Supporting Information

Photochemical water oxidation with visible light using a cobalt containing catalyst

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Detailed Methods

General

The ligand M2P was prepared from the tetraisoprolyl ester of methylenediphosphonic acid (Aldrich) by a literature procedure.[1] M2P forms a complex with cobalt(II) (K = 12.03).[2] The ligand has been used in a 1.4 times excess to ascertain that the amount of cobalt(II) that is not bound to M2P (for example as $Co_3(PO_4)_2$) is kept at a very low level. Using known stability constant and the following parameters: $[Co^{2+}]$ = 20 μM, [M2P] = 28 μM, $[PO_4^{3-}]$ = 50 mM, pH 7, it was calculated that ~99.3% of the cobalt is present as CoM2P, ~0.7% as $Co(M2P)_2$ and <0.001% as $Co_3(PO_4)_2$ (Fig. S1). $[Ru^{III}(bpy)_3](ClO_4)_3$ was prepared according to literature,[3] $[Ru^{II}(bpy)_3](ClO_4)_2$ was prepared by anion exchange form $[Ru^{II}(bpy)_3]Cl_2$ (Aldrich) and recrystallized from $MeCN/Et_2O$. $Co(ClO_4)_2\cdot 6H_2O$ (Aldrich) and $Na_2S_2O_8$ (Aldrich) were bought and used as received. The program Hyperquad Simulation and Speciation from Protonic Software was used to calculations the distribution of Co species in the presence of M2P.

Oxygen evolution measurements

The oxygen evolution was followed using a standard Clark-type oxygraph electrode (Hansatech Instruments), separated from the sample solution by a Teflon membrane. The signal was recorded for the entire duration of the experiment at 0.1 sec intervals using the Oxygraph+ software (Hansatech Instruments). The maximum turnover frequency (TOF_{max}) was determined at the steepest slope of the oxygen evolution curve. The signal was calibrated using air saturated aqueous solutions ($[O_2]$ = 276 μM, T = 20 °C).[4] In a standard procedure, the desired amount of catalyst ($Co(ClO_4)_2$ + M2P) was mixed and added to a buffer solution at pH 7. To this solution $Ru^{II}(bpy)_3(ClO_4)_2$ and $Na_2S_2O_8$ dissolved in water was added in the dark and the reaction mixture (1 mL) was transferred to the Clark cell and de-aerated using Argon. When sufficiently low O_2 concentrations were reached (~10 μM O_2) the Argon was removed and the cell was closed. The cell was left in the dark for about 15 s to ensure that the oxygen level was constant where after the light was turned on.

The chemical oxidation was done by mixing the catalyst ($Co(ClO_4)_2$ + M2P) in a buffered solution at pH 7 that was transferred to the Clark cell and de-aerated. 350 μL of a concentrated aqueous solution of de-aerated $Ru^{III}(bpy)_3(ClO_4)_3$ was added.

Light scattering.

The light source for the scattering experiments was a Uniphase He-Ne laser emitting vertically polarized light at a wavelength of 632.8 nm and operating at 25 mW. Data was collected at 25 °C with the scattering angle set to 90 degrees, using a Perkin Elmer diode detector (Perkin Elmer, Quebec, Canada) and connected to an ALV5000 multiple digital autocorrelator (ALV-Laser Vertriebgesellschaft mbH, Germany). The data was acquired and evaluated using the ALV Correlator software v3.0.

Electrochemistry.

Cyclic voltammetry and differential pulse voltammetry were carried out using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}. Differential pulse voltammetry was performed with a scan rate of 20 mV s^{-1}, a pulse height of 75 mV and duration of 40 ms. The electrolyte was 50 mM potassium phosphate at pH 7.0. The working electrode was a glassy carbon disc (diameter 3 mm). The surface of the electrode was routinely polished with an alumina(0.05 mm)-water slurry on a felt surface, immediately prior to use. A glassy carbon rod served as counter electrode and as reference electrode an Ag/AgCl electrode with a potential of 0.197 V vs. the NHE was used. The counter and reference electrodes were in compartments separated from the bulk solution by fritted disks.

Isolation of a solid Co/M2P material.

