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Light-Induced Water Oxidation by a Ru complex Containing a Bio-Inspired Ligand

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Abstract: The new Ru complex **8** containing the bio-inspired ligand **7** was successfully synthesized and characterized. Complex **8** efficiently catalyzes water oxidation using Ce^{IV} and Ru^{III} as chemical oxidants. More importantly, this complex has a sufficiently low overpotential to utilize ruthenium polypyridyl-type complexes as photosensitizers.

Introduction

One of the most important challenges of the 21st century is to provide clean and renewable fuels. An attractive option is to model natural photosynthesis and use solar energy to convert water into molecular oxygen and hydrogen based fuels.^[1-3] The development of efficient catalysts for water oxidation is essential for the creation of an artificial watersplitting system. In the natural photosynthesis, a tetranuclear manganese cluster located in the oxygen-evolving complex (OEC) catalyzes the four-electron oxidation of water to molecular oxygen, thereby providing electrons for the reduction of carbon dioxide to biomass.^[4]

Inspired by Nature, considerable efforts have been devoted to finding a robust and efficient manganese-based water oxidation catalyst. To date, this has resulted in limited success.^[5] However, by using noble metals such as ruthenium^[6]

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Keywords: homogeneous catalysis • oxidation • photochemistry • ruthenium • water splitting

and iridium,^[7] progress has been made in the field. Since the pioneering work by Meyer, with the "blue dimer" ([*cis,cis*-{Ru(bpy)₂(H₂O)]₂(μ -O)]⁴⁺) (bpy=2,2'-bipyridine),^[8] a variety of different catalysts have been reported, ranging from mononuclear homogeneous systems^[9] to polynuclear heterogeneous catalysts.^[10] However, the majority of these systems depend on the use of stoichiometric amounts of strong oxidants, such as Ce^{IV}, which has an oxidation potential of approximately +1.5 V versus the normal hydrogen electrode (NHE). In contrast, light-induced water oxidation is rare, there are only a few reported homogeneous catalysts which are able to oxidize water photochemically.^[11] Herein, we would like to report a new type of bio-inspired complex **8**, which is capable of catalyzing light-driven water oxidation in a homogeneous system at neutral pH.

The introduction of negatively charged groups into the ligands of manganese and ruthenium complexes substantially lowers the oxidation potentials relative to the complexes with neutral ligands.^[12] This is clearly demonstrated by the dinuclear Ru complex **1**,^[12b] prepared from ligand **2** (Figure 1).



Figure 1. Structures of dinuclear Ru complex 1 and ligand 2.

This complex has considerably lower redox potentials from $Ru_2^{II,II}$ up to $Ru_2^{III,IV}$, than the corresponding dinuclear

Chem. Eur. J. 2011, 17, 7953-7959

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Ru complex, in which the two terminal phenolic groups are replaced by pyridines.

Although complex 1 turned out to be an interesting oxidation catalyst, it failed to catalyze water oxidation. This is probably due to oxidative degradation of the tertiary amine group in the ligand that occurs at the high oxidation potential required for the oxidation of water. It was therefore decided to synthesize ligand 7, in which the sensitive tertiary amine function of the complex has been replaced by imidazole, which is more resistant towards oxidation and is also present as a ligand in the OEC.

Results and Discussion

Ligand 7 was prepared according to Scheme 1. First, the dicesium salt of diacid 3 was allowed to react with bromoketone 4 to give diester 5 in high yield. This was then treated with ammonium acetate to give the bisimidazole compound 6. Deprotecting compound 6 with BBr_3 afforded ligand 7 in low yield (ca. 10%). However, demethylation with HI afforded ligand 7 as the hydroiodide salt, in high yield. Refluxing 7 with triethylamine and [Ru(DMSO)₄Cl₂] in methanol, followed by the addition of 4-picoline and continued reflux gave, somewhat surprisingly, a complex with an overall ratio of 1:1 between ligand 7 and ruthenium instead of a dinuclear complex, similar to 1. Unfortunately we have been unable to obtain crystals suitable for X-ray crystallography of the complex, but the elemental analysis suggests a structure such as 8, consisting of two mononuclear ruthenium units linked by a bridging iodide ligand. The UV/Vis spectrum (Figure 2) displays a broad signal at approximately 550 nm, implying that the oxidation state is Ru₂^{III,III}.^[12c] The Ru complex 8 was therefore studied with X-band EPR spectroscopy at 77 K. A frozen solution of complex 8 (1 mm) in dichloromethane gave no EPR signal, thus confirming that complex 8 resides in the EPR-silent $Ru_2^{III,III}$ oxidation state, with strong coupling between the ruthenium atoms. The



