Supporting Information for:

Is $[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]^{10-}$ a Genuine Molecular Catalyst in Photochemical Water Oxidation? Answers from Time-Resolved Hole Scavenging Experiments

Mirco Natali,[a] Serena Berardi,[b] Andrea Sartorel,*[b] Marcella Bonchio,[b] Sebastiano Campagna[c] and Franco Scandola*[a]

Materials and Methods.

Laser flash photolysis: Nanosecond transient absorption measurements were performed with an Applied Photophysics laser flash photolysis apparatus, using a frequency-tripled (355 nm, 160 mJ) Surelite Continuum II Nd/YAG laser (half-width 6-8 ns) as excitation source. Transient detection was obtained using a photomultiplier-oscilloscope combination (Hamamatsu R928, LeCroy 9360). Kinetics of bleach recovery were collected in the following experimental conditions: Excitation wavelength = 355 nm; analysis wavelength = 450 nm; $[Ru(bpy)_3]^{2+}$ = $5.0\cdot10^{-5}$ M; $[Na_2S_2O_8]$ = $5.0\cdot10^{-3}$ M; [**1**] = $5.0\cdot10^{-5}$ M in 80 mM phosphate or borate buffers, pH 8. **1** was directly introduced as a solid in order to measure the scavenging of the freshly dissolved sample (< 1 min), while for the aged samples (5-1400 min) it was added into the cuvette by diluting a 10^{-3} M mother solution, prepared in the same buffer of the flash photolysis experiment.

Electrochemistry: Cyclic voltammetry experiments were performed using a BAS EC-epsilon potentiostat. A standard three-electrode electrochemical cell was used. Potentials were referred to an Ag/AgCl/3 M NaCl, reference electrode. Glassy carbon electrode (3 mm diameter, geometric surface area = 7 mm^2) from BAS and a Pt wire were used respectively as working and auxiliary electrode. When time-dependent scans were recorded, the working electrode was accurately polished after every scan.

FT-IR: FT-IR spectra were recorded on a Nicolet 5700 FT-IR instrument.

UV-Vis: UV-Vis kinetic experiments were collected using a Varian Cary-100 Scan spectrophotometer.

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

Synthesis of $[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]^{10-}$ (**1**): the synthesis of **1** was performed according to literature procedure (Hill, et al. *Science*, 2010, **328**, 342). 35.6 g of $Na_2WO_4{\cdot}2H_2O$ (108 mmol), 3.22 g of $Na_2HPO_4{\cdot}7H_2O$ (12 mmol) and 6.98 g of $Co(NO_3)_2{\cdot}6H_2O$ (24 mmol) were added to 100 ml of water. The pH was adjusted to 7.8, with the solution still being turbid, and then refluxed for two hours. After reflux, NaCl was added to achieve 3 M concentration. Crystals were collected after few hours. IR and UV-vis characterization are reported below (figures S1 and S2 respectively). Thermogravimetric analysis (figure S3) evidences 24 water molecules of hydration.

