

Supporting Information

Antimony porphyrins as red-light powered photocatalysts for solar fuel production from halide solutions in the presence of air

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Materials

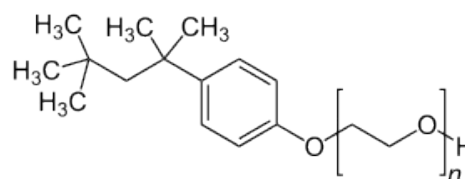
Tetrabutylammonium salts NBu_4X (Fluka, X = Cl, Br, I), HBr (48 wt.% in H_2O , Aldrich) and KBr (Merck, Uvasol quality) and KI (AppliChem, p.A.) were used as the halide anion sources. The commercially available free-base porphyrin ligands *meso*-Tetraphenylporphyrin H_2TPP (Strem Chemicals), *meso*-Tetrakis-4-Methoxyphenylporphyrin $\text{H}_2(\text{Tp-OCH}_3)\text{PP}$ (Aldrich) and Octaethyl-porphyrin $\text{H}_2(\text{OEP})$ (Fluka) were used as received. SbCl_3 (Aldrich, 99.99%) was used as metallation reagent. The low-valent antimony(III) and the high-valent antimony(V) forms of the photocatalysts were prepared according to the methods described in the literature [1,2].

In a typical procedure, 1 mmol of free-base porphyrin (ca. 0.6 g in case of H_2TPP) was added to a suspension of 80 ml pyridine and 5 g molecular sieve (4Å). The mixture was stirred and refluxed for 30 min under Ar. After cooling to r.t., an excess of SbCl_3 (30 mmol) was added. The solution was protected from light, stirred and heated under Ar for another 30 min to reach a final temperature of approximately 70 °C. During this period a colour change to brownish-green indicated the metallation process. At r.t. about 0.4 ml of Br_2 were added, the mixture was stirred for 15 min and then 50 ml of H_2O were added dropwise. The hydrolysed reaction mixture was stirred for 1 h at r.t. and then evaporated to dryness. The crude reaction product was extracted with CH_2Cl_2 and filtered in small portions over silica gel in a chromatography column. After completely washing out remaining free-base porphyrin with CH_2Cl_2 , the product was eluted with EtOH (95 %) and crystallized. Exchange of the counteranion was achieved by treatment of the product with a 1:1 (v:v) mixture of EtOH and an aqueous 1M potassium salt solution followed by extraction with diethylether and crystallization. The nature of the axial hydroxo ligands in the antimony(V) porphyrin cations $[(\text{P})\text{Sb}^{\text{V}}(\text{OH})_2]^+$ studied was confirmed in each case by field desorption (FD)-mass spectroscopy:

- | | | |
|--|---|--|
| 1: $[(\text{TPP})\text{Sb}(\text{OH})_2]^+$: | $\text{C}_{44}\text{H}_{30}\text{N}_4\text{O}_2\text{Sb}^+$ | 767 (100%, M^+), 733 (20%, $[\text{M}-2\text{OH}]^+$) |
| 2: $[(\text{T}(p\text{-OCH}_3)\text{PP})\text{Sb}(\text{OH})_2]^+$: | $\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_6\text{Sb}^+$ | 887 (35%, M^+), 853 (100%, $[\text{M}-2\text{OH}]^+$) |
| 3: $[(\text{OEP})\text{Sb}(\text{OH})_2]^+$: | $\text{C}_{36}\text{H}_{46}\text{N}_4\text{O}_2\text{Sb}^+$ | 687 (16%, M^+), 653 (100%, $[\text{M}-2\text{OH}]^+$) |

Hydrogen peroxide was determined quantitatively by the peroxidase-catalyzed oxidation of 4-aminophenazone in the presence of chromotropic acid [3]. For semiquantitative reaction control, colorimetric test strips (Merck Millipore) indicating light-mediated H₂O₂ accumulation in the range 0.5 - 2 - 5 - 10 - 25 mg/l were also employed.

