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SUPPORTING INFORMATION

Light Driven Styrene Epoxidation and Hydrogen Generation Using H_2O as an Oxygen Source in a Photoelectrosynthesis Cell

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EXPERIMENTAL SECTION

Reagents. All reagents used in this work were obtained from Aldrich Chemical Co. in the highest commercially available grade and were used without further purification. Highly pure water was obtained by passing it through an UltraClear water purifier system from SG Wasseraufbereitung und Regenerierstation GmbH (Conductivity at 25 °C = 0.055 μS/cm). $[Ru(bpy)_3]^{2+}$,[1] $[Ru(bpy)_2(4,4'\text{-}(PO_3H_2)_2bpy)]^{2+}$, abbreviated as **P-bpy-Ru**,[2] and $\{[Ru^{II}(trpy)(H_2O)]_2(\mu\text{-pyr-dc})\}(OAc)$, abbreviated as $[H_2O\text{-}Ru^{II}Ru^{II}\text{-}OH_2]^+$ **(2,2$^+$)**, were prepared according to literature procedures.[3] All synthetic manipulations were routinely performed under argon atmosphere using Schlenck techniques.

Photoanode preparation. The FTO glass used was from Hafordt glass TEC (15 Ω cm^{-2} resistance), was first cleaned in a detergent solution using an ultrasonic bath for 30 min, and then rinsed with water and ethanol and dried under air. Nanocrystalline TiO_2 (20 ± 5 nm particle size, Solaronix T/SP) was deposited onto a FTO by the doctor blade technique. The resulting electrodes were gradually heated under airflow at 325 ºC for 5 min, 375 ºC for 5 min, 450 ºC for 15 min and 500 ºC for 15 min. The heated electrodes were soaked into $TiCl_4$ aqueous solution 0.04 M at 70 ºC for 30 min and then washed with water and ethanol. Electrodes were heated again at 500 ºC for 30 min and cooled before dye adsorption. Film thickness was measured with an Ambios Technology XP-1 Profilometer to be 8 μm. The final area of the device was 1.5 cm^2. The slides were immersed in an aqueous solution (pH 5.0) of $[Ru(bpy)_2(4,4'\text{-}(PO_3H_2)_2bpy)](PF_6)_2$ (0.5 mM) and *tert*-butyl phosphonic acid (0.1 mM) for 15 h at room temperature in the dark to give **FTO/TiO_2-P-bpy-Ru, TiO_2-P-tBu/** photoanodes. Slides were soaked in clean aqueous solutions for an additional 15 h to remove excess complex from the surface before measurements were undertaken. Surface coverages (Γ in mol cm^{-2}) were estimated by absorbance measurements of slides (baseline corrected) by using the expression $\Gamma = A(\lambda)/\varepsilon(\lambda)/1000$.[4] In the measurement, the molar extinction coefficients (ε) for the complex was 10200 M^{-1} cm^{-1}, and A(λ) was the maximum absorbance of the sensitized slides. This gave a maximum surface coverage (Γ_0) of ~8.8 x 10^{-8} mol cm^{-2}.

Instrumentation and Measurements. All electrochemical experiments were performed on an IJ-Cambria CHI-660 potentiostat using a three-electrode cell with either Sodium Saturated Calomel Electrode (SSCE) or Ag/AgCl/NaCl 3.5 M as a reference electrode. The potentials were converted to NHE by using the expressions *V* (NHE) = *V* (SSCE) + 0.205 and *V* (NHE) = *V* (Ag/AgCl) + 0.236. Typical LSV experiments were carried out at a scan rate of 10 mV s^{-1}. 400 MHz Bruker Avance II Ultrashield spectrometer was used to carry out NMR spectroscopy at room temperature. Samples were run in D_2O with 2,2-Dimethyl-2-silapentane-5-sulfonate sodium salt (DSS) as an internal reference. UV–vis spectroscopy was performed on a Cary 50 Bio (Varian) UV–vis spectrophotometer with 1 cm quartz cells. Transient absorption spectroscopy (TAS) measurements were carried out on 1.5 cm^2 photoanode on a system similar to previously described.[5] All kinetic constants are described as half lifetime rates, which correspond to the time in which half of the *ΔO.D.* is found.

