



Supporting Information

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Supporting Information for:

An all-inorganic, stable and highly active tetra-ruthenium homogeneous catalyst for water oxidation

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Instrumentation

UV-vis spectra were acquired on an Analytik Jena SPECORD S600 spectrophotometer equipped with a diode-array detector and an immersible fiber-optic probe. Electrochemical data were obtained at room temperature using a BAS CV-50W electrochemical analyzer equipped with a glassy-carbon working electrode, a Pt-wire auxiliary electrode, and a Ag/AgCl (3 M NaCl) BAS reference electrode. All reduction potentials are measured relative to this reference electrode. 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 O₂ and N₂. Argon was used as a carrier gas. Isotopic gas analysis was performed using a quadrupole HP 5971A Mass Selective Detector coupled with a HP HP5890 series II model gas chromatograph.

Materials

Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Ru(bpy)₃²⁺) was purchased from Aldrich. Tris(2,2'-bipyridyl)perchlororuthenium(III) salt (Ru(bpy)₃³⁺) was obtained by oxidation of Ru(bpy)₃²⁺ with PbO₂ in 0.5 M H₂SO₄ and precipitated from solution by addition of concentrated HClO₄.^[1, 2] The product was dried under vacuum and stored in a

freezer (-18 °C) in a sealed vial for not longer than 1-2 weeks. Quantitative correction for the $\text{Ru}(\text{bpy})_3^{2+}$ that forms spontaneously is described below in the “Catalytic Water Oxidation” section. Water for the preparation of solutions was obtained from a Barnstead Nanopure[®] water-purification system. Isotope labeled water with 97% ^{18}O was purchased from Cambridge Isotope Laboratories, Inc. All other chemicals and salts were of the highest purity available from commercial sources.

Synthesis and Characterization of $\text{Rb}_8\text{K}_2[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]\cdot 25\text{H}_2\text{O}$

Potassium γ - decatungstosilicate, $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ was prepared according to literature methods,^[3] and its identity and purity were checked by infrared spectroscopy. Preparation of $\text{Rb}_8\text{K}_2[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]\cdot 25\text{H}_2\text{O}$ (**1**): A solid sample of $\text{RuCl}_3\cdot\text{H}_2\text{O}$ (0.60 g, 2.67 mmol) was quickly added to a freshly prepared solution of $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ (4.00 g, 1.33 mmol) dissolved in 65 mL of H_2O . The solution immediately turned brown and the pH dropped to ca. 2.6. The solution pH was adjusted to 1.6 by drop-wise addition of 6M HCl. After additional stirring for 5 min, a solution of RbCl (2.4 g, 20 mmol) dissolved in 10-15 mL of H_2O was added to the mixture in small portions. The mixture was filtered and the filtrate left to stand at room temperature. Brown plate crystals began to form after 24 h. Yield ca. 1.8 g (ca. 40% based on W).

Elemental analysis: calcd.: W 55.14, Ru 6.11, Si 0.84, Rb 10.18, K 1.17; found: W 55.2, Ru 5.8, Si 0.73, Rb 10.2, K 0.95. The number of crystal water molecules was determined by thermogravimetric analysis (TGA) (see “Thermal Stability Studies” section below). IR (KBr pellet; 2000-400 cm^{-1}): 1616 (m), 999 (m), 947(m-s), 914(s) 874 (s), 802 (vs), 765 (vs), 690 (sh), 630 (sh), 572 (m-s), 542 (ms) (Figure S1). Raman (in H_2O , $c = 0.153$ mM; $\lambda_e = 1064$ nm): 1066 (w, br), 968 (w), 871 (w), 798 (w, br), 604 (w), 487 (s), 427 (s, br) (Figure S2). The infrared and Raman spectra of **1** are typical of γ -disubstituted polytungstates and a characteristic Ru-O-Ru mode at 487 cm^{-1} is evident in the latter spectrum. Compound **1** is EPR silent (X-band, RT, saturated aqueous solution). Magnetic susceptibility measurements (2–290 K, 0.1 and 1.0 Tesla) showed a diamagnetic signal ($\chi_{\text{dia/TIP}}(\mathbf{1}) = -4.2 \times 10^{-4}$ emu mol⁻¹). Electronic absorption spectra

(400-900 nm, in H₂O (c = 0.153 mM, 0.1 mm cell pathlength)) [λ_{\max} , nm (ϵ , M⁻¹ cm⁻¹)]:
a) at natural pH 4.9: 445 sh (not readily quantifiable); b) at pH 2.5: 445 (2.8 × 10⁴).

X-ray crystallography

Crystal data for **1** at 173 K: orthorhombic, space group *Pnna*, $a = 44.794(4)$, $b = 19.4287(17)$, $c = 11.8049(10)$ Å, $V = 10273.8(15)$ Å³, $Z = 4$. The refinement converged to $R(F_o) = 0.0957$, $wR(F_o^2) = 0.2520$, and $GOF = 1.025$ for 73225 reflections with $I > 2\sigma(I)$.