Reactions and measurements in microheterogeneous medium were carried out in dilute aqueous micellar solutions (1.4 mM) of the nonionic surfactant 4-(1,1,3,3-Tetramethylbutyl)phenylpolyethylene glycol (Triton X-100, Roth), which displays a critical micelle concentration (CMC) of 0.24 mM [4] :



Silica gel supported antimony(V) porphyrin photocatalysts [5] were prepared according to the following modified procedure:

4 mg of [(T(*p*-OCH₃)PP)Sb(OH)₂]Cl (**2**) were dissolved in 25 ml EtOH (Merck, Uvasol). A 10 ml sample of the dark green solution was slowly added to 1.6 g of silica gel (0.060-0.200 mm, pore size 60 Å, Acros) in a beaker and gently mixed. Evaporation of the solvent after 2 days resulted in a bright-green powder carrying the immobilized multielectron transfer sensitizer **2** (surface modified SiO₂ containing 0.1 wt.% [(T(*p*-OCH₃)PP)Sb(OH)₂]⁺).

Spectroscopic properties of the Photocatalysts 1-3 (data from refs. [6,7] unless otherwise stated):

Table S1: Absorption maxima of the [(P)Sb^V(OH)₂]⁺ photocatalysts at 298K in ethanol solution

Porphyrin-ligand (P)	$\lambda_{\max} / \text{nm}$ ($10^{-3} \epsilon / \text{L mol}^{-1} \text{cm}^{-1}$)			HW / cm^{-1} * B (Soret)
	<i>N</i>	<i>B</i> (Soret)	<i>Q</i>	
TPP	314, 356 <i>s</i> (12.9) (7.0)	366 <i>s</i> , 397 <i>s</i> , 419 (4.5) (20.8) (316.2)	512 <i>s</i> , 552, 591 (2.1) (11.8) (6.4)	600
T(<i>p</i> -OCH ₃)PP	319, -- (14.9)	-- , 383 <i>s</i> , 436 (20.4) (149.8)	523 <i>s</i> , 561, 609 (3.1) (10.0) (16.0)	1500
OEP	288, -- (3.0)	346 <i>s</i> , 377 <i>s</i> , 397 (10.7) (33.7) (267.5)	494 <i>s</i> , 530, 570 (1.3) (10.7) (10.6)	500

