

# Efficient Light-Driven Carbon-Free Cobalt-Based Molecular Catalyst for Water Oxidation

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**S** Supporting Information

**ABSTRACT:** The abundant-metal-based polyoxometalate complex  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  is a hydrolytically and oxidatively stable, homogeneous, and efficient molecular catalyst for the visible-light-driven catalytic oxidation of water. Using a sacrificial electron acceptor and photosensitizer, it exhibits a high (30%) photon-to- $\text{O}_2$  yield and a large turnover number (>220, limited solely by depletion of the sacrificial electron acceptor) at pH 8. The photocatalytic performance of this catalyst is superior to that of the previously reported precious-metal-based polyoxometalate water oxidation catalyst  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ .

Efficient water oxidation is a key step in the production of fuel from water by photochemical, electrochemical, and other approaches.<sup>1–3</sup> The development of efficient water oxidation catalysts (WOCs) remains a major scientific challenge despite considerable progress in recent years.<sup>4–21</sup> Recently, a series of molecular, carbon-free, soluble, and fast tetraruthenium and tetracobalt polyoxometalate (POM) WOCs, including  $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$  (**1**) and  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$  (**2**), have been reported.<sup>22–31</sup> Complex **2**, which is based on earth-abundant Co, exhibits a turnover frequency (TOF) for homogeneous catalytic water oxidation using  $[\text{Ru}(\text{bpy})_3]^{3+}$  as the oxidant at pH 8 that is as high as any WOC reported to date, one estimated to be ~20 times higher than that of **1** below pH 7.2 ( $5$  vs  $0.25$   $\text{s}^{-1}$ ).<sup>22,31</sup> We previously demonstrated that **1** and its isostructural phosphorus-centered analogue catalyze oxygen evolution in a homogeneous photon-driven water-oxidation system (Scheme 1) using  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a photosensitizer and  $\text{S}_2\text{O}_8^{2-}$  as a sacrificial electron acceptor.<sup>24,28</sup> We report here that **2** does the same (Scheme 1) but exhibits substantially higher rates and  $\text{O}_2$  evolution quantum yields (~30%) than **1** and all other POM-based WOCs. Significantly, **2** and **1** have different selectivity features, indicating that the reactivities of one POM WOC are not necessarily operable for others.<sup>22–31</sup>

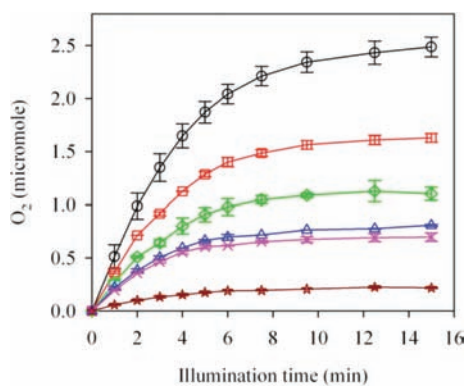
The photocatalytic system was evaluated under the experimental conditions described in Figure 1, where the system was considerably optimized in comparison with that in our previous paper, as shown in the Supporting Information (SI).<sup>24,28</sup> Dioxygen was formed quickly under visible-light illumination (420–470 nm) catalyzed by even  $0.5$   $\mu\text{M}$  **2** (results not shown). A series of control experiments confirmed that fast  $\text{O}_2$  generation requires the presence of all four components: photons,  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,

persulfate, and **2**. In the absence of **2**, the maximum  $\text{O}_2$  yield after 15 min of illumination was ~0.2  $\mu\text{mol}$  (12 times lower than in catalytic runs using  $5$   $\mu\text{M}$  **2**). After 10–15 min of illumination, the amount of  $\text{O}_2$  reached a plateau value, the concentration of  $\text{S}_2\text{O}_8^{2-}$  decreased from its initial value of 5.0 mM to <0.2 mM (the detection limit), and the concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  decreased by <15%. Significantly, photosensitizer decomposition was markedly higher (>50–60% of the initial concentration) in the absence of the catalyst, indicating that the photosensitizer is protected from decomposition by the presence of the catalyst. Furthermore, catalytic oxidation of water resumed upon the addition of  $\text{S}_2\text{O}_8^{2-}$  (Figure S1 in the SI), suggesting that the catalyst remains active and that  $[\text{Ru}(\text{bpy})_3]^{2+}$  is protected and regenerated. The final amount of  $\text{O}_2$  formed and the turnover number [defined as  $\text{TON} = (\text{O}_2 \text{ yield at end of run})/(\text{catalyst concentration}) = [\text{O}_2]_f/[\text{catalyst}]$ ; see Table 1] at the end of each run was limited mainly by depletion of the sacrificial electron acceptor. Catalyst reuse, spectroscopic and dynamic light scattering data were all consistent with the absence of catalyst decomposition during turnover (see the SI). For reasons yet to be understood, the nature of buffer also affected the efficiency of  $\text{O}_2$  formation (Figure S2). In this work, 80 mM borate buffer was found to maintain the pH well, with a pH decrease of only 0.1–0.3 pH unit by the end of the reaction.

