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A Ru-Hbpp-Based Water-Oxidation Catalyst Anchored on Rutile TiO_2**

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Two organic ligands based on bis-(2-pyridyl)pyrazole (Hbpp) functionalized with a *para*-methylenebenzoic acid (Hbpp-R_a) or its ester derivative (Hbpp-R_e) were prepared and characterized. The ester-functionalized ligand was then used to prepare a series of related dinuclear ruthenium complexes of general formula $[Ru^{II}_2(L\text{-}L)(bpp\text{-}R_n)(trpy)_2]^{m+}$ (L-L = *m*-Cl, *m*-acetato, or $(H_2O)_2$; *n* = e or a; trpy = 2,2′:6′,2′′-terpyridine; *m* = 2 or 3). The complexes were characterized in solution by 1D and 2D NMR spectroscopy, UV/Vis spectroscopy, and electrochemical techniques. The $[Ru^{II}_2(m\text{-}Cl)(bpp\text{-}R_e)(trpy)_2](PF_6)_2$ complex was further characterized in the solid state by X-ray diffraction. The complexes containing the free carboxylic acid ligand were anch-ored onto rutile TiO_2 and treated with 0.1 M triflic acid solution to generate the homologous water-oxidation catalysts TiO_2-$[Ru^{II}_2(H_2O)_2(bpp\text{-}R_a)(trpy)_2]^{2+}$. This new hybrid material catalytically oxidizes water to molecular oxygen in a heterogeneous manner using Ce^{IV} as chemical oxidant. The generation of molecular oxygen is accompanied by the formation of carbon dioxide as well as some leaching of the Ru catalyst.

Introduction

Molecular hydrogen is an attractive and clean energy vector, but whilst the storage and separation of hydrogen have al-ready been achieved with a certain degree of success[1] the question of where to get a sustainable hydrogen source re-mains unanswered.[2] Molecular hydrogen can be obtained from water splitting according to Equation (1).

$$2\,H_2O \rightarrow 2\,H_2+O_2 \qquad (1)$$

This reaction is thermodynamically unfavorable by 474.4 kJmol^{-1} (237.0 kJmol(H_2O)). In principle, this energy could be supplied by sunlight; however, water does not absorb the electromagnetic radiation emitted by the sun to promote water splitting in a kinetically facile manner. To over-come this hurdle, a set of reactions should be coupled to a light-harvesting device/molecular assembly in such a manner that overall water splitting is achieved from sunlight. It is desirable that the two redox half-reactions involved in water splitting [Eq. (2) and Eq. (3)] take place at physically separated locations so that oxygen gas and hydrogen gas can be stored in different containers.

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

$$2\,H^+ +2\,e^- \rightarrow H_2 \qquad (3)$$

The achievement of water splitting thus necessitates master-ing three main components: 1) a light-harvesting device, 2) a water-oxidation catalyst that speeds up the half-reaction shown in Equation (2), and 3) a proton-reduction catalyst that does the same for the half-reaction shown in Equation (3). Furthermore, those three components should be assembled into a single cell with a proton-exchange membrane (PEM), and all of these parts have to properly work in a harmonized manner. A drawing of a such a potential cell is shown in Figure 1 and can be thought of as a modification of a Grätzel cell, in which

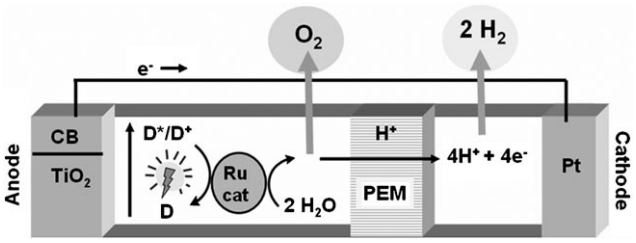


Figure 1. Schematic drawing of a water-splitting photochemical cell. It can be roughly described as a device that consists of three components: 1) a light-harvesting device, in this case the dye (D) molecule attached to a semi-conductor photoanode (CB: conduction band); 2) a water-oxidation catalyst that is oxidized to its active oxidation state by D^+ and from which molecular oxygen is evolved; and 3) a Pt cathode where hydrogen is evolved. The cell is designed with two compartments that are physically separated by a proton-exchange membrane.

Instead of simply making electricity the electricity is used to generate a chemical fuel, in this particular case molecular hy-drogen.[3] The separation of the anodic and cathodic compart-ments through a PEM is not only useful to separate H_2 and O_2 but also to prevent short-circuiting of the cell. Note that for this particular system it is imperative to design a sufficiently rugged PEM that is capable of resisting relatively severe conditions of pH and redox potentials.

Although an important amount of work has been carried out to develop components (1) and (3), well-defined molecular catalysts that are capable of efficiently oxidizing water to molecular oxygen are scarce and, as a consequence, hamper the development of devices based on this technology. On the other hand, the generation of hydrogen and oxygen from water and light can also be achieved by using semiconductors only.[4] In this latter field, improvements are directed towards the development of semiconductors with higher solar radiation absorption efficiencies, minimizing catalyst degradation, and finding readily accessible semiconductors with appropriate properties.[5]

The difficulty of obtaining efficient water-oxidation catalysts stems from two points: first, the reaction is tremendously un-favorable from a thermodynamic point of view, and second, there is a high intrinsic molecular complexity associated with this process, which essentially involves the removal of four pro-tons and four electrons from two water molecules together with the formation of an O—O bond [Eq. (2)].[6] The latter aspect can be responsible for the sluggish kinetics generally associated with this process in comparison with the millisecond timescale in which nature operates.