* HW: half-width

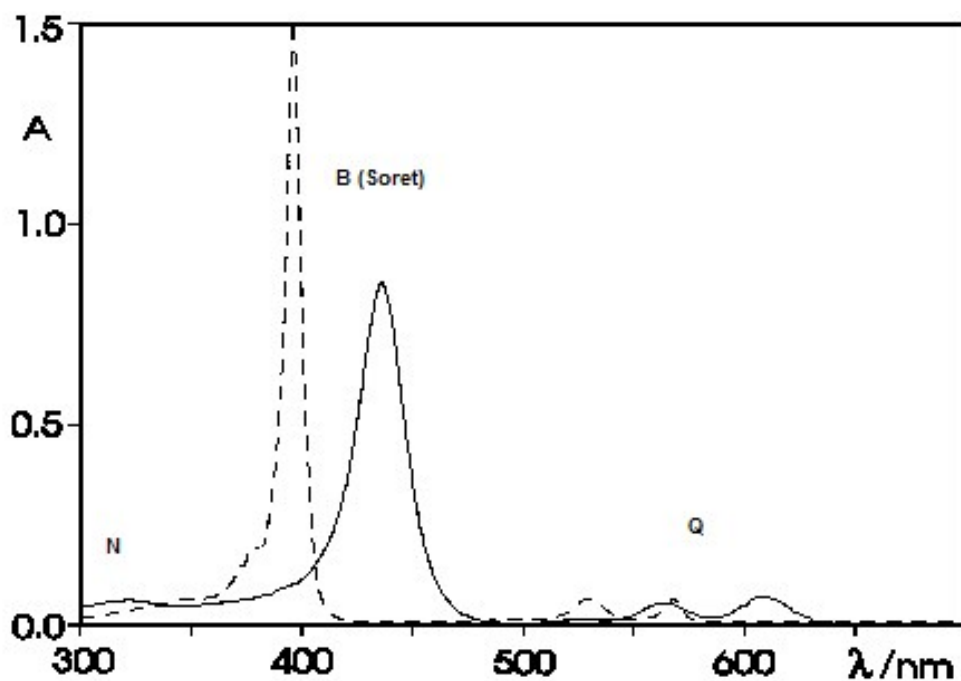


Fig. S1: UV-Vis absorption spectra of $[(T(p\text{-OCH}_3)\text{PP})\text{Sb}^{\text{V}}(\text{OH})_2]\text{Cl}$, **2** (—) and $[(\text{OEP})\text{Sb}^{\text{V}}(\text{OH})_2]\text{Cl}$, **3** (---) at 298K in ethanol solution ($5.6 \times 10^{-6}\text{M}$, 1cm cell). For compound **1** see ref. [7].

Table S2: Fluorescence properties of the $[(\text{P})\text{Sb}^{\text{V}}(\text{OH})_2]^+$ photocatalysts at 298K in ethanol solution

Porphyrin-ligand (P)	$\lambda_{\text{max}} / \text{nm}$		ϕ_{F}		$\tau_{\text{F}} / \text{ns}$	Stokes shift / cm^{-1}	
	S_2	S_1	S_2	S_1	S_1	S_2	S_1
TPP	428	596, 651, 720 s	0001	0.035	1.46	500	100
T(<i>p</i> -OCH ₃)PP	450	627, 670 s, --	$\sim 10^{-4}$	0.012	1.1 *	700	400
OEP	--	573, 628, 680 s	--	0.025	1.05	--	100

* in water containing Triton X100

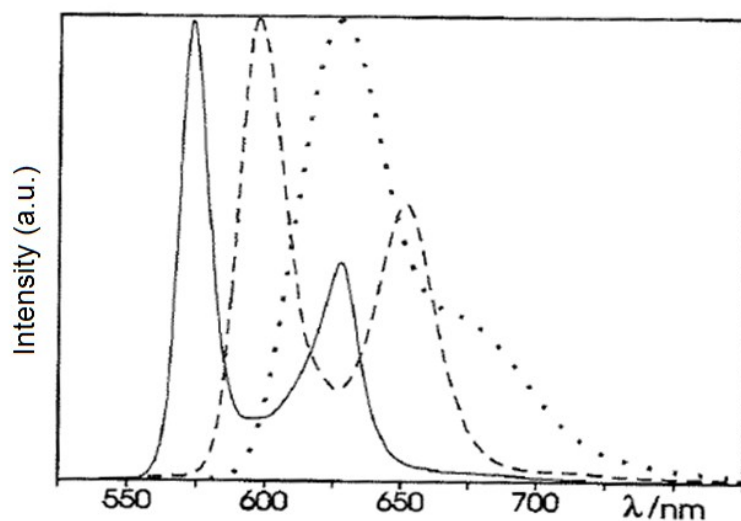


Fig. S2: S_1 -state (Q-band) fluorescence spectra of $[(\text{TPP})\text{Sb}^{\text{V}}(\text{OH})_2]\text{Cl}$, **1** (---), $[(\text{T}(p\text{-OCH}_3)\text{PP})\text{Sb}^{\text{V}}(\text{OH})_2]\text{Cl}$, **2** (···) and $[(\text{OEP})\text{Sb}^{\text{V}}(\text{OH})_2]\text{Cl}$, **3** (—) at 298K in ethanol solution.

