Supporting information

Ascorbate as Electron Relay Between an Irreversible Electron Donor and a Ru(II) or Re(I) Photosensitizer

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Experimental

All photocatalytic reactions were performed in deionized water, that was doubly distilled before use. Sodium ascorbate was purchased from Sigma Aldrich, Ascorbic acid from Acros, NaOH from Erne surface AG, and TCEP from Apollo scientific.

Standard procedure for catalytic reactions:

TCEP hydrochloride (286.6 mg) and the corresponding amount of sodium ascorbate (0 - 396 mg, 0 - 200 mM) were dissolved in water (3-5 mL) and 1-2 mL (depending on the desired final pH) of a 1 M NaOH solution was added. For experiments without TCEP, the corresponding amounts of AscOH and NaAscO were dissolved in H_2O to a final concentration of 0.1 M. Then PS **2** (2.5 mL of a 2 mM stock solution, 0.5 mM) or $[Ru(BPy)_3]Cl_2$ pentahydrate (**3**, 3.65mg, 0.5 mM) and WRC **1** (1 - 100 µL of a 10 mM stock solution, 1 - 100 µM) were added. In the case of TCEP, the mixture was then titrated under virgous stirring on a pH meter (Mettler Toledo seven multi) with NaOH (1 M) to the corresponding pH. Finally the reaction solution was diluted with water up to the final reaction volume. The reaction solution was connected to a Ar line with a controlled flow of 6 ml/min, and the dried purge gas was analysed by GC (automated Bruker GC-450 or 456, see below). As soon as the solution was degassed (no oxygen and nitrogen detected by GC), irradiation was started with an LED lamp (385 nm, 100 mW, $3.4 \cdot 10^{-7}$ mol/s, used for PS **2** and 470 nm, 100 mW, $4.0 \cdot 10^{-7}$ mol/s, used for PS **3**). Hydrogen evolution was continuously monitored by GC (see below). When hydrogen evolution had ceased, the data were analyzed with the software ORIGIN. Conversions in TCEP were directly measured from the reaction solution by ^{31}P-NMR spectroscopy (200 MHz Varian Mercury or 300 MHz Varian Gemini-2000 spectrometer): 15.7 ppm (bs, $[R_3\mathbf{P}\text{-}H]^+$); 56.1 ppm (s, $R_3\mathbf{P}$=O).

Gas chromatograms were recorded using either a Varian CP-3800, automated Bruker GC-450 or 456 gas chromatograph with argon as carrier gas and a 3 m x 2 mm packed molecular sieve 13X 80-100 column. The column and reference gas flow (Ar) was set to 20 ml/min. The oven was operated isothermal at 100 °C. An argon flow of usually 6 ml/min (adjusted with a manual flow controller (Porter, 100) or an onboard EFC device for the GC-456 and referenced with a F-200CV-002 from Bronkhorst) was passed through the reaction mixture and into the GC, where 1000 µl gas samples were automatically injected in defined time intervals (usually 5 min) using a 6-Port-2-Position Valve from Vici. The gases were detected using a thermal conductivity detector operated at 150 C (retention time is about 1 min for H_2). Calibration was achieved by mixing Ar and H_2 in known ratios with two mass flow controllers (Bronkhorst, F-201CV-200 for Ar and F-200CV-002 for H_2 resp. 0.51 % H_2 in Ar (pangas)). This setup allowed the detection of H_2 to $2 \cdot 10^{-5}$ resp $2 \cdot 10^{-6}$ (molfraction) for GC-450 or 456, respectively. At Ar flows of 6 ml/min through the reaction the detection limit was $H_2/s \geq 1 \cdot 10^{-10}$ resp. $\geq 1 \cdot 10^{-11}$ mol s^{-1} for GC-450 resp. 456.

HPLC measurements were performed on a VWR Hitachi Elite LaChrome with a C_{18} nucleodur column and H_2O/MeOH as eluent (gradient starting with 10% MeOH, 0.1% TFA in H_2O to pure MeOH).

Luminescence lifetime measurements were recorded on an Edinburgh LP920 Laser Flash Photolysis transient absorption spectrometer using a flashlamp pumped Q-switched Nd:Yag laser (355 nm) as excitation source.

