Supporting Information

Electron Transfer Dynamics in Semiconductor–Chromophore–Polyoxometalate Catalyst Photoanodes

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1. UV-visible Spectra of Films

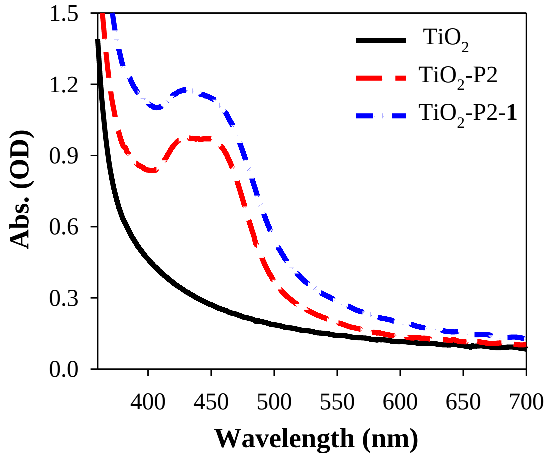

Figure S1. UV-vis absorption spectra of TiO_2 (black), TiO_2-P2 (red) and TiO_2-P2-**1** (blue).

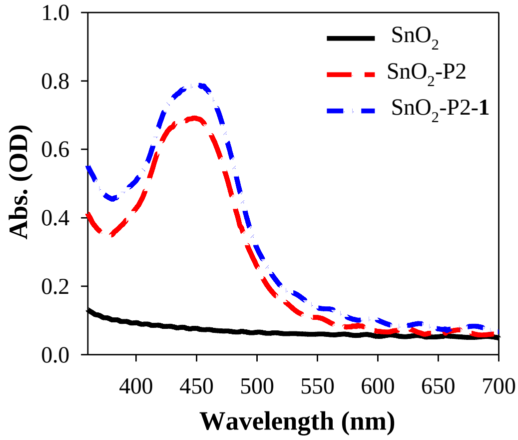

Figure S2. UV-vis absorption spectra of SnO_2 (black), SnO_2-P2 (red) and SnO_2-P2-**1** (blue).

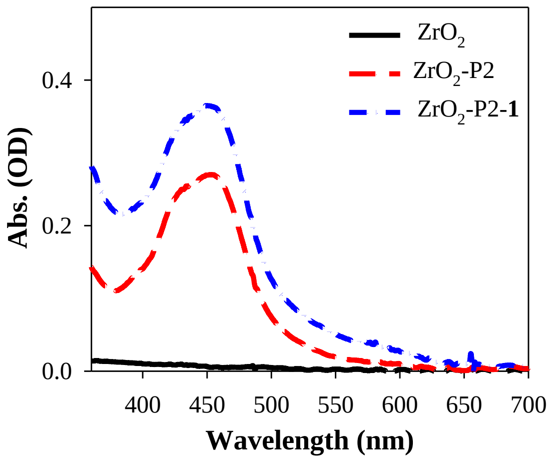

Figure S3. UV-vis absorption spectra of ZrO_2 (black), ZrO_2-P2 (red) and ZrO_2-P2-**1** (blue).

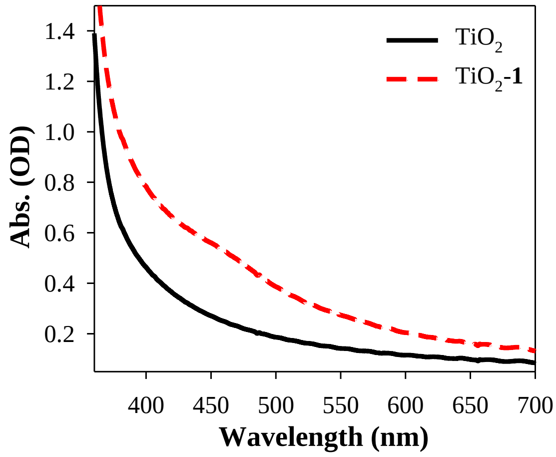

Figure S4. UV-vis absorption spectra of TiO_2 (black) and TiO_2-**1** (red)