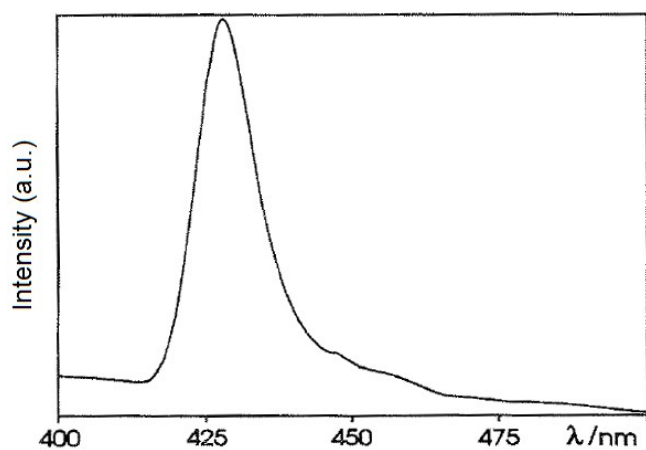


Fig. S3: S_2 -state (B-band) fluorescence spectrum of $[(\text{TPP})\text{Sb}^{\text{V}}(\text{OH})_2]\text{Cl}$, **1** at 298K in ethanol solution (data from ref.[6], for more details see also ref. [8]).

Table S3: Low-temperature luminescence properties of the [(P)Sb^V(OH)₂]⁺ photocatalysts **1-3** at 77K in 95% ethanol glass matrix.

Porphyrin-ligand (P)	$\lambda_{\max} / \text{nm}$		Φ_{rel} (S_1/T_1)	$\tau_{\text{P}} / \text{ms}$ T_1	Stokes shift / cm^{-1} T_1	E / eV	
	$S_1(0,0)$	$T_1(0,0)$				S_1	T_1
TPP	594	760	~80	0.8 / 12 *	3700	2.09	1.64
T(<i>p</i> -OCH ₃)PP	618	810	~140	1.1 / 6.2 *	3800	2.01	1.53
OEP	570	704	2.7	37	3300	2.18	1.76

* double exponential fit

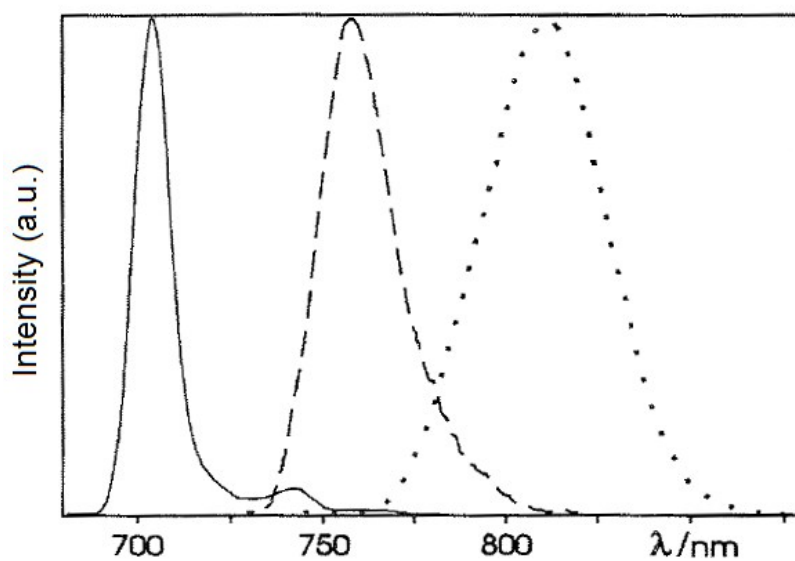


Fig. S4: T₁-state phosphorescence spectra of [(TPP)Sb^V(OH)₂]Cl, **1** (---), [(T(*p*-OCH₃)PP)Sb^V(OH)₂]Cl, **2** (···) and [(OEP)Sb^V(OH)₂]Cl, **3** (—) at 77K in 95% ethanol glass matrix (data from ref.[6]).

