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

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Instrumentation

UV-Vis spectra were acquired using Agilent 8453 spectrophotometer equipped with a diode-array detector and with a magnetic stirrer and temperature controller (Agilent 89090A). Analysis of dioxygen in the reaction headspace was performed using a HP5890A model gas chromatograph equipped with thermal conductivity detector and a GC column (1.5m x 3 mm) packed with 5Å molecular sieves to separate O_2 and N_2. Argon was used as a carrier gas. A Hamamatsu Xe-lamp (model C2577) was used as the light source for the photocatalysis measurements. A steady state luminescence quenching was studied using a SPEX® FluoroLog®-3 self-contained and fully automated spectrofluorometer.

Materials

Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($Ru(bipy)_3^{2+}$), ruthenium (IV) oxide hydrate (RuO_2xH_2O), and sodium persulfate (98+%) were purchased from Aldrich. A suspension of RuO_2 in H_2O was prepared as follows: 7.5 mg of RuO_2 was added to 0.2 L of H_2O and sonicated for 1 hr. Then, under vigourous agitation a required amount of this suspesion was withdrawn by a pipette and added to a catalytic solution. A final amount of Ru in the system (contained in RuO_2 colloidal partilces) was 175 micromole, which was 1.09 times more per Ru than in a typical experiment with **1** (40 micromole of **1** or 160 micromole of Ru). Preparation and characterization of $Rb_8K_2[\{Ru_4O_4(OH)_2(H2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]$ (**1**) was described earlier[1]. Water for the preparation of solutions was obtained from a Barnstead Nanopure® water-purification system, and all other chemicals and salts were of the highest purity available from commercial sources.

General procedure

Light induced water oxidation was performed in the round bottom-reaction vessel with a diameter ~3 cm and with a total volume of ~15 mL equipped with a side arm stopcock and 14/20 outer joint. The vessel was filled with 8 mL of solution with the desired concentrations of $Ru(bipy)_3^{2+}$ (0.5-1.0 mM), $Na_2S_2O_8$ (2.5-10 mM), catalyst (**1**) (1.25-10 μM) and buffer (20-50 mM sodium phosphate, initial pH 7.2). The reaction

vessel was then sealed with a rubber septum, carefully deairated and filled with Ar. All procedures were performed with a minimum exposure to ambient light. The reaction was initiated by turning on the Xe-lamp. The output of the Xe-Lamp was filtered with a 420-520 nm band-pass filter and was focused onto the reaction vessel. Light intensity was adjusted by varying the beam size at the sample (by an aperture) and/or applying a neutral density filter(50% transmission). At high light intensity (28 mW/cm^2), the reaction in solution proceeded very fast and the O_2 concentration in the head space was not in equilibrium with O_2 formed in solution. Therefore, to follow the kinetics of O_2 formation, the reaction was stopped after the desired illumination time by turning off the lamp. The reaction vessel was then vigorously shaken to equilibrate dioxygen concentrations in liquid and gas phases, and the headspace was analyzed for O_2 content. After that, the reaction vessel was wrapped in aluminum foil and opened. The solution pH was measured. A small amount of the reaction solution, 0.15-0.30 mL, was withdrawn and diluted in 0.1% aqueous EtOH solution and analyzed by UV-Vis for the remaining $[Ru(bipy)_3]^{2+}$. The quantification of unreacted persulfate was performed as described below. By decreasing the light intensity by *ca.* three-fold, the kinetics of O_2 formation could be followed continuously by withdrawing a gas sample from the head space without stopping the reaction.

The O_2 yield was quantified as described earlier[1]. Briefly, 0.1 mL of the gas in the headspace gas of the reaction vessel was withdrawn through a septum using a deairated gas-tight syringe and injected into gas chromatograph. Contamination of the head-space by air was corrected by quantification of N_2 present in the head-space (from the N_2 peak in the GC traces).

Quantification of persulfate

The total amount of unreacted persulfate in reaction solution was determined after turning off the light. The reaction solution was added (in 0.5-1.0 mL increments) into 10 mL of 10 mM $Fe(NH_4)_2(SO_4)_2$ solution in 0.1 M H_2SO_4. Under these conditions 1 eq of persulfate oxidizes 2 eqs of Fe(II) to Fe(III). [2] The Fe(II)/Fe(III) ratio was determined by measuring the solution reduction potentials using a VWR symPhony Epoxy Combination Redox Electrode (VWR Scientific Products, USA). The readings of potentials were

calibrated using a series of stock solutions of persulfate with concentrations in the range 0.5-5.0 mM. All these persulfate stock solutions contained 1.0 mM Ru(bipy)$_3^{2+}$, 5 µM catalyst (**1**), and 20 mM sodium phosphate buffer.