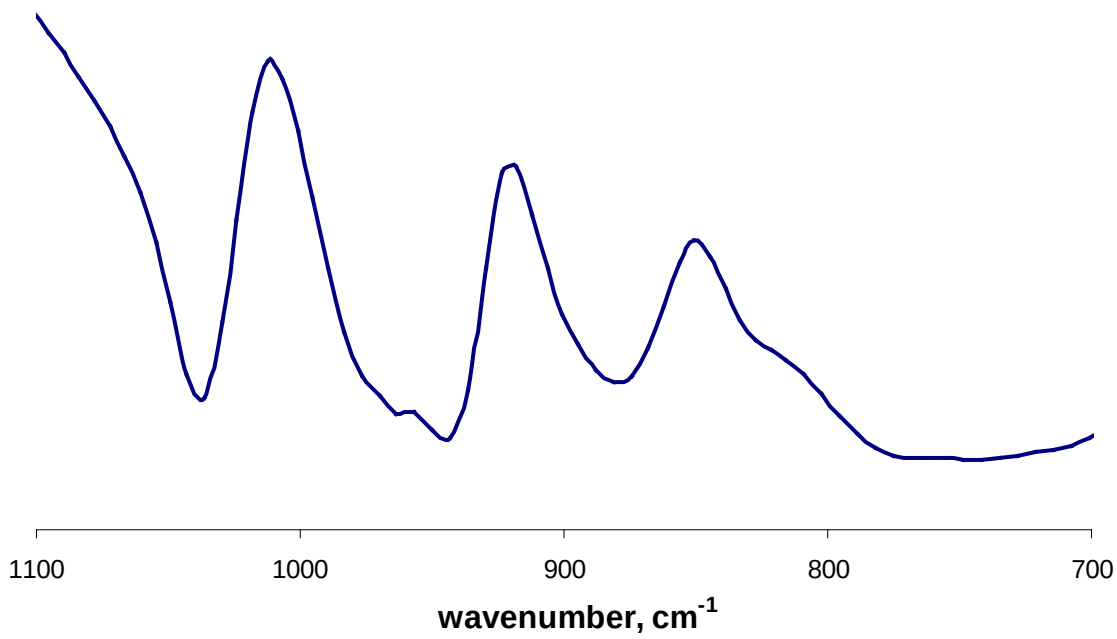

Figure S1. Infrared spectra of crystals of **1** (2% in KBr pellet).

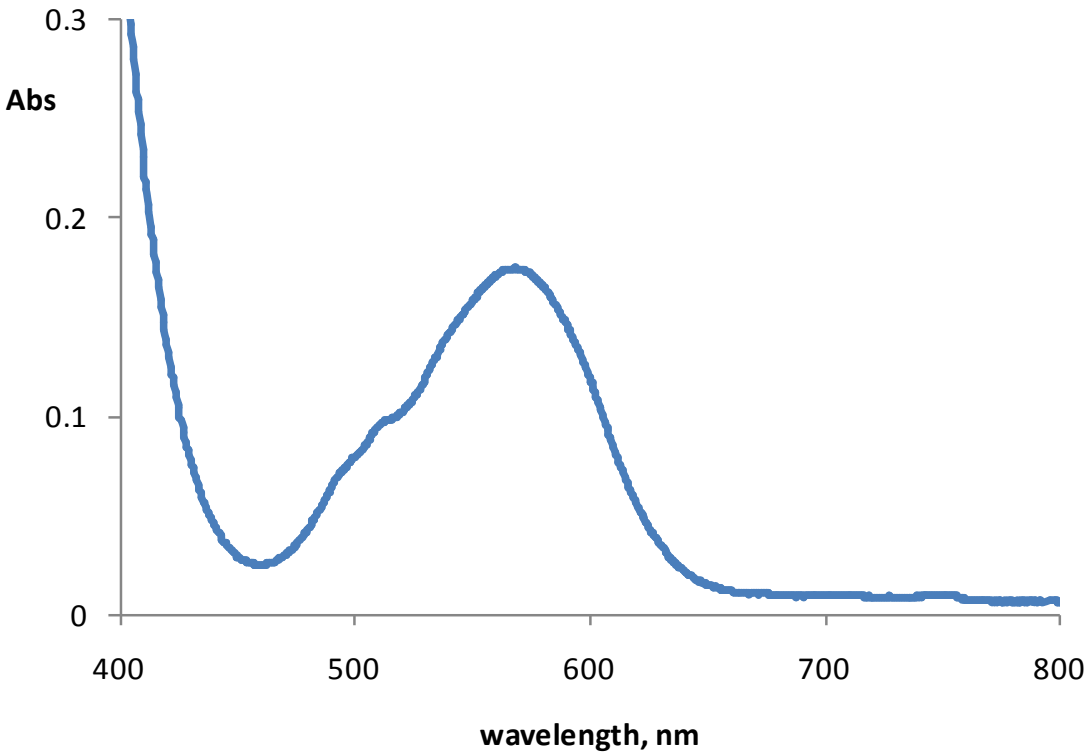

Figure S2. UV-vis spectra of a freshly prepared 1 mM solution of **1** in water.

