Supporting Information

Enabling Light-Driven Water Oxidation via a Low Energy Ru^{IV}=O Intermediate

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1. Comparison of the UV-vis spectra of photosensitizer and catalyst

Fig. S1. Comparison of the UV-vis spectra of $[Ru(bpy)_3]^{2+}$ and catalyst 1

2. Reaction between sensitizer and persulfate

$$Photoexcitation$$

$$2 [Ru(bpy)_{3}]^{2+} + 2hv \longrightarrow 2 [Ru(bpy)_{3}]^{2+*}$$

$$(1)$$

$$Oxidant generation$$

$$2 [Ru(bpy)_{3}]^{2+*} + 2[S_{2}O_{8}]^{2-} \xrightarrow{\phi_{q}} 2 [Ru(bpy)_{3}]^{3+} + 2SO_{4}^{2-} + 2SO_{4}^{-\bullet}$$

$$(2)$$

$$2 [Ru(bpy)_{3}]^{2+} + 2SO_{4}^{-\bullet} \xrightarrow{\phi_{r}} 2 [Ru(bpy)_{3}]^{3+} + 2SO_{4}^{2-}$$

$$(3)$$

$$Water oxidation$$

$$4 [Ru(bpy)_{3}]^{3+} + 2H_{2}O \xrightarrow{\phi_{c}} 4 [Ru(bpy)_{3}]^{2+} + 4H^{+} + O_{2}$$

$$(4)$$

The photoinduced electron transfer reaction between $[Ru(bpy)_3]^{2+}$ and $[S_2O_8]^{2-}$ (reaction 2) has recently attracted considerable interest in view of its practical application in light driven water oxidation systems. The reaction of $[Ru(bpy)_3]^{2+*}$ with $[S_2O_8]^{2-}$ has been investigated in detail by Bard et al. in aqueous and mixed CH₃CN-H₂O solutions by steady state luminescence quenching and emission lifetime techniques.¹ The Stern-Volmer (SV) plots of I_0/I (where $I_0(I)$ are the emission intensity values in the absence and presence of persulfate, respectively) vs $[S_2O_8]^{2-}$ showed downward curvature for solutions of low ionic strength. On the basis of Bard's work, two quenching mechanisms have been proposed: "unimolecular and "bimolecular".¹ The "unimolecular" quenching corresponds to the excitation of a ground state ion pair between $[Ru(bpy)_3]^{2+}$ and $[S_2O_8]^{2-}$ and proceeds via intramolecular electron transfer. The "bimolecular" mechanism operates for free excited $[Ru(bpy)_3]^{2+*}$ molecules as well as for excited ion pair complexes. It assumes that electron transfer occurs in a collision between $[Ru(bpy)_3]^{2+*}$ and $[S_2O_8]^{2-}$ or between an excited ion pair complex and another $[S_2O_8]^{2-}$ molecule. The SV plots were successfully fitted with the expression for the emission quenching derived from the proposed model.¹

On the other hand, our recent study of the quenching of $[Ru(bpy)_3]^{2+*}$ by $[S_2O_8]^{2-}$ in aqueous solutions of a constant ionic strength ($\mu = 0.12$) using steady-state luminescence revealed that the experimental data can be treated according to a different mechanism that is more consistent with the classical description of similar photochemical reactions.² The alternative mechanism (Scheme S1) assumes that electron transfer occurs only within the excited precursor complex, which can be formed from the excitation of the ground state ion pair or from the diffusion controlled reaction between the free excited molecule of $[Ru(bpy)_3]^{2+*}$ and $[S_2O_8]^{2-}$. With the electron transfer being the rate determining step, the entire process can be considered as an activation-diffusion controlled reaction. Due to the increased interest in this reaction in light of photosensitized water oxidation studies, it seems extremely important to fully understand the mechanism and the ambiguity in the interpretation of experimental data, which has led us to a more detailed investigation of the reaction between the excited state of $[Ru(bpy)_3]^{2+}$ and $[S_2O_8]^{2-}$. While the derived model is used to describe experimental findings in this work, the detailed analysis falls beyond the scope of this paper and will be published elsewhere.