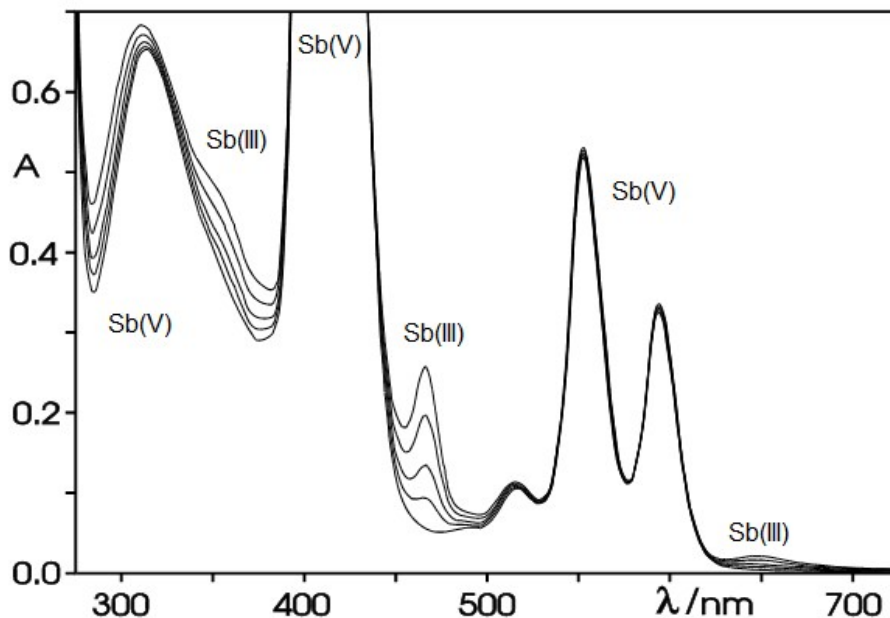


Fig. S5: Formation of the low-valent complex $[(\text{TPP})\text{Sb}^{\text{III}}]^+$ with a Soret-band maximum at 465nm [1] during 590 nm irradiation of $[(\text{TPP})\text{Sb}^{\text{V}}(\text{OH})_2]^+$, **1** in the presence of iodide in excess. Reaction conditions: 1cm cell, 6×10^{-5} M compound **1**, 10^{-2} M Bu_4NI , acetonitrile, air, 298K at $t = 0, 5, 10, 20$ and 60s photolysis times ($5.8\text{mW}/\text{cm}^2$).

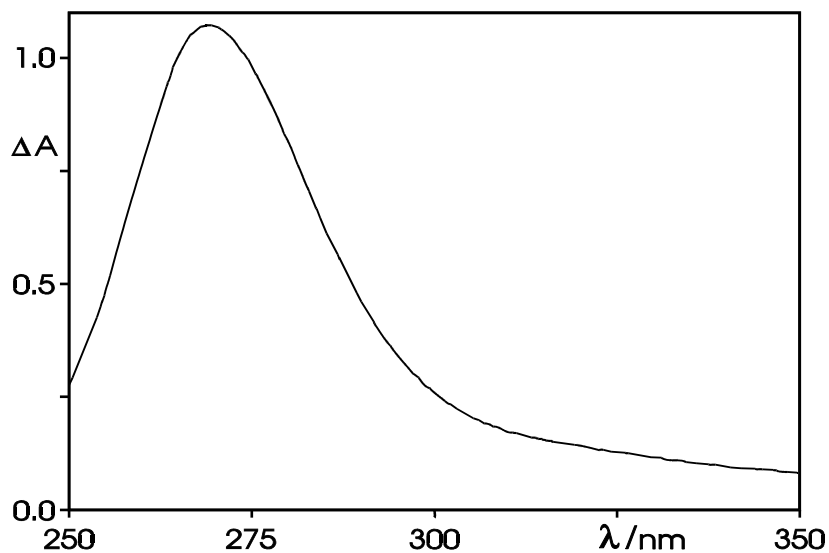


Fig. S6: Difference spectrum of a photolyzed solution containing 9.3×10^{-5} M $[(\text{OEP})\text{Sb}^{\text{V}}(\text{OH})_2]^+$, **3** and 5×10^{-2} M Bu_4NBr in air saturated acetonitrile at 298K. Irradiation at 546nm resulted in the production of the two-electron oxidation product tetrabutylammonium tribromide ($\lambda_{\text{max}} = 269$ nm).

