Electronic Supporting Information

Photocatalytic H_2 Evolution from Neutral Water with a Molecular Cobalt Catalyst on a Dye-sensitised TiO_2 Nanoparticle

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Experimental Section

Materials and Methods. All starting reagents for the synthetic part of the work were purchased from commercial suppliers and used without any further purification. Chemicals used for the analytical part were of the highest available purity. TiO_2 nanoparticles (AEROXIDE® TiO_2 P25 particles from Evonik Industries) were an anatase / rutile (8:2) mixture with an average particle size of 21 nm. Triethanolamine hydrochloride buffer solutions (TEOA, 0.10 M) were titrated with dilute NaOH to the desired pH value at 25 ºC. $[CoCl_2(dmgH)(dmgH_2)]$ ($dmgH_2$ = dimethylglyoxime),[1] $[Co^{III}Cl(dmgH)_2(pyridine)]$,[1] pyridyl-4-phosphonic acid,[2] and $[Ru^{II}$(2,2'-bipyridine)$_2$(2,2'-bipyridine-4,4'-diylbis(phosphonic acid)]Br_2, [**RuP**]Br_2,[3] were prepared as described previously.

Physical measurements. UV-vis spectra were recorded on a Varian Cary 50 UV-vis spectrophotometer using samples dissolved in water or TEOA buffer (pH 7, 0.10 M). Electrospray ionisation mass spectrometry was carried out in MeOH. Expected and experimental isotope distributions were compared. ^1H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer at room temperature. The signal from the residual ^1H present in D_2O was used as internal reference.[4] Elemental analysis was carried out by the microanalytical laboratory of The University of Manchester.

X-ray Crystallographic Studies of $(Et_3NH)[CoP]\cdot\frac{1}{2}MeOH$. Intensity data were recorded on an Oxford X-calibur 2 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the CrysAlisPro software package.[5] The single crystal was mounted in Paratone N oil on the tips of a glass fiber and kept under a stream of N_2. Full matrix least-squares refinement was carried out on F^2 values using the SHELXTL software.[6,7] All non-hydrogen atoms were located and their positions were refined with anisotropic thermal parameters by successive least-square cycles and Fourier syntheses. Carbon-bound hydrogen atoms were assigned to idealised positions and non-carbon bound hydrogens localised on difference Fourier maps (Figure 2, main text). All hydrogen atoms were isotropically refined given thermal parameters of 1.5 (methyl hydrogens) or 1.2 (non-methyl hydrogens) times the thermal parameter of the atom to which they were attached. The structure was validated by using the CheckCIF programme[8] (free of A and B alerts) from the International Union of Crystallography and the PLATON software.[9] Crystal data, data collection parameters, and structure refinement details can be found in Table S1, and selected bond distances and angles in Table S2. The **CoP** anion crystallises with a counter-cation, Et_3NH^+, and one MeOH lattice molecule at half occupancy per cobalt complex (Figure S1).

Adsorption of CoP to TiO_2. A solution of (Et_3NH)[**CoP**] or $[Co^{III}Cl(dmgH)_2(pyridine)]$ (0.1 μmol in 0.5 mL of TEOA, 0.10 M, pH 7) was added to a stirred dispersion of TiO_2 (5 mg in 1 mL TEOA). The mixture was left stirring for one h, was subsequently centrifuged, and the filtered, clear supernatant was then analysed by UV-vis spectrophotometry. The amount of **CoP** adsorbed to TiO_2 was quantified by the absorbance difference at λ_{max} (244 nm) before and after exposure to TiO_2 nanoparticles (Figure S2). The amount of **CoP** and $[Co^{III}Cl(dmgH)_2(pyridine)]$ adsorbed to TiO_2 particles after one h was 33±2% and ≤ 5%, respectively. **RuP** adsorbs quantitatively (>95%) to TiO_2 under the experimental conditions (TEOA buffer, pH 7).[10]