Crystals of **1** were taken directly from the mother liquor, mounted on a cryoloop and immediately cooled to 173(2) K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated Mo-K α (0.71073 Å) radiation. A total of 73255 reflections were collected of which 12815 were independent [$R(\text{int}) = 0.1244$]. An empirical absorption correction using equivalent reflections was performed with the program SADABS V2.10.^[4] The structure was solved with the SHELXTL, V 6.14 software to the quality indices above. The statistics for the structure are quite reasonable; for all data, $R_1 = 0.1200$ and $wR_2 = 0.2697$. Max/min residual electron density 4.803 and -5.488 e Å⁻³. Structure solution, refinement and generation of publication materials were also performed using SHELXTL, V 6.14, software.^[5] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe (FIZ, 76344 Eggenstein-Leopoldshafen (Germany); tel.: (+49)7247-808-205, fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-419095 for file name, H23 K2 O95.50 Rb8 Ru4 Si2 W20.

Titration Studies

The pH titrations of UV-vis spectra of **1** were performed on a 0.15 mM solution (0.051 g of **1** dissolved in 50 mL water) starting at pH 4.9 (the natural pH of **1** in water). The pH was lowered to 2.5 by drop-wise addition of 0.1 M HCl and then increased to 9.9 by drop-wise addition of 0.1 M NaOH (see Figures S3 and S4 below).

Conventional (pH versus volume of titrant) acid-base titration of 2.8 μmol (18.7 mg) of **1** was performed by adding 0.1 M HCl or 0.1 M NaOH. The initial solution volume was 4.5 mL and the initial pH was 4.2. The pH of the solution was then raised to

7.5 by adding 5.9 μmol of NaOH (~2.1 equiv per **1**). After that, the solution was titrated with HCl; the titration curves are given in Figure S5. A consumption of two protons per **1** is seen from Figure S6.

Thermal Stability Studies

The thermal stability and decomposition characteristics of **1** were assessed by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA curve shows a weight loss of 7.8% between 30 and 250 $^{\circ}\text{C}$ that is associated with the loss of 29 water molecules (water molecules of crystallization and terminally bound aqua ligands on the Ru centers), Figure S7. The DTA curve shows an endothermic process between 50 and 130 $^{\circ}\text{C}$ attributed to desorption of water molecules of crystallization from the lattice structure, Figure S7.

Cyclic Voltammetry

Cyclic voltammograms (CVs) were obtained at room temperature under Ar using 0.5-2 mM concentrations of **1** in 0.1 M HCl and 0.4 M sodium acetate buffer (pH 4.8) or in 25 mM phosphate buffer (pH 7.0; 0.15 M NaCl was added to the phosphate buffer). Potentials are relative to the Ag/AgCl (3.0 M NaCl). Scan rates were 25 and 100 mV s^{-1} .

Catalytic Water Oxidation

Stock solutions of $\text{Ru}(\text{bpy})_3^{3+}$, 1.5-2.5 mM, were prepared in 1 mM HClO_4 . The solution was diluted ~1:20 with water and the usual contamination with $\text{Ru}(\text{bpy})_3^{2+}$ was estimated from its absorbance at 454 nm ($\epsilon = 1.45 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). This $\text{Ru}(\text{bpy})_3^{3+}$ solution was subsequently reduced by a slight excess of ascorbic acid and the total amount of $\text{Ru}(\text{bpy})_3^{2+}$ was determined from the absorbance at 454 nm. The $\text{Ru}(\text{bpy})_3^{2+}$ contamination in $\text{Ru}(\text{bpy})_3^{3+}$ never exceeded 3-5%. A small amount (0.1-0.2 mL) of the $\text{Ru}(\text{bpy})_3^{3+}$ stock solution was quickly mixed in a quartz UV-vis cell filled with 2.8-2.9 mL of the catalyst solution in a phosphate buffer. The kinetics for the catalytic reduction of $\text{Ru}(\text{bpy})_3^{3+}$ was studied by following the accumulation of the reaction product, $\text{Ru}(\text{bpy})_3^{2+}$. The mixing time was 5-10 s, and the data were collected every 3-10 s. Typically, the initial concentrations of $\text{Ru}(\text{bpy})_3^{3+}$ were in the range of 0.09-0.12 mM.

The characteristics of the kinetics (e.g. nonexponential rate law, etc.) are addressed in the text.

Oxidation of water to O₂ was performed on a larger scale. The reaction vessel with a total volume of ~20 mL was filled with 8 mL of 1.5 mM Ru(bpy)₃³⁺, sealed with a rubber septum, carefully deaerated, and filled with Ar gas. The second vessel was filled with a deaerated catalyst solution containing phosphate buffer. Then, 2.0 mL of the catalyst solution was withdrawn with a deaerated gas-tight syringe and injected into the first vessel. After 3-5 min, the headspace was analyzed for O₂ content: 0.1 mL of headspace gas was withdrawn through a septum by a deaerated gas-tight syringe and injected into the gas chromatograph. Contamination of the head-space by air was always quantified by measuring the N₂ present in the head-space (from the N₂ peak on GC traces). The O₂ from catalytic H₂O oxidation, equation 1 in the text, was quantitatively corrected for the slight contamination of O₂ from air. A typical GC trace is shown in Figure S8. The amount of O₂ dissolved in the reaction solution was ignored.