Nature has been using water and sunlight as a source of energy in its photosynthetic processes in green plants and algae for billions of years.[7] The overall photosynthetic process can be written as Equation (4).

$$H_2O+CO_2 \rightarrow 1/n\,(CH_2O)_n+O_2 \qquad (4)$$

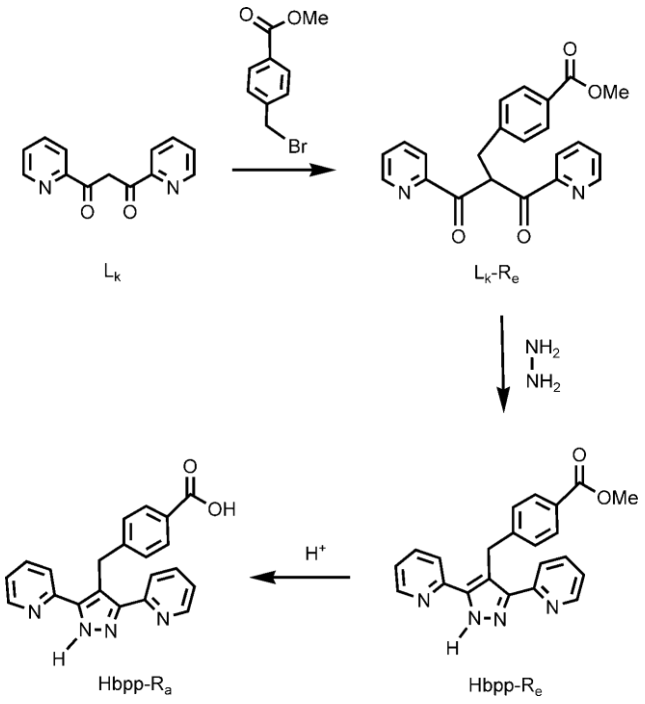
This reaction involves the reduction of CO_2 to carbohydrates and again the oxidation of water by the $4\,H^+/4\,e^-$ pathway [Eq. (2)]. The latter is the terminal reaction that occurs at photosystem II (PSII) in green plants and takes place at a polynuclear Ca-Mn_4 complex. Recently, the X-ray crystal structure, at

3.5 Å resolution, was solved and many new amino acid residues have been assigned; in addition, complementary instrumental techniques have allowed further structure refining, especially of the oxygen-evolving complex (OEC) and its sur-rounding environment.[8] While details of the structure of the OEC is becoming more precise, the mechanism through which this reaction proceeds is still subject

to controversy and necessitates a great deal of attention. For this reason, it is important to build low-molecular-weight functional models with perfectly characterized molecular structures and redox processes to be able to understand the different pathways through which those reactions proceed. This knowledge should bring about valuable information to further our understanding of the potentially viable water-splitting mechanisms. The purely biological interest in understanding the water-oxidation mechanism at OEC–PSII is thus matched by the urgent need our present society has for clean and renewable energy. The discovery of a sufficiently rugged and efficient water-split-ting catalyst will represent a significant advancement towards building a complex device for clean energy harvesting and storage. Furthermore, the possibility to have solid-state devices for modular assembly greatly simplifies the related construction and engineering of the device.[9]

In 1985, Meyer and co-workers reported the first structurally characterized water-oxidation catalyst, known as the blue dimer.[10] Several years ago, in 2004, we significantly improved Meyer's catalyst (kinetics of oxygen generation and turnovers increased roughly by a factor of four under the same conditions) based on the rational development of organic ligands and basic inorganic principles.[11] This work set up a revolution of new catalysts with different structural motifs that have considerably enhanced the number of metal cycles, although the kinetics are still slow.[12]

For the reasons described above, our group has undertaken a project to anchor our Ru catalyst onto solid supports to demonstrate the viability of the reaction with the catalyst in the solid state, and also to get a deeper understanding of how the catalyst behaves under solid-state conditions and in highly restricted translational mobility.[13] Furthermore, attaching the catalyst to a suitable semiconductor substrate allows for the preparation of a photoelectrochemical device. The first out-come of this project involved the anchoring of our ruthenium bis-(2-pyridyl)pyrazole (Ru-Hbpp) catalyst onto conducting organic polymers deposited on a graphite electrode by anodic electropolymerization of N-substituted pyrroles.[14] For this purpose, we modified the 2,2':6',2''-terpyridine (trpy) ligands with



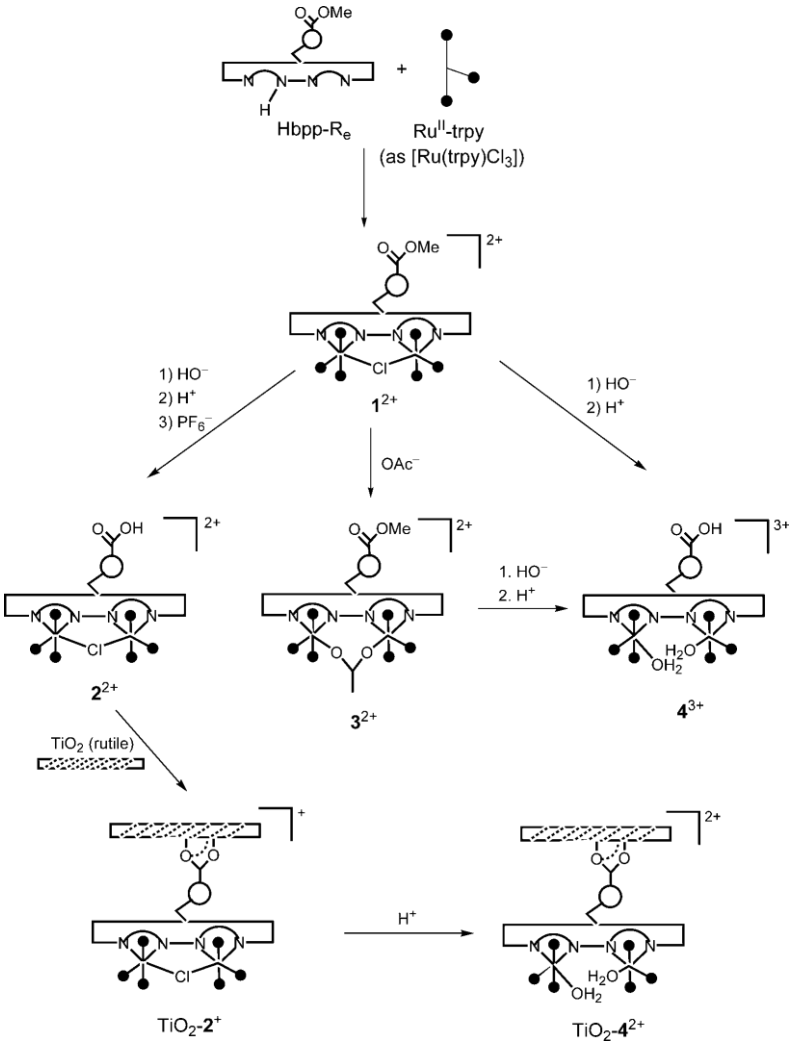
Scheme 1. Ligand synthesis.