Syntheses: PS **2**, WRC **1** and $[Ru(BPy)_3]Cl_2 \cdot 5H_2O$ (PS **3**) were synthesized according to reported procedures.[1-3]

The **maximal steady state DHA concentration** was estimated according to the following calculation: $d[DHA]/dt = 2 \cdot 10^{-6}$ M/s - $k \cdot [TCEP] \cdot [DHA] = 0$, where $2 \cdot 10^{-6}$ M/s refers to the maximal hydrogen evolution rate and k the reduction rate constant of DHA by TCEP (1 $M^{-1}s^{-1}$), according to the literature.[4]

Table SI1. Summarized results of the pH dependency study in water with 0.1 M TCEP, 50 mM NaAscO, 100 µM **1** and 0.5 mM PS **2** or **3**.

pH	PS	Maximal rate [a] (nmol H_2/s)	Reaction time [b] (h)	TCEP Conversion (%, ^{31}P-NMR)	TON_{AscO^-} (H_2/$AscO^-$)
3	**2**	7.7 ± 0.5	17 ± 1.5	15	0.3
	3	1.1 ± 0.1	54 ± 5	15	0.3
4	**2**	21.7 ± 1.1	23 ± 2	100	2
	3	3.5 ± 0.1	96 ± 8	100	2
5	**2**	22.8 ± 1.2	36 ± 3	100	2
	3	13.5 ± 0.7	34 ± 3	100	2
6	**2**	18.5 ± 0.9	54 ± 5	100	2
	3	8.2 ± 0.6	58 ± 5	100	2

[a] Reaction volumes: 10 mL (PS **2**) and 9 ml (PS **3**), [b] Time required to form of 95 % of totally measured H_2 (GC).

Table SI2. Summarized results of the [WRC] dependency study in 9 mL water with 0.1 M TCEP, 100 mM NaAscO and 0.5 mM **3** at pH 5.

WRC (µM)	Maximal rate[a] (nmol/s)	TON_{Co} [a] (H_2/Co)	Max. TOF_{Co} [a] H_2/Co/h	Total H_2 [a] (µmol)	Reaction time [b] (h)	TCEP conv. [c] (%)	TON_{AscO^-} (H_2/$AscO^-$) [d]
100	16.6 ± 0.8	1080 ± 50	66.6 ± 4.8	970 ± 55	35 ± 3	100	0.97 ± 0.06
50	18.5 ± 0.9	1830 ± 80	150 ± 6	825 ± 40	23 ± 2.5	100	0.83± 0.04
25	21.0 ± 0.9	3200 ± 200	340 ± 18	720 ± 65	21 ± 2	100	0.72 ± 0.07
20	21.1 ± 1.1	4000 ± 250	425 ± 25	715 ± 60	22 ± 2	90	0.72 ± 0.06
10	19.7 ± 1.0	6300 ± 400	800 ± 50	570 ± 35	19 ± 1.5	75	0.57 ± 0.04
5	19.3 ± 0.9	9000 ± 500	1550 ± 75	410 ± 30	13 ± 1.5	55	0.41 ± 0.03
1	14.7 ± 0.8	33300 ± 1500	5880 ± 360	290 ± 20	11 ± 1	35	0.29 ± 0.02
0	0.21 ± 0.03	-	-	3.5 ± 2	22 ± 3	5	< 0.1

[a] Measured by GC, [b] 95 % conversion, [c] determined by ^{31}P-NMR, [d] According to total H_2 measured by GC

Table SI3. Potentials (V vs. NHE) of the different redox couples involved in the photocatalytic hydrogen production.

TCEP/ TCEP=O	DHA/ AscOH	$AscO^-$/ $AscO^{\cdot}$	$*Re^{I/0}$	$Re^{I/0}$	$*Ru^{II/I}$	$Ru^{II/I}$	$Co^{II/I}$	H^+ / $^1/_2$ H_2 (pH 4-5)
-0.29 [5]	+0.40 [6]	+0.70 [6]	+1.33 [a]	-0.82 [1]	0.82 [7]	-1.28 [7]	-0.65 [2]	-0.46 - -0.52

[a] Lower estimate was obtained by subtracting the triplet emission energy (E_T, at λ_{maxem}) from $Re^{I/0}$.