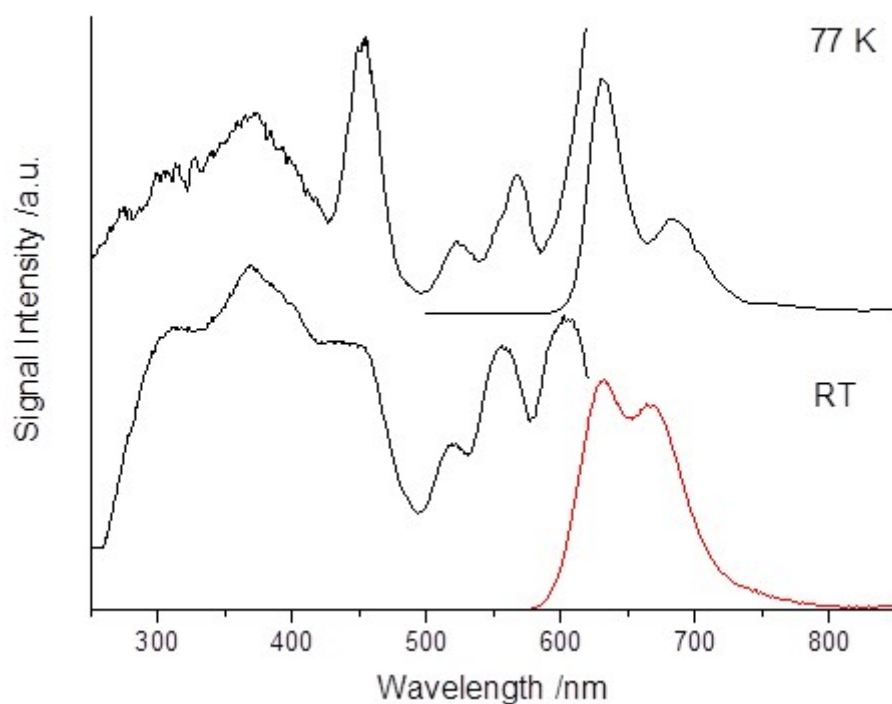


Fig. S7: Emission and excitation spectra of the silica gel immobilized antimony porphyrin complex **2** (solid sample of the surface modified SiO₂ containing 0.1 wt.% [(T(*p*-OCH₃)PP)Sb(OH)₂]⁺).

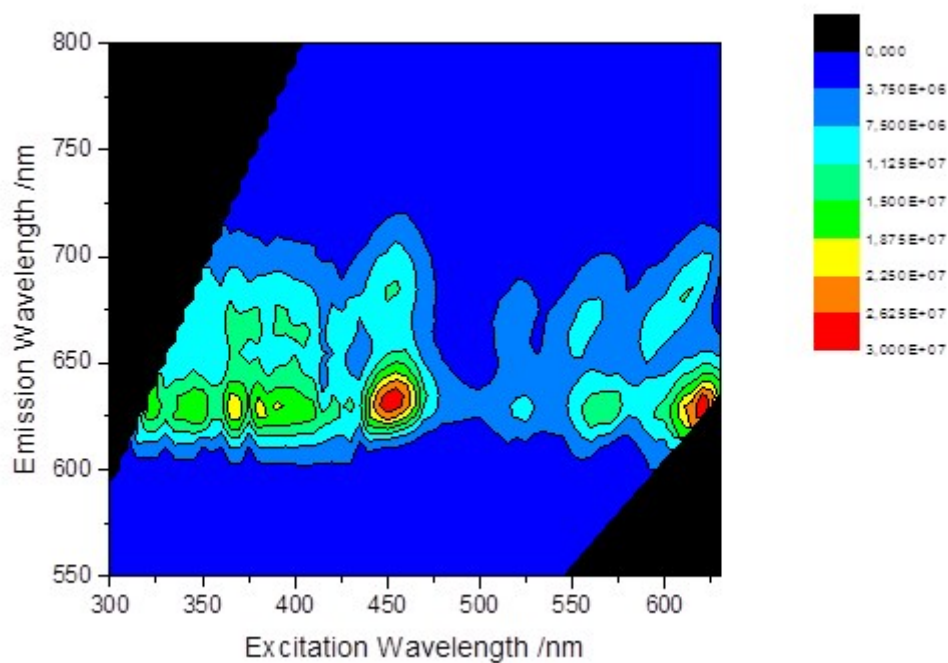


Fig. S8: 2D-plot of the 77K emission and excitation spectra of the silica gel immobilized antimony porphyrin complex **2** (solid sample of SiO₂ containing 0.1 wt.% [(T(*p*-OCH₃)PP)Sb(OH)₂]⁺).