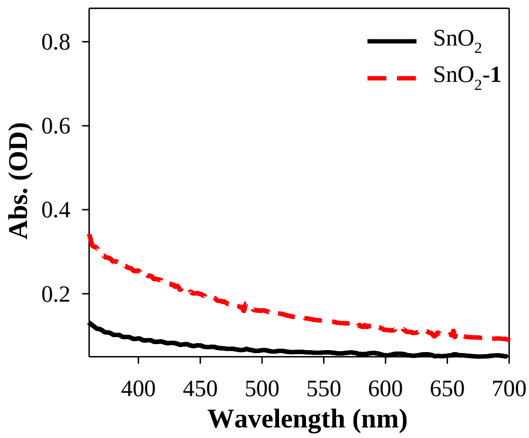

Figure S5. UV-vis absorption spectra of SnO_2 (black) and SnO_2-**1** (red)

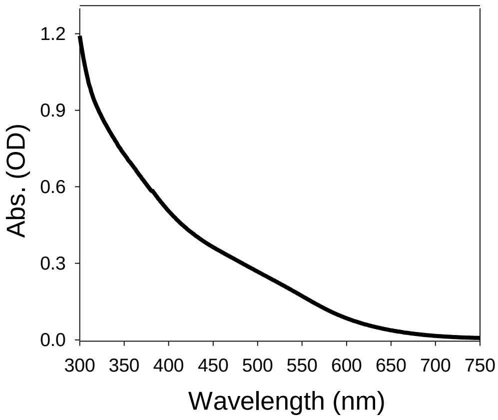

Figure S6. UV-vis absorption spectrum of **1** in an aqueous solution of 0.2 mM (1 mm path length)

2. Absorption and Emission Spectra of P2

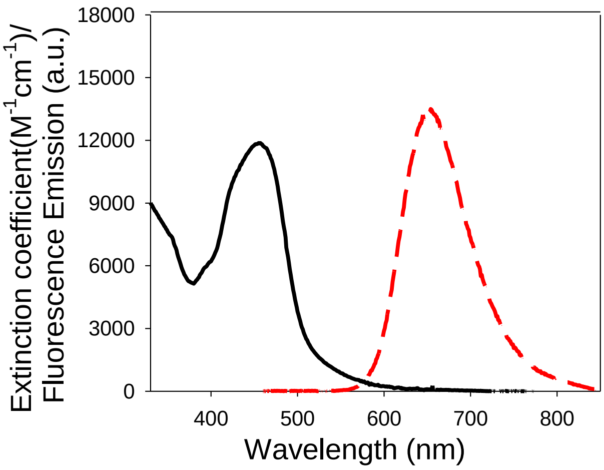

Figure S7. Absorption (solid line) spectrum of P2 in 0.1 M $HClO_4$, and emission spectrum (dotted line) of 10^{-5} M P2 in water (1 cm path length).

3. Additional Transient IR Kinetics

The following control measurements confirm that **1** cannot inject electrons into the metal oxide in the absence of P2, and that P2 cannot inject electrons into ZrO_2. Samples were pumped at 515 nm and probed at 5000 nm.

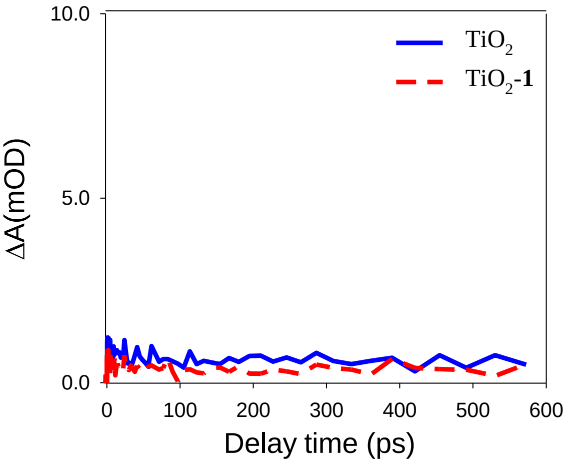

Figure S8. Electron injection kinetics of TiO_2 (blue) and TiO_2-**1** (red), in the absence of sensitizer.