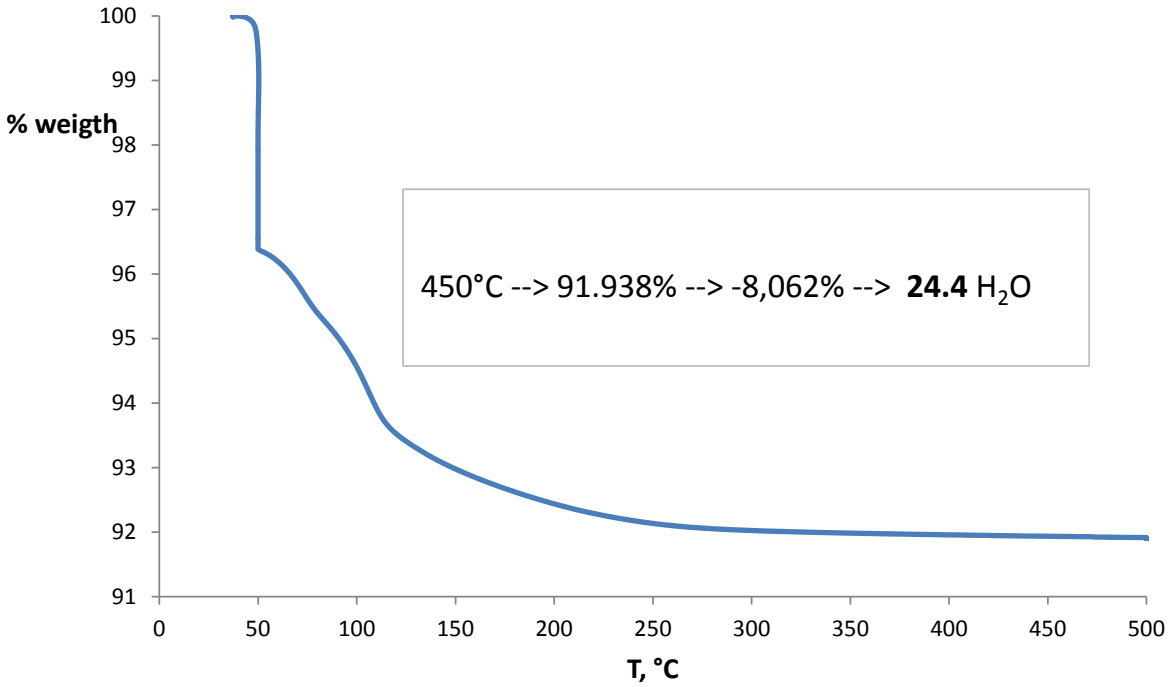

Figure S3. TGA analysis of crystals of **1**. The decrease of weight is due to loss of 24 hydration water molecules per molecule of **1**.

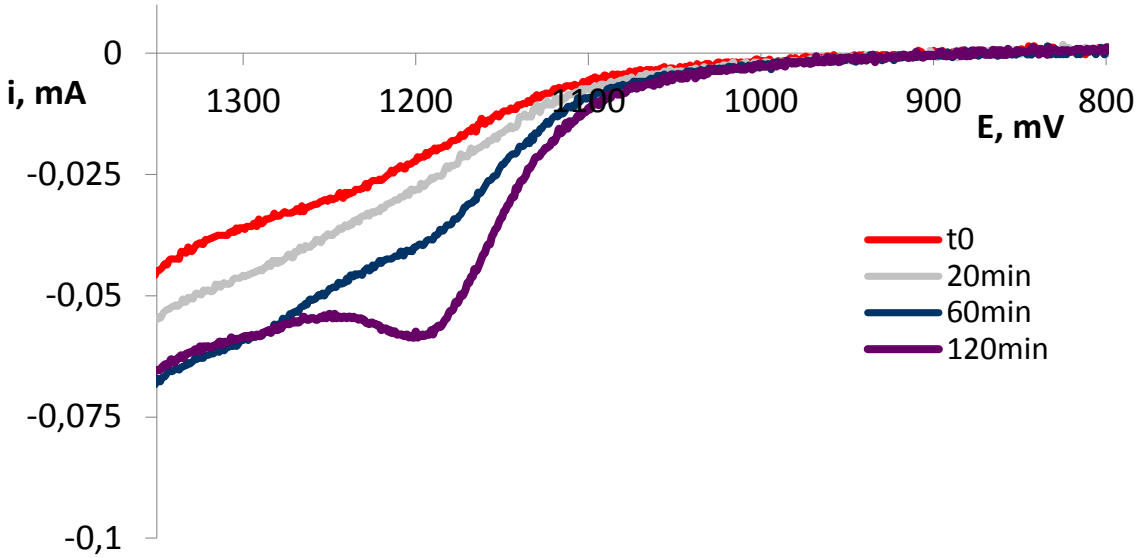

Figure S4. Time dependent CV scans of 2 mM **1** in 0.2 M borate buffer (pH 8).

