Supporting Information for:

Oxygenic Polyoxometalates: a New Class of Molecular Propellers

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Materials and Methods.

Thermogravimetric Analysis (TGA): Thermogravimetric analyses were performed on a TGA Q500 (TA Instruments) and recorded under N_2 or under air, upon equilibration at 100 °C, followed by a ramp of 10 °C/min up to 1000 °C.

Resonance Raman (rRaman): Micro-Raman spectra were recorded with a inVia Reflex Renishaw spectrometer equipped with three lasers (532, 632.8 and 785 nm). The laser beam was focused on an area of about $2x2 \ \mu m$ and with power lower than 1 mW.

Analysis of O_2 content: An Ocean Optics oxygen sensor system (FOXY R-AF) was used for the quantitative detection of O_2 . The experiments were performed in a custom built reactor, closed with a special cap in which the sensor is inserted. The calibration was performed using a temperature sensor.

UV-Vis: UV-Vis spectra were recorded using a Perkin-Elmer Lambda 45 spectrophotometer.

Syntheses of transition metal substituted polyoxometalates.

The synthesis of the polyoxometalates used in this work was performed as described in the literature. In particular:

Ru₄(**SiW**₁₀)₂: A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. Mc Daniel, S. Bernhard and M. Bonchio, *J. Am. Chem. Soc.*, 2008, **130**, 5006.

Cu₄(PW₉)₂: R. G. Finke, M. W. Droege and P. J. Domaille, *Inorg. Chem.*, 1987, 26, 3886.

Co₄(PW₉)₂: T. J. R. Weakley, H. T. Evans, J. S. Showell, G. F. Tourné and C. M. Tourné, *J. Chem. Soc., Chem. Commun.*, 1973, 139; R. G. Finke, M. W. Droege and P. J. Domaille, *Inorg. Chem.*, 1987, 26, 3886.

Ni₄(PW₉)₂, J. M. Clemente-Juan, E. Coronado, J. R. Galán-Mascarós and C. J. Gómez-García, *Inorg. Chem.*, 1999, **38**, 55.

Mn₄(PW₉)₂: C. J. Gómez-García, E. Coronado, P. Gómez-Romero and N. Casañ-Pastor, *Inorg. Chem.*, 1993, **32**, 3378.

Fe₄(PW₉)₂: X. Zhang, Q. Chen, D. C. Duncan, R. J. Lachicotte, and C. L. Hill, *Inorg. Chem.*, 1997, 36, 4381.

The identity of the complexes was confirmed by infrared spectroscopy by comparison with literature data.



Figure S1. Structure of $[M_4(\mu-O)_4(H_2O)_2(PW_9O_{34})_2]^n$; Blue atoms: W; yellow atoms: Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}; orange atoms: P; red atoms: O.

General procedure for catalytic hydrogen peroxide dismutation.

Catalytic hydrogen peroxide dismutation to H_2O and O_2 was performed in a custom built reaction vessel with a total volume of 24 mL. The home-made reactor was designed by the Technical Staff at the Department of Chemical Sciences at the University of Padova. We thank Roberto Inilli an Mauro Meneghetti for technical assistance. The vessel was filled with the appropriate amount of the catalyst and 12 mL of sodium phosphate buffer (50 mM, pH = 7.0) while stirring, then closed with the cap, in which the O_2 sensor is inserted. After the equilibration of the system, the appropriate amount of H_2O_2 was added from a side tap, which was suddenly closed. O_2 evolution was detected by the sensor.

The dependence of oxygen evolution rate from the concentrations of H_2O_2 and $Ru_4(SiW_{10})_2$ is reported in Figures S2 and S3, respectively. The kinetic law for hydrogen peroxide decomposition was shown to be first order dependent on the concentration of $Ru_4(SiW_{10})_2$ and on the initial concentration of hydrogen peroxide. Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2011



Figure S2. (a) dependence of the rate of hydrogen peroxide decomposition on $[H_2O_2]$. Conditions: 12 ml of 50 mM phosphate buffer (pH = 7.0); $[H_2O_2] = 13-33$ mM; $[\mathbf{Ru}_4(\mathbf{SiW}_{10})_2] = 15 \ \mu\text{M}$; $T = 27^{\circ}\text{C}$. (b) dependence of log(rate) versus log($[H_2O_2]$).

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Figure S3. (a) dependence of the rate of hydrogen peroxide decomposition on $[\mathbf{Ru}_4(\mathbf{SiW}_{10})_2]$. Conditions: 12 ml of 50 mM phosphate buffer (pH = 7.0); $[H_2O_2] = 33$ mM; $[\mathbf{Ru}_4(\mathbf{SiW}_{10})_2] = 10.8-29.2 \ \mu\text{M}$; T = 27°C. (b) dependence of log(rate) versus log($[\mathbf{Ru}_4(\mathbf{SiW}_{10})_2]$).