General Catalytic Procedures

Homogeneous photochemical oxidation: The photochemical experiments involved a three-component system: catalyst, photosensitizer and sacrificial electron acceptor. Irradiation was carried out with a 150 W xenon arc lamp equipped with a 400 nm cut-off filter to remove UV and IR radiation. The intensity of the radiation was approximately 0.1 W cm^{-2}. In a typical photocatalytic experiment were mixed **2,2$^+$** 0.01 mM, **$[Ru(bpy)_3]^{2+}$** 0.1 mM, 10 mM **$[Co(NH_3)_5Cl]Cl_2$** in a total volume of 4 mL of a D_2O:CF_3SO_3D mixture (pD 1.0), 10 mM 4-HSS and 5 mM DSS. The mixture was irradiated with visible light for 30 minutes. ^1H NMR in D_2O was registered and calculation of the yield of alkene conversion was made using the DSS resonances that is used as internal reference.

Nafion membrane modification.

The Nafion® membrane separating the two compartments of the cell was activated by the following procedure: a piece of about 12 mm diameter was cut from a larger sheet (H2Planet, N-117, 183 mm thick) and was submerged in a 0.1 M aqueous solution of H_2O_2 at 80 °C for 1 h. Then it was cleaned with water followed by 1 h at 80 °C in 0.1 M H_2SO_4 and finally for 1 more hour at 80 °C in pure water. After this procedure, it was stored at ambient temperature in pure water. The active section of the membrane, when mounted on the reactor, had a diameter of about 10 mm.

The polymerization of EDOT on the surface of the membrane was performed by the diffusion method, in a cell with two identical chambers where the solution of the reagents, EDOT and $FeCl_3$, were placed separately. The membrane

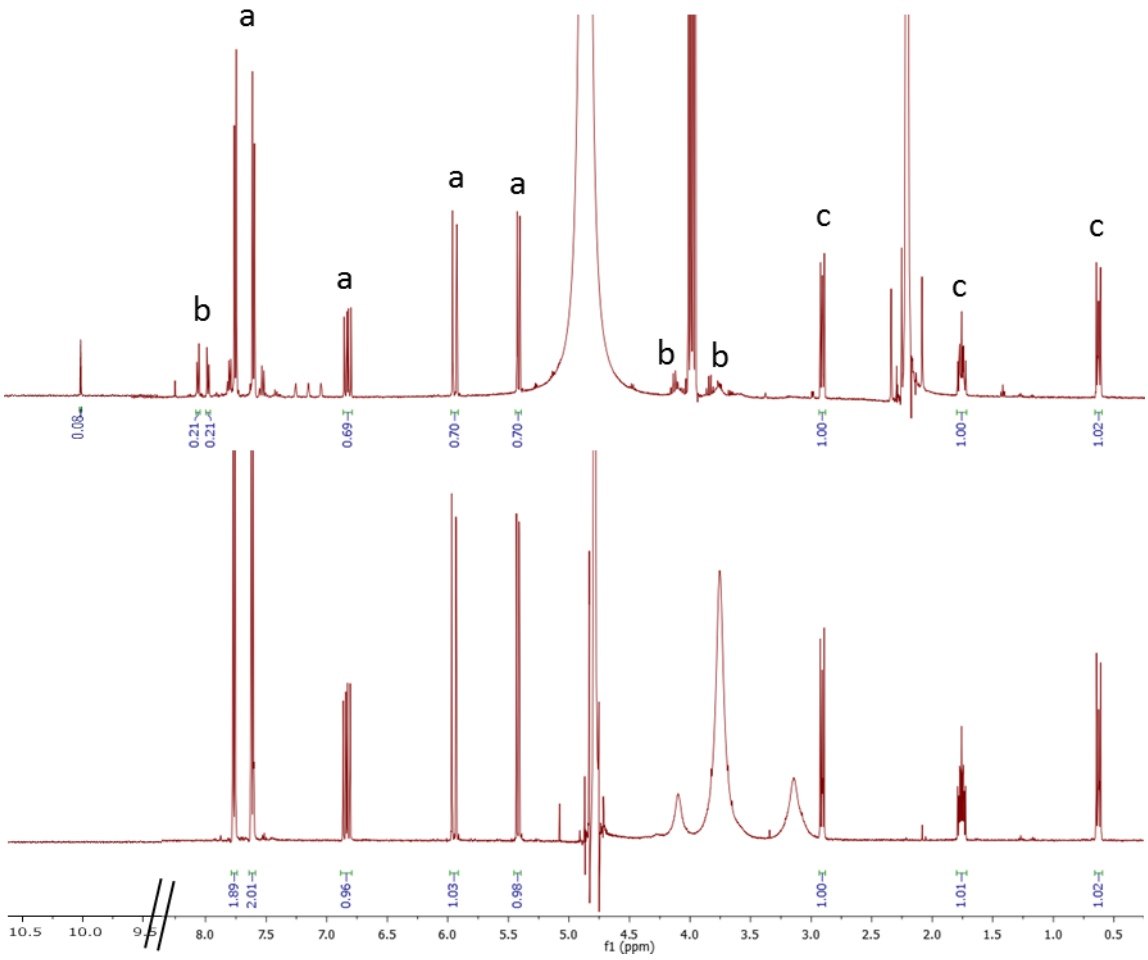
was set between both chambers. With this strategy, the EDOT diffuses through the membrane and it is oxidized in contact with $FeCl_3$, leading to the formation of the polymer on the surface of the membrane.

