JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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A Molecular Light-Driven Water Oxidation Catalyst

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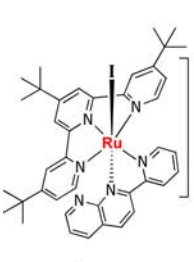
Supporting Information

ABSTRACT: Two mononuclear Ru(II) complexes, [Ru(ttbt)(pynap)(I)]I and [Ru(tpy)(Mepy)$_2$(I)]I (tpy = 2,2′;6,2″-terpyridine; ttbt = 4,4′,4″-tri-*tert*-butyltpy; pynap = 2-(pyrid-2′-yl)-1,8-naphthyridine; and Mepy = 4-methylpyridine), are effective catalysts for the oxidation of water. This oxidation can be driven by a blue (λ_{max} = 472 nm) LED light source using [Ru(bpy)$_3$]Cl$_2$ (bpy = 2,2′-bipyridine) as the photosensitizer. Sodium persulfate acts as a sacrificial electron acceptor to oxidize the photosensitizer that in turn drives the catalysis. The presence of all four components, light, photosensitizer, sodium persulfate, and catalyst, are required for water oxidation. A dyad assembly has been prepared using a pyrazine-based linker to join a photosensitizer and catalyst moiety. Irradiation of this intramolecular system with blue light produces oxygen with a higher turnover number than the analogous intermolecular component system under the same conditions.

One of the primary goals in the area of solar energy utilization is the development of an effective molecular catalyst to carry out artificial photosynthesis.[1] For solar water decomposition such a catalyst would consist of three critical components: a chromophore to absorb light in the available region of the solar spectrum and provide a reasonably long-lived, charge-separated excited state; an oxidation catalyst to facilitate the decomposition of water into dioxygen; and a reduction catalyst to carry out the analogous process for the reduction of protons to dihydrogen. From a chemical standpoint, the oxidation of water is the more challenging process since it involves the transfer of four electrons and the combination of two oxygens coming from different water molecules. Our group[2] and others[3] have had some recent success in the development of water oxidation catalysts based on transition metal complexes involving Ru(II), Mn(III), Ir(III), and other metals. These catalysts are driven chemically by the use of a sacrificial oxidant such as Ce(IV) which activates the water oxidation catalyst (WOC). Issues related to the role of cerium in the oxidation process have somewhat complicated this approach.[4] Alternatively, surface modified electrodes may also be used for this same purpose.[5]

Here we report the use of a photosensitizer in conjunction with a sacrificial electron acceptor to activate a mononuclear Ru(II) complex that has previously demonstrated good performance as a WOC.[6] Furthermore, the catalyst and photosensitizer have been combined into a single molecule using a pyrazine-derived linker to provide a system that uses light to directly produce oxygen from water, although a stoichiometric electron acceptor is still required. We have undertaken a systematic study that varies the light source, photosensitizer, and oxidation catalyst to help better understand the catalytic process and to optimize the performance of our system.

In recent work we have investigated a family of 28 mononuclear Ru(II) complexes as water oxidation catalysts.[6] These complexes belong to two general groups: [Ru(bpy)(tpy)X]$^+$ (type 1) and [Ru(tpy)(Mepy)$_2$X]$^+$ (type 2) (bpy = 2,2′-bipyridine, tpy = 2,2′;6,2″-terpyridine, Mepy = 4-methylpyridine), X = halogen or water). For Ce(IV) promoted water oxidation, we often found that X = iodide complexes were unusually active. We also found that a type 1 catalyst using 2-(pyrid-2′-yl)-1,8-naphthyridine (pynap) as the bidentate ligand was exceptionally active[7] while the use of 4,4′,4″-tri-*tert*-butyltpy (ttbt) as a tridentate ligand sometimes improves activity.[6] For these reasons we initially chose complexes **1** and **2** for use as catalysts in a bimolecular light-driven process.



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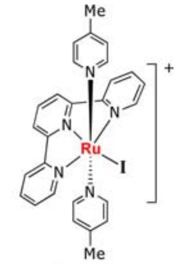