Assembly of photocatalytic H_2 production particles. The TiO_2 nanoparticles were loaded with **CoP** and **RuP**, and the photocatalytic system prepared by the following procedure: (Et_3NH)[**CoP**] (typically 0.1 μmol in 0.1 mL water) was added slowly to a stirred (volume of stir bar: 0.15 mL) dispersion of TiO_2 nanoparticles (5 mg) in 4.3 mL TEOA buffer (100 mM, pH 7) in a Pyrex pressure reaction vessel (total volume 9.5 mL). After one h, [**RuP**]Br_2 (typically 0.1 μmol in 0.1 mL water) was added dropwise to the stirred mixture of **CoP**-modified TiO_2 nanoparticles. After 20 min, the reaction vessel was sealed tightly with a rubber septum. The loading ratio for **RuP** and **CoP** on TiO_2 of three to one is estimated from electronic absorption studies (**RuP** adsorbs quantitatively and approximately one third of **CoP** attaches to TiO_2, see above). **RuP** adsorbs quantitatively to TiO_2 and only one third of **CoP** adsorbs to TiO_2. The total amount of **RuP** and **CoP** in the system is the same (0.1 μmol each). The turnover numbers and frequencies are given for the total amount of **CoP** in the system. For the UV irradiation experiments, [**RuP**]Br_2 was not added. The volume of the headspace of the vessel is 4.85 mL. All manipulations until this point were done in air, and an Al foil protected the vessel from light.

Photocatalytic H_2 production. Photocatalytic experiments were performed with a Solar Light Simulator (Newport Oriel, 150 W, 100 mW cm^{-2}) equipped with an air mass 1.5 global filter. IR irradiation was filtered in all experiments with a water filter, and the UV irradiation was filtered with a 420 nm cut-off filter (UQG Optics), unless otherwise noted (UV experiments). To reduce the light intensity to 20 mW cm^{-2} a neutral density filter with 20% transmission was used in one of the experiments. The stirred and light-protected reaction vessel was purged with 2% CH_4 in N_2 for 10 min prior light experiments. Methane acts as an internal standard for H_2 quantification (see below). The reaction vessel was thermostated with a water circulator connected to a water-jacketed reservoir at 25 °C. The amount of photo-generated H_2 was detected and quantified by headspace gas analysis with an Agilent 7890A Series gas chromatograph (GC) equipped with a 5 Å molecular sieve column (N_2 carrier gas at a flow rate of approximately 3 mL min^{-1}). The column temperature was held isothermally at 40 ºC, and a thermal conductivity detector was used. The instrument was calibrated with various known amounts of H_2 against CH_4 and the linearity and stability of the instrument and method were checked regularly. The total irradiation time for each light experiment was four h, with 10 μL aliquots of the headspace gas removed for GC analysis after 0, 0.5, 1, 1.5, 2, 3 and 4 h (and 5, 6, 7, 8 and 24 h for the long-term experiment). The results are summarised in Table S3. In the absence of either light, **RuP**, TiO_2, **CoP**, TEOA (sacrificial electron donor) only small traces or no H_2 were detected. The turnover frequencies are based on the average H_2 production within the first hour. Each experiment was carried out at least three times with the following treatment of data: considering a sample of n observations x_i, the unweighted mean value (x_u) with its standard deviation (σ) was calculated using the following equations:

$$x_u = \Sigma_i\, x_i/n;\ \sigma = \{\Sigma_i\, (x_i - x_u)^2 / [n(n-1)]\}^{1/2}$$

Centrifugation Experiments. A solution of (Et_3NH)[**CoP**] (0.1 μmol) was added to a stirred dispersion of TiO_2 (5 mg) and stirred for one h, then a solution of [**RuP**]Br_2 (0.1 μmol) was added and the mixture stirred for an additional 20 min. The dispersion contained a total of 4.5 mL TEOA (0.10 M, pH 7), was subsequently centrifuged, and the clear supernatant with free **CoP** removed. Then, the separated **RuP/CoP** modified TiO_2 NPs were dispersed in fresh TEOA buffer (4.5 mL) in a Pyrex vessel, purged with 2% CH_4 in N_2 and the stirred reaction mixture irradiated for four h with visible light and analysed by GC. The result is given as Experiment 7 in Table S3. The same experiment was also performed with **CoP**-modified particles (in the absence of **RuP**) and UV-light irradiation (Experiment 8 in Table S3).