Solar photochemical experiments with immobilized photocatalysts:

“AM 1.5” samples were exposed to simulated sunlight (SolSim, Luzchem) closely matching the intensity of one sun at a solar zenith angle of $z = 48.2^\circ$ (1.5 AirMass filter):

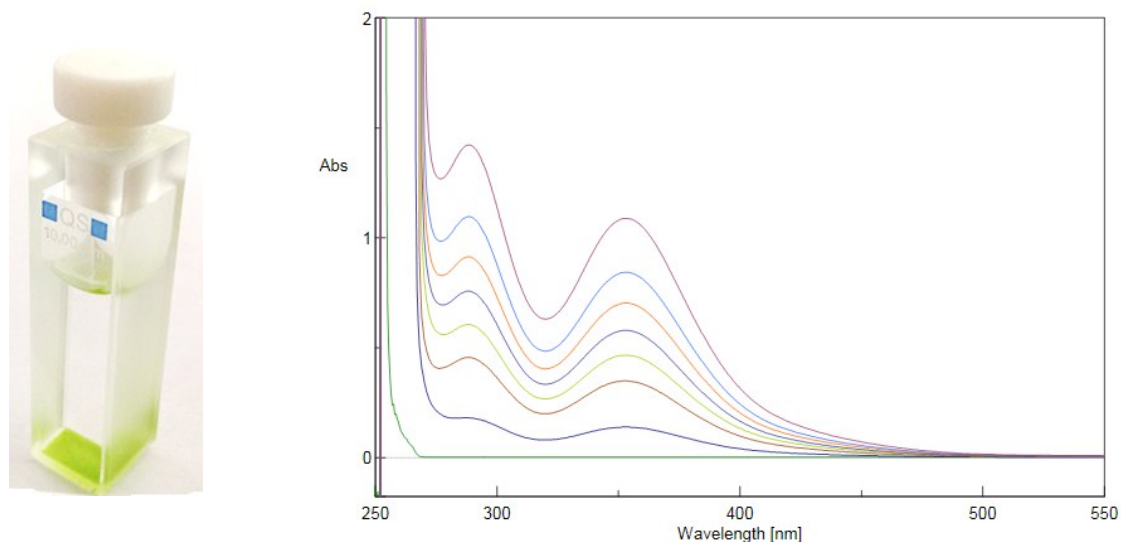


Fig. S9: Cuvette containing a 1M KI solution covering a 30 mg sample of the surface modified SiO_2 with 0.1 wt.% $[(\text{T}(p\text{-OCH}_3)\text{PP})\text{Sb}(\text{OH})_2]^+$ (**2**) before exposure to AM 1.5 light of the solar simulator. Right side: Photocatalyzed formation of potassium triiodide in the first 40 min of simulated sunlight exposure.