$$[\operatorname{Ru}(\operatorname{bpy})_{3}^{3^{+}} \cdots S_{2}O_{8}^{3^{-}}]$$

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}*} + S_{2}O_{8}^{2^{-}} \xleftarrow{k_{d}} *[\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}} \cdots S_{2}O_{8}^{2^{-}}]$$

$$\operatorname{hv} \underbrace{1/\tau_{\circ}}_{K_{a}} \qquad \operatorname{hv} \underbrace{1/\tau_{\circ}}_{K_{a}}^{\operatorname{IP}}$$

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}} + S_{2}O_{8}^{2^{-}} \xleftarrow{K_{a}} [\operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}} \cdots S_{2}O_{8}^{2^{-}}]$$

Scheme S1.

First, we report results on the strong dependence of the quenching efficiency, φ_q on the buffer concentration. Steady-state luminescence quenching was used to probe the reaction of $[Ru(bpy)_3]^{2+}$ with $[S_2O_8]^{2-}$ under experimental conditions similar to those employed for light-driven water oxidation in H₂O/TFE (4/1, v/v) solutions containing 20, 80 and 200 mM aqueous phosphate buffer (pH 7.0). The

results revealed that the quenching efficiency ($\varphi_q = 1 - I/I_o$) increases with decreasing buffer concentration at constant $[S_2O_8]^{2-}$ (Fig S2)



Figure S2. Quenching efficiency of the photoreaction of $[Ru(bpy)_3]^{2+}$ with $[S_2O_8]^{2-}$ in a mixture of H₂O and TFE (4/1, v/v) containing 200 mM aqueous phosphate buffer (black); 80 mM phosphate buffer (blue); and 20 mM phosphate buffer (green). Red squares show the data obtained from flash photolysis measurements and black squares show the data obtained from emission lifetime measurements.

Transient absorption experiments were performed in order to independently measure the relationship between φ_q and the $[S_2O_8]^{2-}$ concentration. The transient absorption spectra of $[Ru(bpy)_3]^{2+}$ after 470 nm excitation in the absence of persulfate show a ground state bleach at 450 nm, an isosbestic point at 500 nm and a weakly absorbing species above 500 nm that can be assigned to the excited state of $[Ru(bpy)_3]^{2+*}$ (Fig. S3). Excited state relaxes back to its ground state, resulting in the recovery of the bleach kinetic (Fig. S3, inset). The lifetime of $[Ru(bpy)_3]^{2+*}$ was estimated to be 580 ns by a singleexponential fit to the kinetic trace at 455 nm.



Fig. S3. Transient absorption spectra for H_2O/TFE (4/1, v/v) solution containing 50 μ M [Ru(bpy)₃]²⁺ and 20 mM aqueous phosphate buffer (pH 7.0) after 470 nm excitation after different times delays. Inset: decay profile monitored at 455 nm; the solid red line represents monoexponential fit to the decay curve.