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Table S1. Crystal Data and Details of Data Collection for (Et_3NH)[**CoP**]·½MeOH

chemical formula	$C_{19.5}H_{37}ClCoN_6O_{7.5}P$	crystal size (mm)	0.25 x 0.10 x 0.05
M_r (g mol^{-1})	600.90	color, shape	brown, block
Crystal system	Triclinic	sec per frame	110
space group	$P\bar{1}$	T (K)	100
a (Å)	8.171(5)	μ (Mo Kα, mm^{-1})	0.833
b (Å)	12.998(5)	Θ range, deg	3.12 to 25.02
c (Å)	14.602(5)	total no. of data	8129
α (deg)	113.768(5)	no. of unique data	4830
β (deg)	99.000(5)	no. of parameters	380
γ (deg)	97.294(5)	completeness to theta	99.8%
V ($Å^3$)	1370.5(11)	R1[a]	0.0499
Z	2	wR2[b]	0.1369
ρ_{calc} (g cm^{-3})	1.456	GOF[c]	1.024

[a]R1 = $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b]wR2 = $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, [c] GOF = $\{\Sigma[w(F_o^2-F_c^2)^2] /(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table S2. Selected Bond Distances (Å) and Angles (deg) for (Et_3NH)[**CoP**]·½MeOH

Co1–Cl1	2.219(2)	N1–Co1–Cl1	178.60(9)
Co1–N1	1.955(3)	N1–Co1–N2	90.71(13)
Co1–N2	1.896(3)	N1–Co1–N3	91.22(13)
Co1–N3	1.901(3)	N2–Co1–N3	81.06(14)
Co1–N4	1.886(3)	N2–Co1–N4	179.31(13)
Co1–N5	1.876(3)	N2–Co1–N5	98.51(14)

Table S3. Photocatalytic H_2 Production with **RuP** and **CoP** attached to TiO_2 NPs in TEOA buffer at pH 7 and 25 °C

#	Catalytic Nanoparticle System[a]	Experimental Conditions[b]	H_2 (4 h)[c] ± σ / %	TOF (**CoP**) ± σ / h^{-1}	H_2 ± σ / μmol H_2 h^{-1}	H_2 ± σ / μmol H_2 h^{-1} (g TiO_2)$^{-1}$
*Standard system – electron transfer from **RuP** to **CoP***						
1	**CoP** (0.1 μmol), **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2})	2.29±0.15	19.4±1.0	1.94±0.10	388±20
*UV irradiation - electron transfer from TiO_2 to **CoP***						
2	**CoP** (0.1 μmol), no **RuP**, TiO_2 (5 mg)	TEOA, UV-visible light (100 mW cm^{-2}), pH 7	6.07±0.42	42±3	4.21±0.30	842±59
*Phosphate inhibition - **CoP** not attached to TiO_2*						
3	**CoP** (0.1 μmol), no **RuP**, TiO_2 (5 mg)	TEOA + phosphate, UV-visible light (100 mW cm^{-2})	0.08±0.08	—[d]	—	—
*Reduced light absorption and **CoP** loading on TiO_2*						
4	**CoP** (0.1 μmol), **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 20 mW cm^{-2})	1.47±0.08	7.70±0.4	0.77±0.04	154±8
5	**CoP** (0.1 μmol), **RuP** (0.02 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2})	1.16±0.06	10.7±0.6	1.07±0.06	214±11
6	**CoP** (0.02 μmol), **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2})	0.18±0.07	9.83±6	0.20±0.12	39±24
*Centrifugation experiments. **CoP** concentration before centrifugation, 0.1 μmol.*						
7	**CoP**, **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2})	0.24±0.02	*n.d.*	0.28±0.08	57±16
8	**CoP** (0.1 μmol), no **RuP**, TiO_2 (5 mg)	TEOA, UV-visible light (100 mW cm^{-2})	1.6±0.08	*n.d.*	0.71±0.04	142±41
pH variation - pH 6 and 8						
9	**CoP** (0.1 μmol), **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2}), pH 6	0.06±0.01	1.12±0.1	0.11±0.01	0.02±0.01
10	**CoP** (0.1 μmol), **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2}), pH 8	1.1±0.06	18±0.9	1.8±0.1	0.36±0.02
Control Experiments						
11	no **CoP**, **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2})	0.02±0.01	—	—	—
12	**CoP** (0.1 μmol), **RuP** (0.1 μmol), no TiO_2	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2})	—	—	—	—
13	**CoP** (0.1 μmol), no **RuP**, TiO_2 (5 mg)	TEOA, visible light (λ > 420 nm, 100 mW cm^{-2})	—	—	—	—
14	**CoP** (0.1 μmol), **RuP** (0.1 μmol), TiO_2 (5 mg)	no TEOA, vis. light (λ > 420 nm, 100 mW cm^{-2})	—	—	—	—
15	**CoP** (0.1 μmol), **RuP** (0.1 μmol), TiO_2 (5 mg)	TEOA, no irradiation	—	—	—	—