Synthesis and characterization of Ru₄(SiW₁₀)₂@MWCNT were performed as described in F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parisse, C. Maccato, S. Rapino, B. Rodriguez Gonzalez, H. Amenitsch, T. Da Ros, L. Casalis, A. Goldoni, M. Marcaccio, G. Scorrano, G. Scoles, F. Paolucci, M. Prato and M. Bonchio, *Nature Chem.*, 2010, **2**, 826–831. The loading of the catalyst in the material was 60% w/w (TGA analyses).

Synthesis of Polyaniline (PANI).

A literature procedure, describing the preparation of PANI fibers has been followed (Q. Tang, J. Wu, X. Sun, Q. Li, J. Lin and M. Huang, *Chem. Commun.*, 2009, 2166).

The PANI was prepared by an aqueous solution polymerization method. Under air atmosphere and magnetic stirring, to a 25 mL of $4.9 \cdot 10^{-2}$ M aniline solution (ANI), 1.23 mL of a 1 M HCl solution were added, in order to obtain a molar ratio [ANI] : [HCl] = 1:1 in deionized water. The final solution was heated to 80°C in a oil-bath, and then 332.48 mg of potassium peroxydisulfate (KPS), as initiator, with a molar ratio [ANI] : [KPS] of 1:1 was quickly added to the ANI solution. After the system was kept at 80°C for 10 minutes, all the KPS was dissolved, and green PANI was formed, the system was immediately cooled to 0 ± 3 °C and left overnight without stirring. The product was carefully filtered off, washed five times with deionized water, and finally dried under vacuum for 24 h to obtain a dark-green solid.

Synthesis of Ru₄(SiW₁₀)₂@PANI.

A straightforward metathesis technique was adopted in aqueous media to anchor $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$ to positively charged PANI. 5 mg of solid PANI were mixed with 1 ml of a 1.6 mM aqueous solution of $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$. The mixture was sonicated for 15 minutes, stirred overnight and then the final material was recovered upon centrifugation, washed with water and finally dried under vacuum. The uptake of $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$ was checked by TGA measurement of the final material by comparison with the TGA of the PANI (blank) and it was found to be 20% w/w (cfr. Figures S4 and S5). It is worth noting that higher concentrations of the $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$ solutions produced similar loadings in the final material.



Figure S4. TGA of pristine **PANI**.



Figure S5. TGA of Ru₄(SiW₁₀)₂@PANI.

Poly(diallyldimethylammoniumchloride) PDDA.

PDDA with very low molecular weight $((C_8H_{16}ClN)_n CAS-26062-79-3, MW < 10^5)$ is commercially available in aqueous solution 35 % w/w (Sigma-Aldrich).

Synthesis of and Ru₄(SiW₁₀)₂@PDDA.

A straightforward metathesis technique was adopted in aqueous solution to anchor $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$ to the positively charged **PDDA**. 1 ml of an aqueous solution containing 10 mg of **PDDA** was mixed with 1 ml of a 3.2 mM aqueous solution of $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$. The black and sticky precipitate was sonicated for 15 minutes and stirred overnight. The product was recovered upon centrifugation, washed with water and finally dried under vacuum. Thermogravimetric analysis of $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$ @PDDA (Figure S7) indicated a 70% w/w catalyst loading in the hybrid material.



Figure S7. TGA of Ru₄(SiW₁₀)₂@PDDA.

The materials were also characterized by rRaman and ATR-IR and the resulted spectra were reported in Figure S8-S9.



Figure S8. rRaman spectra of $Ru_4(SiW_{10})_2$ (blue line), $Ru_4(SiW_{10})_2$ @PDDA (red line), $Ru_4(SiW_{10})_2$ @MWCNT (purple line) and $Ru_4(SiW_{10})_2$ @PANI (green line). Given the high absorbance of PANI, the typical peaks of $Ru_4(SiW_{10})_2$ are not well resolved in $Ru_4(SiW_{10})_2$ @PANI spectra (green line).



Figure S9: FT-IR/ATR spectra of PANI (black line), $Ru_4(SiW_{10})_2$ @PANI (green line) and $Ru_4(SiW_{10})_2$ (yellow line). The peaks at 967, 920 and 886 cm⁻¹ pertaining to the inorganic POM are retained in the $Ru_4(SiW_{10})_2$ @PANI material.

UV-vis experiments of the reaction mixtures after the catalysis by the hybrid materials were also performed in order to check for catalyst $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$ leaching from the different supports. The results are reported in Figure S10.



Figure S10. UV-vis spectra of reaction solutions after H_2O_2 dismutation (phosphate buffer 50 mM, pH=7.0). $Ru_4(SiW_{10})_2$ (blue line, entry 3 in table 1), $Ru_4(SiW_{10})_2@MWCNT$ (purple line, entry 13 in table 1 in the paper), $Ru_4(SiW_{10})_2@PANI$ (green line, entry 14 in table 1) and $Ru_4(SiW_{10})_2@PDDA$ (red line, entry 15 in table 1).



Figure S11. Transmission Electron Microscopy (TEM) images of (a) **PANI** and (b) $\mathbf{Ru}_4(\mathbf{SiW}_{10})_2$ @**PANI**. Bar scale = 200 nm.



(a) (b) Figure S12. Transmission Electron Microscopy (TEM) images of (a) **PDDA** and (b) **Ru**₄(SiW₁₀)₂@**PDDA**. Bar scale = 200 nm.