Figure 2. UV/Vis absorption spectrum of complex 8 (0.25 mm) in CH₂Cl₂.

complete lack of ${}^{1}H$ NMR signals is also compatible with a $Ru_{2}^{III,III}$ oxidation state.

Two additional elemental analyses were performed, one sample in which compound **8** had been dried under reduced pressure at 100 °C overnight and one at 150 °C. They indicated the loss of two picolines and four picolines, respectively. The unusual affinity for water that complex **8** displays is not easily explained.

The MALDI-TOF mass spectrum (Figure 3) shows two major signals corresponding to the two halves of complex 8, that is, complexes 9 (m/z 546) and 10 (m/z 637). A high resolution ESI-MS showed a major signal at m/z 804.19 (Figure 4). This could correspond to a compound in which one of the picolines has been oxidized to the corresponding aldehyde (11),^[11a] or in which an imidazole or a picoline has been oxidized to the corresponding *N*-oxide.^[13]

The catalytic activity of complex **8** in water oxidation was studied in acidic solution, using the Ce^{IV} oxidant $[Ce(NH_4)_2-(NO_3)_6]$. A deoxygenated aqueous solution of Ce^{IV} was



Scheme 1. Synthesis of ligand 7 and complex 8.

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Figure 3. MALDI-TOF mass spectrum of complex 8.



Figure 4. High-resolution ESI-MS spectrum of complex 8 in CH₂Cl₂.

added to an aqueous solution of **8** with pH1 (0.1 M CF₃SO₃H). Immediate oxygen evolution was observed, with an approximate turnover number (TON) of 1000/10 h based on complex **8** (Figure 5). The TON is strongly dependent on the concentration of the catalyst and the TON decreased upon dilution of the catalyst.

One explanation could be that the complex dissociates at lower concentration to give a mononuclear complex, which is a less efficient catalyst. As in most published studies of water oxidation, the oxygen evolution levels off after some time, under our conditions after ca 6 hours. The major reason is probably decomposition of the ligand backbone of the catalyst, as indicated by the formation of carbon dioxide during the water oxidation.

In an attempt to obtain information about the mechanism of water oxidation complex **8** was dissolved in an aqueous solution (pH ca. 1, H_3PO_4 0.1 M), in the presence and absence of Ce^{IV} (10 equiv). The reaction mixtures were left to

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stand overnight. Aliquots were then taken and analyzed by MALDI-TOF mass spectrometry. The mass spectra displayed no significant difference, suggesting that significant ligand exchange does not occur during water oxidation.

The cyclic voltammogram of complex **8** in aqueous phosphate buffer at pH 7.2 shows a current from catalytic oxygen evolution starting at approximately 1.2 V versus NHE (Figure 6). The electrochemistry of complex **8** suggests that [Ru-(bpy)₃]³⁺-type complexes, photogenerated from [Ru(bpy)₃]²⁺, could be used to drive the water oxidation.



Figure 5. Oxygen evolution catalyzed by complex **8** ($1.4 \,\mu$ M/ $0.14 \,\mu$ M) employing [Ce(NH₄)₂(NO₃)₆] (26 mM) as the oxidant in an aqueous CF₃SO₃H solution (pH 1, 3.9 mL). $\odot = 0.14 \,\mu$ M, $\blacklozenge = 1.4 \,\mu$ M.