To quantify the photocatalytic performance, we compared the average stoichiometric dioxygen chemical yields ( $\Phi_{\text{CY}} = 2[\text{O}_2]_f/[\text{Na}_2\text{S}_2\text{O}_8]_0$ , where  $[\text{O}_2]_f$  and  $[\text{Na}_2\text{S}_2\text{O}_8]_0$  are the final yield of  $\text{O}_2$  and the initial concentration of persulfate, respectively) and the initial photon-to- $\text{O}_2$  generation quantum yields  $\{\Phi_{\text{QY}}(0) = 2[\Delta(\text{O}_2)]/\Delta(h\nu)\}_0$ , where  $\Delta(\text{O}_2)$  and  $\Delta(h\nu)$  are the change in the total amount of  $\text{O}_2$  and the number of photons absorbed, respectively. According to eq 2 in Scheme 1, two photons and two  $\text{S}_2\text{O}_8^{2-}$  ions can lead to the evolution of one  $\text{O}_2$  molecule in the absence of loss pathways. The value of  $\Phi_{\text{QY}}(t)$  can also be calculated from the ratio of the rates of  $\text{O}_2$  generation and photon absorption and is related to the slope of the plot of  $\text{O}_2$  versus illumination time shown in Figure 1. It is clear that  $\Phi_{\text{QY}}(t)$  is largest at the onset of the reaction and decreases with time, approaching zero at ~15 min. For this reason, only the initial quantum yields were compared in this work. It was shown previously that the ratio of  $[\text{O}_2]$  formed to  $[\text{Na}_2\text{S}_2\text{O}_8]$  consumed changes negligibly throughout the course of the catalytic runs.<sup>24</sup> Only the average value of  $2[\text{O}_2]/[\text{Na}_2\text{S}_2\text{O}_8]$  (over the course of the reaction) was

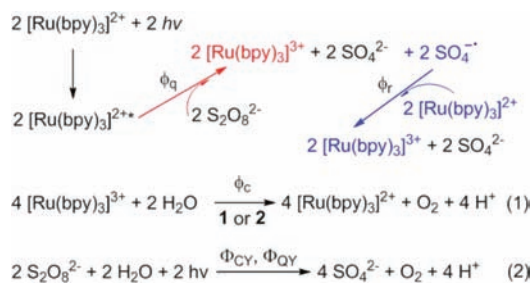
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**Figure 1.** Kinetics of O<sub>2</sub> formation in the photocatalytic system at different concentrations of **2**: 0 (brown ☆), 1.5 (pink ×), 2 (blue △), 3 (green ◇), 4 (red □), and 5 μM (black ○). Conditions: Xe lamp, 420–470 nm, 16.8 mW light beam with a diameter of ~0.75 cm focused on the reaction solution; 1.0 mM [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 5.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 80 mM sodium borate buffer (initial pH 8.0); total reaction volume 2 mL; vigorous stirring (5 × 10<sup>3</sup> rpm).

### Scheme 1. Principal Processes of O<sub>2</sub> Evolution in a Homogeneous Light-Driven Water Oxidation System

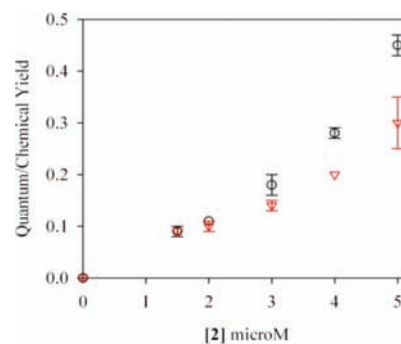


**Table 1.** Turnover Numbers (TON), Chemical Yields, and Initial Quantum Yields for Homogeneous Visible-Light-Driven Water Oxidation Catalyzed by **2**<sup>a</sup>

catalyst (μM)	TON <sup>b</sup>	chemical yield <sup>c</sup>	initial quantum yield <sup>d</sup>
0	N/A	0.04 ± 0.01	0.03 ± 0.01
1.5	158 ± 15	0.09 ± 0.01	0.09 ± 0.01
2	143 ± 3	0.11 ± 0.01	0.10 ± 0.01
3	149 ± 15	0.18 ± 0.02	0.14 ± 0.01
4	175 ± 6	0.28 ± 0.01	0.20 ± 0.01
5	224 ± 11	0.45 ± 0.02	0.30 ± 0.05
5 (1) <sup>e</sup>	136 ± 5	0.27 ± 0.01	0.24 ± 0.01