The isotope labeling experiment was conducted using 5 and 10 atom % H₂¹⁸O. The procedure used was similar to the one described above but the reaction was carried out under He. The MS detector was tuned for maximum sensitivity. Single ion mode was used to scan for the ions m/z = 28, 30, 32, 34, 36, 40 with a dwell time of 40 μs, resulting in 3 cycles per second. The total flow rate into the spectrometer was limited to 0.6 mL/min. A 5 μL sample of gas was introduced into the instrument. MS ChemStation analysis software was used to extract the single ion chromatograms. Typical results are given in Figure S9.

The voltammetric behavior of **1** as a function of pH and solution conditions is described in the text. The efficiency of **1** as a catalyst for electrochemical water oxidation as such was not investigated in this study.

In order to explore further the catalytic properties of **1** towards water oxidation we attempted to use Ru(bpy)₃²⁺ as an electron transfer catalyst. As noted in the text, the CV of Ru(bpy)₃²⁺ shows reversible behavior with E_a = 1100 and E_c = 940 mV and I_a/I_c ~1, Figure 2, which is higher than the value of the most negative peak observed for **1** (at pH 2.0) and is higher than the standard potential for 4-electron oxidation of water to O₂, E_o = 0.82 V vs NHE at pH 7. If a very small amount of **1** is added (0.006-0.029 mM)

catalytic currents are observed at potentials corresponding to the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^{3+}$, Figure 2.

Finally, we used $\text{Ru}(\text{bpy})_3^{3+}$ as a stoichiometric oxidant to demonstrate that O_2 is a reaction product. In order to minimally optimize the reaction conditions we examined the kinetics of $\text{Ru}(\text{bpy})_3^{3+}$ decay by following the formation of $\text{Ru}(\text{bpy})_3^{2+}$ (the main product of $\text{Ru}(\text{bpy})_3^{3+}$ reduction) in 10 mM sodium phosphate buffer solution (final pH 6.9). In the absence of **1** the typical reaction time, $\tau_{1/2}$, is longer than 30 min. Addition of very small amounts of **1** (in the range 0.5 - 1.5 μM) considerably shortens the reaction time.

Finally, the O_2 yield was determined under the following conditions: 18 mM sodium phosphate buffer solution (final pH = 6.9; final total volume = 10 mL), 1.2 mM (12 μmol) $\text{Ru}(\text{bpy})_3^{3+}$ and 0.1 μmol of **1**.

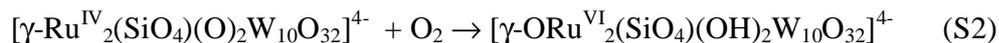
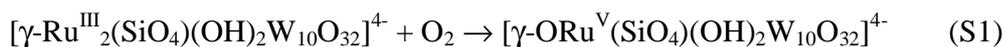
Computational Studies

All calculations were performed using the Gaussian 03 program.^[6] The geometries of the reported structures were optimized without any symmetry constraints at the B3LYP/[Lan12dz + d(Si)] level of theory with additional d polarization functions for Si atom ($\alpha = 0.55$) and the corresponding Hay-Wadt effective core potential (ECP) for Ru and W atoms.^[7-10] The final energies of the optimized structures were further improved by performing single point calculations including additional d and p polarization functions for O ($\alpha = 0.96$) and H ($\alpha = 0.36$) atoms, respectively, i.e. at the B3LYP/{Lan12dz + d(Si,O) + p(H)} level of theory.

The dielectric effects from the surrounding environment were estimated using the self-consistent reaction field IEF-PCM method^[11] at the B3LYP/[Lan12dz + d(Si)] level. In these calculations we used water as a solvent. We used the B3LYP/{Lan12dz + d(Si,O) + p(H)} energies including solvent effects, while the energies without solvent effects are provided in parentheses (values below). In our calculations we used the experimentally reported structures of the studied species without counter cations.

Previously, we have shown that the proposed computational approach adequately describes the geometrical and electronic structures of the di-d-transition-metal-substituted γ -Keggin POMs, $[\gamma\text{-M}_2\text{-(SiO}_4\text{)W}_{10}\text{O}_{36}]^n$.^[12-14]

Some computational findings: The studies of the geometrical and electronic structure of reactants and products, as well as the thermodynamics of the reactions in eqs S1-S2 below clearly show that reaction S1 is highly exothermic (by 55.4 (45.1) kcal/mol), while the reaction S2 is 28.1 kcal/mol exothermic in the gas-phase, but becomes 13.4 kcal/mol endothermic in water. In other words, O₂ evolution via a Ru^V-to-Ru^{III} redox process does not appear to be feasible, but it does appear to be so via a Ru^{VI}-to-Ru^{IV} redox process in this Ru₂ “monomer”, [$\{\text{Ru}^{\text{III}}_2(\text{OH})_2(\text{H}_2\text{O})_2\}(\gamma\text{-SiW}_{10}\text{O}_{36})\}^{4-}$] (which is half of **1**) and **1** itself. Furthermore, our preliminary calculations of (Ru₂^{IV}POM) oxidation to (Ru₂^VPOM) indicate that this is a relatively facile process and requires only 20-25 kcal/mol of energy (Kuznetsov, A.; Gueletti, Y. V.; Hill, C. L.; Musaev, D. G., unpublished work.)