In accordance with the results of the cyclic voltammetry (CV), it was found that water oxidation was catalyzed by complex 8 using $[Ru(bpy)_3]^{3+}$ as the oxidant. In a typical experiment, a deoxygenated solution of complex 8 in an aqueous phosphate buffer solution (pH 7.2) was added to $[Ru(bpy)_3]^{3+}$. This resulted in an instantaneous evolution of O₂, with a maximum TON of approximately 100/14 min (Figure 7). The TON is, again, extremely depending on the catalyst concentration and when this was decreased from 5.5 µm to 1.1 µm, the TON dramatically decreased to ca. 8/13 min. The TON is considerably lower than with Ce^{IV} as oxidant. One reason is clearly that $[Ru(bpy)_3]^{3+}$ is unstable at neutral pH. Under our reaction conditions, in aqueous phosphate buffer at pH 7.2 it decomposes, giving carbon dioxide as the main volatile product. Carbon dioxide was also formed in the presence of catalyst 8. Interestingly, the TON for carbon dioxide formation is only moderately depending on the catalyst concentration (Figure 8).

To ensure that H_2O is the sole source of the oxygen atoms in O_2 , isotopically labeled H_2O (¹⁸O, 5.4%) was used.

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Figure 6. Cyclic voltammogram in the presence (—) and absence (---) of complex **8** (55 μ M) in an aqueous phosphate buffer solution (pH 7.2, 0.1 M) using a glassy carbon working electrode and an Ag/AgCl reference electrode.



Figure 7. Chemical water oxidation catalyzed by complex **8** (5.5 μ M/ 1.1 μ M) employing [Ru(by)₃](PF₆)₃ (40 mM) as the oxidant in an aqueous phosphate buffer (0.1 M, pH 7.2, 0.5 mL). $\diamond = 5.5 \ \mu$ M, $\bullet = 1.1 \ \mu$ M.



Figure 8. Carbon dioxide evolution during water oxidation, in the presence of complex 8 (5.5 μ M/1.1 μ M) and [Ru(bpy)₃](PF₆)₃ (40 mM) as the oxidant in an aqueous phosphate buffer solution (0.1 M, pH 7.2, 0.5 mL). $\diamond = 5.5 \mu$ M, $\bullet = 1.1 \mu$ M.

This resulted in proportionally enriched O₂ (Figure 9). The isotopomeric ratio of ${}^{16,18}\text{O}_2/{}^{16,16}\text{O}_2$ (*m/z* ratio 34/32) was determined to be 0.118 (theoretically 0.114=2.0.054/(1-0.054)). An increase in *m/z* 36 was also seen, but the relative error in *m/z* 36 was too large for a quantitative determination. These results confirm that H₂O is the oxygen source of the evolved O₂.



Figure 9. Chemical water oxidation catalyzed by complex 8 (5.5 μ M) employing [Ru(byy)₃](PF₆)₃ (40 mM) as the oxidant in an aqueous phosphate buffer solution (0.1 M, pH 7.2, 0.5 mL) containing 5.4 % ¹⁸O. $\bullet = O_2$, $\Box = {}^{16.16}O_2$, $\blacksquare = {}^{16.18}O_2$.

We also decided to study photocatalytic oxygen evolution. In the initial experiments, $[Ru(bpy)_3]Cl_2$ was utilized as the photosensitizer. This should generate $[Ru(bpy)_3]^{3+}$ by photo-electron transfer to persulfate, $S_2O_8^{2-}$, as the sacrificial electron acceptor. To our surprise no evolution of oxygen was detected. However, when the anion in the photosensitizer was changed from Cl⁻ to PF₆⁻, oxygen evolution was observed with a TON of ca 30/20 min (Figure 10). This dramatic difference could be due to the competing oxidation of chloride to chlorine.^[8]

By substituting $[Ru(bpy)_3](PF_6)_2$ by the more strongly oxidizing photosensitizer, $[Ru(bpy)_2(deeb)](PF_6)_2$ (deeb=4,4'bis(ethoxycarbonyl)-2,2'-bipyridine), the photocatalytic system rapidly generated O₂ under illumination by visible light (Figure 10). Oxygen evolution lasted for 20 min and the TON was determined to ca 250/20 min. Addition of more photosensitizer led to the generation of more O₂, confirming that decomposition of the photosensitizer is a major limitation.