pyrrole monomers, but in such a way that the intrinsic coordination properties of trpy were unaltered so that it was bound to the Ru metal center in a similar manner, and thus guaranteed a comparable performance of the corresponding Ru-Hbpp complex.[15] In that study, we demonstrated the feasibility of the solid-state design, and it constitutes the best molecular water-oxidation catalyst ever reported in the solid state using a chemical oxidant. Unfortunately, it suffers from oxidation of the polypyrrole backbone and, thus, deactivation of the catalyst. We are currently working on the design of ligands, the intrinsic coordination properties of which are not modified, and which can be anchored into rugged inorganic solid supports that do not suffer oxidative degradation. From this point of view, TiO_2 is an excellent candidate. Herein, we report on the preparation of new organic ligands Hbpp-R (Scheme 1), their coordination ability to form the corresponding dinuclear Ru com-plexes, their attachment onto rutile TiO_2 solid surfaces, and the performance of these new hybrid materials with regard to their capacity to oxidize water to molecular oxygen.

Results and Discussion

Synthesis of Ligands and Complexes

The synthetic strategy to prepare the new Hbpp-modified ligands (Scheme 1) involved nucleophilic addition of the bromomethylbenzoate to the *a*-carbon atom of the *b*-diketone precursor, followed by reaction with hydrazine to generate the heterocy-clic pyrazolate ring. Both reactions occurred in good yield, and the Hbpp-R_e (e =ester) ligand was easily obtained in this manner. Basic hydrolysis of the latter



Scheme 2. Synthesis of the Ru complexes.

Characterization of the Ru Complexes 1–4

The structural, spectroscopic, and electrochemical properties of generates the corresponding carboxylic ligand Hbpp-R_a (a = acid) in nearly quantitative yield. To prepare the Ru complexes, the ester form of the ligand (Hbpp-R_e) was used because of the lower capacity of the ester group to coordinate to the metal center and, thus, to minimize the generation of undesired compounds. Furthermore, the higher solubility of the ester derivative in organic solvents as compared to the carboxylic acid allows a simpler workup procedure. The synthetic strategy for the preparation of the dinuclear Ru—Cl—Ru com-plex 1^{2+} (Scheme 2) involved the direct reaction of [$RuCl_3$-(trpy)] and the Hbpp-R_e ligand in the presence of a reducing agent and exposure to radiation from a tungsten lamp over-night. Basic treatment both replaces the Cl bridging ligand by $H_2O/OH^{—}$ groups, depending on the pH, and also hydrolyzes the ester group on the Hbpp-R_e ligand to give 4^{3+}. The latter can also be obtained through the acetato-bridged synthetic intermediate Ru—OAc—Ru, 3^{2+}, followed by acid–base treatment. the new family of Ru complexes 1–4 were thoroughly characterized by applying the usual techniques. For complex 1, solid-state structural characterization was achieved by X-ray diffraction analysis. Two ORTEP views of its cationic moiety are shown in Figure 2, and the diffraction parameters are listed in Table 1. The

Ru metal centers are doubly bridged by the Hbpp-R_e chelating ligand and also by the chloro ligand occupying the meridional position of a hypothetical coordination octahedron. The other meridional position is occupied by the tridentate trpy ligand, which is thus situated perpendicularly with regard to Hbpp-R_e. In this arrangement, note that the two trpy ligands are disposed, forming an angle of 66.058. As expected, the methyl benzoate attached to the pyrazolate group is not involved in the first coordination sphere of Ru. The metal–ligand bond distances and angles for complex 1 (see Supporting Information) are typical and situated within the values obtained for related Ru complexes.[16]