Steady state luminescence quenching

The solutions of Ru(bpy)$_3^{2+}$, S$_2$O$_8^{2-}$, and their mixtures were prepared and stored under darkroom conditions to avoid photoreaction. All solutions were purged with Ar before measurements. A 10x1 mm dual-path-length quartz cuvette and 1.8-nm excitation and emission slits were used in all steady-state luminescence measurements. Samples were excited at 450 nm, and emission intensity data were collected at 20 °C at 617-620 nm. Integration time was set at 0.05 s. To minimize light induced reactions during the measurements, the acquisition time was kept to less than 1 s. Repetitive measurements showed that the emission intensity decreased by less than 2% during this acquisition time.

Quantum yield measurements

The quantum yield of O$_2$ formation, Φ, defined as the number of O$_2$ molecules formed per two absorbed photons, was calculated using eq S1:

$$\Phi = N(O_2)/[N(hv)/2] \qquad (S1)$$

where N(O$_2$) is the moles of O$_2$ formed, and N(hv) is the moles of photons absorbed by the reaction solution. The quantum yield is defined for per two absorbed photons because the formation of one molecule of O$_2$ requires four oxidative equivalents supplied by two molecules of persulfate after absorption of two photons, as shown in Scheme 1. The amount of O$_2$ formed was quantified as described above at the reaction time <15 min (Figure 1, main text). The total amount of photons absorbed for a given reaction time *t* was calculated from the irradiation power and the absorbance by the reaction solution.

The irradiation power measured at the point right in front of the reaction vessel using a laser power meter (Molectron, model Max 500A) was 50 mW. The spectrum of light emitted by the Xe-lamp in the 420-520 nm range as well as the absorption spectra of cut-off filter were considered to be flat in this spectral region. During illumination, the reaction solution remained orange colored, indicating that the photosensitizer was mostly present in reduced form as Ru(bpy)$_3^{2+}$. Since the optical density of the reaction solution

was much larger than 3 in 420-520 nm range, all light entering the reaction solution was considered to be absorbed. The amount of absorbed light can be determined from the measured power in front of the reaction vessel and the reflection loss at the glass/air interface. The latter was estimated to be *ca.* 6 % for the round reaction vessel. The experimental quantum yield was found to be *ca.* 9%.

Estimation of ion-pairing equilibrium constant K_3

Quenching of excited $Ru(bpy)_3]^{2+}$ by persulfate can proceed via both static and dynamic pathways. In the dynamic pathway, the excited chromophore encounters the quencher by a diffusion process. In the static pathway, the excited chromophore is quenched by a quencher molecule that forms a contact ion pair with the chromophore in the ground state:

$$[Ru(bpy)_3]^{2+} + S_2O_8^{2-} \leftrightarrow [Ru(bpy)_3]^{2+} \bullet S_2O_8^{2-} \qquad (S2)$$
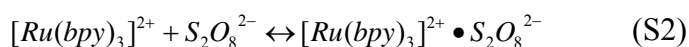
The ion-pairing equilibrium constant $K_3 = 1.1 \times 10^3$ M^{-1} was obtained by fitting of data in Figure S1 using a procedure identical to that described by Bard et al.[3]
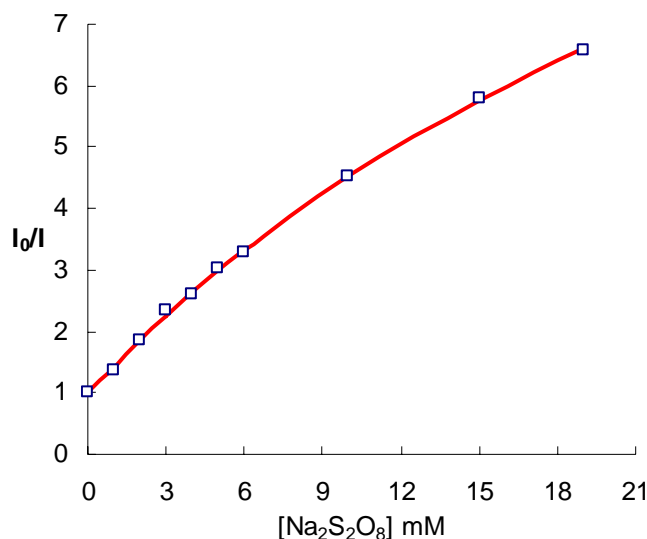

Figure S1. I_0/I as a function of $[S_2O_8^{2-}]$ (Stern-Volmer plot) in 20 mM sodium phosphate buffer solutions. All solutions contained 1.0 mM $[Ru(bpy)_3]^{2+}$ and were purged with Ar. The solid line is a fitting obtained using the reaction mechanism and fitting procedure described in reference 3.[3]

Computational studies

All calculations were performed using the Gaussian 03 program[4]. The geometries of all species were optimized without any symmetry constraint at the B3LYP[6] level of theory. In these calculations we used Hay-Wadt effective core potentials (ECPs) and associated Lanl2dz basis set for Ru[6] and the standard 6-31G* split-valence-polarization basis set for all other atoms. The solvent effects were estimated by using the self-consistent reaction field IEF-PCM method[7] with water as a solvent (dielectric constant ε = 78.39).

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