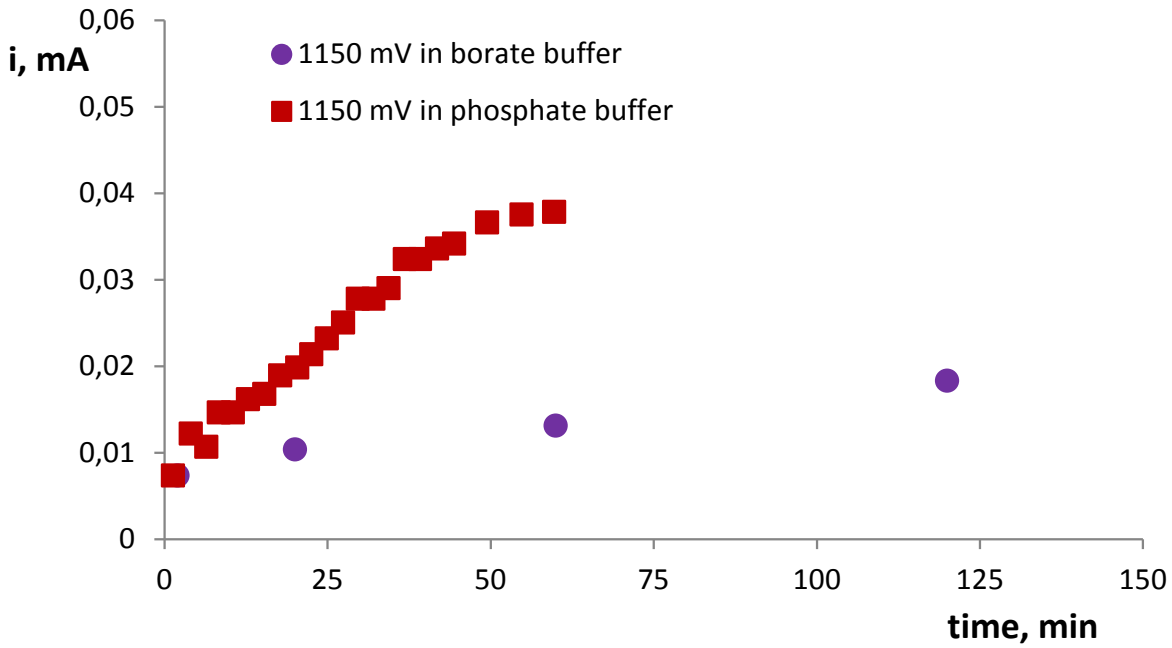

Figure S5. Plot of the anodic current at 1150 mV vs time observed in the CV of 2 mM **1** in 0.2 M phosphate (red squares) and borate (violet dots) buffers (pH 8).