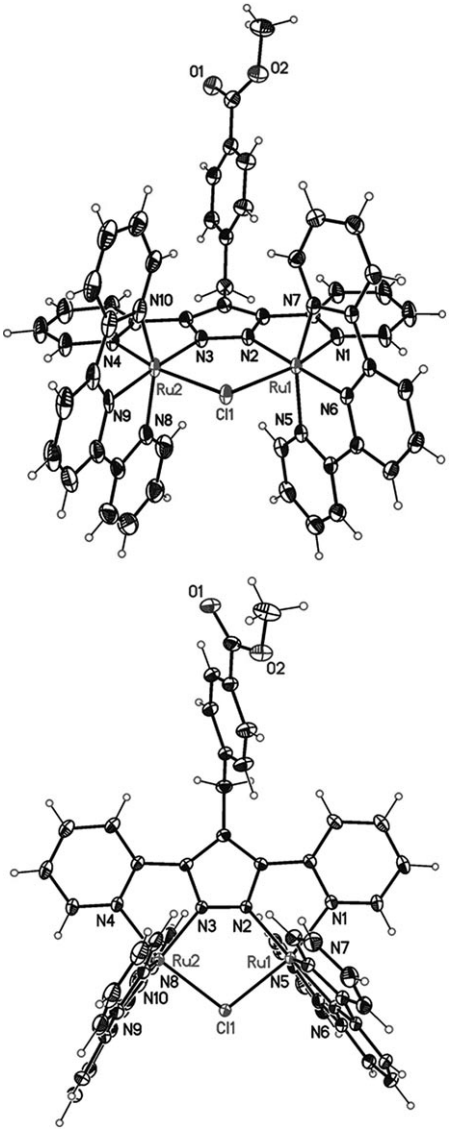


Table 1. Crystal data for $1(PF_6)_2 \cdot 1.5\,CH_3COCH_3 \cdot 1\,H_2O$.

Parameter	
Empirical formula	$C_{52}H_{47}ClN_{10}O_2P_2Ru_2 \cdot 2\,PF_6 \cdot 1^1/_2\,C_3H_6O_1 \cdot 1\,H_2O$
Molecular weight	1468.59
Crystal system	triclinic
Space group	*P-1*
a [Å]	13.6739(5)
b [Å]	14.4629(5)
c [Å]	15.0131(5)
a[8]	101.037(2)
b [8]	94.9510(10)
g [8]	93.951(2)
V [Å^3]	2892.16(17)
Formula units/cell	2
T [K]	100(2)
1_{calcd} [mgm^{-3}]	1.686
R_1[a]	0.0339
wR_2	0.0858

[a] $R_1 = C||F_o|-|F_c||/C|F_o|$. [b] $wR_2=[C\{w(F_o^2-F_c^2)^2\}/C\{w(F_o^2)^2\}]^{1/2}$, where $w= 1/[s^2(F_o^2)+(0.0042P)^2]$ and $P=(F_o^2+2F_c^2)/3$.

Figure 2. Two ORTEP views (50 % probability) of complex 1^{2+}. Selected dis-tances: Ru1-Cl1: 2.4712(3) Å, Ru1-N1: 2.0539(10) Å, Ru1-N2: 2.0009(10) Å, Ru1-N5: 2.0560(11) Å, Ru1-N6: 1.9625(10) Å, Ru1-N7: 2.0572(10) Å, Ru2-Cl1:2.4665(3) Å, Ru2-N3: 1.9980(10) Å, Ru2-N4 2.0636(11) Å, Ru2-N8: 2.087(2) Å, Ru2-N9: 1.9664(13) Å, Ru2-N10: 2.0315 Å.

1D and 2D NMR spectroscopy was performed to structurally characterize complexes 1–4 in solution (see Figure 3 and the Supporting Information). A very similar structural arrangement as in the solid state was observed in solution through 1D and 2D NMR spectroscopy as expected for a diamagnetic low-spin Ru^{II} d^6 ion. In solution at room temperature, owing to the fast dynamic behavior and/or the absence of packing interactions as in the solid state, complexes 1–4 display pseudo-C_{2v} symmetry in their NMR spectra, where a symmetry plane would bisect the bpp-R_e ligand and would transform the

two trpy ligands. Another symmetry plane perpendicular to the previous one would contain the bpp-R_e ligand and bisect each trpy unit. As a consequence, the four external pyridyl groups of the trpy ligands are magnetically equivalent, as are the two internal pyridyl groups. The symmetry, together with the 2D NMR spectra,

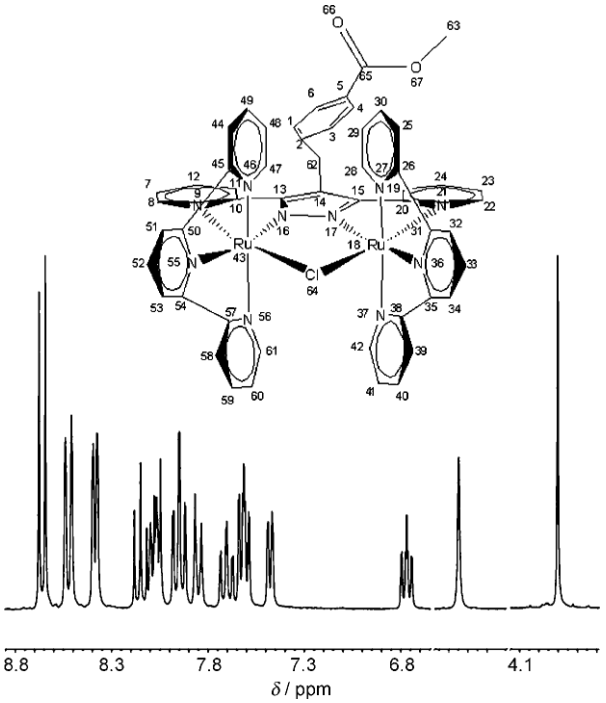


Figure 3. ^{1}H NMR spectrum of 1^{2+} in [D_6]acetone and numbering scheme for NMR assignment.

allows all of the observed resonances in the spectra of complexes 2–4 to be assigned without any ambiguity.