In the presence of a sacrificial electron acceptor such as a potassium persulfate, the remaining bleach signal reflects the efficiency of the $[Ru(bpy)_3]^{3+}$ formation in the photochemical step (Fig. S5). Initial bleach in the transient absorption experiments at 455 nm represents the difference between [Ru(bpy)₃]²⁺ $(\varepsilon = 14600 \text{ M}^{-1} \text{ cm}^{-1})$ and $[\text{Ru}(\text{bpy})_3]^{2+*}$ of the $[\text{Ru}(\text{bpy})_3]^{2+}$. Using extinction coefficients of the excited and ground states experimentally determined $\Delta \varepsilon$ (at 450 nm) was 11000 M⁻¹cm⁻¹. Based on this $\Delta \varepsilon$, the initial depletion of the $[Ru(bpy)_3]^{2+}$ was calculated which also equals the concentration of the $[Ru(bpy)_3]^{2+*}$. $[Ru(bpy)_3]^{2+*}$ can relax back to its ground state or be quenched by persulfate to form $[Ru(bpy)_3]^{3+}$ ($[Ru(bpy)_3]^{3+}$ has negligible absorption at 450 nm, ε around 200 M⁻¹cm⁻¹). The concentration of the $[Ru(bpy)_3]^{2+}$ that was not recovered equals to the $[Ru(bpy)_3]^{3+}$ formed. The ratio of the $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+*}$ gave the quenching efficiency. The quenching efficiencies calculated from the bleach recovery at 455 nm (red symbols in Fig. S4) are in agreement with the quenching efficiencies calculated from the steady-state fluorescence quenching for the same solvent composition. At 30 mM K₂S₂O₈, the highest initial concentration used in the light driven water oxidation experiments, the quenching efficiency obtained from the flouresence data reaches 75 % for 20 mM phosphate buffer and 65 % for 80 mM phosphate buffer respectively (green and blue symbols, Fig. S2). The quenching efficiencies obtained from the measurements of emission lifetime of the $[Ru(bpy)_3]^{2+}$ at 610 nm vs $[S_2O_8]^{2-}$ concentration are in agreement with the quenching efficiency from the steady-state fluorescence quenching (Fig. S2 and Fig. S4). Steady state luminescence studies together with the time-resolved spectroscopy show that lower buffer concentrations favor higher efficiency for the formation of oxidant $[Ru(bpy)_3]^{3+}$.



Fig S4. I_0/I (red) and τ_0/τ (measured at 610 nm) (black) as a function of $[S_2O_8]^{2-}$ of the photoreaction of $[Ru(bpy)_3]^{2+}$ with $[S_2O_8]^{2-}$ in a mixture of H_2O and TFE (4/1, v/v) containing 20 mM aqueous phosphate buffer

The transient absorption spectra of $[Ru(bpy)_3]^{2+}$ after 470 nm excitation in the presence of potassium persulfate show a ground state bleach at 450 nm that partially recovers due to non-unity φ_q and then continues to grow for ca. 2 µs (Fig. S5). The reaction between the photogenerated sulfate radical anion $(SO_4^{-\bullet})$ and $[Ru(bpy)_3]^{2+}$ is a thermal pathway for $[Ru(bpy)_3]^{3+}$ generation (reaction 3) and is the reason for additional ground-state depopulation (Fig. S5). The radical-to-oxidant reaction yield (φ_r) is often taken to be unity, but there are some reports pointing to lower yields that can be attributed to side reactions of $SO_4^{-\bullet}$ with water, chloride, phosphate anions, TFE and the persulfate molecule (reactions (S1)-(S6)).³⁻¹⁰



Figure S5. Transient kinetics monitored at 455 nm after 470 nm excitation at different $[S_2O_8]^{2-}$ concentrations. Experimental conditions: 50 μ M $[Ru(bpy)_3]^{2+}$, 0 – 45 mM $[S_2O_8]^{2-}$ in the mixture of H₂O/TFE (4/1 v/v) containing 20 mM aqueous phosphate buffer.

For our experimental conditions, φ_r was estimated from the kinetic trace for a 30 mM concentration of persulfate as follows. The initial bleach in the transient absorption (Figure S5, t < 0.2 µs) represents the difference between $[Ru(bpy)_3]^{2+*}$ and $[Ru(bpy)_3]^{2+}$, and the final signal (Figure S5, t > 2 µs) is the difference between $[Ru(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{2+}$. The quenching efficiency of $[Ru(bpy)_3]^{2+*}$ in the initial step was obtained from fluorescence quenching experiments yielding φ_q = 0.75. This value of φ_q obtained from fluorescence quenching was found to be in good agreement with φ_q estimated from transient absorption, despite complex kinetics at 450 nm. From the additional bleach at 455 nm, the amount of $[Ru(bpy)_3]^{2+*}$ consumed in both steps (photochemical and thermal) can be estimated, assuming that the contribution from absorbance of $[Ru(bpy)_3]^{3+}$ is negligible (ε_{450} around 200 M⁻¹ cm⁻¹). The ratio of the $[Ru(bpy)_3]^{3+}$ / $[Ru(bpy)_3]^{2+*}$ provided the φ_{tq} , total quantum efficiency for the formation of $[Ru(bpy)_3]^{3+}$, as 1.16. The efficiency of the thermal reaction φ_r can be calculated as (φ_q (1+ φ_r) = 1.16 and was found to be 0.55.