$Co(ClO_4)_2 \cdot 6H_2O$ (183 mg, 0.5 mmol), H_4M2P (88 mg, 0.5 mmol) and $[Ru(bpy)_3](ClO_4)_2$ (100 mg, 0.13 mmol) were dissolved in 150 ml of water. The pH was adjusted to 7.0 by addition of a KOH solution (0.1 M). After that, $Na_2S_2O_8$ (476 mg, 2.0 mmol) in 10 ml of deionized water was added and the solution was illuminated using a 500 Watt tungsten lamp. The pH was kept in the 6.9-7.1 range by continuous injection of a KOH solution (0.1 M). The illumination was stopped when pH ceased to decrease which took approximately 20 min (~40 ml of KOH solution). After the illumination 200 ml of acetone was added and the resulted suspension was centrifuged for 5 min at 5000 rpm. The supernatant was discharged and pellets were ultrasonicated with 50 ml of acetone. Centrifugation of the acetone suspension gave a dark-green material that was dried on air yielding 90 mg of material. Elemental analysis: C, 2.57%; Co, 27.22%; H, 2. 94%; P, 12.84% corresponding the approximate composition (of these four elements) $C_xH_{14x}P_{2.0x}Co_{2.2x}$ and to a Co/M2P ratio of 2.2/1.

The photosensitizer/electron acceptor system.

The light-induced reaction starts with that $Ru(bpy)_3^{2+}$ is excited by the light to form $Ru(bpy)_3^{2+*}$ (eq. S1) which sends an electron to $S_2O_8^{2-}$ and gives $Ru(bpy)_3^{3+}$, SO_4^{2-} and $SO_4^{\cdot-}$ (eq. S2).

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \qquad \text{(S1)}$$

$$Ru(bpy)_3^{2+*} + S_2O_8^{2-} \longrightarrow Ru(bpy)_3^{3+} + SO_4^{2-} + SO_4^{\cdot-} \qquad \text{(S2)}$$

The oxidized $Ru(bpy)_3^{3+}$ can now oxidize the Co/M2P catalyst one step and returns to $Ru(bpy)_3^{2+}$ (eq. S3).

$$Ru(bpy)_3^{3+} + Co/M2P^{n} \longrightarrow Ru(bpy)_3^{2+} + Co/M2P^{n+1} \qquad \text{(S3)}$$

The sulfate radical formed in eq. S2 is strongly oxidizing and will oxidize $Ru(bpy)_3^{2+}$ (eq. S4). If the $Ru(bpy)_3^{2+}$ is present in a higher concentration than any cobalt containing species this will be the most likely reaction.

$$Ru(bpy)_3^{2+} + SO_4^{\cdot-} \longrightarrow Ru(bpy)_3^{3+} + SO_4^{2-} \qquad \text{(S4)}$$

The $Ru(bpy)_3^{3+}$ formed in eq. S4 will react according to eq. S3 to give the $Ru(bpy)_3^{2+}$ and oxidized catalyst.

In this manner each persulfate molecule will accept two electrons and allow for two oxidation steps on the catalyst.

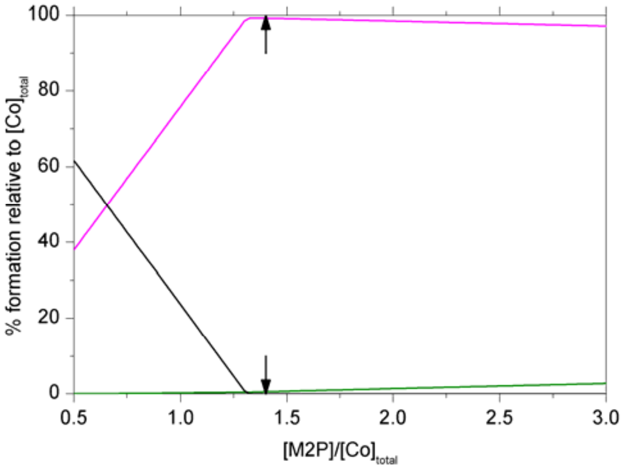

Fig. S1. Distribution of cobalt species as a function of $[M2P]/[Co]_{total}$. $Co(M2P)^{2-}$ (pink), $\{Co(M2P)_2\}^{6-}$ (green) and $Co_3(PO_4)_2$ (black). The arrows indicate a $[M2P]/[Co]_{total}$ ratio of 1.4, this condition was used in all the experiments described unless otherwise stated. Parameters used for the calculation: $[Co]_{total} = 20$ µM, $[M2P] = 10$-60 µM, $[PO_4^{3-}]_{total} = 50$ mM, pH 7.0.[2]