Additional experiments were made in a weaker phosphate buffer (0.01 M instead of 0.1 M), which after addition of catalyst, sensitizer, and persulfate gave a pH of 5. Illumination of this solution produced no oxygen. However, after neutralizing the pH to 7 with calcium hydroxide and upon illumination, oxygen evolution was observed. It is not clear if this simply reflects the pH dependence of the oxidation potential of water or if a reasonable concentration of hydroxide is required for the nucleophilic addition to an intermediate ruthenium oxo-species. During the catalytic cycle the ruthe-

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Figure 10. Light-driven oxygen evolution catalyzed by complex **8** (5.4 μ M), in an aqueous phosphate buffer solution (0.1 M, pH 7.2, 1.0 mL), in the presence of [Ru(bpy)₂(deeb)](PF₆)₂ (\bullet) or [Ru(bpy)₃](PF₆)₂ (\blacktriangle) (99 μ M) as photosensitizer and Na₂S₂O₈ (20 mM) as sacrificial electron acceptor.

nium is presumably oxidized from the initial $Ru_2^{III,III}$ state to $Ru_2^{V,V}$. Earlier work by Meyer, with the "blue dimer", shows that the mechanism for water oxidation is kinetically very complicated.^[9d] This may also be true for catalyst **8**, thus partly explaining the sensitivity of catalyst **8** to the reaction conditions in water oxidation.

To show that the oxygen is indeed derived from water, also in the light-driven oxidation, an experiment with labeled water (4.5 % ¹⁸O) was performed (Figure 11). The experimental ratio ^{16,18}O₂/^{16,16}O₂ was determined to 0.094, which is exactly the theoretical ratio.



Figure 11. Light-driven water oxidation catalyzed by complex **8** (4.8 μ M), in an aqueous phosphate buffer solution (0.1 M, pH 7.2, 0.46 mL) containing 4.5 % ¹⁸O, in the presence of [Ru(bpy)₂(deeb)](PF₆)₂ (110 μ M) as photosensitizer and Na₂S₂O₈ (21 mM) as sacrificial electron acceptor. $\bullet = O_2$, $\Box = {}^{16,16}O_2$, $\blacksquare = {}^{16,18}O_2$.

To demonstrate that water oxidation is indeed catalyzed by $\mathbf{8}$ a series of control experiments were conducted: 1) In the absence of catalyst $\mathbf{8}$, no oxygen was produced. 2) Irradiation in the absence of sensitizer did not generate any oxygen. 3) Replacing catalyst **8** by RuO_2 (same molar quantity of Ru), a well-known water oxidation catalyst,^[14] led to

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Conclusion

the generation of only substoichiometric amounts of oxygen.

In conclusion, we have prepared a new Ru complex **8** based on the bio-inspired ligand **7**. Complex **8** was found to efficiently catalyze water oxidation with Ce^{IV} as well as $[Ru(bpy)_3]^{3+}$ as chemical oxidants. More importantly, water oxidation could also be driven by visible light, employing $[Ru(bpy)_2(deeb)]^{2+}$ as photosensitizer, to give a high TON of approximately 250/20 min.

Future work will focus on linking the photosensitizer and the water oxidation catalyst to improve the electron transfer from the oxidation catalyst to the photooxidized photosensitizer. Also attempts to attach this system to an acceptor surface will be initiated.

