Electronic Supplementary Information

Cs₉[(γ-PW₁₀O₃₆)₂Ru₄O₅(OH)(H₂O)₄], a new all-inorganic, soluble catalyst for the efficient visible-light-driven oxidation of water

Claire Besson,a,b Zhuangqun Huang,b Yurii V. Geletii,b Sheri Lense,b Kenneth I. Hardcastle,b Djamaladdin G. Musaev,b Tianquan Lian,b Anna Proustac and Craig L. Hill*b

a Institut Parisien de Chimie Moléculaire, UMR CNRS 7201, UPMC Univ Paris 06, 4 place Jussieu, Case 42, 75005 Paris, France.
b Department of chemistry, Emory University, 1515 Dickey Drive, Atlanta GA 30322, USA. Fax: 404-727-6076; Tel: 404-727-6611; E-mail: chill@emory.edu.
c Institut Universitaire de France

Synthesis of Cs₉[(γ-SiW₁₀O₃₆)₂Ru⁴IV₄O₅(OH)(OH₂)₄]17 H₂O (2)

Ruthenium trichloride hydrate (281 mg, 1.25 mmol based on RuCl₃•H₂O) was dissolved in 10 mL of water to give a very dark green solution with pH = 0.6. Finely ground Cs₇[γ-PW₁₀O₃₆]•H₂O (1.5 g, 0.44 mmol, prepared according to the literature) was added to the solution in small portions over about 40 minutes, under vigorous agitation. Water (10 mL) was then added and the dark brown suspension was left stirring for twelve hours in an open Erlenmeyer flask. Dark microcrystalline 2 was then collected by filtration (1 g, 0.14 mmol, 65 % based on W). Recrystallization was performed by dissolving 1.0 g of 2 in 70 mL of water at 80 ºC, adding cesium chloride (2.5 g, 15 mmol) and cooling to 0 ºC, yielding dark red plates (250 mg, 0.04 mmol, 25 % based on 2). IR (ν, cm⁻¹, 2% in KBr) 489 (w), 525 (w), 702 (sh), 890 (sh), 812 (s), 887 (sh), 950 (s), 976 (sh), 1044 (m), 1075 (m), 1095 (sh), 1135 (m). UV (λ, nm, in HCl 0.1 M) (log ε) 445 (4.3). DPV (mV, reference electrode Ag/AgCl (3.0 M NaCl), 0.1 M sodium sulfate buffer pH 2.0 with 0.1 M NaNO₃ as electrolyte, scan rate 25 mV.s⁻¹) 1029, 684, 563, 425, 98, -66, -346, -480. DPV (0.1 M sodium phosphate buffer pH 7.0 with 0.1 M NaNO₃ as electrolyte, scan rate 25 mV.s⁻¹) 510, ca. 300, -163 (two electrons), -446, -678, -820.

IR spectrum of Cs\(_9\)(\(\gamma\)-SiW\(_{10}\)O\(_{36}\))\(_2\)Ru\(_{IV}\)\(_4\)O\(_5\)(OH)(OH\(_2\))\(_4\)] (2)

![IR spectrum](image)

**Figure S1.** IR spectrum of Cs\(_9\)(\(\gamma\)-PW\(_{10}\)O\(_{36}\))\(_2\)Ru\(_{IV}\)\(_4\)O\(_5\)(OH)(OH\(_2\))\(_4\)]

**X-Ray crystallography of Cs\(_9\)(\(\gamma\)-SiW\(_{10}\)O\(_{36}\))\(_2\)Ru\(_{IV}\)\(_4\)O\(_5\)(OH)(OH\(_2\))\(_4\)]·17H\(_2\)O**

X-ray quality crystals of Cs\(_9\)(\(\gamma\)-PW\(_{10}\)O\(_{36}\))\(_2\)Ru\(_{IV}\)\(_4\)O\(_5\)(OH)(OH\(_2\))\(_4\)]·17H\(_2\)O were grown by slow evaporation of a saturated aqueous solution.

A suitable crystal was coated with Paratone N oil, suspended on a small fiber loop and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 APEX II CCD sealed tube diffractometer with graphite monochromator Mo K\(_{\alpha}\) (\(\lambda = 0.71073\) Å) radiation. Data were measured using a combination of \(\varphi\) and \(\omega\) scans with 10 s frame exposure and 0.3° frame widths. Data collection, indexing and initial cell refinements were all carried out using APEX II software.\(^1\) Frame integration and final cell refinements were done using SAINT software.\(^2\) The final cell parameters were determined from least-square refinements on 9834 reflections. The structure was solved using direct methods and difference Fourier techniques (SHELXTL, v 6.12).\(^3\) All atoms except oxygens were refined anisotropically. Scattering factors and anomalous dispersion coefficients are taken from the International tables for X-Ray Crystallography.\(^4\) Structure solution and refinement were performed using SHELXTL, v 6.12 software.\(^3\)

1. *APEX II, 2005*, Bruker ASX Inc. Analytical X-Ray systems, %$^\text{\#}$% East Cheryl parkway, Madison WI 53711-5373, USA.
Crystallographic data for Cs$_9$[($\gamma$-SiW$_{10}$O$_{36}$)$_2$Ru$^{IV}_4$O$_5$(OH)(OH$_2$)$_4$]$\cdot$17H$_2$O