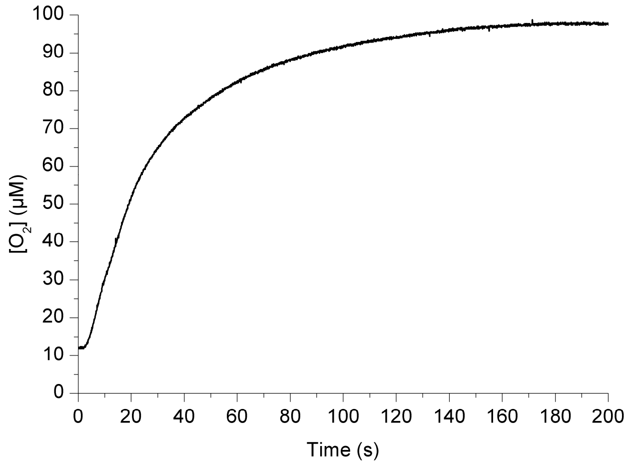

Fig. S2. Chemical oxidation of water in phosphate buffer with Co/M2P (10 µM Co^{2+}, 14 µM M2P, 2000 µM Ru(bpy)$_3^{3+}$, 20 mM phosphate buffer, pH 7.0). The [Ru(bpy)$_3$]$^{3+}$ was added at t = 0. Due to the large volume of [Ru(bpy)$_3$]$^{3+}$ added (200 µl) addition took ~1.5 s, explaining the initial slow rise of the O$_2$ evolution. The oxygen evolution started directly after the addition.

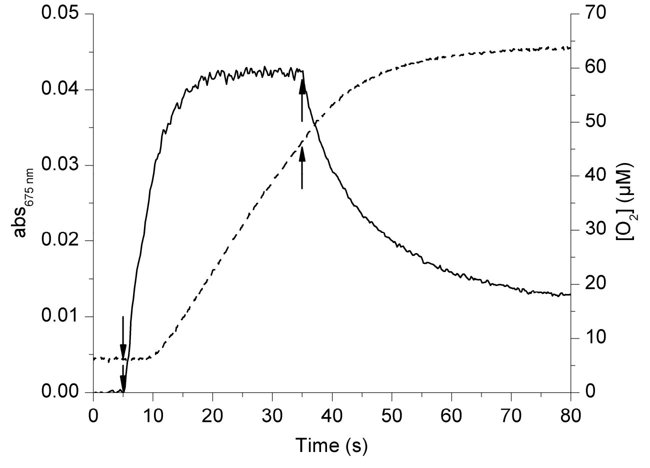

Fig S3. Following photochemical Ru(bpy)$_3^{3+}$ formation (full line) and oxygen evolution (dashed line) with the Co/M2P system. An argon-flushed mixture containing Co^{2+} (20 µM), M2P (28 µM), Ru(bpy)$_3^{2+}$ (100 µM), and $S_2O_8^{2-}$ (2 mM) in phosphate buffer (50 mM, pH 7) was kept in the dark in a UV-vis cell or Clark cell. Visible light illumination (LEDs, λ = 470±10 nm, ~280 µE) was applied at the down arrows and stopped at the up arrows. The Clark cell was thermostated at 20 °C.