Experimental Section

Materials and general methods: [Ru(DMSO)₄Cl₂]^[15] and [Ru(bpy)₃]-(PF₆)₃^[16] were prepared according to literature procedures. All other reagents including solvents were obtained from commercial suppliers and used directly without further purification. All solvents were dried by standard methods when needed. ¹H and ¹³C NMR spectra were recorded at 400 MHz and at 100 MHz, respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak [CDCl₃ (δ (H)=7.26 and $\delta(C) = 77.16$, [D₆]DMSO ($\delta(H) = 2.50$ and $\delta(C) = 39.52$), CD₃OD $(\delta(H)=3.31$ and $\delta(C)=49.00)$] as internal standard. Splitting patterns are denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Flash chromatography was carried out with 60 Å (particle size 35-70 µm) normal phase silica gel. High resolution mass spectra measurements were recorded on a Bruker Daltonics microTOF spectrometer with an electrospray ionizer. Cyclic voltammetric (CV) measurements were carried out with an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie), using a glassy carbon disk (diameter 3 mm) as the working electrode, and a platinum spiral as counter-electrode. The reference electrode was an Ag/AgCl electrode (3 M KCl aqueous solution). The electrolyte used was a pH 7.2 phosphate buffer (0.1 M). All potentials are reported vs. NHE, using the $[\operatorname{Ru}(\operatorname{bpy})_3]^{3+}/[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$ couple $(E_{1/2}=1.26 \text{ V vs. NHE})$ as an internal standard. Half-wave potentials $(E_{1/2})$ were determined by cyclic voltammetry as the average of the anodic and cathodic peak potentials ($E_{1/2}$ = $(E_{pa}+E_{pc})/2)$. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer, using samples prepared as KBr discs. The UV/Vis absorption spectra were measured on a CARY 300 Bio UV/Visible spectrophotometer. Elemental analyses were carried out at Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr, Germany, and Analytische Laboatorien, Prof. Dr. H. Malissa und G. Reuter GmbH, Lindlar, Germany. EPR spectra were recorded at 77 K on a Varian E9 spectrometer equipped with a quartz insert for liquid nitrogen. Measurements were made with a microwave frequency of 9.12 GHz, a microwave power of 2 mW and a modulation amplitude of 2 mT.

2-Methoxyisophthalic acid (3): A solution of KOH (34.0 g, 606 mmol) in H_2O (200 mL) was added to a suspension of 2,6-dimethylanisole (25.0 g, 184 mmol), KMnO₄ (191.5 g, 1.21 mol) and H_2O (500 mL). After heating at 80°C overnight, the mixture was cooled to RT and the solid was filtered off. Upon acidification of the filtrate with concentrated HCl to pH 1, a white precipitate was formed and filtered off, washed with H_2O and Et_2O , and dried under vacuum to obtain **3** as a white solid (13.3 g,

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37%). Spectral data were in accordance with those previously reported in the literature. $^{\left[17\right] }$

2-(Bromoacetyl)anisole (4): 2-Methoxyacetophenone (0.75 g, 5.0 mmol) and *N*-bromosuccinimide (0.89 g, 5.0 mmol) were triturated together with *p*-toluenesulfonic acid (0.095 g, 0.50 mmol) in a porcelain mortar for 5 min to form a yellow viscous reaction mixture which was left to stand at room temperature for 3 h. H₂O (5 mL) was added, followed by extraction with CH₂Cl₂ (2×10 mL). The organic phases were combined and washed with water (10 mL), dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. The pale grey oil was recrystallized from EtOH to yield **4** as white crystals (0.97 g, 84%). ¹H NMR (CDCl₃, 400 MHz): δ =3.95 (s, 3H; OCH₃), 4.61 (s, 2H; CH₂), 6.99 (dd, *J*=8.53, 0.76 Hz, 1H; Ph-H), 7.04 (ddd, *J*=8.37, 6.88, 0.95 Hz, 1H; OH-H), 7.52 (ddd, *J*=8.52, 7.28, 1.85, 1H; Ph-H), 7.83 ppm (dd, *J*=7.74, 1.85 Hz, 1H; Ph-H); ¹³C NMR (100 MHz, CDCl₃): δ =192.4, 158.9, 134.9, 131.6, 125.0, 128.3, 121.2, 111.7, 55.9, 37.8 ppm; HRMS (ESI): *m/z* calcd for C₉H₉O₂Br+Na⁺: 250.9678 [*M*+Na⁺]; found: 250.9681.