Dye-Sensitized Photoelectrochemical cell (DSPEC) construction and measurements.

A two compartment (H-shaped) reactor made of Pyrex glass with a water jacket to maintain constant the temperature was used as DSPEC. The photoanode described above was used as the working electrode. A platinum mesh was used as auxiliary electrode, and a Ag/AgCl/NaCl 3.5 M as a reference electrode. The electrolyte of both compartments contained 0.1 M $LiClO_4/HClO_4$ aqueous solution (pH 1.0).

For photochemical hydrogen evolution experiments, irradiation was carried out with a 150 W Xenon arc lamp equipped with a 400 nm cutoff filter to remove UV radiation. The intensity of the radiation was approximately 0.1 W/cm^{-2}. The temperature of the cell was maintained constant at 20 ^{o}C thanks to water circulation through the jacketed cell. Hydrogen evolution was analyzed with a gas-phase Clark-type hydrogen electrode (Unisense H2-N needle microsensor). The electrode was calibrated using nitrogen saturated and hydrogen saturated aqueous solutions, and further calibrated in the gas phase by known amounts of hydrogen inserted in the cell in the same set-up as used in our experiments. The conversion of the organic substrate was measured by ^{1}H-NMR.

Figure S1. ^{1}H-NMR of the photocatalytic oxidation of *para*-styrene sulfonic acid with **2,2^{+}** (400 MHz, 298 K, D_2O). Reaction conditions: **2,2^{+}** 0.01 mM/**4-HSS** 10 mM/**[Ru(bpy)$_3$]$^{2+}$** 0.1 mM/Co^{III} 10 mM/DSS 5 mM in 4 mL of a D_2O:CF_3SO_3D mixture (pD 1.0). Before (bottom) and after (top) irradiation with visible light for 30 min. For the NMR measurements, 0.5 mL of the reaction mixture was transferred to an NMR tube and a ^{1}H NMR experiment was done. The peaks corresponding to the NMR reference DSS were averaged as 2 in both samples, and were compared to the signals labeled as **a** and **b**, 4-HSS and diol derivative, respectively. The reaction conversion was calculated based on the disappearance of 4-HSS taking DSS as an internal reference, in a similar method described by Fukuzumi *et al*.[6] Therefore, the initial integration of **a** *vs.* **c** (2:1) corresponded to the initial concentrations of each substance, 10 and 5 mM. After the reaction, the integration of **a** *vs.* **c** was 1.4:1, corresponding to a concentration of 4-HSS of 7.0 mM and, thus, a conversion yield of 30%. An estimation of the formation of the diol is as follows: the integration of **b** *vs.* **c** was 0.21:1, corresponding to a concentration of the diol of 1.1 mM (11% yield), and the selectivity was 37%. The peak at 10.0 ppm corresponds to the formation of the aldehyde as a side product, with a concentration of 0.8 mM (8% yield). The aldehyde is formed because of substrate oxidation by $[Ru(bpy)_3]^{3+}$, as with a blank experiment without catalyst, the latter is formed in a 5% yield.



a Ressonances corresponding to 4-HSS. **b** Ressonances corresponding to the diol derivative. **c** Peaks for the aqueous NMR reference DSS.

