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Homogeneous Light-Driven Water Oxidation Catalyzed by a Tetraruthenium Complex with All Inorganic Ligands

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Providing renewable pollution-free fuels is one of the most important scientific challenges of the 21st century, and in this context, the direct, efficient, sustained sunlight-driven splitting of water into H_2 and O_2 remains one of the most desirable targets. Development of O_2 evolution/H_2O oxidation catalysts (WOCs) in artifical photosynthesis (AP) schemes [comprising coupled visible-light photosensitizers, H_2 evolution catalysts (HECs), and WOCs] has frequently been success-limiting, despite significant progress on heterogeneous[1−4] and homogeneous[5−13] WOCs. Recently, H_2O oxidation by $[Ru(bpy)_3]^{3+}$ (eq 1)[14] and Ce(IV)[15] catalyzed by the tetraruthenium polyoxometalate complex $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ (**1**) has been reported. This complex exhibits the stability advantages of heterogeneous catalysts with the tunability and other advantages of homogeneous catalysts. In this work, we demonstrate that **1** catalyzes efficient water oxidation in a totally homogeneous visible-light-driven AP system at neutral (physiological) pH (Scheme 1).

$$4[Ru(bpy)_3]^{3+} + 2H_2O \rightarrow 4[Ru(bpy)_3]^{2+} + O_2 + 4H^+ \qquad (1)$$

Figure 1 plots the kinetics of O_2 formation and persulfate ($S_2O_8^{2-}$) consumption catalyzed by **1** (the net reaction is eq 2). The quantum efficiency (defined as the number of molecules of O_2 formed per two absorbed photons) is ∼9%, which, to our knowledge, is among the highest reported for photocatalytic water oxidation using molecular catalysts.[6]

$$2S_2O_8^{2-} + 2H_2O + 2h\nu \rightarrow 4SO_4^{2-} + O_2 + 4H^+ \qquad (2)$$

In the photocatalytic system reported here, $[Ru(bpy)_3]^{3+}$ is generated from $[Ru(bpy)_3]^{2+}$ ($\lambda_{max} = 454$ nm, $\varepsilon = 1.4 \times 10^4$ M^{-1} cm^{-1}) by photooxidation using $S_2O_8^{2-}$ as a sacrificial electron acceptor. This process has been well-studied and is believed to proceed via $S_2O_8^{2-}$ quenching of the visible-light-accessible metal-to-ligand charge-transfer excited state, $[Ru(bpy)_3]^{2+}*$.[16] The products, $[Ru(bpy)_3]^{3+}$ and $SO_4^{\bullet-}$ [$E°(SO_4^{\bullet-}/SO_4^{2-}) \approx 2.4$ V][17] are both strong oxidants, and the latter oxidizes $[Ru(bpy)_3]^{2+}$ to form a second $[Ru(bpy)_3]^{3+}$.[18] The absorption of two photons and the consumption of 2 equiv of $S_2O_8^{2-}$ generates four $[Ru(bpy)_3]^{3+}$ (eq 3), sequentially oxidizing **1**, which in turn oxidizes H_2O to O_2 (eq 1) and regenerates $[Ru(bpy)_3]^{2+}$ (net reaction in eq 2 via Scheme 1).

$$4[Ru(bpy)_3]^{2+} + 2S_2O_8^{2-} + 2h\nu \rightarrow 4[Ru(bpy)_3]^{3+} + 4SO_4^{2-} \qquad (3)$$

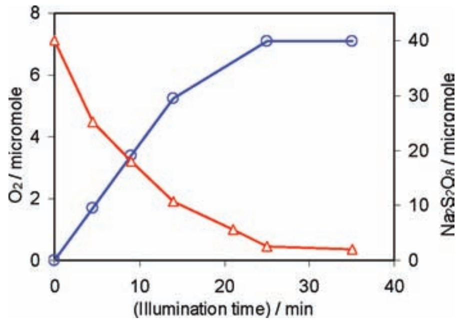
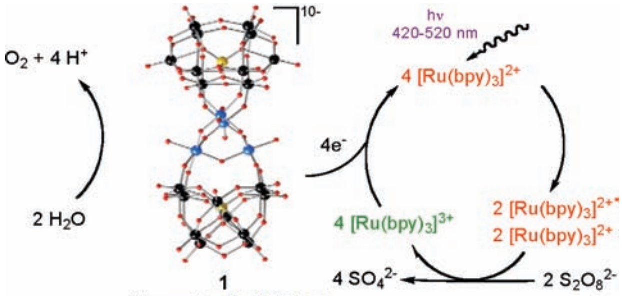