<sup>a</sup>For experimental conditions, see the Figure 1 caption. TONs and chemical yields were averaged for results at 12.5 and 15 min. <sup>b</sup>TON = (O<sub>2</sub> yield at end of run)/(catalyst concentration) = [O<sub>2</sub>]<sub>f</sub>/[catalyst]. <sup>c</sup>Φ<sub>CY</sub> = 2[O<sub>2</sub>]<sub>f</sub>/[Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]<sub>0</sub>. <sup>d</sup>Φ<sub>QY</sub>(0) = 2[Δ(O<sub>2</sub>)]/Δ(hν)<sub>0</sub> = initial O<sub>2</sub> formation rate/photon flux. <sup>e</sup>Using 5 μM **1**; reported values, excluding 0 μM, were corrected for the amount of O<sub>2</sub> generated in the control experiment.

measured in this study. The values of Φ<sub>CY</sub> and Φ<sub>QY</sub>(0) as functions of catalyst concentration are plotted in Figure 2 and listed in Table 1. In calculating these reported values, we subtracted the maximal contribution of O<sub>2</sub> generated from noncatalytic pathways (obtained from the control experiment without catalyst).<sup>38</sup>



**Figure 2.** Dependence of chemical yield (black ○) and initial quantum yield (red ▽) on catalyst concentration, **[2]**. For experimental conditions, see the Figure 1 caption.

Both the chemical yield and the initial quantum yield increased with catalyst concentration.

The photocatalytic O<sub>2</sub> evolution in this system is believed to follow the well-established reaction mechanism presented in Scheme 1.<sup>24,27,28</sup> The reaction is initiated upon the absorption of two photons by two [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complexes. Because of the large extinction coefficient (ε<sub>454</sub> = 1.4 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) and high concentration of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (1 mM), all of the incident photons are captured by [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in the solution. Following photoexcitation, the excited [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup> is quenched by S<sub>2</sub>O<sub>8</sub><sup>2-</sup> through both bimolecular and unimolecular electron transfer (ET) pathways.<sup>32–34</sup> The quenching (or ET) efficiency (φ<sub>q</sub>) increases with the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> concentration (as shown in Figure S3) and is 67% at 5.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, the initial concentration used in the catalytic runs. The photoinduced ET results in the generation of two [Ru(bpy)<sub>3</sub>]<sup>3+</sup> complexes and two SO<sub>4</sub><sup>•-</sup> radical anions. The latter subsequently oxidize two additional [Ru(bpy)<sub>3</sub>]<sup>2+</sup> to give two [Ru(bpy)<sub>3</sub>]<sup>3+</sup>, with a yield of φ<sub>r</sub>. Finally, four [Ru(bpy)<sub>3</sub>]<sup>3+</sup> complexes oxidize water to make one O<sub>2</sub> with a yield of φ<sub>c</sub>.

On the basis of Scheme 1, the chemical yield and quantum efficiency of O<sub>2</sub> generation can be related to the yields of individual steps according to eqs 3 and 4 (see the SI for detailed derivations):

$$\Phi_{\text{CY}} = 2 \frac{[\text{O}_2]_f}{[\text{Na}_2\text{S}_2\text{O}_8]_0} = 0.5(1 + \phi_r)\phi_c \quad (3)$$

$$\Phi_{\text{QY}}(t) = 2 \left[ \frac{\Delta(\text{O}_2)}{\Delta(h\nu)} \right]_t = 0.5\phi_q(t)(1 + \phi_r)\phi_c \quad (4)$$