Figure S2. UV-vis of **2,2**$^{+}$ 0.05 mM (black), **3,3**$^{+}$ (red) and **4,4**$^{+}$ (blue) generated in a bulk electrolysis experiment (approx two and four mols of electrons, respectively) at an applied potential of 0.79 V and 1.12 V in a 0.1 M triflic acid solution at pH 1.0.

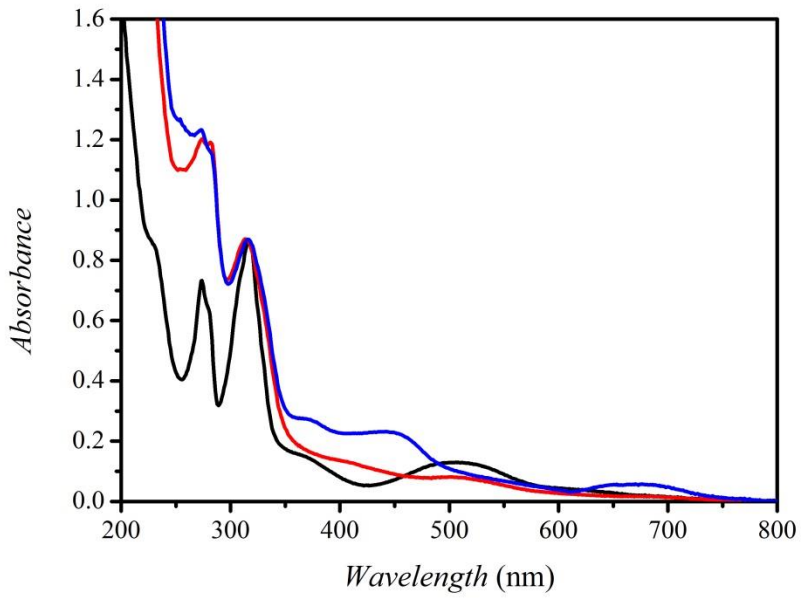


Figure S3. UV-vis spectra of a sensitized TiO_2 film (1 cm^2) obtained from a solution of 0.5 mM **P-bpy-Ru**$^{II,2+}$ and 0.5 0.5 mM *tert*-butylphosphonic acid (blue) or 0.1 mM *tert*-butylphosphonic acid (green).

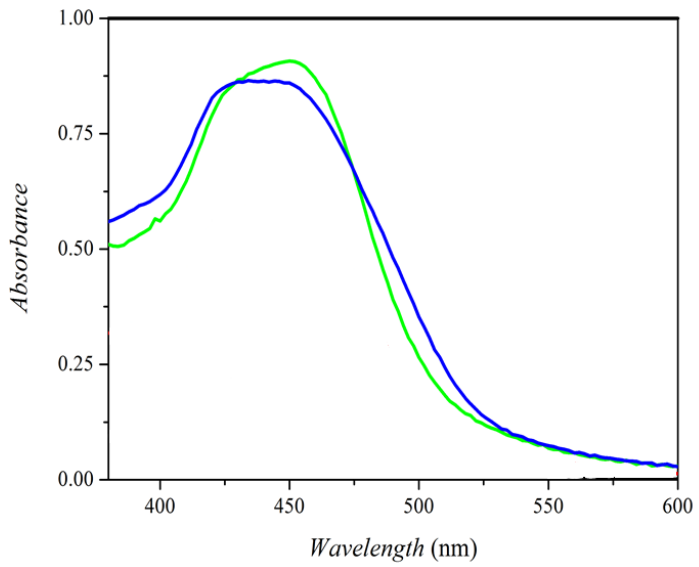


Figure S4. The Nafion-PEDOT membrane. (top left) SEM image of the modified proton exchange membrane prepared using 0.5 mM of EDOT and 60 minutes polymerization time. (bottom left) pH change *vs*. time for a two-compartment cell containing 10 mL of a 0.1 M sodium phosphate solution (pH 7.0) on one side and 10 mL of a 0.1 M triflic acid solution (pH 1.0) on the other, separated by a proton exchange membrane. The pH is measured on the side in which the pH at time 0 s is 7.0. The membranes used are Nafion® (black) and Nafion:PEDOT 0.5 mM/60 min polymerization (red). (bottom right) UV-vis kinetic traces followed at 452 nm for the adsorption of an aqueous solution of **bpy-Ru$^{II,2+}$** in the membrane (λ_{max} = 452 nm) using Nafion® (black line) and 0.5 mM/60 min polymerization time (red line).

