Electronic Supplementary Information

$Cs_9[(\gamma\text{-}PW_{10}O_{36})_2Ru_4O_5(OH)(H_2O)_4]$, a new all-inorganic, soluble catalyst for the efficient visible-light-driven oxidation of water

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Synthesis of $Cs_9[(\gamma\text{-}SiW_{10}O_{36})_2Ru^{IV}{}_4O_5(OH)(OH_2)_4]\cdot 17\ H_2O$ (2)

Ruthenium trichloride hydrate (281 mg, 1.25 mmol based on $RuCl_3\bullet H_2O$) was dissolved in 10 mL of water to give a very dark green solution with pH = 0.6. Finely ground $Cs_7[\gamma\text{-}PW_{10}O_{36}]\bullet H_2O$ (1.5 g, 0.44 mmol, prepared according to the literature[1]) 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 $NaNO_3$ 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 $NaNO_3$ as electrolyte, scan rate 25 $mV.s^{-1}$) 510, *ca. 300*, -163 (two electrons), -446, -678, -820.

1. P. J. Domaille, *Inorg. Synth.* 1990, **27**, 101-102.

IR spectrum of $Cs_9[(\gamma\text{-}SiW_{10}O_{36})_2Ru^{IV}{}_4O_5(OH)(OH_2)_4]$ (2)

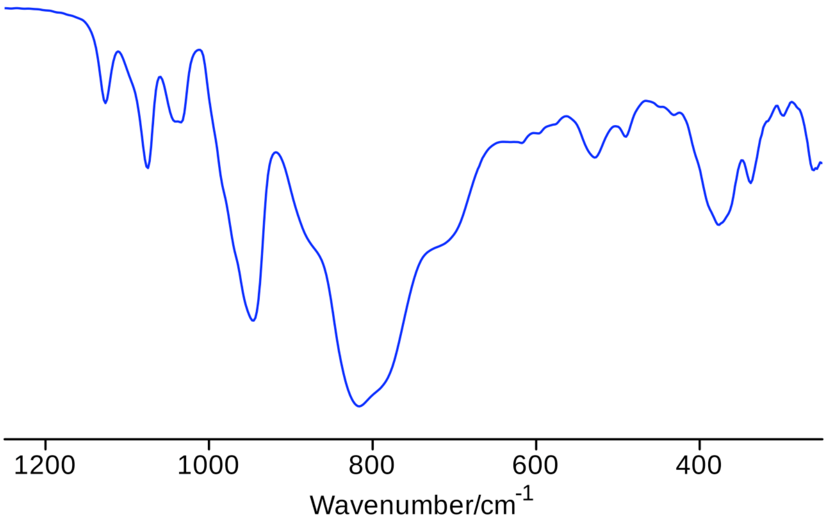

Figure S1. IR spectrum of $Cs_9[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_5(OH)(OH_2)_4]$.

X-Ray crystallography of $Cs_9[(\gamma\text{-}SiW_{10}O_{36})_2Ru^{IV}{}_4O_5(OH)(OH_2)_4]\cdot 17H_2O$

X-ray quality crystals of $Cs_9[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}O_5(OH)(OH_2)_4]\cdot 17H_2O$ 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 Kα (λ = 0.71073 Å) radiation. Data were measured using a combination of φ and ω 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, %$^% East Cheryl parkway, Madison WI 53711-5373, USA.
2. *SAINT v. 6.45 A, 2003*, Bruker ASX Inc. Analytical X-Ray systems, East Cheryl parkway, Madison WI 53711-5373, USA.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.,* 2008, **64**, 112-122.
4. *International tables for X-Ray Crystallography, volume C*, A. J. C. Wilson ed. Klüwer Academic publishers, Dordrecht, the Netherlands, 1992.

Crystallographic data for $Cs_9[(\gamma\text{-}SiW_{10}O_{36})_2Ru^{IV}_4O_5(OH)(OH_2)_4]\cdot 17H_2O$

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	α= 90°.
	b = 41.66(3) Å	β= 93.056(9)°.
	c = 20.378(12) Å	γ = 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 $Cs_9[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_5(OH)(OH_2)_4]$ (2)

An aqueous solution of $Cs_9[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_5(OH)(OH_2)_4]$ (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).

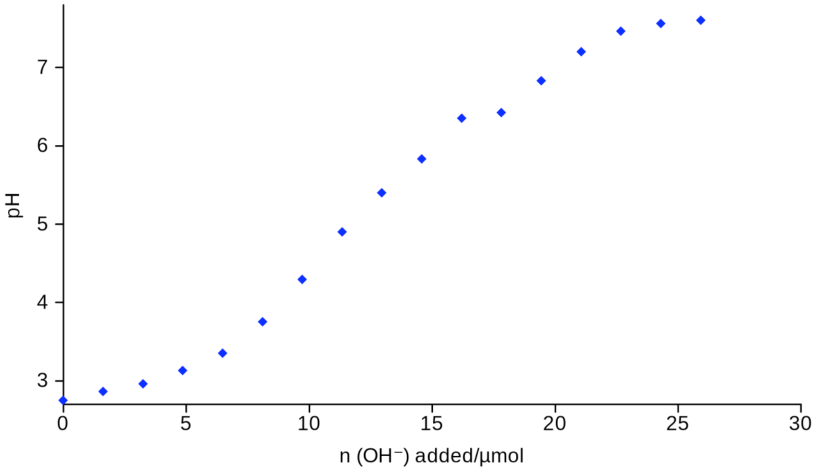

Figure S2. Titration of an acidified solution of $Cs_9[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_5(OH)(OH_2)_4]$ by NaOH.

