Supplementary Information

Wilkinson's Iridium Acetate Trimer as a Water-Oxidation Catalyst

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Figure S1. Rate of oxygen evolution vs. concentration of **1**. Conditions: 10.0 mM NaIO₄, 230 mM NaOAc, pH 5.6. Error bars indicate two standard deviations from the mean.



Figure S2. Log of the rate of oxygen evolution vs. log [1]. Conditions: 10.0 mM NaIO₄, 230 mM NaOAc, pH 5.6. Error bars indicate two standard deviations from the mean.



Figure S3. Normalized rate of oxygen evolution vs. sodium acetate concentration for 120 nM iridium acetate (triangles) and 430 nM iridium oxide (squares). Conditions: 10.0 mM sodium periodate, pH 5.6.



Figure S4. Visible spectrum of 960 μ M 1 in milliQ water (pH ~6).



Figure S5. Visible spectrum of 107 μ M 1 28 s after addition of sodium iodate. Final sodium iodate concentration: 8.89 mM.



Figure S6. Visible spectrum of 595 μ M 1 23 hr after addition of sodium iodate, showing continued growth in intensity, and formation of the peak at ~590 nm. Final sodium iodate concentration: 25.0 mM.



Figure S7. TEM images of: (a) a solution of 620 μ M of 2 nm IrO₂ nanoparticles, (b) a solution containing 635 μ M **1** and 28 mM sodium periodate after 3 weeks, showing the formation of small nanoparticles, (c) a solution 10.7 μ M **1** in 6.9 mM butylmalonate, 7.9 mM sodium periodate, and 204 mM NaOAc buffer pH 5.2 after 2 weeks reaction, showing a small amount of aggregated material, and (d) a solution of 230 mM NaOAc buffer pH 5.5. Magnification: 250000x. In the absence of butylmalonic acid, nanoparticles similar to those prepared by conventional methods form from the reaction of **1** with sodium periodate (compare images (a) and (b)). When butylmalonic acid is present in solution (c), larger aggregates form comparable to those seen in a sodium acetate solution containing no iridium (d).



Figure S8. Visible spectra of 96.0 μ M **1** in 6.9 mM butylmalonate, 204 mM NaOAc buffer pH 5.2 without addition of NaIO₄ (solid line) and 1 month after addition of 8.9 mM NaIO₄ followed by extraction with dichloromethane (dashed line).



Figure S9. Visible spectra time course of 124μ M IrO₂ nanoparticles (per Ir basis) in 8.00 mM sodium periodate. Conditions: 7.44 mM sodium butylmalonate, 184 mM sodium acetate, pH 5.6.



Figure S10. Electrochemical quartz crystal nanobalance measurement of 2 mM 1 (blue: voltage ramp; black: measurements with 1; and gray: background measurements).



Figure S11. LC-MS of 1 prepared through method A. The peak at 1125 m/z is due to trace carbonate.

Materials and Methods:

Iridium chloride hydrate was purchased from Pressure Chemical Company. Silver acetate was purchased from J. T. Baker. Acetic acid was purchased from EMD Chemicals. Sodium acetate, Celite 545, butylmalonic acid, sodium iodate, and cerium(IV) ammonium nitrate were purchased from Sigma-Aldrich. Sodium periodate was purchased from Acros. Potassium hexachloroiridate(IV) was purchased from Strem Chemicals, Inc. All chemicals were used without additional purification. Water was purified using a milliQ water system provided by Millipore. Elemental analysis was performed by Atlantic Microlab, Inc. High resolution LC-MS was performed by the Keck Biotechnology Resource Center at Yale. TEM images were taken using a Zeiss EM-900 TEM operating at 80 kV. Images were recorded using an SIS Megaview III digital camera.

Wilkinson's iridium acetate trimer $[Ir_3O(OAc)_6(H_2O)_3](OAc)$ (1) was synthesized using two methods based on the original synthesis.¹ Both methods were found to yield 1 with identical catalytic activity within the error of the measurements.

Method A: Iridium chloride hydrate (960 mg) and silver acetate (1.82 g) were combined in 35 mL acetic acid and refluxed for 3 hours under air. The solution was then basified using sodium bicarbonate, and filtered. Rotary evaporation of the aqueous solution was followed by extraction with an ethanol-methanol mixture. **1** was then obtained as a dull green solid after rotary evaporation and drying of the EtOH-MeOH mixture. The complex was assayed for purity by elemental analysis (Calc: 15.76 C, 3.21 H; Found: 15.92 C, 3.17 H), and high resolution LC-MS (Fig. S10).

Method B: Iridium chloride hydrate (981 mg) and silver acetate (2 g) were combined with 50 mL of acetic acid and refluxed under nitrogen for 3 hours. The solution was filtered through Celite 540 to remove silver chloride, and the solvent was removed via rotary evaporation to yield a yellow glass. The crude product was dissolved in methanol and filtered to remove excess silver acetate, and the solvent was removed via rotary evaporation to yield a brown powder (378 mg).

Iridium oxide nanoparticles were synthesized according to Mallouk's procedure² using a 60 fold excess of butylmalonic acid as the surfactant. The resultant colloidal solution was diluted to a known volume and the concentration was determined assuming complete conversion of potassium hexachloroiridate to iridium oxide and no loss during transfers. The UV-visible

spectrophotometric properties of the colloidal solution were found to be in good agreement with the literature values.

General procedure for Clark-type O_2 electrode measurements: A solution of oxidant in buffer (5.00 mL) is placed in the electrode chamber, and the system is allowed to equilibrate until a stable baseline is attained. After the baseline has stabilized, 10.0 μ L of catalyst solution is injected into the electrode chamber and the change in electrode current over time is recorded. This procedure is repeated a minimum of three times per reaction condition. Error bars represent two standard deviations from the mean when present, and are generally between 10 and 20% of the measured value.

Simultaneous cyclic voltammetry and piezoelectric gravimetry measurements were collected with an Elchema EQCN-600 nanobalance and an Elchema PS-605B potentiostat. Both instruments were computer-controlled with the Elchema Voltscan program (version V.4.1). A conventional three-electrode cell configuration was used; the counter electrode was a platinum foil, and an Ag/AgCl electrode (Bioanalytical Systems, Inc.) served as the reference. The working electrode was a 14-mm diameter quartz crystal (AT cut, plano-plano, 10 MHz) coated with a gold/chromium conducting surface (approximate electroactive surface area: 0.256 cm²). The quartz crystal disc was mounted in an EQCM-5710 quartz crystal holder (Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland). The frequency response of the quartz crystal was additionally monitored before and during experiments using a Fluke PM6680B high-resolution frequency counter. No deposition of heterogeneous material was observed upon cycling.

- 1. S. Uemura, A. Spencer, and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1973, 2565.
- P. G. Hoertz, Y.-I. Kim, W. J. Youngblood, and T. E. Mallouk, J. Phys. Chem. B, 2007, 111, 6845-6856.