The UV/Vis spectral features in dichloromethane for complexes 1–3 are listed in the Experimental Section, and the UV/ Vis spectrum of complex 4 is shown in Figure 4. The main fea-tures of these complexes are relatively similar and therefore only that of complex 4 is discussed here. Three main regions can be distinguished: one between 200 and 350 nm, in which very intense bands are observed due to intraligand *p*–*p** transitions;[17] one between 350 and 550 nm, in which there are

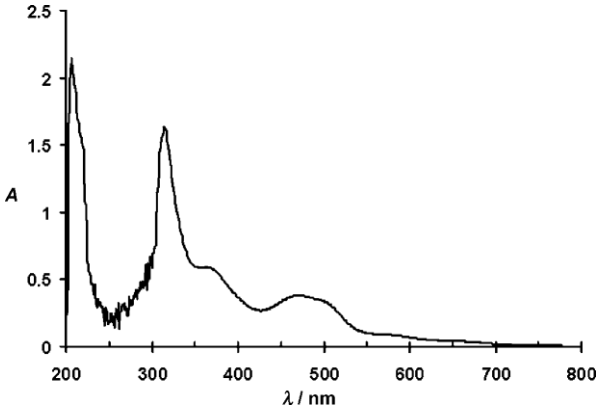


Figure 4. UV/Vis spectrum of a 3.3×10^{-5} M solution of complex 4^{3+} in 0.1 M triflic acid.

mainly broad unsymmetrical Ru(d*p*)-trpy/bpp-R_e(*p**) metal-to-ligand charge transfer (MLCT) bands;[18] and finally one region above 550 nm in which d–d transitions are observed.

Electrochemical experiments were carried out by means of cyclic voltammetry (CV; see Figure 5 and the Supporting Information). For complex 1, which contains no aqua groups, the cyclic voltammograms in organic solvents show two chemically reversible and electrochemically quasi-reversible redox waves. The first redox process at 0.77 V is assigned to the formation of the mixed-valence species II,II/II,III, whereas the second one at 1.25 V involves the removal of a second electron associated with the II,III/III,III redox process. The 480 mV difference is indicative of relatively strong electronic coupling between the metal centers through the bridging ligands. The electrochemistry of complex 4, which contains two aqua groups, was per-formed at pH 1.0 in 0.1 M aqueous triflic acid solution and is very different to that of complex 1 owing to the fact that now the electron-transfer processes can be coupled to proton trans-fer. The three redox processes observed in the voltammogram are assigned by comparison with the parent Ru-Hbpp analogue under the same conditions.[9] The first redox wave at 0.57 V involves only electron transfer and is assigned to the process shown in Equation (5). The second redox wave at 0.65 V is now an overall hydrogen-atom transfer and is as-signed to the process shown in Equation (6). The third wave at 0.95 V is assigned to the process shown in Equation (7).

$$Ru^{II}(H_2O)\text{-}Ru^{II}(H_2O) - 1\ e^- \rightarrow Ru^{II}(H_2O)\text{-}Ru^{III}(H_2O) \quad (5)$$

$$Ru^{II}(H\ O)\text{-}Ru^{III}(H\ O) - 1\ e^- - 1\ H^+ \rightarrow Ru^{III}(H\ O)\text{-}Ru^{III}OH \quad (6)$$

$$Ru^{III}(H_2O)\text{-}Ru^{III}OH - 1\ e^- - 1\ H^+ \rightarrow Ru^{III}(H_2O)\text{-}Ru^{IV}O \quad (7)$$

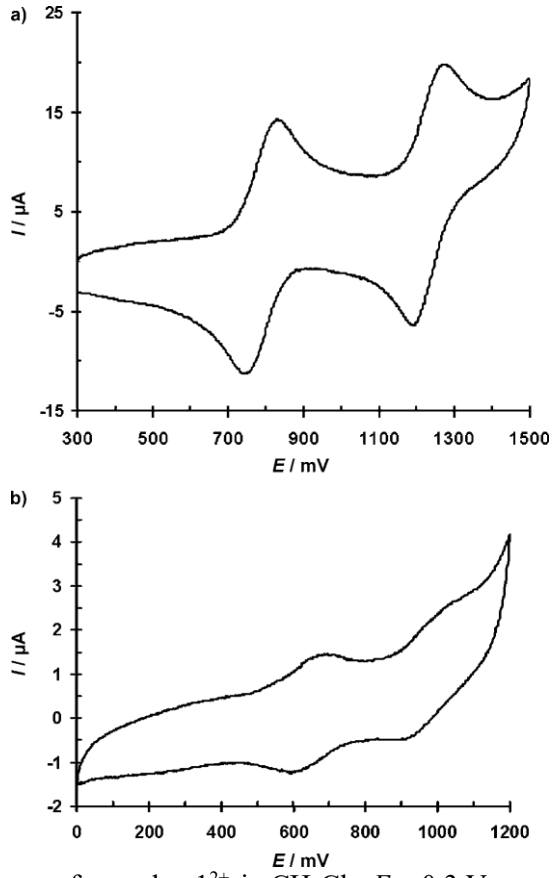


Figure 5. a) Cyclic voltammogram of complex 1^{2+} in CH_2Cl_2. $E_i = 0.3$ V scan-ning anodically at a scan rate of 200 mV s^{-1}. b) Cyclic voltammogram of complex 4^{3+} at pH 1 in 0.1 M triflic acid. $E_i = 0.0$ V scanning anodically at a scan rate of 100 mVs^{-1}.

The next redox process, which is not observed in the vol-tammogram, generates the dioxido species

$Ru^{IV}O$-$Ru^{IV}O$ that is responsible for the generation of molecular oxygen. The easy access to higher oxidation states of complex 4^{3+} is due to fact that the simultaneous removal of electrons and protons does not allow the build-up of high Coulombic charges in the com-plex and also to the *s*- and *p*-donor nature of the oxido group, which stabilizes higher oxidation states of the Ru metal center.[19]

Attachment of Ru Catalysts on Rutile TiO_2 and Water Oxidation

The free ligand Hbpp-R_a was anchored onto TiO_2 by the addi-tion of the latter into a solution of the ligand in MeCN and stir-ring the mixture at room temperature. After a few hours, the ligand was totally anchored onto the support, as seen by the disappearance of the ligand from the solution. The mixture was then centrifuged, and the remaining solid was filtered and washed several times with MeCN to finally obtain TiO_2-(bpp-R_a). Both the free ligand (Hbpp-R_a) and the supported ligand (TiO_2-(bpp-R_a)) were completely stable under oxidative condi-tions (in the presence of Ce^{IV}) at pH 1 in triflic acid. Further-more, in the latter case no leaching of the complex into the so-lution was observed, indicating the high stability of the TiO_2—O_2CR bond.