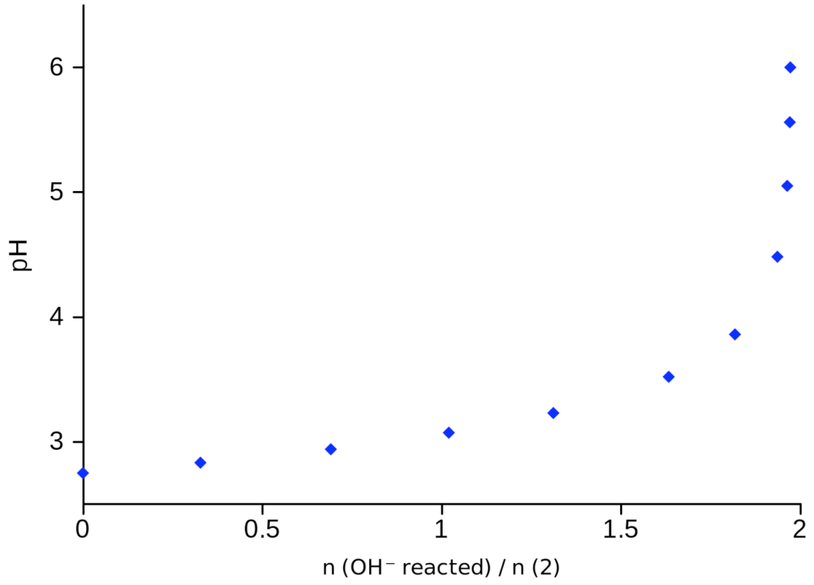

Figure S3. Calculation of NaOH-equivalents reacting with the acidified **2**.

The number of hydroxide anions reacting with $[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_6(OH_2)_4]^{10-}$ (calculated from the number introduced by correcting for the variation of pH) is two per molecule of **2** present (Figure S3).

The protonation of $[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_6(OH_2)_4]^{10-}$ therefore requires 2 protons and yields $[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_6(OH)_2(OH_2)_2]^{12-}$. The two p$K_a$ 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.

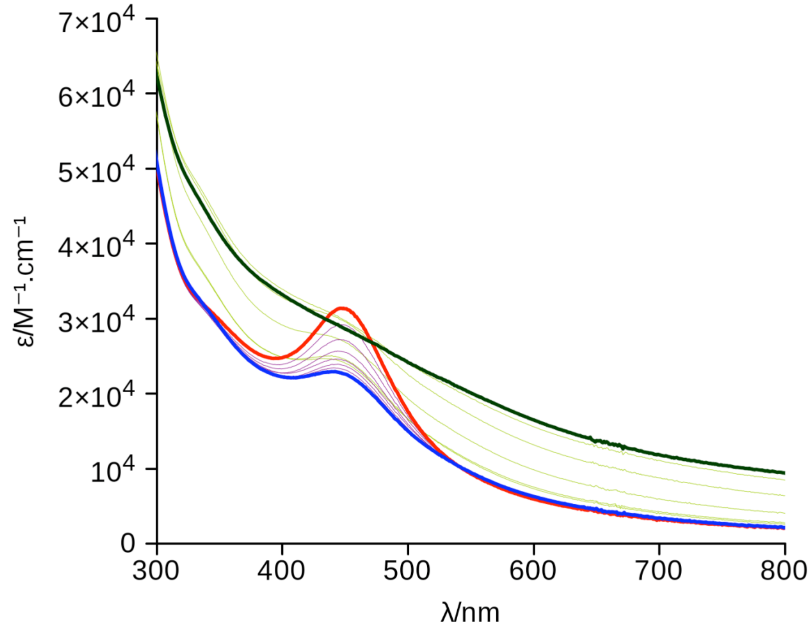

Figure S4. pH dependence of UV-visible spectra of **2**: $[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_6(OH)_2(OH_2)_2]^{12-}$ (dark green, pH 4.9), $[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_6(OH_2)_4]^{10-}$ (blue, pH 1.9) and $[(\gamma\text{-}PW_{10}O_{36})_2Ru^{IV}{}_4O_4(OH)_2(OH_2)_4]^{8-}$ (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 $Na_2S_2O_8$, 20 mM Na_2SiF_6 buffer at pH 5.8[1], and the desired concentration of catalyst. The solution was thoroughly deairated 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.

1. M. Hara, C. C. Waraksa, J. T. Lean, B. A. Lewis, T. E. Mallouk, *J. Phys. Chem. A* 2000, **104**, 5275-5280.