Figure 1. Kinetics of O_2 formation (○) and persulfate consumption (△) in the Scheme 1 photocatalytic system. Conditions: Xe lamp, 420−520 nm bandpass filter, 50 mW light beam with a diameter of ∼1.5 cm focused on the reaction solution, 1.0 mM $[Ru(bpy)_3]^{2+}$, 5.0 mM $Na_2S_2O_8$, 5.0 μM **1**, 20 mM sodium phosphate buffer (initial pH 7.2), total reaction volume 8 mL, vigorous agitation using a magnetic stirrer.

Scheme 1. Light-Induced Catalytic Water Oxidation by Tetraruthenium Polyoxometalate **1** Using $[Ru(bpy)_3]^{2+}$ as a Photosensitizer and Persulfate as a Sacrificial Electron Acceptor



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(atom code: Ru, O, W, Si)

The photocatalytic system was evaluated under the experimental conditions described in Figure 1. Dioxygen was formed quickly under visible-light illumination (420−520 nm), while persulfate was consumed. A gradual decrease in pH from 7.2 to 6.3 and a gradual <10−15% decomposition of $[Ru(bpy)_3]^{2+}$ were also observed. The final dioxygen yield (per the stoichiometry in eq 2, $\Phi_S = [O_2]/2[S_2O_8^{2-}]$) was ∼38%. The turnover number (TON = $[O_2]/[Ru_4\text{−}POM]$) was ∼1.8 × 10^2 with an initial turnover frequency (TOF) of ∼8 × 10^{-2} s^{-1}. Higher TONs (up to ∼3.5 × 10^2) were achieved at lower catalyst and higher persulfate concentrations. For continuous determination of the O_2 concentration in the reactor head space after the desired illumination periods without reaction stoppage, the reaction kinetics was measured with lower (one-third) light intensity. Under these conditions, the reaction rate decreased 2-fold when the light intensity was further reduced to half the initial value. The rate and O_2 yield increased when the concentration of **1** was increased from 1.25 to 2.5 μM. Very little change was observed when the catalyst concentration was varied from 2.5 and 5.0 μM. A further increase in catalyst concentration resulted in a significant decrease in the reaction rate and precipitation of an

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adduct between **1** and $[Ru(bpy)_3]^{2+}$. Full characterization of this adduct is in progress. A 2-fold decrease in the $[Ru(bpy)_3]^{2+}$ concentration reduced the rate by a factor of ~1.4. An increase in persulfate concentration (from 2.5 to 10 mM) resulted in an almost linear increase in the rate of O_2 formation. All of these observations are qualitatively consistent with the processes in Scheme 1.

A series of control experiments confirmed that fast O_2 generation requires the presence of all four components: photons, $[Ru(bpy)_3]^{2+}$, persulfate, and **1**. In the absence of **1**, the O_2 yield after 30 min of illumination was below the O_2 detection level in our system (<0.15 μM), or 25−50 times lower than in the catalytic runs. No O_2 was formed when **1** was replaced by a similar molar quantity of Ru in the form of $RuCl_3$, a precursor of RuO_2 (a known and efficient WOC). Replacement of **1** with RuO_2 particles (Aldrich; same molar quantity of Ru) resulted in a 10−20-fold lower rate of O_2 formation. The observed high TONs and the absence of induction periods in the kinetics of O_2 formation suggest that **1** is stable under these photochemical turnover conditions. It is noteworthy that photosensitizer decomposition was significantly higher (>40−50%) in the absence of **1**, indicating an efficient reduction of $[Ru(bpy)_3]^{3+}$ by **1** during photocatalytic turnover. Further mechanistic experiments are underway.