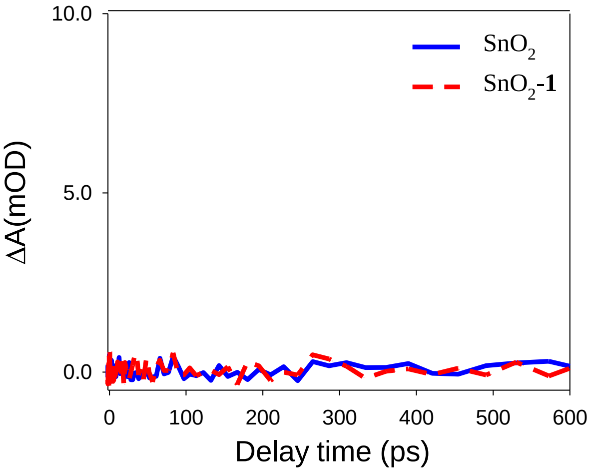

Figure S9. Electron injection kinetics of SnO_2 (blue) and SnO_2-**1** (red), in the absence of sensitizer.

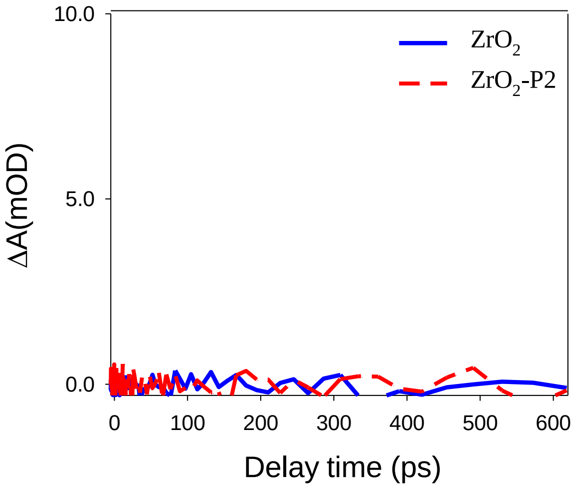

Figure S10. Electron injection kinetics of ZrO_2 (blue) and ZrO_2-P2 (red).

4. Kinetics of P2 Excited State Decay in Solution

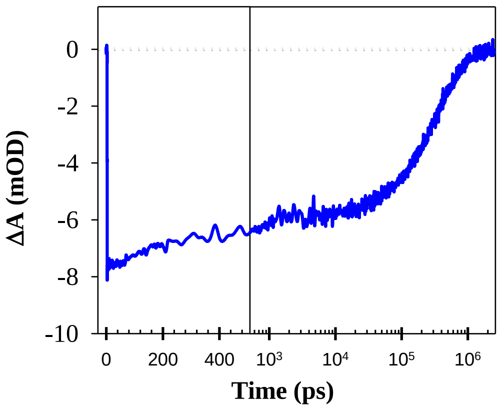

Figure S11. GSB recovery kinetics for P2 in an aqueous solution averaged over 460-470 nm (400 nm excitation). The time axis is linear for the left panel and logarithmic scale for the right panel.

5. Steady-state Fluorescence Studies of P2 and 1 in Solution

Steady state fluorescence studies on mixtures of P2 and **1** in MeCN:H_2O indicate that the fluorescence of P2 may be quenched by the presence of **1**.

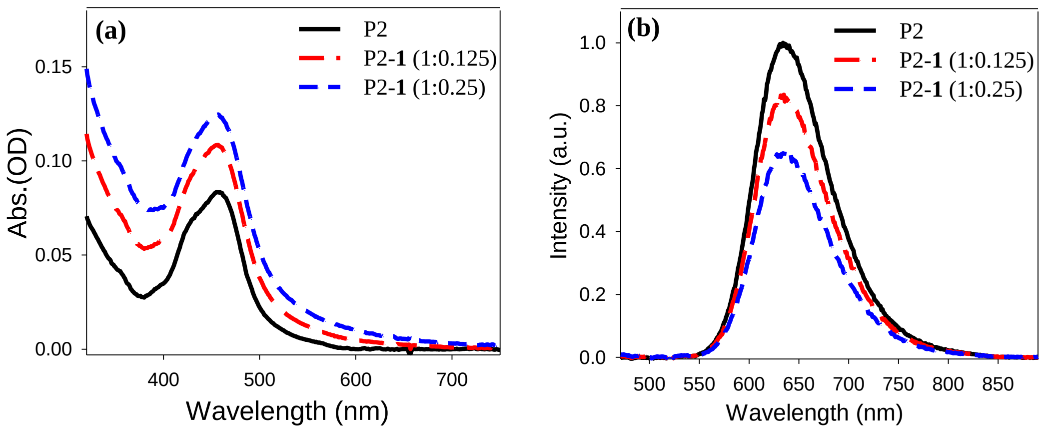

Figure S12. **(a)** UV-vis absorption spectra and **(b)** steady-state fluorescence emission spectra of mixtures of P2 and **1** in acetonitrile–water (1:1). The molar ratios of P2 to **1** are indicated.