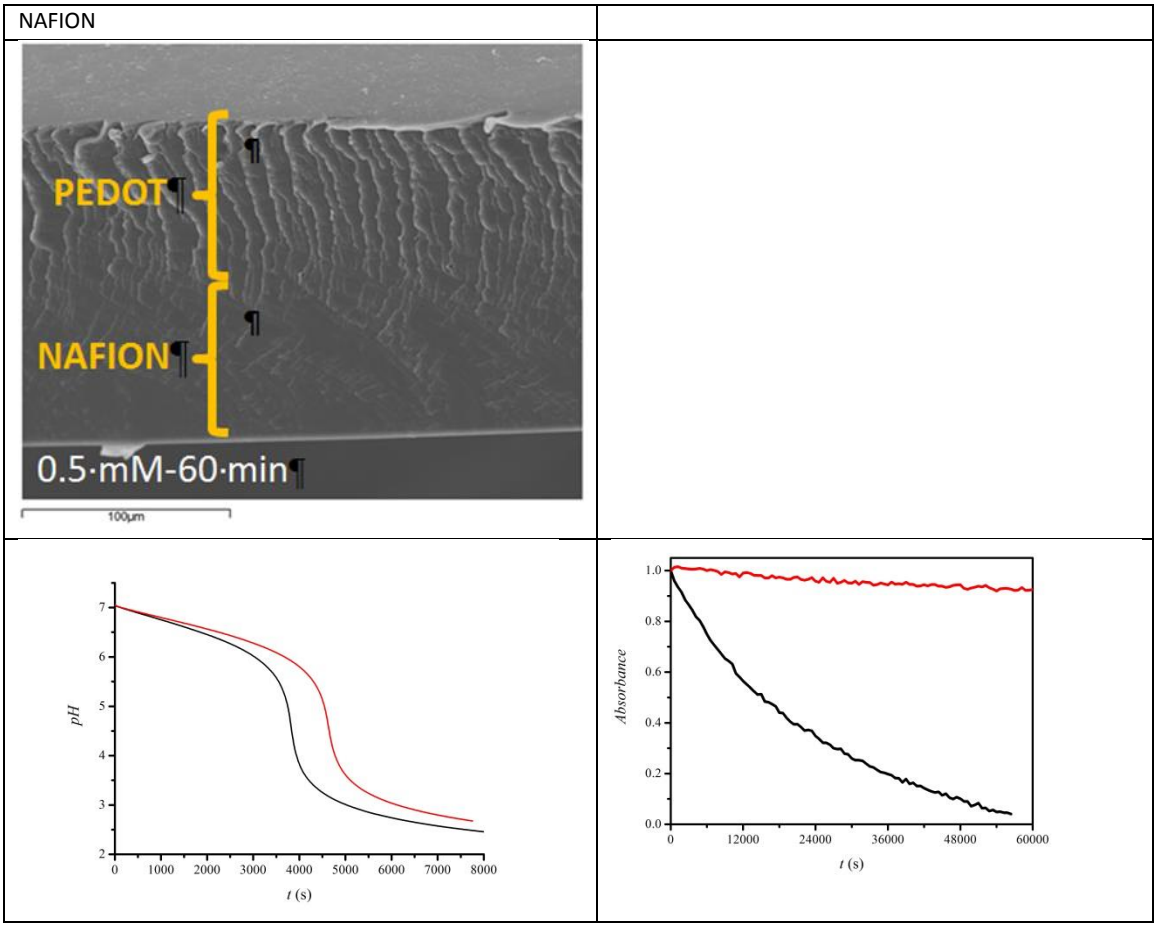


Figure S5. Photocurrent traces obtained by linear sweep voltammetry in a DSPEC cell upon irradiation with a Xe lamp (λ > 400 nm, 0.1 W cm^{-2}) at an applied bias of 0.3 V upon incremental addition of the catalyst **2,2**$^{+}$ in 0.1 M triflic acid solution (black line) or 0.1 M $LiClO_4$ in a 0.1 M $HClO_4$ solution (red line). The anodic half-cell contains **FTO/TiO_2-P-bpy-Ru, TiO_2-P-tBu/** (Γ = 8.8 x 10^{-8} mol cm^{-2}), **2,2**$^{+}$ at different concentrations and 4-HSS (10 mM), while the cathodic half-cell consists of a Pt mesh.