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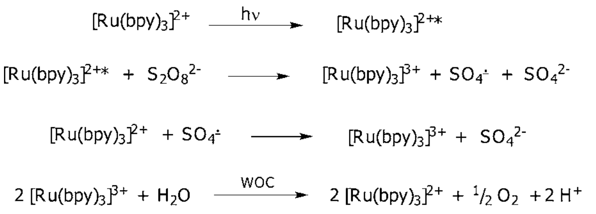
This investigation was greatly facilitated by the use of a light emitting diode (LED) as the irradiation source. LEDs are available as inexpensive strips and have well-defined emission properties (Figure S1 in the SI). For the photosensitizer we chose [Ru(bpy)$_3$]Cl$_2$ which has been previously employed in this regard[8] and which provides an excited state that after the loss of an electron can readily oxidize our catalyst. Figure S1 shows the absorption spectrum of [Ru(bpy)$_3$]Cl$_2$ in water along with the emission spectra of blue, green, amber, and red LEDs. Light absorption by the photosensitizer clearly decreases as the emission maximum of the excitation source shifts to the red. To obtain [Ru(bpy)$_3$]$^{3+}$ after photoexcitation, an electron must be expelled from the sensitizer complex and for this we use sodium persulfate as a sacrificial electron acceptor. The addition of one electron to sodium persulfate provides sodium sulfate and a sulfate anion radical that can oxidize [Ru(bpy)$_3$]$^{2+}$ to provide a second equivalent of sulfate and [Ru(bpy)$_3$]$^{3+}$ (Scheme 1).[9] The intermediate persulfate anion radical that is

Received: January 24, 2012
Published: June 14, 2012

dx.doi.org/10.1021/ja300797g | *J. Am. Chem. Soc.* 2012, 134, 10721−10724

Scheme 1. Photosensitized water oxidation using $[Ru(bpy)_3]Cl_2$, $Na_2S_2O_8$, and a WOC.[9]



formed in step 2 of Scheme 1 is a strong oxidant, and we cannot rule out it reacting directly with the WOC. We did confirm, however, that $[Ru(bpy)_3]^{3+}$, generated thermally[10] by oxidation of $[Ru(bpy)_3]Cl_2$ with PbO_2, was sufficient to activate the WOC and generate O_2. It is necessary to buffer the solution to prevent it from becoming too acidic and thus retarding the catalysis. After some experimentation we settled on a Na_2SiF_6/$NaHCO_3$ buffer system as suggested by Mallouk et al.[11]

In a typical experiment, a 50 μL acetonitrile solution of the catalyst was injected into an aqueous solution (5 mL) of the photosensitizer and sodium persulfate buffered to pH 5.3 ± 0.2 by Na_2SiF_6/$NaHCO_3$. A water-jacketed beaker was used to maintain a temprature of 20 °C, and a strip of 18 LED lights was wrapped around the beaker. A Clark electrode immersed in the solution was used to monitor the evolution of oxygen which was then recorded as a function of time. When an aqueous solution of catalyst **1** or **2** (0.04 mM) was irradiated by blue LEDs in the presence of $[Ru(bpy)_3]Cl_2$ (0.16 mM) and $Na_2S_2O_8$ (8 mM) for 6 h, TON = 6 (for **1**) and 57 (for **2**) were measured (Figures S2 and S3 in SI). We also prepared the photosensitizer $[Ru(pynap)(bpy)_2]Cl_2$, having a higher excited state oxidation and lower excited state reduction potential than $[Ru(bpy)_3]Cl_2$ (Table 1). Under identical conditions as used for $[Ru(bpy)_3]Cl_2$, $[Ru(pynap)(bpy)_2]Cl_2$ ($E^*_{1/2}$(red) = 0.65 V) was much less effective in activating both catalysts **1** and **2** for oxygen production. If any one of the four critical components in these bimolecular experiments (catalyst, photosensitizer, sodium persulfate, or blue light) is omitted, no oxygen evolution is observed. Ambient room light also provides a very small amount of oxygen.

Using the more active catalyst **2**, we examined the effect of varying the concentration of the $[Ru(bpy)_3]Cl_2$ and found that oxygen evolution showed first-order behavior in the photosensitizer (Figure 1). It is noteworthy that the catalyst and photosensitizer are both polypyridine Ru(II) complexes. Their functions are most likely differentiated by their excited state lifetimes. A longer lifetime for $[Ru(bpy)_3]Cl_2$ as compared to a Ru-tpy complex would allow for more facile electron loss to persulfate. A bifunctional water reduction system in which a single Pt complex combines the functions of both sensitizer and catalyst has also been reported.[13]

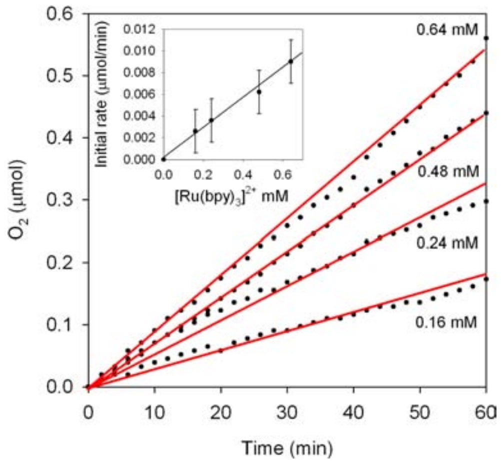


Figure 1. Initial rate of oxygen production by **2** (0.04 mM) and $Na_2S_2O_8$ (8 mM) in the presence of amber light (λ_{max} = 599 nm) as a function of sensitizer concentration.