Furthermore, from eqs 3 and 4, the chemical yield, quantum yield, and quenching efficiency are related by eq 5:

$$\Phi_{\text{QY}}(t) = \phi_q(t)\Phi_{\text{CY}} \quad (5)$$

This relation was confirmed to good measure by our experimental data (Table 1) and accounts for the observed decrease in the rate (quantum yield) of O<sub>2</sub> formed as a function of time and the catalyst concentration. For example, with the measured initial φ<sub>q</sub> and Φ<sub>CY</sub> (0.67 and 0.45, respectively, for 5 μM **2**; see Table 1), the initial Φ<sub>QY</sub> is 0.30, which agrees well with the measured value (0.30). As the reaction proceeds, φ<sub>q</sub>(t) and therefore Φ<sub>QY</sub>(t) decrease as a result of the depletion of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. In measurements with different catalyst concentrations, the initial quenching efficiency φ<sub>q</sub> should be identical (67%) because the same initial concentrations of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> were used. According to eq 5, the reduced initial quantum yield for O<sub>2</sub> generation can be attributed to

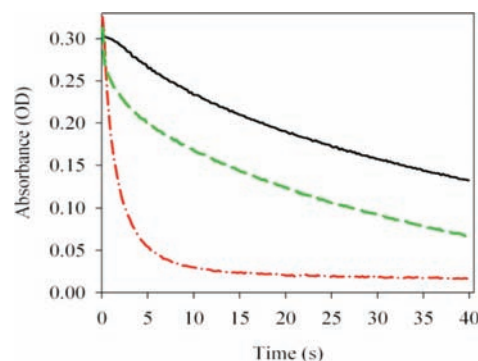
the decrease in the chemical yield at lower catalyst concentrations, consistent with the experimental observations shown in Figure 1 and Table 1.

Our result suggests that a key factor that limits the quantum yield is the chemical yield  $\Phi_{CY}$ , which is significantly less than unity in the current systems. According to eq 3,  $\Phi_{CY}$  is determined by both  $\phi_r$  and  $\phi_c$ . The  $\phi_r$  is generally taken to be *near unity*, although several reports have indicated that it is less than unity and highly dependent on the solution environment.<sup>35–37</sup> In a previous study, we determined that  $\phi_c = 67\%$  for **2** at pH 8 in stoichiometric water oxidation in the dark by  $[\text{Ru}(\text{bpy})_3]^{3+}$ .<sup>31</sup> From the measured  $\Phi_{CY}$  (0.45 at  $5 \mu\text{M}$  **2**), the minimal  $\phi_c$  (when  $\phi_r = 1$ ) can be estimated to be 0.45, consistent with the previously reported  $\phi_c$  value.<sup>31</sup>  $\Phi_{CY}$  and hence  $\phi_c$  increase with the catalyst concentration, implying a competition between catalytic (see Scheme 1) and noncatalytic pathways for the photogenerated  $[\text{Ru}(\text{bpy})_3]^{3+}$ .

To gain further insight into the factors limiting the quantum and chemical yields for catalytic  $\text{O}_2$  generation, we also compared the catalytic activities of **1** and **2** under identical conditions. As shown by both Figure S4 and Table 1, the chemical yield and TON in the reactions catalyzed by **2** are  $\sim 1.7$  fold higher than those catalyzed by **1**, with a 1.25 higher quantum yield. These three criteria demonstrate that **2**, an abundant-metal-based material, catalyzes visible-light-driven water oxidation more rapidly than **1**, which contains a precious metal, ruthenium. Furthermore, the photochemical reactions using **1** and **2** were carried out under the same conditions, so  $\phi_r$  should be the same in both systems. Therefore, a higher  $\Phi_{CY}$  for **2** suggests a higher  $\phi_c$  using this catalyst. These data suggest that **2** has a higher selectivity toward water oxidation than **1**, which is consistent with a higher TOF for dark water oxidation by **2** than by **1**.<sup>31</sup>