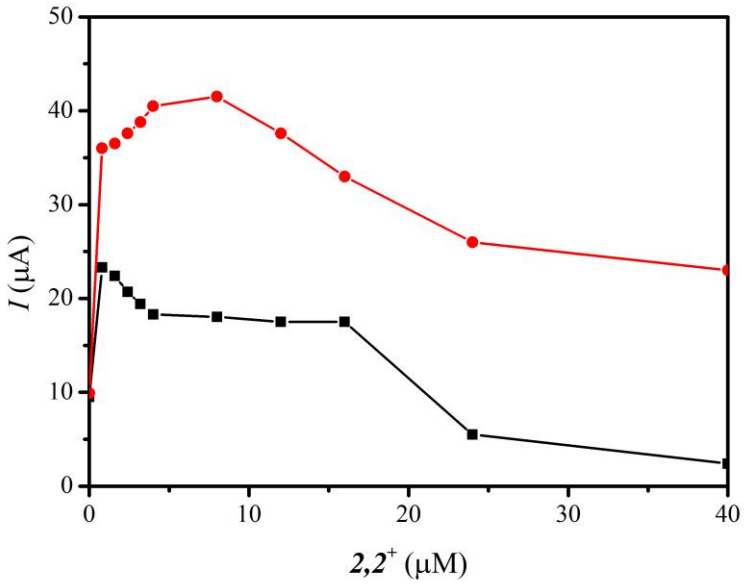


Figure S6. Linear sweep voltammetry or *I-V* curve of the DSPEC cell upon 1.5 AMG with a Xe lamp (λ > 400 nm, 0.1 W cm^{-2}) or without light (black line) at a scan rate of 10 mV s^{-1}. The anodic half-cell contains **FTO/TiO_2-P-bpy-Ru, TiO_2-P-tBu/** (Γ = 8.8 x 10^{-8} mol cm^{-2}) as the working electrode and 4-HSS 10 mM while the cathodic half-cell consists of a Pt mesh as auxiliary electrode. The supporting electrolyte solution is made of a 0.1 M $LiClO_4$ in a 0.1 M $HClO_4$ aqueous solution (pH 1.0) up to a total volume of 9 mL in each compartment. The concentration of **2,2**$^+$ varies from 0 μM (red line), 8 μM (green line) and 24 μM (blue line). It can be observed that without catalyst, the photocurrent obtained is negligible and almost comparable to the dark current. On the other hand, at high concentrations of the catalyst the photocurrent diminishes, most possibly due to higher recombination reactions between the TiO_2 and the catalyst.