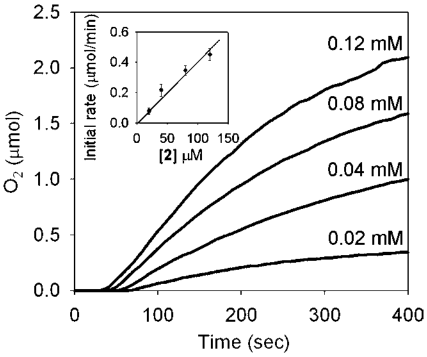


Figure 2. Initial rate of oxygen production (measured after induction period) upon blue light irradiation of various concentrations of **2** containing $[Ru(bpy)_3]Cl_2$ (0.16 mM) and $Na_2S_2O_8$ (8 mM).

The effect of varying the concentration of catalyst **2** is shown in Figure 2. If the concentration of **2** is plotted against the initial rate of oxygen production (inset), a linear (R^2 = 0.97) relationship is maintained, indicating first-order behavior in the catalyst. The photocatalytic effect is clearly illustrated in Figure 3 that shows the effect of turning the light source on and off. The slight decrease in oxygen during the "off" period has been observed previously[14] and results from equilibration of

Table 1. Electronic Absorption[a] **and Electrochemical Potential (Ground**[b] **and Excited State (E^*)) Data for $[Ru(bpy)_3]^{2+}$, $[Ru(pynap)(bpy)_2]^{2+}$, and Catalysts 1, 2, and 5**

Compound	λ_{max} (log ε)	$E_{1/2}^{ox}$ (ΔE)	$E_{1/2}^{red}$ (ΔE)	$E^*_{1/2}{}^{red}$	$E^*_{1/2}{}^{ox}$
$[Ru(bpy)_3]^{2+}$	453 (4.16)	1.27 (84)	−1.34(73), −1.52 (77)	0.77[c]	−0.81[c]
$[Ru(pynap)(bpy)_2]^{2+}$	443 (3.93), 508 (3.89)	1.21 (77)	−1.00 (69), −1.45 (90)	0.65[d]	−0.44[d]
1	561 (4.06)	0.72 (80)	−1.12 (80), −1.62^{ir}		
2	520 (4.56)	0.79(77)	−1.38(77)		
5	486 (4.18), 692 (4.10)	0.84 (135), 1.54^{ir}	−0.56^{ir}, −1.0^{ir}		

[a] Measured in H_2O/CH_3CN (4:1) (5.0×10^{-5} M) at 20 °C; λ in nm and log ε in $L \cdot mol^{-1}\ cm^{-1}$. [b] Measured with a glassy carbon eletrode at 100 mV/s in CH_3CN containing 0.1 M NBu_4PF_6 and $E_{1/2}$ reported in volts relative to SCE; $E_{1/2} = (Epa + Epc)/2$ in volts, and $\Delta E = (Epa - Epc)$ in mV; ir = irreversible. [c] Reference 12. [d] Estimated using $E^*_{1/2}{}^{ox} = E_{1/2}{}^{ox} - E_{em}$ and $E^*_{1/2}{}^{red} = E_{1/2}{}^{red} + E_{em}$, where E_{em} = 1.65 eV for $[Ru(pynap)(bpy)_2]^{2+}$ (λ_{ex} = 508 nm, in CH_3CN at 5.0×10^{-5} M).

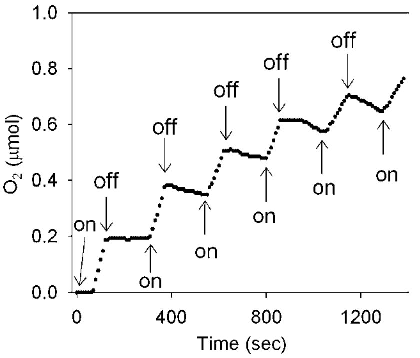
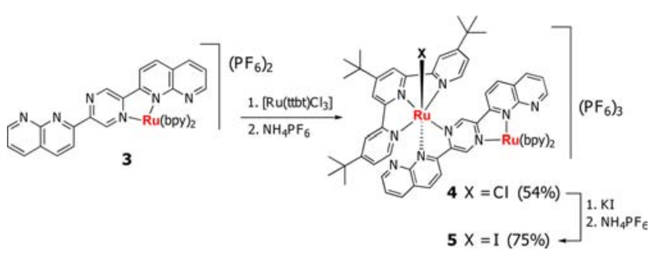


Figure 3. Oxygen evolution catalyzed by **2** (0.04 mM) with $[Ru(bpy)_3]Cl_2$ = 0.16 mM and $Na_2S_2O_8$ = 8 mM in the presence and absence of blue light.

dissolved oxygen with oxygen in the headspace. The slope of the line during the "on" periods also decreases, and after the initial induction period, no further induction period is observed. Thus there appears to be slight catalyst or photosensitizer decomposition during the "off" cycles, and the original and resting states of the catalyst are very likely not the same.

