

Electronic Supplementary Information

Comparison of homogeneous and heterogeneous catalysts in dye-sensitised photoelectrochemical cells for alcohol oxidation coupled to dihydrogen formation

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Experimental Procedures

Materials and devices

All reagents and solvents were obtained from Sigma-Aldrich, Fluorochem, or VWR and used without purification unless described otherwise. Reactions were performed under atmospheric conditions unless otherwise noted. Dye-sensitised solar cells (DSSCs) and dye-sensitised photoelectrochemical cells (DSPECs) were illuminated with the following light source a LED light source (Zahner, TLS3, 50 or 100 mW cm⁻²), with the spectral output given in Figure S7. Quantification of the conversion of PhCH₂OH and PhCHO by Gas Chromatography (GC) was performed on a Trace GC Ultra machine (Interscience) with an RTX-1 column (30 m, 0.25 mm internal diameter, 0.25 μm film thickness), inlet temperature 70°C hold 2.00 minutes ramp 10°C min⁻¹ to 340°C with chlorobenzene as an internal standard (calibration curve, Figure S13). Hydrogen gas was quantified on a CompactGC (Interscience) equipped with a 5Å molecular sieve column (20 m length, 3.2 mm internal diameter), an oven temperature of 34°C, and a flow rate of argon of 2 mL min⁻¹.

Electrochemistry

Cyclic voltammograms were recorded on a PGSTAT10 potentiostat (Autolab) with either a glassy carbon working electrode (MetrOhm, diameter 3 mm) or FTO|TiO₂(|**S-TEMPO** or |**S-Benzene**) electrodes (0.19 cm²) clipped to a holder, a leakless Ag/AgCl reference electrode (eDAQ, ET069) and a Pt wire as a counter electrode. As electrolyte a 100 mM LiTFSI in MeCN solution is used and ferrocene^{0/+} (0.37 V vs. Ag/AgCl) was added after experiments

DRIFT measurements

Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was performed at room temperature on a Nicolet iS50 FTIR (Thermo Fisher, United States) spectrometer equipped with a fast-recovery deuterated triglycine sulfate (DTGS) detector. Samples were diluted to approximately 5 wt% in KBr powder (non-absorbing matrix) and finely ground in a mortar. The samples were placed in a Micro-sampling Cup (DRP-SX3), loaded into the Praying Mantis™ (Sample Holder, Harrick, United States). Pure KBr powder, also finely ground by a mortar, was measured to obtain a background spectrum. Before each measurement, the N₂ purge of the sample chamber was allowed to stabilise for 5 minutes after placing the Micro-sampling cup into The Praying Mantis™. A KBr beam-splitter was used to obtain spectra in the range between 4000 and 400 cm⁻¹ with a spectral bandwidth of 4.0 cm⁻¹ in diffuse reflection mode. Each spectrum was recorded by averaging 32 scans and displayed in absorbance or transmittance mode.

Cleaning of the FTO electrodes

The Fluorine doped Tin Oxide (FTO) electrodes (Solaronix, 2.2 mm, $15 \Omega \text{ sq}^{-1}$) were scrubbed with Deconex and rinsed with hot water, followed by wiping with an acetone-soaked tissue and air drying. The FTO electrodes were then rinsed with acetone, toluene, and ethanol and left to air dry in between. The FTO electrodes were then placed inside a glass container in a solution of a teaspoon of Deconex in Milli-Q and sonicated for 30 minutes. The sonication procedure was repeated with Milli-Q, and then ethanol and the electrodes were left to dry, after which the electrodes were treated with a UV–ozone generator (Ultra-Violet Products, PR-100) for a minimum of 30 minutes.