6. Additional Transient Visible Spectra

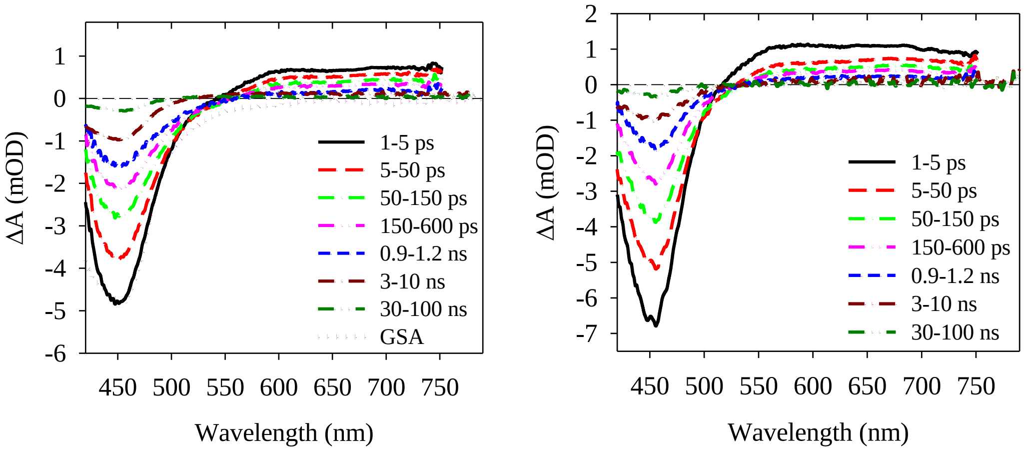

Figure S13. Averaged transient differential absorption spectra of ZrO_2-P2 (left) and ZrO_2-P2-**1** (right) at indicated delay time windows after 400 nm excitation. For ZrO_2-P2 the ground-state absorption (GSA, dotted line) has been inverted and scaled for a better comparison with the corresponding bleach.

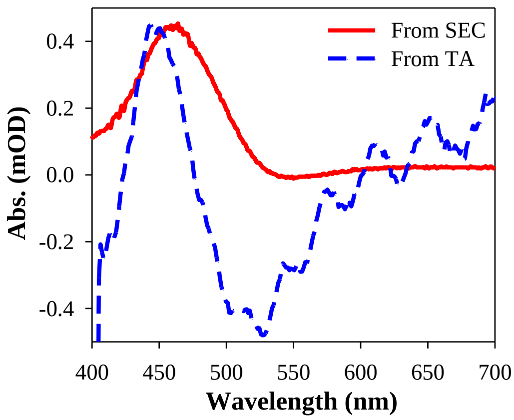

Figure S14. UV-vis absorption differential spectrum of SnO_2-P2-**1** from spectroelectrochemical (SEC) measurements (red) and transient differential absorption (TA) spectra at delay time of 50-100 ns (blue). The former spectrum has been scaled for a better comparison.

7. Photoelectrochemical Studies in Acetonitrile

Photoelectrochemical studies on TiO_2-P2 and TiO_2-P2-**1** electrodes in acetonitrile were performed using the same equipment as the aqueous studies, but with 0.1 M NBu_4PF_6 as electrolyte. The measurements show much lower photocurrents, and no significant enhancement by **1**, in the absence of water and a suitable buffer.