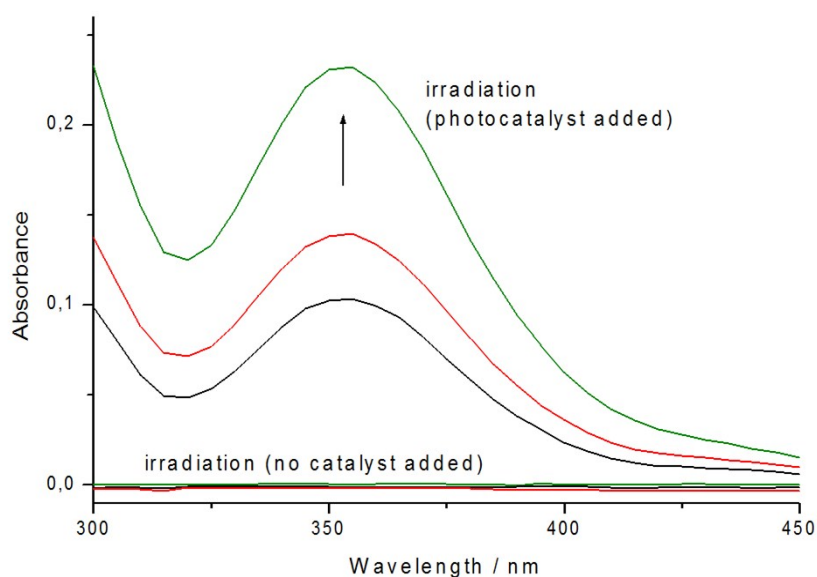


Fig. S10: Control experiment comparing the results of simultaneous visible light exposure of two samples of an aerobic 1M KI solution in the absence and presence of 30 mg of surface modified SiO_2 with 0.1 wt.% of photocatalyst **2** (irradiation > 590 nm).

Triiodide monitored by the product absorption band emerging at 352 nm (Fig. S10) is only formed in the sample containing the photocatalyst. Conditions: 1 cm quartz cells with teflon stopper placed on an optical bench in the beam of a 150W Xe lamp equipped with a IR-water filter to avoid heating of the solutions and a cutoff filter (> 590 nm) to ensure exposure to long-wavelength light only. For the experiment shown, both samples containing a freshly prepared KI solution were exposed next to each other centered in one sample holder to the red-light beam under essentially identical conditions.

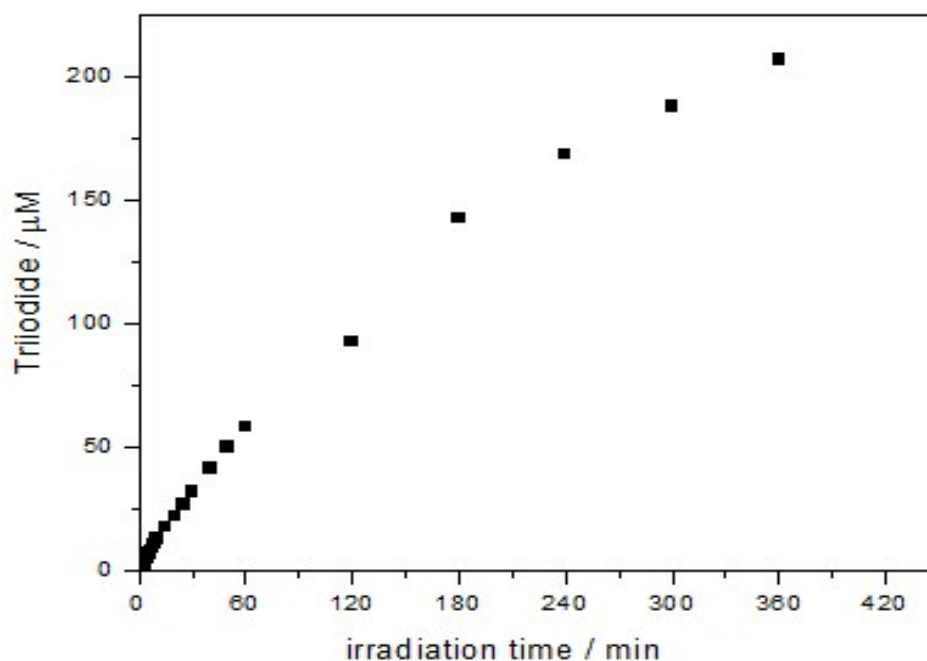


Fig. S11: Formation of triiodide upon 6h exposure to simulated sunlight (AM 1.5) in a stoppered Cuvette containing a 1M KI solution and 30 mg of the surface modified SiO_2 with 0.1wt.% **2**.

The photocatalyst showed an identical initial rate after harvesting the triiodide solution and exchanging the supernatant for a fresh 1M potassium iodide solution.

References:

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