A combination of the above computational data with the experimental observations on water oxidation by [$\{\text{Ru}^{\text{III}}_2(\text{OH})_2(\text{H}_2\text{O})_2\}(\gamma\text{-SiW}_{10}\text{O}_{36})\}^{4-}$] and by **1** indicate, once again, that the most likely resting oxidation state of the 4 Ru centers in **1** is 4+, rather than 3+.

Reviews of POMs:

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- c) M. T. Pope, in *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology, Vol. 4* (Ed.: A. G. Wedd), Elsevier Ltd., Oxford, UK, **2004**, pp. 635
- d) C. L. Hill, in *Comprehensive Coordination Chemistry-II: From Biology to Nanotechnology, Vol. 4* (Ed.: A. G. Wedd), Elsevier Ltd., Oxford, UK, **2004**, pp. 679

Reviews of catalysis by POMs:

- a) C. L. Hill, C. M. Prosser-McCarthy, *Coord. Chem. Rev.* **1995**, *143*, 407
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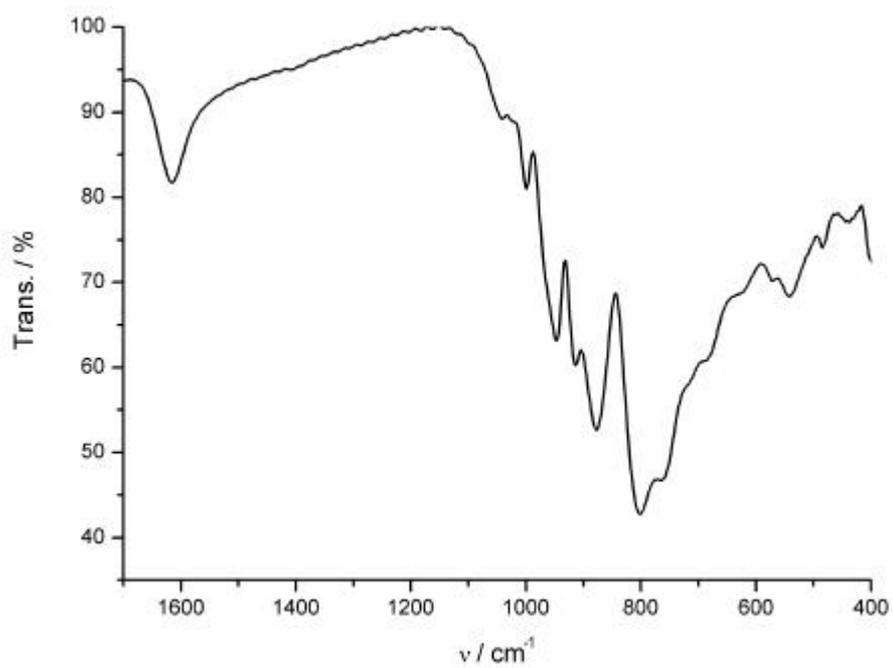


Figure S1. FT-IR spectrum of **1** (KBr pellet).