Light-driven water oxidation utilizes  $[\text{Ru}(\text{bpy})_3]^{3+}$  as an intermediate oxidant (eq 1 in Scheme 1). A higher  $\phi_c$  indicates a faster conversion of  $[\text{Ru}(\text{bpy})_3]^{3+}$  to  $[\text{Ru}(\text{bpy})_3]^{2+}$  in the presence of the catalyst. The concentration of  $[\text{Ru}(\text{bpy})_3]^{3+}$  can be followed by the absorption at 670 nm ( $\epsilon_{670} = 4.2 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ ), where  $[\text{Ru}(\text{bpy})_3]^{2+}$  has only a very low extinction coefficient ( $\epsilon_{670} = 5 \text{ M}^{-1} \text{ cm}^{-1}$ ). Hence, the catalytic efficiencies of **1** and **2** for water oxidation ( $\phi_c$ ) can also be compared using the kinetics of the disappearance of  $[\text{Ru}(\text{bpy})_3]^{3+}$  in the stoichiometric dark water oxidation system. These kinetics traces (shown in Figure 3) were measured by the stopped-flow technique, in which solutions containing  $[\text{Ru}(\text{bpy})_3]^{3+}$  and the catalysts, respectively, were rapidly mixed. It was found that  $[\text{Ru}(\text{bpy})_3]^{3+}$  is consumed via two competing pathways: catalytic water oxidation (eq 1) and the self-decomposition reaction.<sup>25</sup> At pH 8, the  $[\text{Ru}(\text{bpy})_3]^{3+}$  half-life of  $\sim 30$  s (no catalyst) was reduced to 11 and 1.3 s upon addition of **1** and **2**, respectively. Here, the half-life, defined as the time at which the concentration has decreased to one-half of the initial value, was used to compare the relative decay rates of  $[\text{Ru}(\text{bpy})_3]^{3+}$  because the kinetics are complex (not single-exponential). While oxidative catalysis of the bpy ligand cannot be ruled out as a pathway for the consumption of  $[\text{Ru}(\text{bpy})_3]^{3+}$ ,<sup>38</sup> this along with the results in Figure 1 and Figure S4 suggests that **1** and **2** are both efficient WOCs. This result shows that **2** is almost 10 times more efficient than **1** in catalyzing the dark reaction (eq 1), suggesting that **2** should also be a more efficient catalyst in the photodriven systems. Indeed, the  $\text{O}_2$  formation kinetics shows this to be the case.

In summary, we have demonstrated that **2**, a carbon-free molecular WOC consisting of only earth-abundant metals, is a very efficient and stable molecular catalyst for photodriven water



**Figure 3.** Kinetics of  $[\text{Ru}(\text{bpy})_3]^{3+}$  reduction to  $[\text{Ru}(\text{bpy})_3]^{2+}$ , measured as the decrease in absorbance at 670 nm for the noncatalytic reaction (solid black line, no catalyst),  $5 \mu\text{M}$  **1** (dashed green line), and  $5 \mu\text{M}$  **2** (dot-dashed red line). Conditions: 1 mM  $[\text{Ru}(\text{bpy})_3]^{3+}$  (initial), 80 mM sodium borate buffer, pH 8.0,  $20^\circ\text{C}$ .

oxidation. Under the same conditions (pH 8), **2** is more efficient than **1** in oxidizing water, which can be attributed to the higher turnover frequency of **2** relative to **1**.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Experimental procedures, dioxygen measurements, steady-state luminescence quenching, quantum yield measurements, derivation of eqs 3 and 4, comparison of catalytic efficiencies, and complete ref 30. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ REFERENCES

- (1) Barber, J. *Chem. Soc. Rev.* **2009**, *38*, 185.
- (2) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729.
- (3) Gray, H. B. *Nat. Chem.* **2009**, *1*, 7.
- (4) Binstead, R. A.; Chronister, C. W.; Ni, J.; Hartshorn, C. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 8464.
- (5) Yagi, M.; Kaneko, M. *Chem. Rev.* **2001**, *101*, 21.
- (6) Hurst, J. K. *Coord. Chem. Rev.* **2005**, *249*, 313.
- (7) Zong, R.; Thummel, R. *J. Am. Chem. Soc.* **2005**, *127*, 12802.
- (8) Eisenberg, R.; Gray, H. B. *Inorg. Chem.* **2008**, *47*, 1697.
- (9) McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. *J. Am. Chem. Soc.* **2008**, *130*, 210.
- (10) Brimblecombe, R.; Swiegiers, G. F.; Dismukes, G. C.; Spiccia, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 7335.
- (11) Concepcion, J. J.; Jurss, J. W.; Brennaman, M. K.; Hoertz, P. G.; Patrocino, A. O. T.; Iha, N. Y. M.; Templeton, J. L.; Meyer, T. J. *Acc. Chem. Res.* **2009**, *42*, 1954.
- (12) Hurst, J. K.; Cape, J. L.; Clark, A. E.; Das, S.; Qin, C. *Inorg. Chem.* **2008**, *47*, 1753.