(a) TiO_2 NPs were modified with **CoP** and **RuP** as described in the Experimental Section. (b) TEOA buffer was used (4.5 mL, 0.10 M, pH 7; except in experiment 14) in a Pyrex vessel (headspace volume, 4.85 mL). The vessel was sealed with a rubber septum and contained a N_2 atmosphere with 2% CH_4 (GC standard) during irradiation. Irradiation from a solar light simulator (100 mW cm^{-2}) was used, and UV light was filtered with a 420 nm filter in all experiments (except 2 and 8, where UV band gap irradiation was required). The light intensity was reduced to 20 mW cm^{-2} (experiment 4) with a neutral density filter (transmission 20%). Phosphate (25 mM)/TEOA (0.10 M, pH 7) was used in experiment 3. (c) Photoproduced H_2 (in reactor vessel headspace, in percent) after four hours (± σ, standard deviation). Turnover frequency (TOF = molecules of H_2 produced per hour and per molecule **CoP**), H_2 production rate (μmol H_2 h^{-1}) and per g TiO_2 [μmol H_2 h^{-1} (g TiO_2)$^{-1}$] based on the first hour of irradiation. (d) The limit of H_2 detection by GC is below 0.02% H_2.

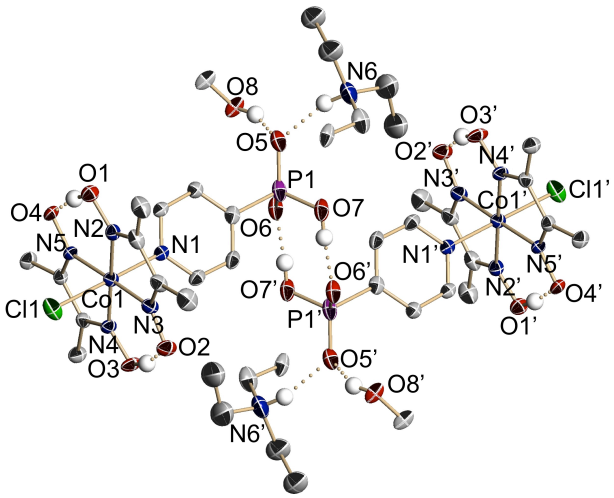

Figure S1. Hydrogen-bonding network in two units of (Et_3NH)[**CoP**]·½MeOH showing 50% probability thermal ellipsoids and the atom-numbering scheme for all non-carbon and non-hydrogen atoms. A disordered ethyl (C18A and C19A) and a methyl group (C15B) in Et_3NH^+ are omitted for clarity.

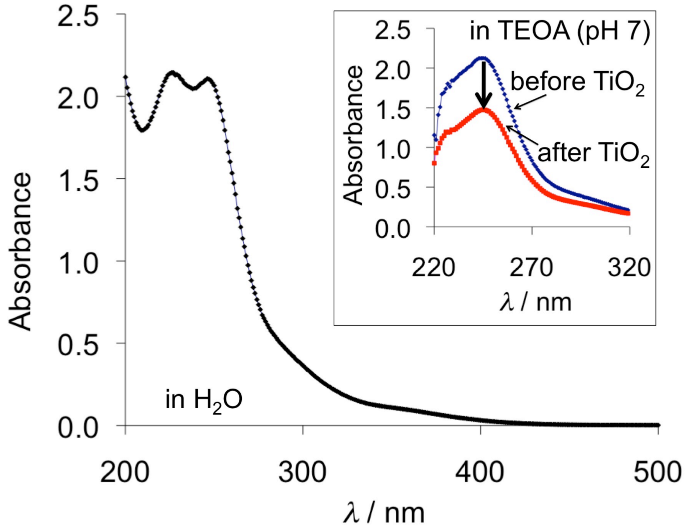

Figure S2. Electronic absorption spectrum of (Et_3NH)[**CoP**] (0.05 mM) in water. The insert shows the determination of adsorption of **CoP** to TiO_2 in 0.10 M TEOA buffer at pH 7.0: UV-vis spectrum of (Et_3NH)[**CoP**] (0.05 mM) (in the absence of TiO_2; blue trace) and after stirring with TiO_2 (5 mg per 0.1 μmol (Et_3NH)[**CoP**]) for one h following centrifugation and filtration (red trace). 33% **CoP** adsorbed on TiO_2 (indicated by arrow).