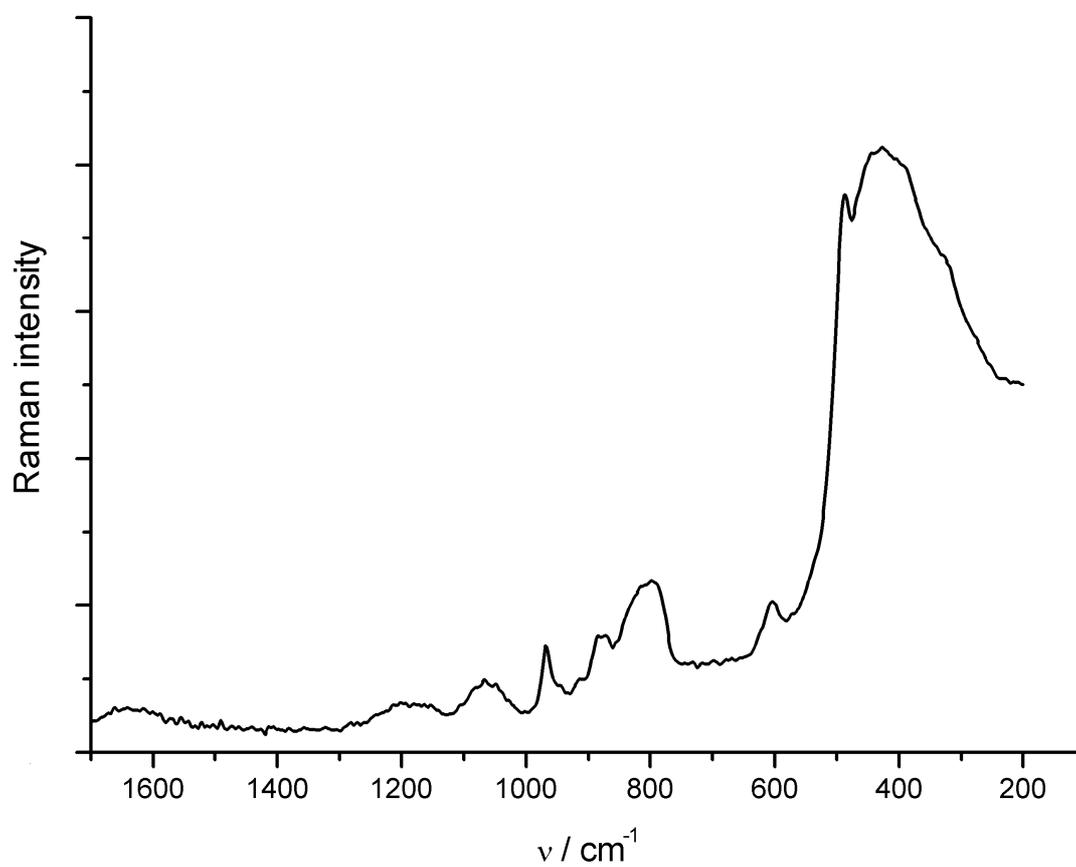


Figure S2. Raman spectrum of **1** in water (0.15 mM sample; $\lambda_e = 1064$ nm). The intense band observed at 487 cm^{-1} is due to a symmetric Ru-O-Ru vibrational mode.

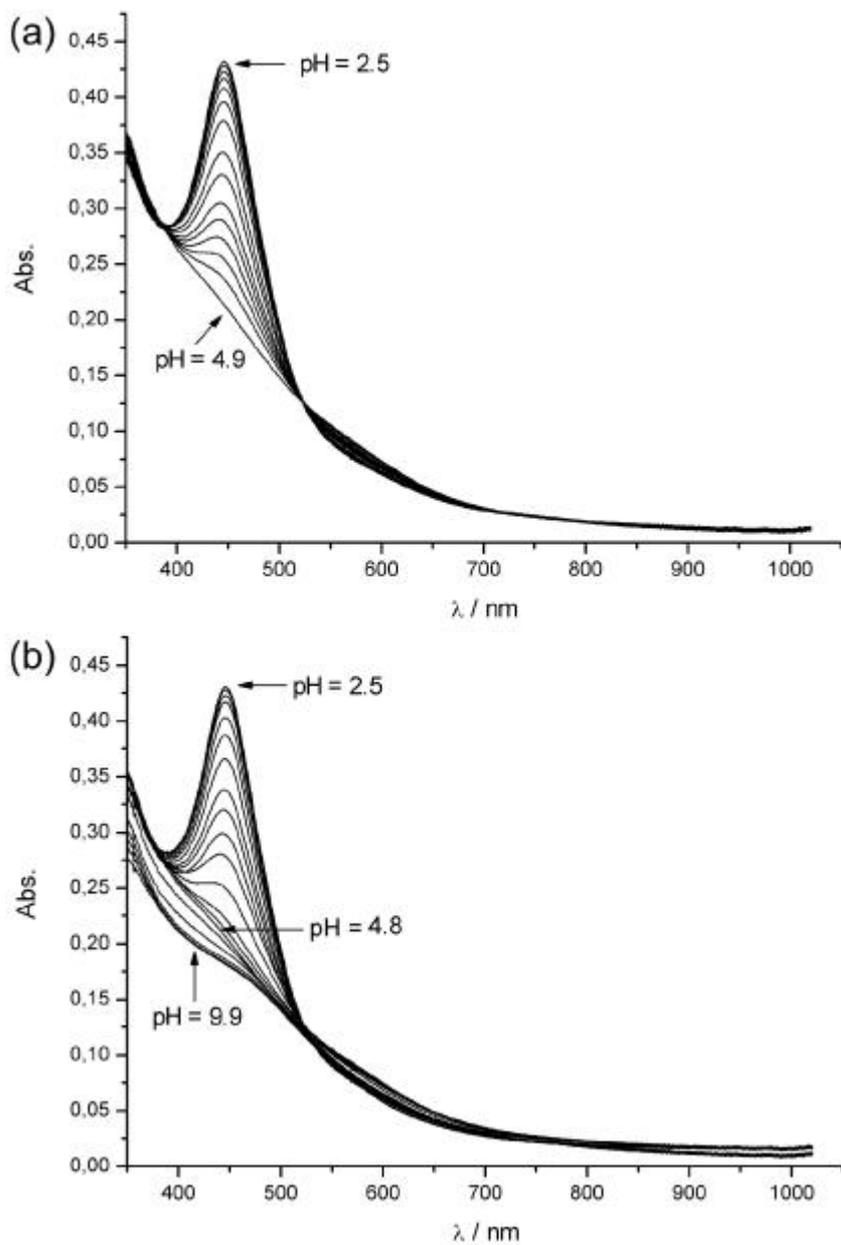


Figure S3. Dependence of the UV-vis spectrum of **1** (0.015 mM solution) with pH. (a) pH decrease from 4.9 (natural pH) to 2.5 (by drop-wise addition of 0.1 M HCl) followed by (b) immediate increase to pH to 9.9 (by drop-wise addition of 0.1 M NaOH).