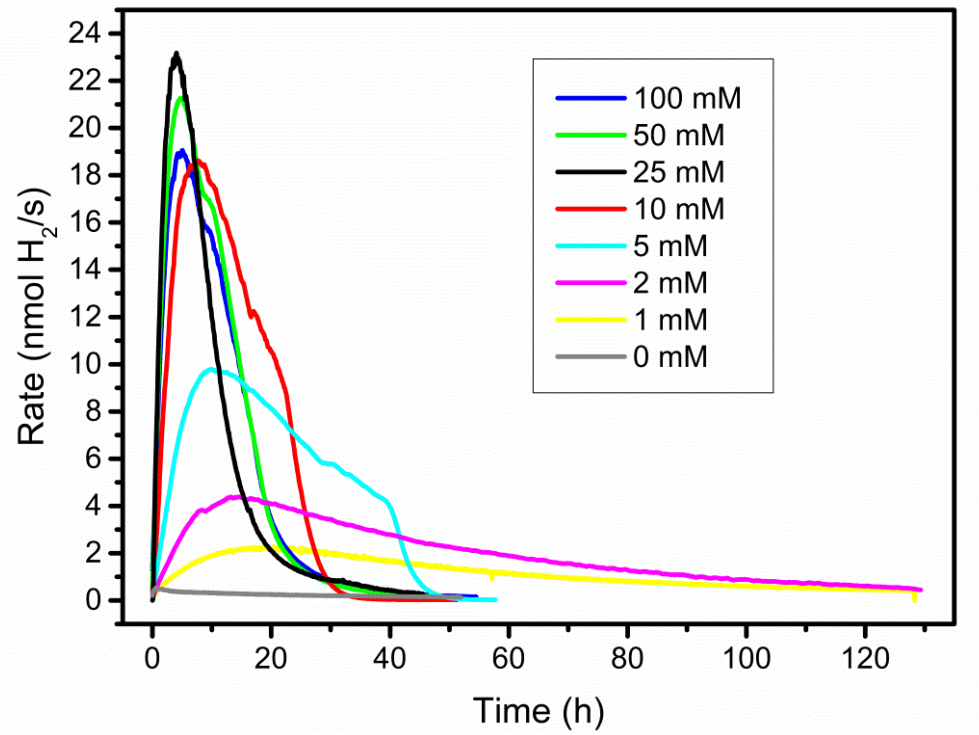

Figure SI1. NaAscO concentration dependency study in 10 mL water with 0.1 M TCEP, 100 µM **1** and 0.5 mM PS **2** at pH 4. Conversions in TCEP: 100 % (2-100 mM), 45 % (1 mM) and 3 % (0 mM).

Table SI4. Summarized results of the [NaAscO] dependency study in water with 0.1 M TCEP, 100 µM **1** and 0.5 mM PS **2** at pH 4.

[NaAscO] (mmol)	Maximal rate (nmol H_2/s)	Reaction time (h) [a]	TCEP Conversion (%, ^{31}P-NMR)	TON_{AscO^-} (H_2/$AscO^-$)
100	18.8 ± 1.9	25.5 ± 2.4	100	1
50	21.1 ± 2	23 ± 2.4	100	2
25	22.5 ± 2.2	25 ± 2.5	100	4
10	18 ± 0.18	24.5 ± 2.5	100	10
5	9.7 ± 0.9	38 ± 3.5	100	20
2	4.3 ± 0.4	108 ± 10	100	50
1	2.2 ± 0.2	274 ± 25	45	45
0	0.4 ± 0.03	-	3	-

[a] Time required to form of 95 % of totally measured H_2 (GC).