Bis(2-(2-methoxyphenyl)-2-oxoethyl)-2-methoxyisophthalate (5): 2-Methoxyisophthalic acid (18.3 g, 93.3 mmol) and Cs₂CO₃ (32.6 g, 93.3 mmol) were suspended in EtOH (250 mL) and stirred vigorously at RT for 2 h. The solvent was evaporated and the white solid was dried over phosphorus pentoxide before being suspended in DMF (300 mL). When compound 4 (43.0 g, 186 mmol) was added, the reaction mixture turned light brown. After stirring at RT overnight the solvent was evaporated, resulting in a pale brown solid which was extracted with CH_2Cl_2 (300 mL). The white salt was removed by filtration and the solvent was evaporated to give a brown solid. Recrystallization from EtOAc yielded 5 as pale brown crystals (42.2 g, 92%). ¹H NMR (400 MHz, CDCl₃): $\delta = 3.98$ (s, 6H; OCH₃), 4.04 (s, 3H; OCH₃), 5.49 (s, 4H; CH₂), 7.04 (dd, J=8.35, 0.68 Hz, 2H; Ph-H), 7.06 (ddd, J=7.58, 7.29, 1.02 Hz, 2H; Ph-H), 7.24-7.29 (m, 1H; Ph-H), 7.54 (ddd, J=8.41, 7.31, 1.85 Hz, 2H; Ph-H), 7.97 (dd, J=7.79, 1.85 Hz, 2H; Ph-H), 8.15 ppm (d, J=7.74 Hz, 2H; Ph-H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 55.7$, 64.2, 70.7, 111.7, 121.2, 123.6, 124.43 126.4, 131.2, 135.1, 135.8, 159.7, 160.4, 165.2, 192.8 ppm. HRMS (ESI): m/z calcd for $C_{27}H_{24}O_9+Na^+$: 515.1313 [$M+Na^+$]; found: 515,1323

2,6-(2-Methoxyphenylimidazolyl)anisole (6): Compound 6 was prepared according to a modified published procedure for conversion of ketoesters into imidazoles. $^{[18]}$ The diester $\boldsymbol{5}$ (3.76 g, 7.6 mmol) and NH4OAc (17.66 g, 228 mmol) were suspended in o-xylene (35 mL) and the mixture was refluxed using a Dean-Stark trap. Periodic aliquots were taken and analyzed by MS to determine the presence of the monocyclized intermediate. When reaction was complete, after a time period varying between 40 min and 2 h, the mixture was cooled to RT. The reaction mixture was then diluted with EtOAc (50 mL) and washed with a saturated aqueous solution of NaHCO₃. The organic phase was dried with MgSO₄ and the solvents were evaporated under reduced pressure, resulting in a yellow residue which was purified by flash chromatography. Elution with a gradient from pentane (100%) to EtOAc (100%) gave compound 6 as a yellow oily solid (1.12 g, 33 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.25$ (d, J = 7.80 Hz; 2H), 7.88 (br, 2H), 7.65 (s, 2H), 7.35 (t, J = 7.80 Hz, 1H), 7.28 (ddd, J=8.34, 7.54, 1.61 Hz, 2H), 7.08 (dt, J=7.54, 1.02 Hz, 2H), 7.03 ppm (d, J = 8.34 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 155.1$, 153.4, 142.9, 134.3, 129.3, 128.3, 127.0, 126.1, 123.9, 121.8, 111.7, 62.2, 55.9 ppm; HRMS (ESI) m/z calcd for $C_{27}H_{25}N_4O_3$: 453.1921 [$M+H^+$]; found: 411.1924.

2,6-(2-Hydroxphenylimidazolyl)phenol (7)-1.5 HI-1.5 (CH₃)₂CO-H₂O: A suspension of compound 6 (1.81 g, 4.0 mmol) in hydriodic acid (57 wt% in H₂O, 40 mL) was refluxed under argon for 17 h. After cooling the reaction mixture to RT the yellow precipitate was filtered off and washed with water. Recrystallization from methanol/acetone gave the desired compound as an orange solid (1.82 g, 64%). ¹H NMR (400 MHz, [D₆]DMSO): δ =14.67 (br, 2H), 14.11 (br, 2H), 10.52 (br, 2H), 8.14 (d, *J*=7.84 Hz, 2H), 7.97 (s, 2H), 7.85 (dd, *J*=7.65, 1.35 Hz, 2H), 7.25 (ddd,