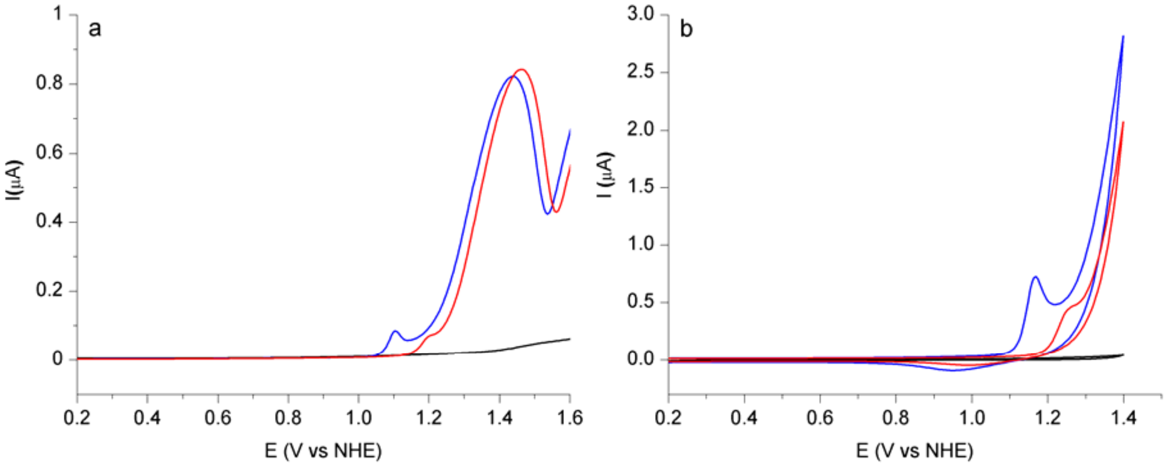

Fig. S4. a) Differential pulse and b) cyclic voltammagrams of pure 50 mM KH_2PO_4/K_2HPO_4 electrolyte at pH 7.0 (black), electrolyte containing 1 mM Co^{2+} (blue) and electrolyte containing 1 mM Co^{2+} and 1.4 mM M2P (red). The potential was measured against a Ag/AgCl reference electrode and converted to NHE potentials by using E(NHE) = E(Ag/AgCl) + 0.197 V.

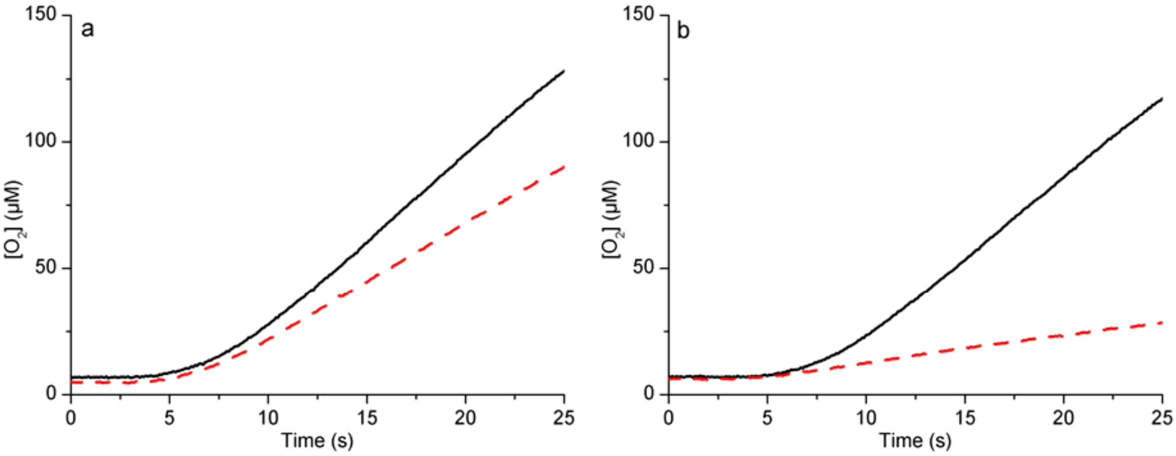

Fig. S5. Light oxidation in phosphate buffer with a) Co/M2P (100 μM Co^{2+}, 140 μM M2P, 250 μM $Ru(bpy)_3^{2+}$ 4 mM $S_2O_8^{2-}$, 50 mM phosphate buffer, pH 7) and b) Co^{2+} alone (100 μM Co^{2+}, 250 μM $Ru(bpy)_3^{2+}$ 4 mM $S_2O_8^{2-}$, 50 mM phosphate buffer, pH 7.0). The samples were illuminated for 20 s (solid black line, light applied at t = 0 s) after which the light was turned off. When the oxygen evolution had stopped the solution was centrifuged (14000 rpm, 15 min) and the supernatant returned to the cell and a second illumination started (dashed red line). The results are reported in Table 1, runs **8** (a) and **9** (b).