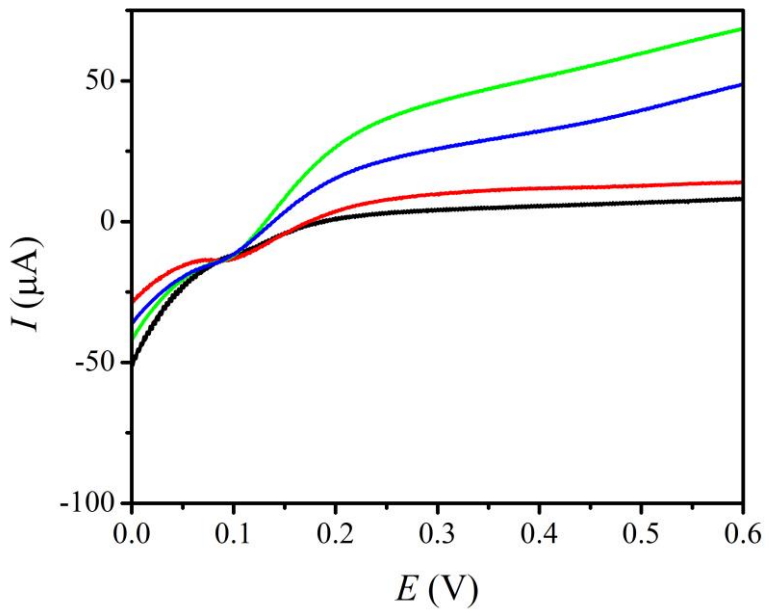
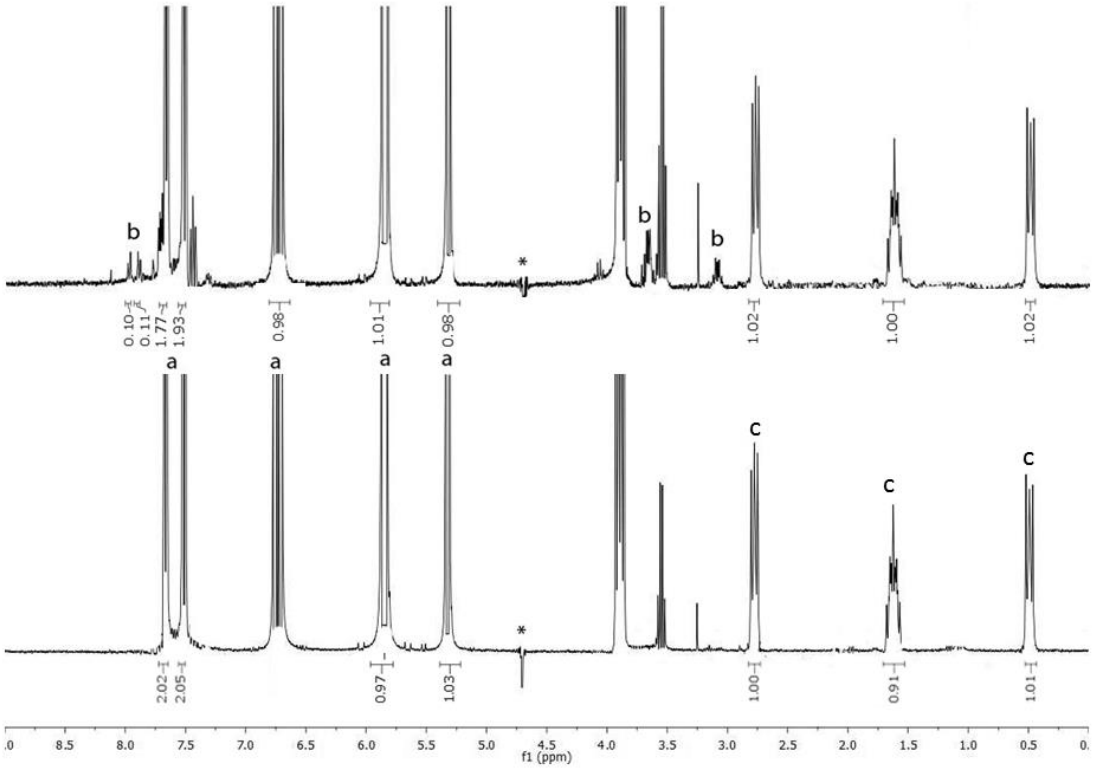


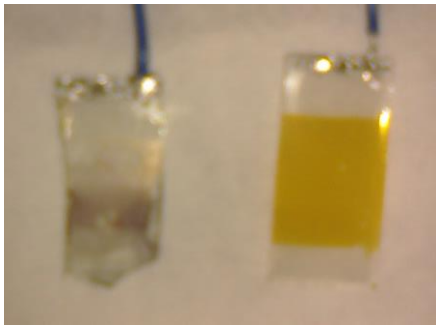
Figure S7. ^{1}H-NMR of photocatalytic oxidation of 4-HSS with **2,2^{+}** (400 MHz, 298 K, no solvent) in a DSPEC upon 1.5 AMG with a Xe lamp (λ > 400 nm, 0.1 W cm^{-2}). The anodic half-cell contains **FTO/TiO_2-P-bpy-Ru, TiO_2-P-tBu/** (Γ = 8.8 x 10^{-8} mol/cm^{2}) as the working electrode, 0.01 mM **2,2^{+}** as catalyst, 4-HSS 10 mM as substrate and 5 mM DSS as the reference. The cathodic half-cell consists of a Pt mesh as auxiliary electrode. In both cases the supporting electrolyte solution is made of a 0.1 M $LiClO_4$/$HClO_4$ aqueous solution (pH 1.0) up to a total volume of 9 mL in each compartment.