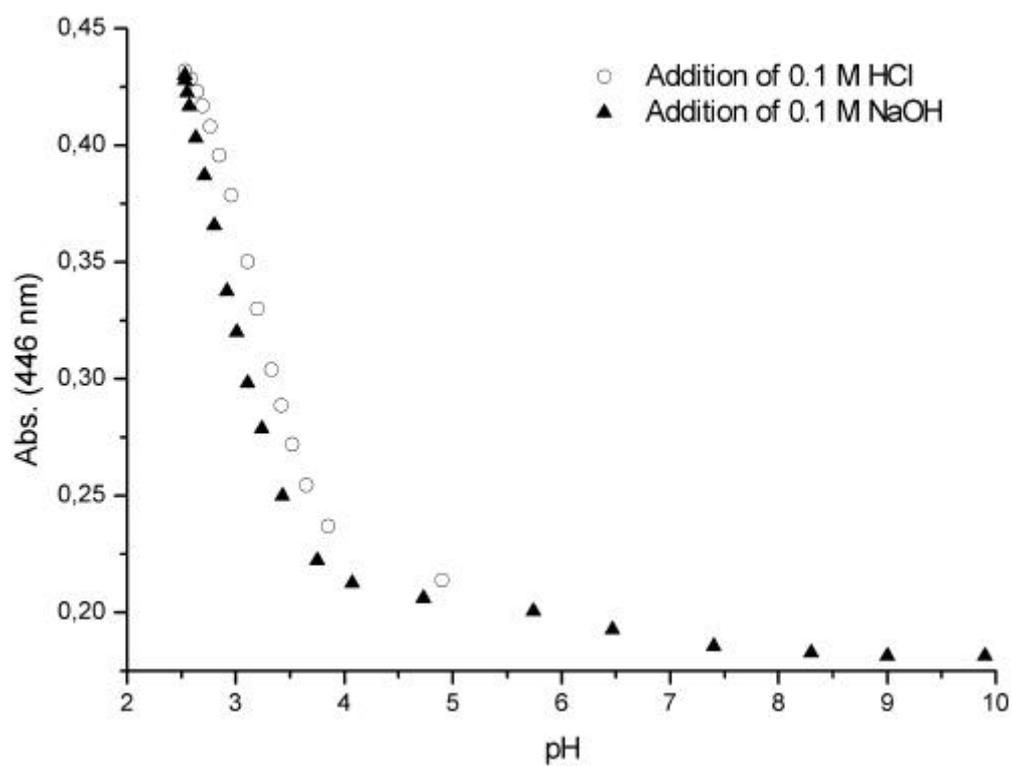


Figure S4. Plot of the UV-vis absorbance (determined at $\lambda_{\text{max}} = 445$) of a 0.15 mM solution of **1** vs. pH: pH decrease from 4.9 (natural pH) to 2.5 (o) followed by immediate increase to 9.9 (σ).