We reasoned that a more efficient oxidation system might result if the catalyst and photosensitizer could be incorporated into the same molecule. Although dyad assemblies containing a photosensitizer and catalyst have been reported for the oxidation of alcohols to ketones and aldehydes[15] and sulfides to sulfoxides[16] as well as the reduction of water to dihydrogen,[17] similar assemblies for the oxidation of water are not well-known.[14] Based on our success with the intermolecular systems $[Ru(bpy)_3]$-**1** and $[Ru(bpy)_3]$-**2**, we have synthesized and evaluated a dyad integrating a $[Ru(bpy)_2]$ moiety with the catalyst **1**. We chose to use 2,6-di-(1′,8′-naphthyrid-2′-yl)pyrazine as the bridging ligand. In earlier work we have reported the formation in a 55% yield of **3**, the mononuclear $Ru(bpy)_2$ complex of this bridging ligand.[18] Treatment of this species with $[Ru(ttbt)Cl_3]$ (ttbt = 4,4′,4″-tri-*tert*-butyl tpy) results in the formation of complex **4**. This complex may be treated with excess KI to replace chloride with iodide, giving complex **5** (Scheme 2). Although the complexation to form **5** could lead to two stereoisomers with regard to the disposition of iodide (*cis* to pyrazine or *cis* to 1,8-naphthyridine), we only observe the indicated isomer with iodide *cis* to the pyrazine[7] as substantiated by the appearance of a pyrazine singlet at 12.56 ppm in the ^{1}H NMR (Figure S10 in SI).

Scheme 2. Synthesis of the Dyads 4 and 5



We found that when an aqueous solution of **5** containing sodium persulfate was irradiated with blue LEDs, oxygen was liberated with a TON (6 h) = 134. This dyad is a far more effective catalyst than the analogous combination of **1** and $[Ru(bpy)_3]Cl_2$ (used at a 4× greater concentration) that provides a TON of only 6 (Figure S4 in SI). It is noteworthy that, unlike catalysts **1** and **2**, the dyad **5** can be activated by the strong oxidant $Na_2S_2O_8$ and a small amount of oxygen is formed even in the absence of light (Figure 4). It should be noted that the dyad **5** performance is particularly impressive in that we have demonstrated that $[Ru(bpy)_2(pynap)]Cl_2$ is not well matched as a photosensitizer (Table 1). We are investigating related dyads that overcome this possible shortcoming.

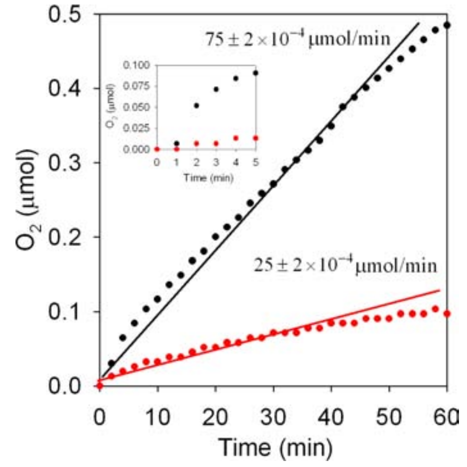


Figure 4. Oxygen evolution by the dyad **5** (0.025 μmol) and $Na_2S_2O_8$ (8 mM) in the presence (black) and absence (red) of blue light.

This study takes a significant step forward in the accomplishment of artificial photosynthesis. We have demonstrated that a dyad assembly containing a water oxidation catalyst and an appropriate photosensitizer linked through a central pyrazine, using a complementary light source and a sacrificial electron acceptor in a buffered aqueous solution, can effectively use light to decompose water and generate oxygen. We are now examining various water reduction catalysts in hopes of substituting such a species for the sacrificial oxidant and thus obtaining a truly catalytic water splitting system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details regarding synthesis, catalysis, and oxygen monitoring; Figure S1; and ^{1}H NMR spectra for $[Ru(pynap)(bpy)_2]Cl_2$, catalyst **1**, and dyads **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work at the University of Houston was funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-FG02-07ER15888 and the Robert A. Welch Foundation through Grant E-621. We also thank Professor Craig Hill and one of the reviewers for helpful remarks.

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