The attachment of the Ru complex onto rutile TiO_2 was also carried out in MeCN by introducing a sample of TiO_2 (250 mg) to the Ru—Cl—Ru complex 2^{2+} (acid form; 2.7 mg, 2.0 *m*mol) in MeCN (4 mL). In just 5 min, the solution decolorized indicating the total absorption of the complex into the TiO_2, thus gener-ating TiO_2-2^{+}. This new material was thoroughly washed with CH_2Cl_2 and then air-dried at room temperature. The obtained solid was then added to 0.1 M triflic acid (1.5 mL), and the mix-ture was left stirring at room temperature for 24 h to substi-tute the chloro-bridging ligand by two aqua groups to gener-ate the supported water-oxidation catalyst TiO_2-4^{2+} (Scheme 2). The colorless nature of the solution after 24 h clearly indicates that the TiO_2-4^{2+} complex is stable under these acidic conditions. An analogous material anchored into a transparent and conducting device FTO-TiO_2-4^{2+} (FTO: fluo-rine-doped tin oxide; see Supporting Information) was pre-pared for the purpose of characterizing the anchored species electrochemically and spectroscopically. The results of UV/Vis spectroscopy and CV studies of the complex generated in this manner are very similar to those obtained for $[Ru^{II}_2(bpp)(trpy)_2\text{-}(H_2O)_2]^{3+}$ in the homogeneous phase (see Supporting Information), and thus it is expected to behave in a similar manner. The addition of Ce^{IV} (200 *m*mol) in 0.1 M triflic acid (4 mL) to this solution immediately generated molecular oxygen accord-ing to Equation (8).

$$2\,H_2O + 4\,Ce^{IV} \rightarrow 2\,O_2 + 4\,H^{+} + 4\,Ce^{III} \qquad (8)$$

The reaction was followed by online manometry, and a pres-sure profile as a function of time is shown in Figure 6 a. Fur-thermore, the gases produced in this reaction were analyzed by online mass spectrometry and it was found that besides molecular oxygen the catalytic reaction also generated carbon dioxide (Figure 6 b). The combination of the two experiments allowed the amounts of the gases formed to be calculated, which turned out to be roughly 7 *m*mol O_2 (3.5 turnovers) and

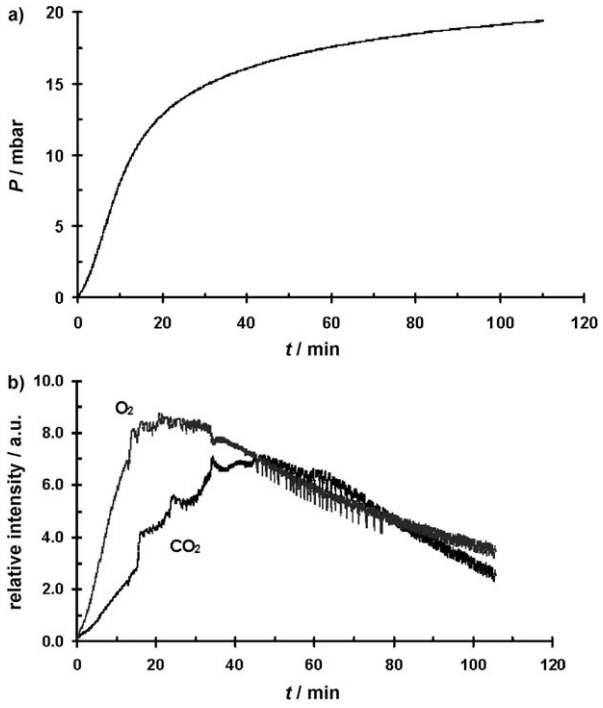


Figure 6. Monitoring of the catalytic gases generated upon oxidative treatment of TiO_2-4^{2+} with Ce^{IV} as a function of time. a) Manometry profile, and b) mass spectrometry profile.

5.8 *m*mol CO_2 (the presence of other gases such as NO, NO_2, N_2O_4, and Cl_2 was also checked by online MS, but none were found; see Supporting Information). It is interesting that O_2 is formed at an initial velocity that is 2.8 times faster than that for CO_2 (Figure 6 b). This result implies that initially the first re-action is the formation of oxygen in a heterogeneous manner and that later on Ce^{IV} is also capable of reacting with the attached metal complex. The generation of CO_2 can arise from the oxidation of the benzylic methylene group[20] or also through a decarboxylation event[21] with concomitant leaching of the metal catalyst into the solution. This is clearly inferred by the fact that initially the TiO_2-4^{2+} supported catalyst is brown in color and the solution is light yellow owing to the presence of Ce^{IV}. After 2 h, when the reaction is completely finished, the solution is brown and the solid is white. This brown solution has a similar UV/Vis trace to the homologous $[Ru^{II}$-(bpp)$(trpy)_2(H_2O)_2]^{3+}$ complex when treated under similar con-ditions in the homogeneous phase. Unfortunately, the nature of this deactivated/degraded complex remains elusive. Blank experiments with only TiO_2, or TiO_2-(Hbpp-R_a) under similar oxi-dative/pH conditions gave no O_2 or CO_2 (see Supporting Information).