- (13) Betley, T. A.; Surendranath, Y.; Childress, M. V.; Alliger, G. E.; Fu, R.; Cummins, C. C.; Nocera, D. G. *Philos. Trans. R. Soc., B* **2008**, 363, 1293.
- (14) Muckerman, J. T.; Polyansky, D. E.; Wada, T.; Tanaka, K.; Fujita, E. *Inorg. Chem.* **2008**, 47, 1787.
- (15) Sala, X.; Romero, I.; Rodríguez, M.; Escriche, L.; Llobet, A. *Angew. Chem., Int. Ed.* **2009**, 48, 2842.
- (16) Cao, R.; Ma, H.; Geletii, Y. V.; Hardcastle, K. I.; Hill, C. L. *Inorg. Chem.* **2009**, 48, 5596.
- (17) Jiao, F.; Frei, H. *Angew. Chem., Int. Ed.* **2009**, 48, 1841.
- (18) Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2009**, 131, 8730.
- (19) Kuznetsov, A. E.; Geletii, Y. V.; Hill, C. L.; Morokuma, K.; Musaev, D. G. *J. Am. Chem. Soc.* **2009**, 131, 6844.
- (20) Duan, L.; Xu, Y.; Gorlov, M.; Tong, L.; Andersson, S.; Sun, L. *Chem.—Eur. J.* **2010**, 16, 4659.
- (21) Masaoka, S.; Sakai, K. *Chem. Lett.* **2009**, 38, 182.
- (22) Geletii, Y. V.; Botar, B.; Kögerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L. *Angew. Chem., Int. Ed.* **2008**, 47, 3896.
- (23) Sartorel, A.; Carraro, M.; Scorrano, G.; Zorzi, R. D.; Geremia, S.; McDaniel, N. D.; Bernhard, S.; Bonchio, M. *J. Am. Chem. Soc.* **2008**, 130, 5006.
- (24) Geletii, Y. V.; Huang, Z.; Hou, Y.; Musaev, D. G.; Lian, T.; Hill, C. L. *J. Am. Chem. Soc.* **2009**, 131, 7522.
- (25) Geletii, Y. V.; Besson, C.; Hou, Y.; Yin, Q.; Musaev, D. G.; Quinonero, D.; Cao, R.; Hardcastle, K. I.; Proust, A.; Kögerler, P.; Hill, C. L. *J. Am. Chem. Soc.* **2009**, 131, 17360.
- (26) Sartorel, A.; Miro, P.; Salvadori, E.; Romain, S.; Carraro, M.; Scorrano, G.; Valentin, M. D.; Llobet, A.; Bo, C.; Bonchio, M. *J. Am. Chem. Soc.* **2009**, 131, 16051.
- (27) Puntoriero, F.; Ganga, G. L.; Sartorel, A.; Carraro, M.; Scorrano, G.; Bonchio, M.; Campagna, S. *Chem. Commun.* **2010**, 46, 4725.
- (28) Besson, C.; Huang, Z.; Geletii, Y. V.; Lense, S.; Hardcastle, K. I.; Musaev, D. G.; Lian, T.; Proust, A.; Hill, C. L. *Chem. Commun.* **2010**, 46, 2784.
- (29) Orlandi, M.; Argazzi, R.; Sartorel, A.; Carraro, M.; Scorrano, G.; Bonchio, M.; Scandola, F. *Chem. Commun.* **2010**, 46, 3152.
- (30) Toma, F. M.; et al. *Nat. Chem.* **2010**, 2, 826.
- (31) Yin, Q.; Tan, J. M.; Besson, C.; Geletii, Y. V.; Musaev, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L. *Science* **2010**, 328, 342.
- (32) White, H. S.; Becker, W. G.; Bard, A. J. *J. Phys. Chem.* **1984**, 88, 1840.
- (33) Kaledin, A. L.; Huang, Z.; Geletii, Y. V.; Lian, T.; Hill, C. L.; Musaev, D. G. *J. Phys. Chem. A* **2010**, 114, 73.
- (34) Kaledin, A. L.; Huang, Z.; Yin, Q.; Dunphy, E. L.; Constable, E. C.; Housecroft, C. E.; Geletii, Y. V.; Lian, T.; Hill, C. L.; Musaev, D. G. *J. Phys. Chem. A* **2010**, 114, 6284.
- (35) Horváth, A.; Bakó, Z.; Papp, S.; Keszei, C. *J. Photochem. Photobiol., A* **1990**, 52, 271.
- (36) Bolletta, F.; Juris, A.; Maestri, M.; Sandrini, D. *Inorg. Chim. Acta* **1980**, 44, L175.
- (37) Henbest, K.; Douglas, P.; Garley, M. S.; Mills, A. *J. Photochem. Photobiol., A* **1994**, 80, 299.
- (38) Ghosh, P. K.; Brunschwig, B. S.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1984**, 106, 4772.