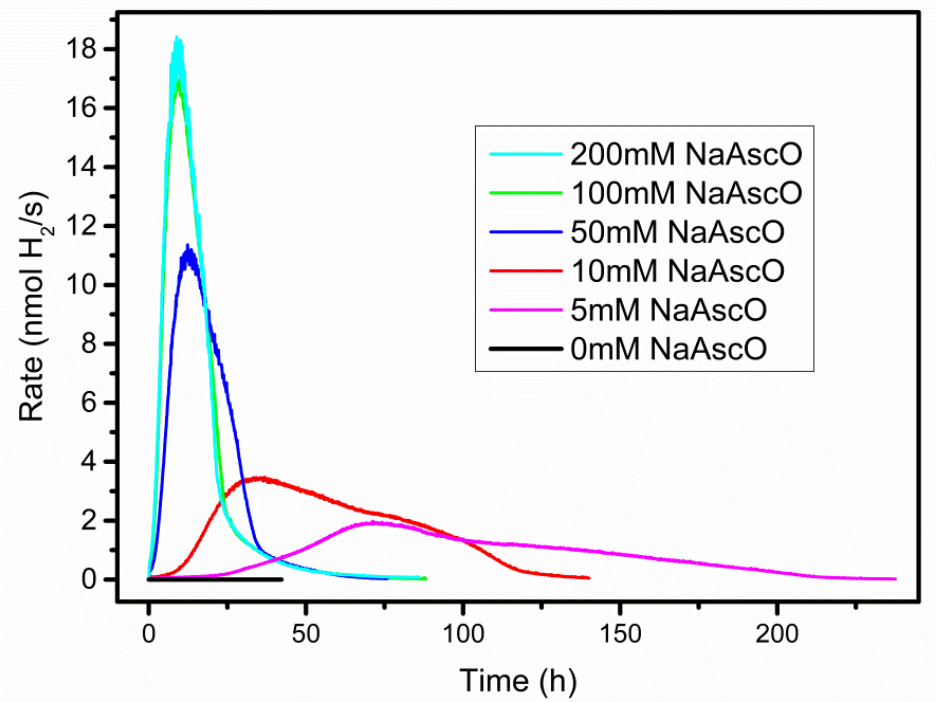

Figure SI2. NaAscO concentration dependency study in 9 mL water with 0.1 M TCEP, 100 µM **1** and 0.5 mM PS **3** at pH 5. Conversions in TCEP: 100 % (5-100 mM) and 0 % (0 mM).

Table SI5. Summarized results of the [NaAscO] dependency study in water with 0.1 M TCEP, 100 µM **1** and 0.5 mM PS **3** at pH 5.

[NaAscO] (mmol)	Maximal rate (nmol H_2/s)	Reaction time (h) [a]	TCEP Conversion (%, ^{31}P-NMR)	TON_{AscO^-} (H_2/$AscO^-$)
200	17.6 ± 1.7	29 ± 3	100	0.5
100	16.7 ± 1.7	35 ± 3.5	100	1
50	10.9 ± 1	36 ± 3.5	100	2
10	3.4 ± 0.35	105 ± 10	100	10
5	1.9 ± 0.18	183 ± 18	100	20
0	0	-	0	-

[a] Time required to form of 95 % of totally measured H_2 (GC).

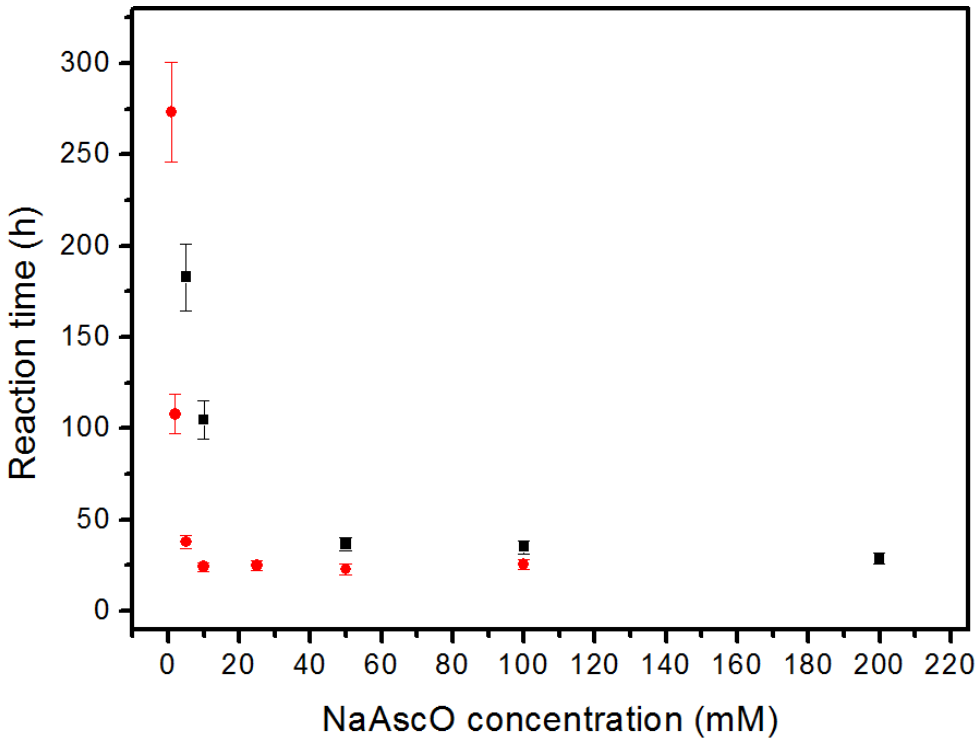

Figure SI3. Estimated reaction times (formation of 95 % of totally evolved hydrogen) in water with 0.1 M TCEP, 0.5 mM PS (black dots: **3**, pH 5; red dots: PS **2**, pH 4) and 100 µM WRC **1**.