Conclusions

The oxidation of water to molecular oxygen is an important re-action both from a biological[22] and technological point of view, especially with regard to the development of commercial light-

harvesting devices for the photoproduction of H_2.[23] Further investigation of its behavior in the solid state is a must to be able to build solid-state modular devices.[24] Previous endeavors in this direction include several strategies to anchor molecular water-oxidation catalysts, but so far none of them have been proven to be fully satisfactory.[9a,15,25] From the present work, two strategies seem the most promising. One strategy is to replace Ce^{IV} as an indiscriminate chemical oxidant by an electric potential appropriately applied to interact only with the Ru centers; this can be achieved by using a conducting solid support based on doped indium oxide, such as ITO or FTO,[9a,15] containing a microcrystalline film of anatase TiO_2, which is also a conductor, into which the complex 4^{2+} could be easily attached in the same manner as described here. The second strategy, which is synthetically much more demanding and thus requires a stronger effort, involves the replacement of the carboxylate group of the modified Hbpp-R_e ligand by a phosphonate group, which is known to be much more rugged with regard to oxidative degradation.[9a]

In conclusion, the results described here demonstrate the feasibility of using rugged inorganic solid supports for the oxi-dation of water to molecular dioxygen and sets up a basis for further developing anchoring strategies for the preparation of efficient and stable hybrid solid-state molecular catalysts.

Experimental Section

Materials: All reagents used in the present work were obtained from Aldrich Chemical Co. and were used without further purification. Reagent-grade organic solvents were obtained from SDS. $RuCl_3 \cdot 3H_2O$ was supplied by Alfa Aesar and was used as received. The titanium oxide used here was supplied by Aldrich and described as Nanopowder TiO_2 rutile (particle size ≈ 10 nm (diameter) × 40 nm (length); specific surface area: 130–190 m^2 g^{-1}; density: 4.17 g mL^{-1} at 25 °C; and bulk density: 0.06–0.10 g mL^{-1}). 1,3-Bis(2'-pyridyl)-1,3-propandione (Lk) [26] and the starting complex [$RuCl_3$(trpy)] [27] were prepared as described in the literature. All synthetic manipulations were routinely performed under nitrogen atmosphere using Schlenk tubes and vacuum-line techniques.

Methyl 4-(3-oxo-2-picolinoyl-3-(pyridin-2-yl)propyl)benzoate (Lk-Re): Acetonitrile (100 mL) and CH_2Cl_2 (15 mL) were added to a round-bottom flask charged with Lk (1.25 g, 5.5 mmol), NaOH (0.3 g, 7.5 mmol), KI (0.3 g, 1.81 mmol), and methyl 4-(bromomethyl)benzoate (1.75 mL, 15 mmol). The suspension was heated at reflux for 12 h and then filtered through celite to remove the inorganic salts. The organic layer was evaporated to dryness under vacuum, and the residue was purified by column chromatography on silica gel using $CHCl_3$ as eluent to afford the title product (2.77 g, 65%).

Methyl 4-[(3,5-di(pyridin-2-yl)-1H-pyrazol-4-yl)methyl]benzoate (Hbpp-Re): Compound 1 (0.6 g, 1.6 mmol) and hydrazine monohydrate (0.42 mL) were successively added to a flask containing a mixture of EtOH (50 mL) and THF (50 mL) and fitted with a reflux condenser. The mixture was heated at reflux for 7 h and then evaporated to dryness. The residue was dissolved in a minimum volume of hot CH_2Cl_2, the solution was poured into cold MeOH (–10 °C) and the mixture was placed in the freezer (–10 °C) until a white precipitate appeared. The precipitate was collected and dried. This process was repeated seven times to obtain pure Hbpp-Re (0.360 g, 60%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.59 (d, 2H, $J_{10,11}$ = 4.80 Hz; H_{10}, H_2), 7.90 (d, 2H, $J_{21,20}$ = 8.40 Hz; H_{21}, H_{23}), 7.68 (m, 4H; H_7, H_5, H_6, H_{12}), 7.29 (d, 2H, $J_{20,21}$ = 8.40 Hz; H_{20}, H_{24}), 7.21 (td, 2H, $J_{11,10/7}$ = 4.80 Hz, $J_{11,12}$ = 8.80 Hz; H_1, H_{11}), 4.83 (s, 2H; H_{18}), 3.86 ppm (s, 3H; H_{27}). ^{33}C{^{1}H} NMR (250 MHz, $CDCl_3$): δ = 167.82 (C_{25}), 150.80 (C_4, C_8), 149.48 (C_{10}, C_2), 146.88 (C_{19}), 137.37 (C_7, C_5), 130.11 (C_{23}, C_{21}), 128.64 (C_{20}, C_{24}), 128.26 (C_{22}), 123.02 (C_1, C_{11}), 121.57 (C_6, C_{12}), 115.28 (C_{14}), 52.34 (C_{27}), 30.48 ppm (C_{18}). ESI-MS: m/z = 370.1, 393.1 $[M+Na]^+$. Elemental analysis (%) calcd for

$C_{22}H_{18}N_4O_2$: C 71.3, H 4.9, N 15.1, O 8.64; found: C 71.1, H 5.0, N 15.3.

4-[(3,5-Di(pyridin-2-yl)-1H-pyrazol-4-yl)methyl]benzoic acid (Hbpp-Ra): A sample of Hbpp-Re (174 mg) was dissolved in acetone (20 mL), aqueous 1 M NaOH solution (20 mL) was added to the solution, and the mixture was stirred overnight at 50 °C. Then, HBF_4 was added until the medium was acidic. The volume was then reduced on a rotary evaporator until a white solid precipitated out of solution. The solid was collected by filtration on a frit (150 mg, 90%).