Notes on the hypothesis of H_2O_2 as an intermediate in the water oxidation cycle of $Ru_4(SiW_{10})_2$.

When the oxidant is $[Ru{(\mu-dpp)Ru(bpy)_2}_3](PF_6)_8$, (bpy = 2,2'-bipyridine; dpp = 2,3-bis(2'pyridyl)pyrazine), hereafter **PS**, the maximum concentration of H₂O₂ in solution is calculated from the Nernst equations, given the standard redox potentials of the equations:

 $\mathbf{PS}^+ + e \Rightarrow \mathbf{PS}, E = 1.79 + 0.0592 \cdot \log([\mathbf{PS}^+]/[\mathbf{PS}])$ Volt

 $H_2O_2 + 2 H^+ + 2 e^- \Leftrightarrow 2 H_2O, E = 1.78 + 0.0592/2 \cdot \log([H_2O_2][H^+]^2)$ Volt

Then, for the reaction:

 $2 \mathbf{PS}^+ + 2 \mathbf{H}_2 \mathbf{O} \Leftrightarrow 2 \mathbf{PS} + \mathbf{H}_2 \mathbf{O}_2 + 2 \mathbf{H}^+$

 $1.79 + 0.0592 \cdot \log([\mathbf{PS}^+]/[\mathbf{PS}]) = 1.78 + 0.0592/2 \cdot \log([\mathbf{H}_2\mathbf{O}_2][\mathbf{H}^+]^2)$

with a 0.1 mM starting concentration of PS^+ , at pH = 7, the equilibrium concentrations are:

 $[\mathbf{PS}] = 1 \cdot 10^{-4} \text{ M}$ $[\mathbf{PS}^+] = 4.79 \cdot 10^{-14} \text{ M}$ $[\mathrm{H}_2\mathrm{O}_2] = 5 \cdot 10^{-5} \text{ M}$

the maximum oxygen evolution rate from H₂O₂ decomposition would then be:

 $d[O_2]/dt = 0.5 \cdot k \cdot [Ru_4(SiW_{10})_2][H_2O_2] = 5.52 \cdot 10^{-8} Ms^{-1}$

with $[\mathbf{Ru}_4(\mathbf{SiW}_{10})_2] = 6 \cdot 10^{-5} \text{ M}, [H_2O_2] = 5 \cdot 10^{-5} \text{ M} \text{ and } \text{k} = 36.8 \text{ M}^{-1} \text{s}^{-1}$

and then the turnover frequency (TOF):

TOF = $(d[O_2]/dt) / [Ru_4(SiW_{10})_2] = 0.00092 \text{ s}^{-1}$

One order of magnitude less than the experimental value of 0.008 s⁻¹ (see reference 8 in the manuscript)

Analogous consideration when the oxidant is $Ru(bpy)_3^{3+}$

$$\text{Ru}(\text{bpy})_3^{3+} + \text{e-} \Leftrightarrow \text{Ru}(\text{bpy})_3^{2+}, E = 1.26 + 0.0592 \cdot \log([\text{Ru}(\text{bpy})_3^{3+}]/[\text{Ru}(\text{bpy})_3^{2+}]) \text{ Volt}$$

Then, for the reaction:

$$2 \operatorname{Ru}(\operatorname{bpy})_{3}^{3^{+}} + 2 \operatorname{H}_{2}O \Leftrightarrow 2 \operatorname{Ru}(\operatorname{bpy})_{3}^{2^{+}} + \operatorname{H}_{2}O_{2} + 2 \operatorname{H}^{+}$$

$$1.26 + 0.0592 \cdot \log([Ru(bpy)_3^{3+}]/[Ru(bpy)_3^{2+}]) = 1.78 + 0.0592/2 \cdot \log([H_2O_2][H^+]^2)$$

with a starting concentration of 0.1 mM $Ru(bpy)_3^{3+}$, at pH = 7, the equilibrium concentrations are:

 $[Ru(bpy)_3^{2+}] = 5.08 \cdot 10^{-4} M$ $[Ru(bpy)_3^{3+}] = 4.92 \cdot 10^{-4} M$ $[H_2O_2] = 2.54 \cdot 10^{-4} M$

the maximum oxygen evolution rate from H₂O₂ decomposition would then be:

 $d[O_2]/dt = 0.5 \cdot k \cdot [Ru_4(SiW_{10})_2] \cdot [H_2O_2] = 2.34 \cdot 10^{-8} Ms^{-1}$

with $[\mathbf{Ru}_4(\mathbf{SiW}_{10})_2] = 5 \cdot 10^{-6} \text{ M}, [H_2O_2] = 2.54 \cdot 10^{-4} \text{ M} \text{ and } \text{k} = 36.8 \text{ M}^{-1} \text{s}^{-1}$

and then the TOF:

TOF = $(d[O_2]/dt) / [Ru_4(SiW_{10})_2] = 0.00468 \text{ s}^{-1}$

Two orders of magnitude lower than the experimental value of 0.44 s^{-1} (see reference 3a in the manuscript).