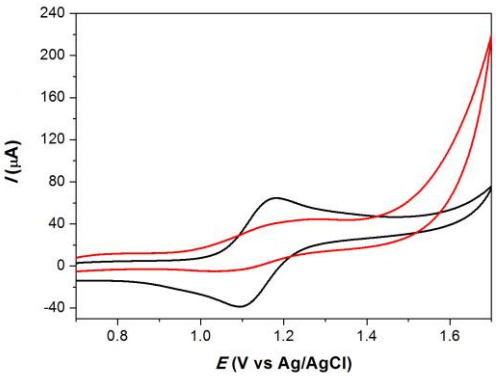
For the NMR measurements, 0.3 mL of the reaction mixture was transferred to an NMR tube and 0.2 mL of D_2O were added prior to the ^{1}H NMR experiment. The peaks corresponding to the NMR reference DSS were averaged as 2 in both samples, and were compared to the signals labeled as **a** and **b**, 4-HSS and diol derivative, respectively. The reaction conversion was calculated based on the disappearance of 4-HSS taking DSS as an internal reference, in a similar method described by Fukuzumi *et al.*[6] Therefore, the initial integration of **a** vs. **c** (2:1) corresponded to the initial concentrations of each substance, 10 and 5 mM. After the reaction, the integration of **a** vs. **c** was 1.86:1, corresponding to a concentration of 4-HSS of 9.3 mM and, thus, a conversion yield of 7%. An estimation of the formation of the diol is as follows: the integration of **b** *vs.* **c** was 0.10:1, corresponding to a concentration of the diol of 0.5 mM, and the selectivity was found to be 70%.



***** Solvent supression experiment, peak corresponding to H_2O is deleted automatically at 4.70 ppm. **a** Ressonances corresponding to NaSS. **b** Ressonances corresponding to the diol derivative. **c** Peaks for the aqueous NMR reference DSS.

Figure S8. (up) Photograph of the **FTO/TiO_2-P-bpy-Ru, TiO_2-P-tBu/** photoanode before (right) and after (left) the photochemical reaction. As can be seen, the orange color of the dye has disappeared due to the hydration of the ligands and subsequent de-attachment from the semiconductor. (down) Cyclic voltammetry before (black) and after (red) the photocatalytic reaction of the photoanode in the DSPEC cell. The working electrode is **FTO/TiO_2-P-bpy-Ru, TiO_2-P-tBu/**, the counter electrode is a platinum mesh and the reference electrode is Ag/AgCl/3.5 M NaCl, at a scan rate of 100 mV s^{-1}.





REFERENCES

[1] J. A. Broomhead, C. G. Young and P. Hood, *Inorg. Synth.,* 2007, **28**, 338-340.

[2] I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C. A. Bignozzi, P. Qu and G. J. Meyer, *Inorg. Chem*., 2001, **40**, 6073-6079.

[3] C. Di Giovanni, A. Poater, J. Benet-Buchholz, L. Cavallo, M. Solà and A. Llobet, *Chem. Eur. J.,* 2014, **20**, 3898.

[4] L. A. Gallagher, S. A. Serron, X. Wen, B. J. Hornstein, D. M. Dattelbaum, J. R. Schoonover and T. J. Meyer, *Inorg. Chem.,* 2005, **44**, 2089-2097.

[5] J. N. Clifford, E. Palomares, M. K. Nazeeruddin, M. Grätzel, J. Nelson, X. Li, N. J. Long and J. R. Durrant, *J. Am. Chem. Soc.,* 2004, **126**, 5225-5233.

[6] Y. Hirai, T. Kojima, Y. Mizutani, Y. Shiota, K. Yoshizawa and S. Fukuzumi, *Angew. Chem. Int. Ed.,* 2008, **47**, 5772-5776.