We also investigated the factors that limit the quantum efficiency of the current system. The solution under light was always orange ($[Ru(bpy)_3]^{2+}$) and not green ($[Ru(bpy)_3]^{3+}$), indicating that there was no buildup of $[Ru(bpy)_3]^{3+}$ and that eq 1 is not rate-limiting. The reaction in eq 3 was comprehensively studied by Bard et al.[16] We used the same steady-state luminescence quenching technique to examine this reaction under conditions similar to those in Scheme 1 and Figure 1. Our data are in good agreement with the earlier noncatalytic report.[16] The Stern−Volmer plot of I_0/I (where I_0 and I are the emissions in the absence and in the presence of persulfate, respectively) versus $[S_2O_8{}^{2-}]$ significantly deviates from linearity and curves downward [Figure S1 in the Supporting Information (SI)], consistent with the formation of a ground-state ion pair between $[Ru(bpy)_3]^{2+}$ and $S_2O_8{}^{2-}$ (see eq S2 in the SI). The ion-pairing equilibrium constant, K_3, was estimated to be $\sim 1.1 \times 10^3$ M^{-1} (see the SI), which is close to that reported earlier (1.8×10^3 M^{-1}).[16] Indeed, density functional (B3LYP) and PCM (water solution) studies showed that the adduct $[Ru(bpy)_3]^{2+}\bullet[S_2O_8]^{2-}$ is stable by 3.7 kcal/mol relative to the $[Ru(bpy)_3]^{2+} + S_2O_8{}^{2-}$ dissociation limit. The steady-state luminescence quenching of $[Ru(bpy)_3]^{2+}*$ by 5.0 mM $Na_2S_2O_8$ in 20 mM sodium phosphate buffer solution gave $I_0/I \approx 3.0$, indicating that ~67% of the excited state was quenched by persulfate. Addition of 5.0 μM **1** did not affect the $[Ru(bpy)_3]^{2+*}$ quenching efficiency.

The overall photon-to-O_2 generation quantum yield, Φ_2, depends on the yields of the reactions in eqs 1 and 3:

$$\Phi_2 = \Phi_3\Phi_1 = (\Phi_q\Phi_r)\Phi_1 = \Phi_q\Phi_S \tag{4}$$

where Φ_1 is the yield of O_2 from 4 equiv of $[Ru(bpy)_3]^{3+}$ (based on eq 1) and Φ_3 is the yield for forming four $[Ru(bpy)_3]^{3+}$ per two absorbed photons and two consumed $S_2O_8{}^{2-}$ (based on eq 3). Φ_3 is the product of the yield of $[Ru(bpy)_3]^{2+}*$ quenching by $S_2O_8{}^{2-}$ (Φ_q) and the yield of the reaction of $SO_4{}^{\bullet-}$ with $[Ru(bpy)_3]^{2+}$ to form the second $[Ru(bpy)_3]^{3+}$ (Φ_r). If $S_2O_8{}^{2-}$ is consumed only upon reduction by $[Ru(bpy)_3]^{2+}*$, the yield of O_2 per two $S_2O_8{}^{2-}$ (Φ_S) is given by $\Phi_r\Phi_1$ and can be related to the photon-to-O_2 yield according to eq 4. From the measured values of Φ_S (~38%) and Φ_q (67%), the overall quantum yield Φ_2 is estimated to be ~26%, which is significantly larger than the measured value of ~9%. The reason for this discrepancy is unclear. Furthermore, the maximal value of Φ_1 was estimated to be ~60% in stoichiometric water oxidation by $[Ru(bpy)_3]^{3+}$ catalyzed by **1**.[14] The nonunity efficiency derives from an ensemble of side reactions resulting in $[Ru(bpy)_3]^{3+}$ decomposition. Assuming that $\Phi_1 = 60\%$ under our photocatalytic conditions and using the measured Φ_S gives estimated values of 65 and 44% for Φ_r and Φ_3, respectively. Thus, the quantum efficiencies for generating $[Ru(bpy)_3]^{3+}$ (~44%) and its reaction with the catalyst to form O_2 (~60%) are major limiting factors in this system. The overall quantum efficiency can be improved with better schemes for generating $[Ru(bpy)_3]^{3+}$. In that regard, $[Ru(bpy)_3]^{2+}$-sensitized nanocrystalline TiO_2 may be an attractive alternative, as a related system was shown to achieve near unity quantum efficiency in generating a long-lived photooxidant.[19] Furthermore, it would eliminate the need for a sacrificial electron acceptor and provide a way to utilize the electron for hydrogen generation, as demonstrated recently in a related system using IrO_2 nanoparticles as the WOC.[4]

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Supporting Information Available: Experimental and computational procedures and additional experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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