Based on determined values for φ_q (65 % for 30 mM $[S_2O_8]^{2-}$ with 80 mM buffer concentration) and $\varphi_r = 0.55$, the maximum quantum efficiency, Φ_{QY} , based on eq 5 is reduced to $\Phi_{QY} = 0.25 \varphi_c$. The total quantum efficiency for generating $[Ru(bpy)_3]^{3+}$, φ_{tq} , in two steps is found to be 1.0, instead of the theoretical value of 2.0, meaning that for our experimental conditions the efficiency for $[Ru(bpy)_3]^{3+}$ generation is only 50 %.



3. Buffer concentration dependence on O₂ evolution

Fig. S6. Kinetics of O₂ formation as a function of illumination time with different phosphate buffer concentration: H₂O/TFE (4/1, v/v) solution containing 1 mM [Ru(bpy)₃]²⁺, 30 mM [S₂O₈]²⁻, 52 μ M catalyst **1** and 20 mM aqueous phosphate buffer (pH 7.0) (red); H₂O/TFE (4/1, v/v) solution containing 1 mM [Ru(bpy)₃]²⁺, 30 mM [S₂O₈]²⁻, 52 μ M catalyst **1** and 80 mM aqueous phosphate buffer (pH 7.0) (black).

4. Stirring dependence on O₂ formation



Fig. S7. Kinetics of O₂ formation as a function of illumination time with different stirring bars. Conditions: 2.9 mL of H₂O/TFE (4/1, v/v) solution containing 1 mM $[Ru(bpy)_3]^{2+}$, 30 mM $[S_2O_8]^{2-}$, 52 µM catalyst 1 and 20 mM aqueous phosphate buffer (pH 7.0)

5. Reaction volume dependence on O₂ formation



Fig. S8. Kinetics of O₂ formation as a function of illumination time with different reaction volume: 2.9 mL (black), 1.9 mL (red). Conditions: H₂O/TFE (4/1, v/v) solution containing 1 mM $[Ru(bpy)_3]^{2+}$, 30 mM $[S_2O_8]^{2-}$, 52 μ M catalyst **1** and 80 mM aqueous phosphate buffer (pH 7.0).





Fig. S9. Kinetics of O₂ formation as a function of illumination time with different laser radiant power: 25 mW (black); 13 mW (red). Conditions: 2.9 mL of H₂O/TFE (4/1, v/v) solution containing 1 mM $[Ru(bpy)_3]^{2^+}$, 30 mM $[S_2O_8]^{2^-}$, 52 µM catalyst 1 and 80 mM aqueous phosphate buffer (pH 7.0)

7. Persulfate concentration dependence on O₂ formation



Fig. S10. Kinetics of O₂ formation as a function of illumination time with various $[S_2O_8]^{2-}$ concentration (5 –30 mM). Conditions: 1.9 mL of H₂O/TFE (4/1, v/v) solution containing 1 mM $[Ru(bpy)_3]^{2+}$, 52 µM catalyst 1 and 80 mM aqueous phosphate buffer (pH 7.0).