 $\begin{array}{l} J{=}8.30,\ 7.65,\ 1.35\ {\rm Hz},\ 2\,{\rm H}),\ 7.20\ ({\rm t},\ J{=}7.84\ {\rm Hz},\ 1\,{\rm H}),\ 7.04\ ({\rm d},\ J{=}8.30\ {\rm Hz},\ 2\,{\rm H}),\ 6.98\ {\rm ppm}\ ({\rm t},\ J{=}7.65\ {\rm Hz},\ 2\,{\rm H});\ ^{13}{\rm C}\ {\rm NMR}\ (100\ {\rm MHz},\ {\rm CD}_3{\rm OD}):\ \delta{=} \\ 157.8,\ 155.7,\ 142.8,\ 133.1,\ 131.2,\ 131.2,\ 128.0,\ 121.2,\ 120.9,\ 117.7,\ 117.2,\ 115.6,\ 114.4\ {\rm ppm};\ {\rm IR}\ ({\rm KBr}):\ \tilde{\nu}_{\rm max}{=} 3100,\ 1692,\ 1627,\ 1584,\ 1497,\ 1463,\ 1233,\ 1210\ {\rm cm}^{-1};\ {\rm HRMS}\ ({\rm ESI}):\ m/z\ {\rm calcd}\ {\rm for}\ C_{24}{\rm H}_{19}{\rm N}_{4}{\rm O}_{3}:\ 411.1452\ [M{+}{\rm H}^{+}];\ {\rm found}:\ 411.1444;\ {\rm Anal.}\ {\rm Calcd}\ (\%)\ {\rm for}\ C_{57}{\rm H}_{61}{\rm I}_{3}{\rm N}_{8}{\rm O}_{11}\ [2(7)\cdot3{\rm Hi}\cdot3({\rm CH}_{3})_{2}{\rm CO}\cdot2{\rm H}_{2}{\rm O}]:\ {\rm C}\ 48.39,\ {\rm H}\ 4.35,\ {\rm I}\ 26.9,\ {\rm N}\ 7.92;\ {\rm found}:\ {\rm C}\ 48.25,\ {\rm H}\ 4.54,\ {\rm I}\ 29.5,\ {\rm N}\ 7.99. \end{array}$

Synthesis of Ru complex 8-MeOH-9H2O. Ligand 7 (67 mg, 0.095 mmol) and Et₃N (0.17 mL, 1.2 mmol) were dissolved in MeOH (2 mL). [Ru- $(DMSO)_4Cl_2$] (121 mg, 0.25 mmol) was added to this solution and the mixture was refluxed for 24 h. Then 4-methylpyridine (0.34 mL, 3.5 mmol) was added, and the mixture was further refluxed for 48 h. After cooling to RT, the reaction mixture was filtered to remove a yellow precipitate. After addition of H2O (2 mL) to the filtrate, the complex precipitated as a dark-green solid. The precipitate was isolated by centrifugation, washed with water (5×4 mL), and dried under vacuum to afford 8 (83 mg, quant.). IR (KBr): $\tilde{\nu}_{\rm max}\!=\!3410,\;3050,\;2920,\;1936,\;1619,\;1500,$ 1445, 1286, 1209, 1033, 812, 753 cm⁻¹; Anal. Calcd (%) for C₇₃H₈₁IN₁₂O₁₆Ru₂ [Complex 8·MeOH·9H₂O]: C 51.2, H 4.8, N 9.8, found: C 51.8, H 4.8, N 9.5; 100 °C; Anal. Calcd (%) for $C_{60}H_{63}IN_{10}O_{15}Ru$ [Complex 8-2 pic 9H2O]: C 48.3, H 4.2, N 9.4; found: C 47.9, H 4.2, N 9.1; 150°C: Anal. Calcd. (%) for C48H49IN8O15Ru2 [Complex 8-4 pic 9 H2O]: C 44.1, H 3.8, N 8.6; found: C 43.9, H 3.8, N 8.7.

Oxygen evolution measurements: Oxygen evolution was measured by mass spectrometry. We have previously used the MS technique to study oxidation/reduction of water.^[6a,19,20] In this study we have used the MS technique to study chemical oxidation and light induced oxidation of water. An aqueous stock solution **X1** was made, containing 55 μ M of complex **8** and 0.05 M of H₃PO₄. Solution **X2** used in the experiments was made by diluting the stock solution **X1** ten times with a phosphate buffer (pH 7.2, 0.1 M). Solution **X2** was then deoxygenated by bubbling with N₂ for at least 5 min before being used in the experiments.

