[31] D. J. Wasylenko, R. D. Palmer, E. Schott, C. P. Berlinguette, *Chem. Commun.* **2012**, *48*, 2107.

[32] D. Hong, J. Jung, J. Park, Y. Yamada, T. Suenobu, Y.-M. Lee, W. Nam, S. Fukuzumi, *Energy Environ. Sci.* **2012**, *5*, 7606.

[33] D. K. Dogutan, R. McGuire, D. G. Nocera, *J. Am. Chem. Soc.* **2011**, *133*, 9178.

[34] R. McGuire, Jr., D. K. Dogutan, T. S. Teets, J. Suntivich, Y. Shao-Horn, D. G. Nocera, *Chem. Sci.* **2010**, *1*, 411.

[35] Z. Chen, J. J. Concepcion, J. W. Jurss, T. J. Meyer, *J. Am. Chem. Soc.* **2009**, *131*, 15580.

[36] J. J. Concepcion, J. W. Jurss, P. G. Hoertz, T. J. Meyer, *Angew. Chem.* **2009**, *121*, 9637; *Angew. Chem. Int. Ed.* **2009**, *48*, 9473.

[37] F. Li, B. Zhang, X. Li, Y. Jiang, L. Chen, Y. Li, L. Sun, *Angew. Chem.* **2011**, *123*, 12484 – 12487; *Angew. Chem. Int. Ed.* **2011**, *50*, 12276 – 12279.

[38] W. J. Youngblood, S.-H. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust, T. E. Mallouk, *J. Am. Chem. Soc.* **2009**, *131*, 926.

[39] C. F. Moore, J. D. Blakemore, R. L. Milot, J. F. Hull, H.-E. Song, L. Cai, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig, *Energy Environ. Sci.* **2011**, *4*, 2389.

[40] L. Lin, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt, L. Sun, *Chem. Commun.* **2010**, *46*, 7307.

[41] R. Brimblecombe, A. Koo, C. Dismukes, G. F. Swiegers, L. Spiccia, *J. Am. Chem. Soc.* **2010**, *132*, 2892; R. K. Hocking, R. Brimblecombe, L.-Y. Chang, A. Singh, M. H. Cheah, C. Glover, W. H. Casey, L. Spiccia, *Nat. Chem.* **2011**, *3*, 461.

[42] S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers, D. G. Nocera, *Science* **2011**, *334*, 645.