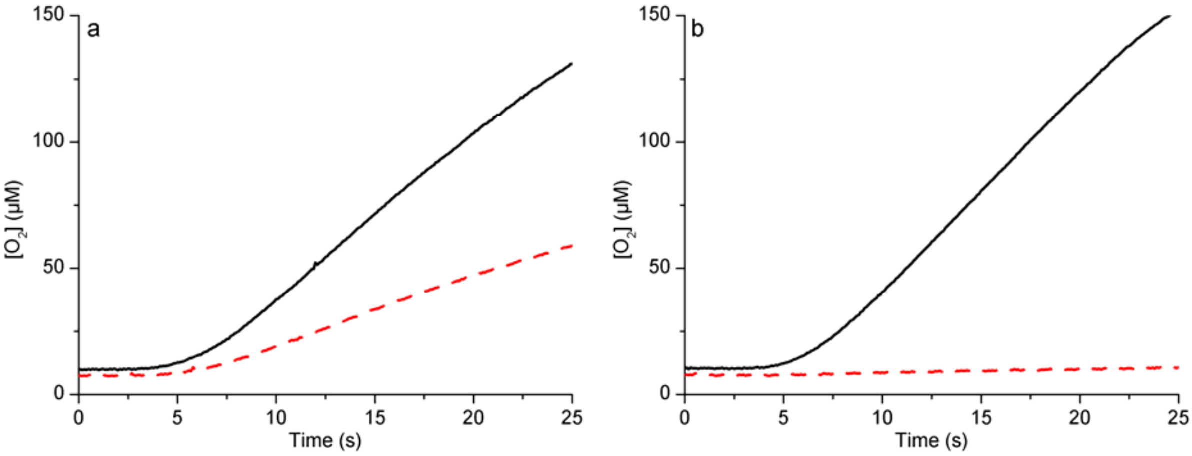

Fig. S6. Light oxidation in cacodylate buffer with a) Co/M2P (100 µM Co^{2+}, 140 µM M2P, 250 µM $Ru(bpy)_3^{2+}$ 4 mM $S_2O_8^{2-}$, 5 mM cacodylate buffer, pH 7) and b) Co^{2+} alone (100 µM Co^{2+}, 250 µM $Ru(bpy)_3^{2+}$ 4 mM $S_2O_8^{2-}$, 5 mM cacodylate buffer, pH 7.0). The samples were illuminated for 20 s (solid black line, Table S2, run **S4** and **S5** for a) and b) respectively, light applied at t = 0 s) after which the light was turned off. When the oxygen evolution had stopped the solution was centrifuged and the supernatant returned to the cell and a second light cycle started (dashed red line, Table S2, run **S6** and **S7** for a) and b) respectively).

Table S1. Maximum turnover frequencies (TOF_{max}) of oxygen evolution for the Co/M2P catalyst in different buffers at pH 7.0.

Conditions[a]			TOF_{max} (s^{-1})	TON
Run	[M2P] (μM)	Buffer		
2	14	Phosphate, 20 mM	0.26±0.01	20
S1	14	Cacodylate, 10 mM[b]	0.24±0.01	13
S2	14	No buffer	0	0
S3	1000	K_3HM2P/K_2H_2M2P, 1 mM	0.09±0.01	2

[a] Using visible light (λ = 470±10 nm), [Co^{2+}] = 20 μM, [$Ru(bpy)_3^{2+}$] = 100 μM, [$S_2O_8^{2-}$] = 2 mM for all experiments. [b] $NaAsO_2(CH_3)_2/HNO_3$.

Table S2. Maximum turnover frequencies (TOF_{max}) of oxygen evolution in cacodylate buffered systems.

Run	[M2P] (μM)	TOF_{max} (s^{-1})
S4	140	0.08±0.01[a]
S5	0	0.08±0.01[a]
S6	140	0.03±0.01[b]
S7	0	0.002±0.001[b]

Performed in a $NaAsO_2(CH_3)_2/HNO_3$ buffer, 5 mM, pH 7.0 using visible light (λ = 470±10 nm), [Co^{2+}] = 100 μM, [$Ru(bpy)_3$]$^{2+}$ = 250 μM, [S_2O_8]$^{2-}$ = 4 mM for all experiments. [a] 20 s of light applied. [b] Second illumination of the sample after 15 min centrifugation.

References

1 S. Mohamady and D. L. Jakeman, *J. Org. Chem.*, 2005, **70**, 10588-10591.
2 Academic Software, 2001.
3 V. Y. Shafirovich, N. K. Khannanov and A. E. Shilov, *J. Inorg. Biochem.*, 1981, **15**, 113-129.
4 G. A. Truesdale and A. L. Downing, *Nature*, 1954, **173**, 1236-1236.