$[Ru_2(\mu\text{-}Cl)(bpp\text{-}Re)(trpy)_2](PF_6)_2$ ($1(PF_6)_2$): $[RuCl_3(trpy)]$ (0.214 g, 0.485 mmol) and LiCl (61.7 mg, 1.455 mmol) were dissolved in a solution of NEt_3 (135.5 µL, 0.97 mmol) in dry MeOH (20 mL). The mixture was stirred at room temperature for 20 min, and then Hbpp-Re (90.5 mg, 0.2445 mmol) and 0.314 M MeONa (0.780 mL, 0.2446 mmol) in dried MeOH (6 mL) were added. The resulting solution was heated at reflux for 4 h and then stirred in the presence of a 100 W tungsten lamp for 12 h. The reaction mixture was filtered, and then saturated aqueous NH_4PF_6 solution (1 mL) and water (3 mL) were added. The volume was reduced on a rotary evaporator until a precipitate appeared, and then the solution was kept cool for one day to obtain a good precipitate. The solid was filtered and purified by column chromatography over neutral alumina; only one orange fraction was eluted with acetone, corresponding to the product. This fraction was evaporated to dryness, the residue was dissolved in a minimum amount of dichloromethane, and the solution was washed three times with distilled water. The organic phase was then dried over anhydrous Na_2SO_4 and evaporated to dryness. The brown powder thus obtained was dissolved in acetone, and again saturated aqueous NH_4PF_6 solution (1 mL) and water (3 mL) were added. The volume was then reduced on a rotary evaporator until a solid precipitated out of the solution. The mixture was cooled in a refrigerator overnight, and the solid was filtered on a frit, washed with cold water (3×5 mL) and diethyl ether (3×5 mL), and dried under vacuum to afford complex $1(PF_6)_2$ (212 mg, 64%).

$[Ru_2(\mu\text{-}O_2CMe)(bpp\text{-}Re)(trpy)_2](PF_6)_2$ ($3(PF_6)_2$): A sample of $1(PF_6)_2$ (0.184 g, 0.135 mmol), sodium acetate (0.097 g, 0.712 mmol), and $AgBF_4$ (60 mg) were dissolved in acetone/water (3:1; 40 mL), and the solution was heated at reflux overnight. The resulting solution was filtered, and saturated aqueous NH_4PF_6 solution (1 mL) was added. A solid precipitated out of the solution upon reducing the volume. The solid was collected and washed with cold water and diethyl ether to afford complex $3(PF_6)_2$ (139 mg, 74%).

$[Ru_2(H_2O)_2(bpp\text{-}Ra)(trpy)_2](PF_6)_3$ ($4(PF_6)_3$): 0.5 M aqueous NaOH solution (10 mL) was added to a sample of $1(PF_6)_2$ (32 mg, 0.023 mmol) dissolved in acetone (10 mL), and the mixture was stirred overnight at 50 °C. Then, HBF_4 was added until the medium was acidic followed by saturated aqueous NH_4PF_6 solution (1 mL). The volume was then reduced on a rotary evaporator until a precipitate appeared. The mixture was then refrigerated overnight, and the solid was collected by filtration on a frit to afford complex $4(PF_6)_3$ (29 mg, 90%).

Preparation of TiO_2-4^{2+}: Rutile TiO_2 (250 mg) was added to a solution of 1^{2+} (2 µmol) in MeCN (4 mL). After stirring the mixture for 5 min, the solution became colorless and was centrifuged. The clean MeCN was discarded, and the remaining brown solid of TiO_2-2+ was washed twice with CH_2Cl_2 and dried in air. The TiO_2-2+ sample obtained in this way was added to 0.1 M aqueous triflic acid solution, and the mixture was stirred in an open vessel overnight to generate TiO_2-4^{2+}.

Instrumentation and Measurements: UV/Vis spectroscopy was performed with a HP8453 spectrometer using 1 cm quartz cells. ^{1}H NMR spectroscopy was performed on a Bruker DPX 200 MHz, a Bruker DPX

250 MHz, or a Varian VRX 500 MHz. Samples were run in $CDCl_3$, CD_2Cl_2 or [D_6]acetone with internal references. Elemental analyses were performed using a Carlo Erba CHMS EA-1108 instrument. ESI-MS experiments were performed on a HP298s GC-MS system. CV experiments were performed with a PAR283 potentiostat using a three-electrode cell. Online manometric measurements were carried out on a Testo 521 differential pressure manometer. Online monitoring of the gas evolution was performed on a Pfeiffer Ominstar GSD 301C mass spectrometer.

X-ray Crystal Structure Determination: Crystals of $1(PF_6)_2 \cdot 1.5\ CH_3COCH_3 \cdot 1\ H_2O$ were obtained by dissolving $1(PF_6)_2$ in mixtures of 1:1 water/acetone at room temperature and allowing the solvents to slowly evaporate. Data collection was made on a Bruker-Nonius diffractometer equipped with an APEX 2 4K CCD area detector.

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[20] In the homogeneous phase, the non-substituted Ru-Hbpp complex $[Ru^{II}_2(bpp)(trpy)_2(H_2O)_2]^{3+}$ in the presence of Ce^{IV} in 0.1 M triflic acid pro-duces only oxygen gas. However, a related aqua complex $[Ru^{II}_2(bpp\text{-}Bz)\text{-}(trpy)_2(H_2O)_2]^{3+}$ (bpp-Bz: 2,2'-(4-benzyl-1*H*-pyrazolate-3,5-diyl)dipyridine) gives significant amounts of CO_2 under similar conditions. This differ-ence indicates that a potential source of CO_2 in the case of $TiO_2\text{-}4^{2+}$ is also the oxidation of the benzylic methylene group. See the Supporting Information for synthetic details and characterization.

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