Fig. S11. Initial rates of O₂ generation as a function of $[S_2O_8]^{2-}$ concentration (black plot). The initial rates were calculated by fitting the generated O₂ curves *vs.* time from 1.5 min to 5 min as a straight line. Conditions: 1.9 mL of H₂O/TFE (4/1, v/v) solution containing 1 mM $[Ru(bpy)_3]^{2+}$, 52 µM catalyst 1 and 80 mM aqueous phosphate buffer (pH 7.0). Stern Volmer plot of I_o/I (red plot) as a function of $[S_2O_8]^{2-}$ concentration. Conditions: 3 mL of H₂O/TFE (4/1, v/v) solution containing 50 µM $[Ru(bpy)_3]^{2+}$ and 80 mM aqueous phosphate buffer (pH 7.0).

8. Chloride concentration dependence on O₂ formation



Fig. S12. Total O₂ production as a function of [Cl⁻] concentration. Conditions: 2.9 mL of H₂O/TFE (4/1, v/v) solution containing 1 mM [Ru(bpy)₃]²⁺, 30 mM [S₂O₈]²⁻, 52 μ M catalyst **1**, KCl (0 – 4 mM) and 80 mM aqueous phosphate buffer (pH 7.0).

9. UV-vis analysis of the sensitizer after illumination

A small amount of the solution (100 μ L) was taken from the reaction mixture containing the sensitizer (1 mM) and K₂S₂O₈ (30 mM) in the absence or presence of complex **1** (52 μ M), and diluted with solution of H₂O/TE (4/1, v/v) (2 mL) and the absorption spectrum was measured. After the reaction mixture was illuminated for 16 min, the same amount (100 μ L) of the reaction mixture was diluted with the same solution, and UV-vis absorption was measured again. The decomposition of the sensitizer after illumination was estimated by analysis the absorption at 450 nm.



Fig. S13. Absorption spectral changes of solutions before and after irradiation.

10. Photostability of complex 1



Fig. S14. Absorption spectral changes of 2.9 mL H₂O/TFE (4/1, v/v) solution containing 30 mM $[S_2O_8]^{2-}$, 52 μ M catalyst **1**, and 20 mM aqueous phosphate buffer (pH 7.0) upon light irradiation.

11. pH dependence on O₂ formation



Fig. S15. Kinetics of O₂ formation with different initial pH: Conditions: 1.9 mL of H₂O/TFE (4/1, v/v) solution containing 1 mM [Ru(bpy)₃]²⁺, 30 mM [S₂O₈]²⁻, 26 μ M catalyst **1**, and 80 mM aqueous phosphate buffer (pH 7.0) (red); 1.9 mL of H₂O/TFE (4/1, v/v) solution containing 1mM [Ru(bpy)₃]²⁺, 30 mM [S₂O₈]²⁻, 26 μ M catalyst **1**, and 80 mM aqueous phosphate buffer (pH 7.8).

12. Reactions of sulfate radical anion

(S1) $SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + H^+ + OH^{\bullet}$ $k = 10-55 \text{ M}^{-1} \text{ s}^{-1} 6.7.9$

(S2)
$$SO_4^{-\bullet} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{-1}$$

 $k = (6.1 \pm 0.6) \times 10^5 \text{ M}^{-1} \text{ s}^{-1.7}$

(S3)
$$SO_4^{-\bullet} + CI^- \rightarrow SO_4^{2-} + CI^{\bullet}$$

 $k = 2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ at pH } 1.4^{-8}$

(S4)
$$SO_4^{-\bullet} + HPO_4^{2-} \rightarrow SO_4^{2-} + HPO_4^{-\bullet}$$

 $k = (1.2 \pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ at pH 9}^{-10}$

(S5)
$$SO_4^{-\bullet} + H_2PO_4^{--} \rightarrow SO_4^{2-} + H_2PO_4^{-0}$$

 $k < 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \text{ at pH 7}^{-10}$

 $(S6) \quad SO_4^{-\bullet} + CF_3CH_2OH \quad \rightarrow SO_4^{2-} + CF_3CHOH^{\bullet} + H^+$