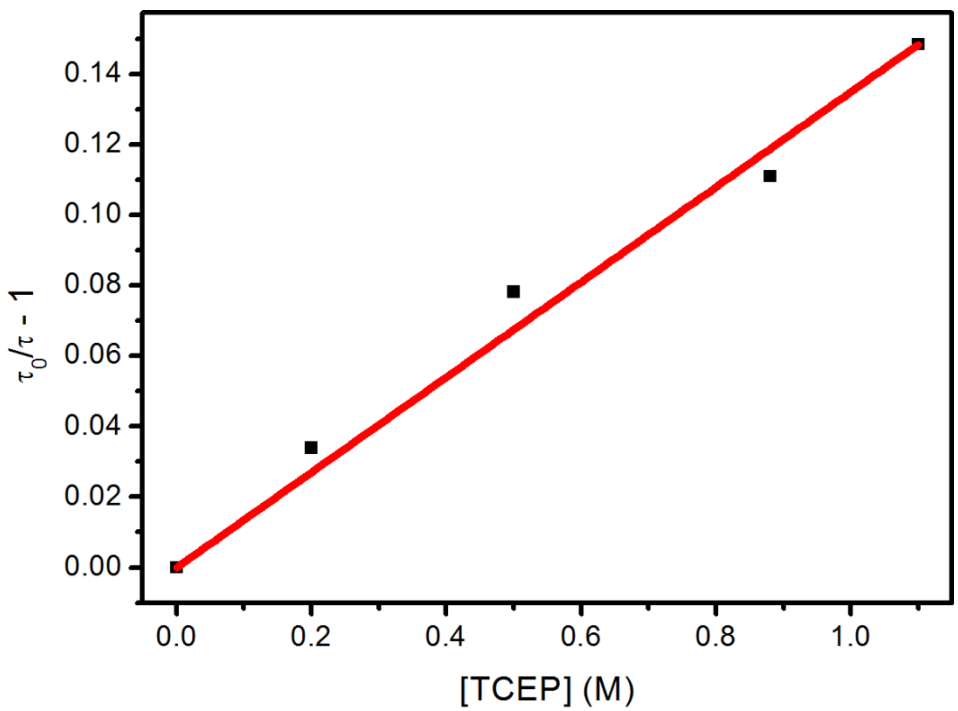

Figure SI4. Stern-Volmer-plot of the quenching study with TCEP and PS **2** in water at pH 4 (τ_0 = 120 ns).

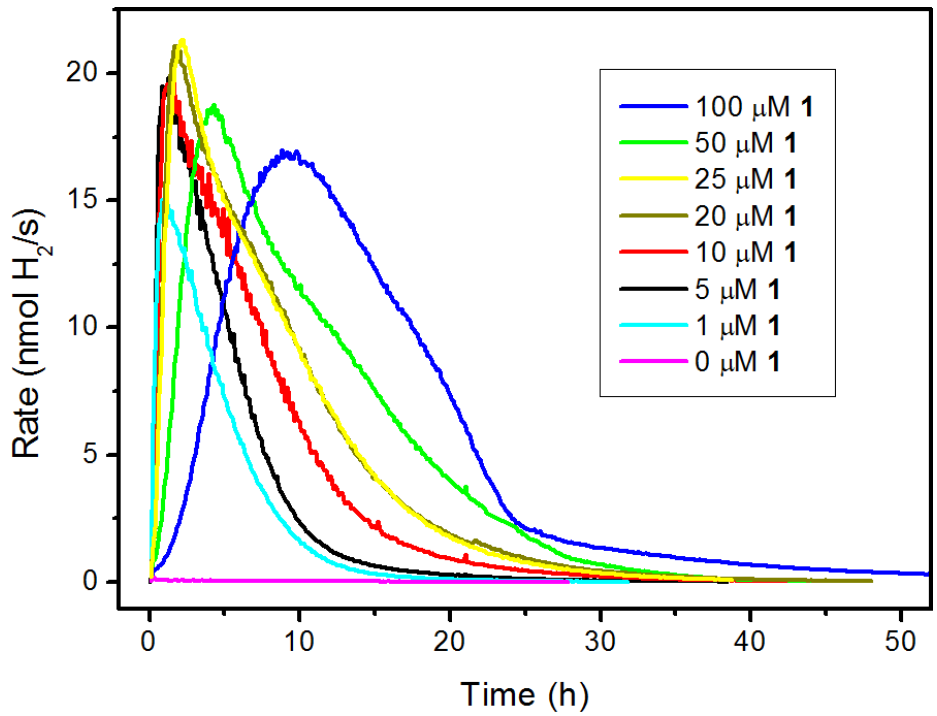

Figure SI5. WRC (**1**) concentration dependency study with 0.1 M TCEP, 100 mM NaAscO, 0.5 mM PS **3** at pH 5.

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