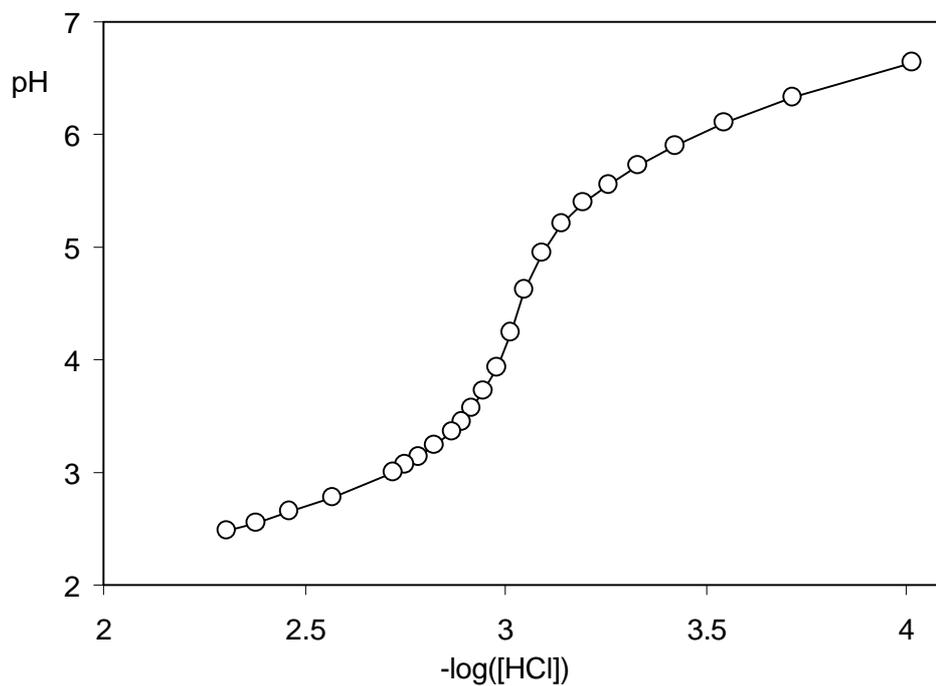


Figure S5. Titration of 2.8 μmol (18.7 mg) of **1** with 0.1 M HCl. Initial volume 4.5 mL, initial pH 4.2 then raised to pH 7.5 by addition of 0.1 M NaOH.

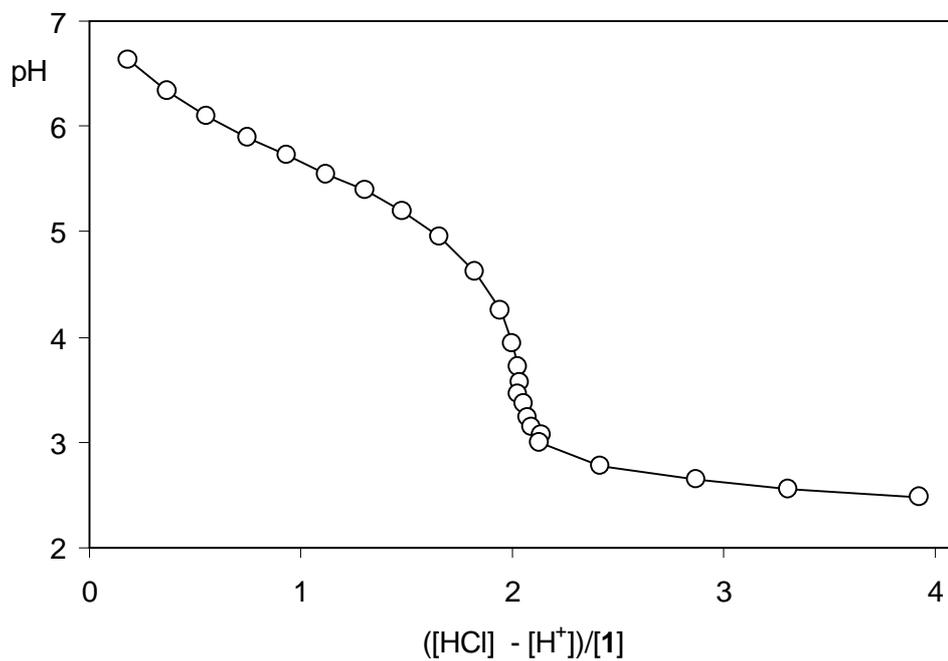


Figure S6. Titration of 2.8 μmol (18.7 mg) of **1** with 0.1 M HCl. The observed pH is plotted versus $([\text{HCl}] - [\text{H}^+])/[\mathbf{1}]$, where $[\text{HCl}]$ is the concentration of HCl in the solution, $[\text{H}^+]$ is the concentration of protons calculated as $[\text{H}^+] = 10^{-\text{pH}}$. Initial volume 4.5 mL, initial pH 4.2 then raised to pH 7.5 by addition of 0.1 M NaOH.