 $k = 10^5 - 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (based on literature data the *k* value is expected to be smaller by 1-2 orders of magnitude in comparison to ethanol for which rate constant for the reaction with sulfate readical is $k = (1.6-7.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ }^6)$

(S7) $SO_4^{-\bullet} + [Ru(bpy)_3]^{2+} \rightarrow SO_4^{2-} + [Ru(bpy)_3]^{3+}$ $k = 4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ at pH} = 4.7^{-4}$

$$(S8) \quad OH^{\bullet} + CF_3CH_2OH \rightarrow H_2O + CF_3CHOH^{\bullet}$$

$$k = 4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1.11}$$

13. Quantum yield measurements

The quantum yield of O_2 formation, Φ_{QY} , defined as the number of O_2 molecules formed per absorbed photons, was calculated using eq S1:

$$\Phi_{QY} = \frac{[O_2]}{hv} \tag{S9}$$

Based on the reaction scheme two photons are needed to produce one O_2 molecule. As a consequence, the limiting value of photochemical quantum yield in a system like this, where persulfate ions are used as sacrificial acceptors, is 0.5. The value of Φ_{QY} can also be calculated from the ratio of the rates of O_2 generation and photon flux and is related to the slope of the plot of O_2 versus illumination time. The Φ_{QY} is the largest at the beginning of the irradiation (Table 1) and decreases with time due to persulfate consumption and pH drop, approaching zero at ~15 min. For this reason, only the initial quantum yields were compared in this work.

The O₂ initial rates were calculated by fitting O₂ vs. time curves from 1.5 min to 5 min as a straight line. The photon flux (q_p) was calculated by eq S10

$$q_p = \frac{n_p}{t} = \frac{(1-\rho)(P_o - P)\lambda}{hc}$$
(S10)

Where n_p is the number of photons absorbed, *t* is the irradiation time, P_o is the radiant power of input light, *P* is the radiant power of output light, $\lambda = 476$ nm, is the wavelength of the light, *h* is Planck's constant, *c* is the speed of light, and ρ is the reflectance of the air/reaction cuvette interface, which is 4 % in our experiment. The radiant power $P_o = 25$ mW, was measured by the power meter built-in the argon ion laser and cross-checked using a laser power meter (ORION/TH, OPHIR). The optical density of the reaction solution was 8 at $\lambda_{exc} = 476$ nm, thus all light entering the reaction solution based on the Beer's Law was considered to be absorbed (*P* = 0).

References:

- 1. H. S. White, W. G. Becker and A. J. Bard, J. Phys. Chem., 1984, 88, 1840-1846.
- 2. W. Rybak, A. Haim, T. L. Netzel and N. Sutin, J. Phys. Chem., 1981, 85, 2856-2860.
- 3. F. Bolletta, A. Juris, M. Maestri and D. Sandrini, Inorg. Chim. Acta, 1980, 44, L175-L176.
- 4. K. Henbest, P. Douglas, M. S. Garley and A. Mills, J. Photochem. Photobiol A, 1994, 80, 299-305.
- 5. A. Horvath, Z. Bako, S. Papp and C. Keszei, J. Photochem. Photobiol A, 1990, 52, 271-280.
- 6. E. Hayon, A. Treinin and J. Wilf, J. Am. Chem. Soc., 1972, 94, 47-57.
- 7. W. J. McElroy and S. J. Waygood, J. Chem. Soc., Faraday Trans., 1990, 86, 2557-2564.
- 8. A. Slama-Schwok and J. Rabani, J. Phys. Chem., 1986, 90, 1176-1179.
- 9. Y. Tang, R. P. Thorn, R. L. Mauldin III and P. H. Wine, J. Photochem. Photobiol A, 1988, 44, 243-258.
- 10. P. Maruthamuthu and P. Neta, J. Phys. Chem., 1978, 82, 710-713.
- 11. C. Walling, G. M. El-Taliawi and R. A. Johnson, J. Am. Chem. Soc., 1974, 96, 133-139.