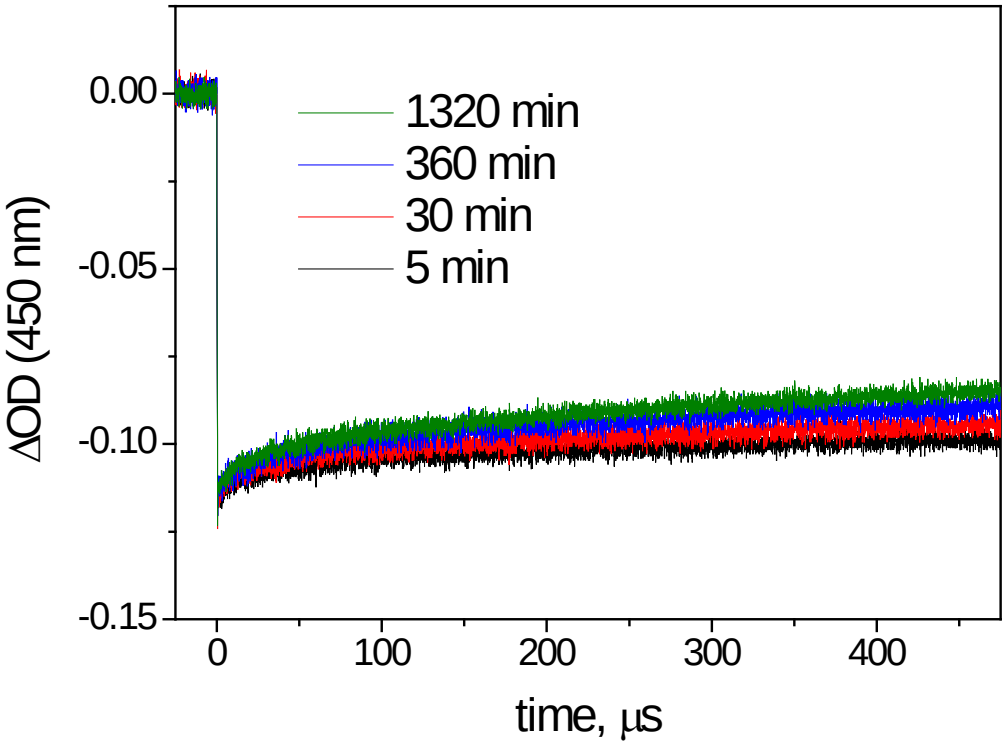

Figure S6. Hole scavenging kinetics measured using 5.0 x 10^{-5} M solutions of **1** of various aging time in 80 mM borate buffer (pH 8). Aging takes place in a 10^{-3} M mother solution of **1** in 80 mM borate buffer (pH 8).

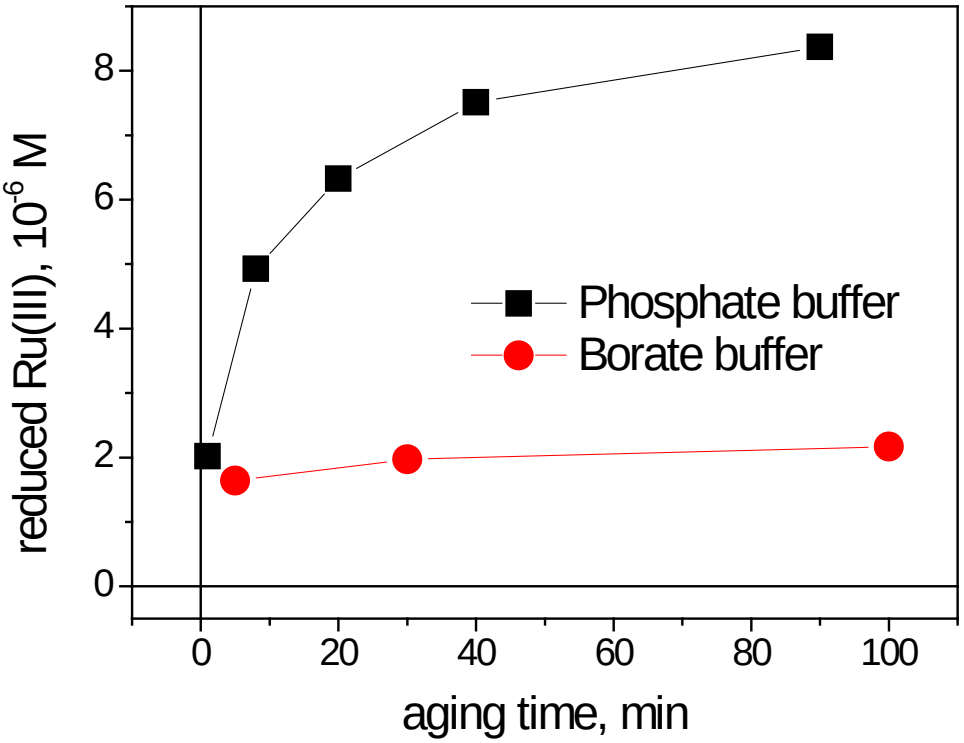

Figure S7. Amount of $Ru(bpy)_3^{3+}$ being reduced by 5.0 x 10^{-5} M **1** in laser flash photolysis (450 μs time window), as a function of the aging time of the solution used in 80 mM phosphate (black squares) and 80 mM borate (red dots) buffers (pH 8). The value of reduced Ru(III) corresponding to 100 min aging in borate buffer is obtained from kinetic traces not shown for clarity in Figure S6.