Chemical oxidation with Ce^{IV}: A Ce^{IV}-oxidant solution was made by dissolving [Ce(NH₄)₂(NO₃)₆] (56 mg, 100 µmol) in water (3.7 mL, pH ca. 1 adjusted with CF₃SO₃H) and the solution was bubbled with N₂ for at least 5 min before being injected into the reaction chamber. Two experiments were made with different solutions of the Ru complex. The first solution was a mixture of **X1** (0.01 mL, 0.55 nmol) and water (0.2 mL, pH ca. 1 adjusted with CF₃SO₃H). The second solution was a mixture of **X1** (0.1 mL, pH 1 adjusted with CF₃SO₃H). These solutions were, one at the time, placed in the reaction chamber and the reaction chamber was evacuated for ca. 10 min to remove O₂ from the water solution. Ca. 30 mbar He was then introduced in to the reaction chamber and after an additional 5 min the Ce^{IV} solution was injected.

Chemical oxidation with Ru^{III}: $[Ru(bpy)_3](PF_6)_3$ (20.4 mg, 20.3 µmol) was placed in the reaction chamber and the reaction chamber was evacuated with a rough pump for 5 min. 43 mbar He was then introduced into the system. Solution **X2** (0.5 mL, 2.8 nmol) was then injected into the reaction chamber (5 min after that He was introduced). The generated oxygen was then measured and recorded versus time with the mass spectrometer.

¹⁸O-Isotopic labeling experiments: $[Ru(bpy)_3](PF_6)_3$ (20.4 mg, 20.3 µmol) was placed in the reaction chamber. The reaction chamber was then evacuated and after 5 min 44 mbar He was introduced into the system. At the same time 97 % ¹⁸O water (0.05 mL) was added to **X2** (0.5 mL, 2.8 nmol). After 5 min the solution was injected into the reaction chamber. The generated oxygen was then measured and recorded versus time with the mass spectrometer. The ¹⁸O concentration in the water was measured with the mass spectrometer from the ratio between *m*/*z* 18 (H₂¹⁶O) and 20 (H₂¹⁸O).

Light-induced oxidation of water: The light source in these experiments was a halogen lamp. The reaction chamber was in these experiments placed in a 100 mL glass vessel filled with water. The function of this glass vessel was to avoid heating of the system and to act as a UV-filter. A solution of $[\text{Ru}(\text{bpy})_2(\text{deeb})](\text{PF}_6)_2$ in acetonitrile $(10 \,\mu\text{L}, 10 \,\text{mM}, 100 \,\text{nmol})$ and $\text{Na}_2\text{S}_2\text{O}_8$ (4.7 mg, 20 μ mol) were placed in the reaction chamber. The system was then evacuated with a rough pump and all the acetonitrile was removed in the pumping. After the background pressure was reached, 47 mbar He was introduced into the system. After 5 min solution **X2** (1 mL, 5.5 mmol) was injected and after an additional 2.5 min the light was switched on.

¹⁸O-isotopic labeling experiments: A solution of $[Ru(bpy)_2(deeb)](PF_6)_2$ in acetonitrile (5 μL, 10 mM, 50 nmol) and Na₂S₂O₈ (2.3 mg, 9.7 μmol) were placed in the reaction chamber. The system was then evacuated with a rough pump and all the acetonitrile was removed in the pumping. After the background pressure was reached, 46 mbar He was introduced into the system. After an additional 5 min a mixture of **X2** (0.4 mL, 2.2 nmol) and 97% ¹⁸O water (0.05 mL) was injected and after an additional 2.5 min the light was switched on. The ¹⁸O concentration in the water was measured with the mass spectrometer from the ratio between mass 18 (H₂¹⁶O) and 20 (H₂¹⁸O).

Acknowledgements

We thank Dr. Y. Xu for a sample of $[Ru(bpy)_2(deeb)](PF_6)_2$, the Knut & Alice Wallenberg Foundation, and The Swedish Energy Agency for financial support.

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Received: December 22, 2010 Published online: May 26, 2011