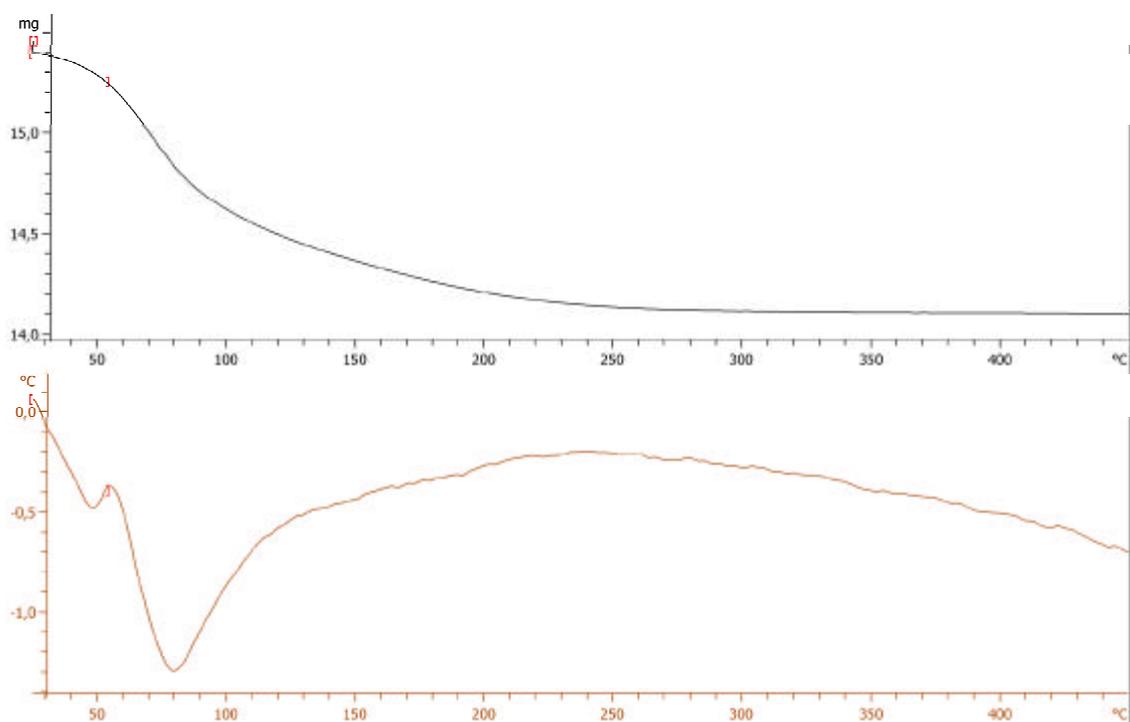


Figure S7. Thermogravimetric analysis (TGA) (top) and differential thermal analysis (DTA) data (bottom) of **1**. The endothermic peak at approx. 80 °C is due to loss of water molecules of crystallization.



RUN # 283

RT	AREA	TYPE	AR/HT	AREA%
0.43	4986	BP	0.091	5.055
0.75	82574	PB	0.099	83.789
1.30	11884	BP	0.136	11.236

TOTAL AREA= 98644
 MUL FACTOR= 1.0000E+00

Figure S8. Typical GC traces of a head space in the reaction of water oxidation with $\text{Ru}(\text{bpy})_3^{2+}$ catalyzed by **1** (equation 1 in the text). HP5890A model gas chromatograph, thermal conductivity detector, packed GC column (1.5 m x 3 mm, 5Å molecular sieves), carrier gas Ar (30 mL/s), 70 °C. The small peak with a retention time 0.43 min is not identified; it is also present in control experiments and in O_2 calibrations. When 0.5% air in Ar is injected, the ratio of O_2 and N_2 peak areas is ~ 0.5.

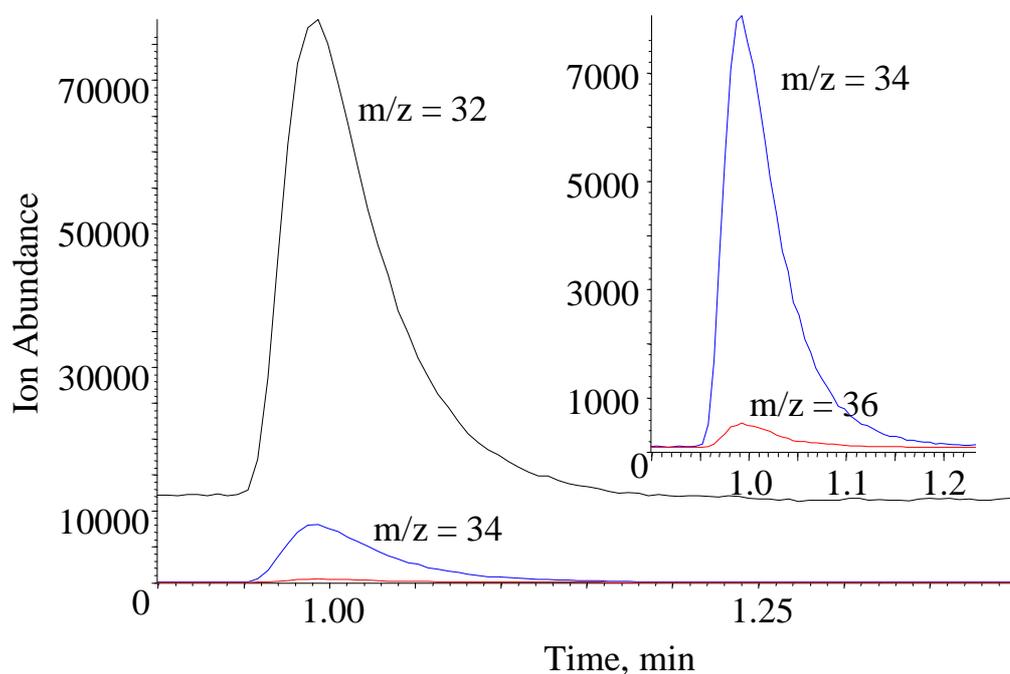


Figure S9. Extracted ion chromatograms of the individually counted ions of a given m/z value (32, 34 or 36 corresponding to $^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{18}\text{O}$ respectively). Both the degree of enrichment and the ratio, $m/z = 34 / m/z = 36$ are consistent with incorporation of ^{18}O into O_2 from H_2O . Experimental conditions : 1.2 mM $\text{Ru}(\text{bpy})_3^{3+}$, 10 μM of **1**, 18 mM phosphate buffer, pH 6.9, room temperature, 10% H_2^{18}O .

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