Empirical formula          Cs$_9$ O$_{98.9}$ P$_2$ Ru$_4$ W$_{20}$
Temperature               172(2) K
Wavelength                0.71073 Å
Crystal system            Monoclinic
Space group               P2(1)/c
Unit cell dimensions      
                          a = 11.452(7) Å, $\alpha$ = 90°.
                          b = 41.66(3) Å, $\beta$ = 93.056(9)°.
                          c = 20.378(12) Å, $\gamma$ = 90°.
Volume                    9709(10) Å$^3$
Z                         4
Density (calculated)      4.736 Mg/m$^3$
Absorption coefficient    27.663 mm$^{-1}$
F(000)                    11889
Crystal size              0.15 x 0.11 x 0.03 mm$^3$
Theta range for data collection 0.98 to 30.43°.
Index ranges             -16<=$h<=$16, -58<=$k<=$59, -28<=$l<=$28
Reflections collected     184349
Independent reflections   28330 [R(int) = 0.0851]
Completeness to theta = 30.43° 96.2 %
Absorption correction     Semi-empirical from equivalents
Max. and min. transmission 0.4913 and 0.1038
Refinement method         Full-matrix least-squares on F$^2$
Data / restraints / parameters 28330 / 0 / 754
Goodness-of-fit on F$^2$   1.071
Final R indices [I>2sigma(I)]  
                          R1 = 0.0469, wR2 = 0.1055
R indices (all data)       
                          R1 = 0.0632, wR2 = 0.1125
Largest diff. peak and hole 8.223 and -4.748 e.Å$^{-3}$
CCDC deposition number    758073
Acid-base titration of Cs$_9$[($\gamma$-PW$_{10}$O$_{36}$)$_2$Ru$^{IV}$$_4$O$_5$(OH)(OH$_2$)$_4$] (2)

An aqueous solution of Cs$_9$[($\gamma$-PW$_{10}$O$_{36}$)$_2$Ru$^{IV}$$_4$O$_5$(OH)(OH$_2$)$_4$] (9.3 mM, 5 mL, 46.5 µM) was titrated back and forth with 0.1 M HCl and 0.1 M NaOH solutions. The difference between successive runs is minimal and can be attributed to dilution. Consequently, only one curve is displayed here for simplicity. The solution of 2 is initially acidified (not displayed), then titrated with 0.1 M sodium hydroxide solution. (Figures S2 and S3).

**Figure S2.** Titration of an acidified solution of Cs$_9$[($\gamma$-PW$_{10}$O$_{36}$)$_2$Ru$^{IV}$$_4$O$_5$(OH)(OH$_2$)$_4$] by NaOH.

![Graph showing pH vs. n(OH$^-$) added/µmol](image)

**Figure S3.** Calculation of NaOH-equivalents reacting with the acidified 2.

![Graph showing pH vs. n(OH$^-$ reacted) / n(2)](image)

The number of hydroxide anions reacting with [($\gamma$-PW$_{10}$O$_{36}$)$_2$Ru$^{IV}$$_4$O$_6$(OH$_2$)$_4$]$^{10-}$ (calculated from the number introduced by correcting for the variation of pH) is two per
molecule of 2 present (Figure S3).

The protonation of \([(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ru}^{IV}_4\text{O}_6(\text{OH}_2)_4]^{10-}\) therefore requires 2 protons and yields \([(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ru}^{IV}_4\text{O}_6(\text{OH})_2(\text{OH}_2)_2]^{12-}\). The two pK\textsubscript{a} values are close enough to be undistinguishable and lie around 3.1.

The pH of an aqueous solution of 2 (22 µM) was set to 4.9 by addition of a few drops of concentrated sodium hydroxide, and then titrated to pH 0.6 by 0.1 M, 1 M and 10 M HCl solutions.

![Figure S4. pH dependence of UV-visible spectra of 2: \([(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ru}^{IV}_4\text{O}_6(\text{OH}_2)_2]^{12-}\) (dark green, pH 4.9), \([(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ru}^{IV}_4\text{O}_6(\text{OH}_2)_4]^{10-}\) (blue, pH 1.9) and \([(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ru}^{IV}_4\text{O}_4(\text{OH}_2)_2]^{8-}\) (red, pH 0.6)
Light-induced water-oxidation.

The conditions used are those described in reference 6 of the main text. Water oxidation was performed in a 15 mL Schlenk flask. The vessel was filled with 8 mL of a solution containing 1.0 mM [Ru(bpy)$_3$]Cl$_2$, 5 mM Na$_2$S$_2$O$_8$, 20 mM Na$_2$SiF$_6$ buffer at pH 5.8$^1$, and the desired concentration of catalyst. The solution was thoroughly deaerated by purging with argon. The reaction was initiated by exposing the reaction vessel to the light of the Xe-lamp using 420-520 nm band-pass filters. After the desired illumination time, the reaction was temporarily stopped by blocking the light, and then the flask was vigorously shaken to allow equilibration of O$_2$ between the solution and the head-space. Analysis of the headspace was performed by withdrawing a 0.1 mL sample from the headspace and injecting this into a 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 the carrier gas. The amount of N$_2$ detected facilitated correction for the air contamination. At the end of the reaction, a sample of the solution was withdrawn, diluted in 0.1 % aqueous ethanol and analyzed by UV-vis spectroscopy to determine the amount of [Ru(bpy)$_3$]$^{2+}$ remaining.