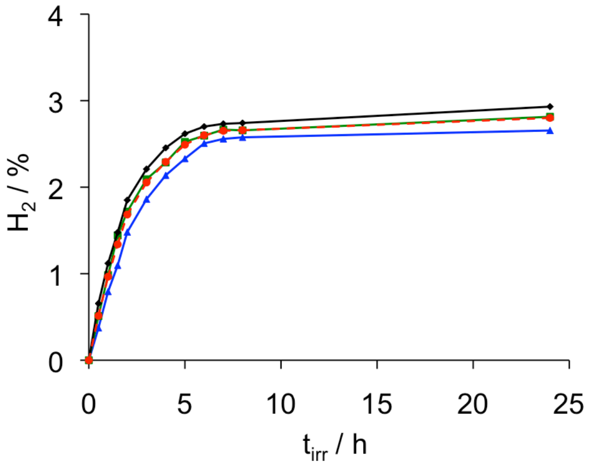

Figure S3. Visible-light driven H_2 production with **CoP** (0.1 *µ*mol) and **RuP** (0.1 *µ*mol) attached to TiO_2 NPs (5 mg) in TEOA buffer (0.10 M) at pH 7 and 25 °C (standard conditions, Experiment 1, Table S3). Three single runs (solid lines) and their average (dotted red line) are shown.

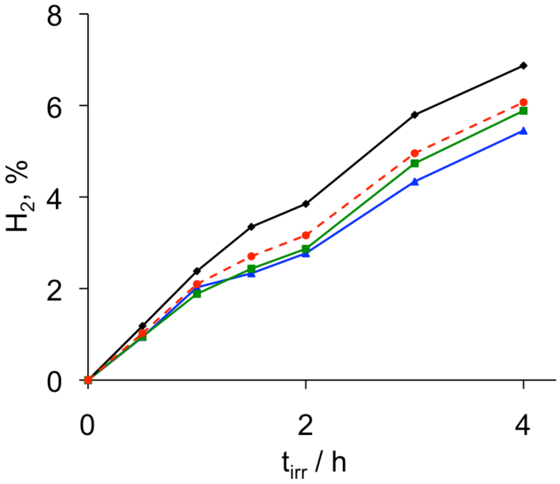

Figure S4. UV-light driven H_2 production with **CoP** (0.1 *µ*mol) attached to TiO_2 NPs (5 mg) in TEOA buffer (0.10 M) in the absence of **RuP** at pH 7 and 25 °C (Experiment 2, Table S3). Three single runs (solid lines) and their average (dotted red line) are shown.

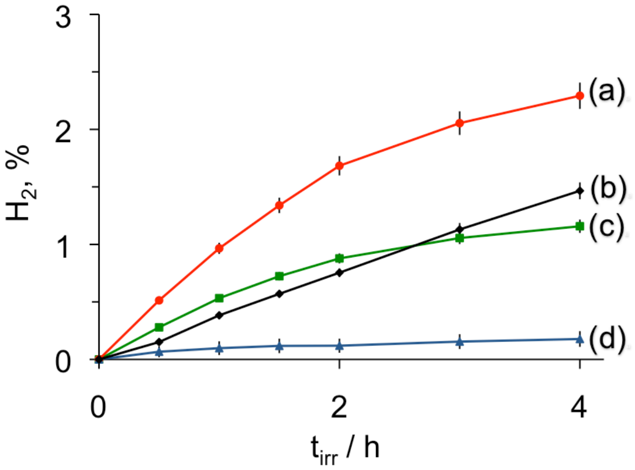

Figure S5. Visible-light driven H_2 production with reduced light intensity or catalyst loading on TiO_2 compared to standard conditions. TiO_2 NPs (5 mg) in TEOA buffer (0.10 M) at pH 7 and 25 °C were employed in all experiments, in addition to (a) **CoP** (0.1 μmol) and **RuP** (0.1 μmol) with 100 mW cm^{-2} irradiation (standard conditions, Experiment 1, Table S3, Figure S3), (b) **CoP** (0.1 μmol) and **RuP** (0.1 μmol) with 20 mW cm^{-2} irradiation (Experiment 4, Table S3), (c) **CoP** (0.1 μmol) and **RuP** (0.02 μmol) with 100 mW cm^{-2} irradiation (Experiment 5, Table S3), and (d) **CoP** (0.02 μmol) and **RuP** (0.1 μmol) with 100 mW cm^{-2} irradiation (Experiment 6, Table S3). The average plots of three independent runs are shown, including error bars).

End of Electronic Supporting Information