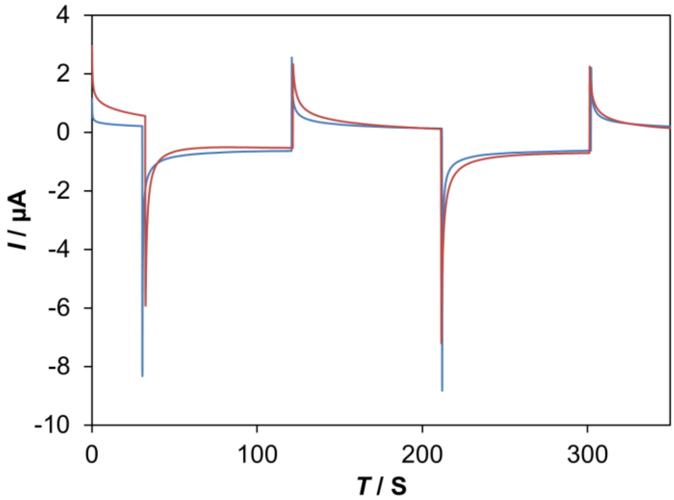

Figure S15. Photoelectrochemical measurements (chronoamperometry) of TiO2-P2 (blue) and TiO2-P2-**1** films (red-brown) in acetonitrile, at an applied bias of 0 mV vs Ag/AgCl, pH 5.8. Illumination (420 – 470 nm, 15 mW cm^{-2}) was provided by a filtered Xenon lamp.

Table S1.

Multiexponential Fitting Parameters for Transient Absorption Kinetics at 2000 cm^{-1} (Figure 1)

SAMPLE	α_1	τ_1 [ps]	α_2	τ_2 [ps]	α_3	τ_3 [ps]	α_4	τ_4 [ps]	α_5	τ_5
SnO_2-P2	-0.33	4.0 ± 1	-0.37	30.3 ± 8	-0.30	224 ± 40	1	> ns		
SnO_2-P2-1	-0.34	3.0 ± 1	-0.37	19.3 ± 6	-0.29	217 ± 34	1	> ns		
TiO_2-P2	-0.63	0.3 ± 0.1	-0.28	10.7 ± 4	-0.09	152 ± 30	1	> ns		
TiO_2-P2-1	-0.60	0.3 ± 0.1	-0.24	1.9 ± 0.8	-0.16	22 ± 5	0.21	219 ± 40	0.79	> ns

Table S2.

Multiexponential fitting Parameters for Transient Absorption Kinetics Shown in Figure 3.

SAMPLE	α_1	τ_1 [fs]	α_2	τ_2 [ps]	α_3	τ_3 [ps]	α_4	τ_4 [ns]	α_5	τ_5 [ns]	α_6	τ_6	Half life [ns]
SnO_2-P2	0.73	55 ± 12	0.13	23 ± 8	0.14	317 ± 45	-0.151	16 ± 3	-0.42	726 ± 40	-0.43	> ms	1100
SnO_2-P2-1	0.89	47 ± 20	-0.36	56 ± 7	-0.52	2004 ± 271	-0.12	15 ± 4	0.07	212 ± 35	0.04	> ms	0.52

	α_1	τ_1 [fs]	α_2	τ_2 [ps]	α_3	τ_3 [ps]	α_4	τ_4 [ps]	α_5	τ_5 [ns]	α_6	τ_6 [ns]	α_7	τ_7	Half life [ns]
TiO_2-P2	0.85	36 ± 12	0.15	7.6 ± 2	-0.183	52 ± 12	-0.27	673 ± 37	-0.29	19.5 ± 3	-0.08	332 ± 62	-0.178	> ms	6.9
TiO_2-P2-1	0.98	32 ± 18	-0.26	0.43 ± 0.3	-0.33	76 ± 18	-0.30	1179 ± 97	-0.092	15.6 ± 4	-0.02	177 ± 59	0.025	> ms	0.13

	α_1	τ_1 [fs]	α_2	τ_2 [fs]	α_3	τ_3 [ps]	α_4	τ_4 [ps]	α_5	τ_5 [ns]	α_6	τ_6 [ns]	α_7	τ_7 [ns]	α_8	t8	Half life [ps]
ZrO_2-P2	1.0	32 ± 12	-0.12	28 ± 20	-0.23	10 ± 7	-0.20	182 ± 30	-0.18	4.5 ± 0.4	-0.11	32 ± 7	-0.11	183 ± 77	-0.05	> ms	102.3
ZrO_2-P2-1	1.0	34 ± 20	-0.11	45 ± 25	-0.19	1.5 ± 0.7	-0.23	46 ± 12	-0.19	0.4 ± 0.1	-0.14	5.2 ± 0.6	-0.13	42 ± 7	-0.02	> ms	41.5