Preparation of the photoanode FTO/TiO₂

A clean FTO plate (Solaronix, 2.2 mm, $15 \Omega \text{ sq}^{-1}$) (10×5 cm) was added to a 40 mM TiCl₄ solution in Milli-Q (100 mL) and placed in the oven at 70°C for 30 min to create a TiO₂ blocking layer. The FTO plate was consecutively rinsed with Milli-Q then ethanol and air-dried. The electrodes were sintered with progressive heating (Programmer PR 5) from ambient temperature to 125°C (over 5 min, 25°C min⁻¹ ramp, hold 125°C for 5 min) then to 202°C (over 15 min, 5.1°C min⁻¹ ramp, hold 202°C for 5 min) to 375°C (over 5 min, 34.6°C min⁻¹ ramp, hold 375°C for 5 min) to 450°C (over 5 min, 15°C min⁻¹ ramp, hold 450°C for 15 min) to 500°C (over 5 min, 10°C min⁻¹ ramp, hold 500°C for 30 min). One mesoporous layer of TiO₂ nanoparticles (particle size 22–25 nm, Dyenamo DN-GPS-22OS, Anatase, Specific surface area 50 - 60 m² g⁻¹) was screen printed (43T screen with 0.79 cm² circles for DSPECs, 0.2 cm² circles for DSSCs) onto the cooled FTO plate thickness of layer after annealing (3.8 μm, Figure S14).¹ The plate was dried for 7 min on a hotplate set at 125°C and cooled to ambient temperature, before printing (43T screen) a scattering layer of TiO₂ (particle size > 100 nm, Solaronix Ti-Nanoxide R/SP, Specific surface area 15 m² g⁻¹) thickness of layer after annealing (6.4 μm, Figure S14) and sintered with progressive heating from ambient temperature to 125°C (over 5 min, 25°C min⁻¹ ramp, hold 129°C for 5 min) then to 202°C (over 15 min, 5.1°C min⁻¹ ramp, hold 202°C for 5 min) to 375°C (over 5 min, 34.6°C min⁻¹ ramp, hold 375°C for 5 min) to 450°C (over 5 min, 15°C min⁻¹ ramp, hold 450°C for 15 min) to 500° C (over 5 min, 10°C min⁻¹ ramp, hold 500°C for 30 min). The cooled sintered plate was soaked for 30 min at 70°C in a 40 mM TiCl₄ in Milli-Q and sintered with progressive heating from ambient temperature to 125°C (over 5 min, 25°C min⁻¹ ramp, hold 125°C for 5 min) then to 202°C (over 15 min, 5.1°C min⁻¹ ramp, hold 202°C for 5 min) to 375°C (over 5 min, 34.6°C min⁻¹ ramp, hold 375°C for 5 min) to 450°C (over 5 min, 15°C min⁻¹ ramp, hold 450°C for 15 min) to 500° C (over 5 min, 10°C min⁻¹ ramp, hold 500°C for 30 min) prior cooling to room temperature for sensitisation. The FTO|TiO₂ electrodes were sensitised with 0.5 mM **AP11** in a 1:1 *t*-BuOH/MeCN solution in the dark for 45 minutes for surface-functionalised experiments and long-term photosynthetic experiments overnight and rinsed afterwards with a 1:1 *t*-BuOH/MeCN solution and kept in the dark before use.

TiO₂ particles or FTO|TiO₂ electrode functionalisation with S-TEMPO or S-Benzene

TiO₂ (Sigma Aldrich, anatase, < 5µm) particles or FTO|TiO₂ electrodes were added to a vial and a mixture of 1% H₂O in MeCN (5 mL) containing either 2 mM **S-TEMPO** or 2 mM **S-Benzene** was added. Reference TiO₂ particles and FTO|TiO₂ electrodes were prepared by adding a blank solution of 1% H₂O in MeCN (5 mL). The solution was purged for 5 minutes with N₂ gas, after which the vial was closed with a screwcap and sealed with Parafilm. The mixture was heated to 70°C for 1, 2, 5, or 21 hours in the dark. The mixture was directly removed from the vial with a glass pipet, after which the TiO₂ particles or FTO|TiO₂ electrodes were rinsed with MeCN yielding (FTO|)TiO₂|**S-TEMPO** or (FTO|)TiO₂|**S-Benzene** particles or electrodes.

Preparation of the platinum counter electrodes

A clean, with one-hole predrilled (Diamond tip nr. 7134, Dremel-400) FTO plate (Solaronix, 2.2 mm, 15 Ω sq⁻¹) was added to a solution of concentrated 1M HCl_(aq) (37% w/v) in EtOH and sonicated for 30 minutes. The electrodes were rinsed with Milli-Q, EtOH and left to dry. Electrochemical deposition of platinum was performed using an aqueous PtCl₄ solution (10 mM PtCl₄, 50 mM HCl, 0.47 mM 3-(2-aminoethylamino)propyldimethoxymethylsilane) in a three-electrode system, with the FTO-plate as the working electrode (WE), Ag/AgCl (leakless, eDAQ, ET069) reference electrode (RE) and a Pt-mesh counter electrode (CE). The platinum was deposited onto the FTO- electrodes by chronoamperometry (galvanostatic) employing a set current of -0.025 A vs. Ag/AgCl over 30 seconds with a PGSTAT10 potentiostat (Autolab), yielding a black hue at the FTO-electrodes. Finally, the FTO|Pt electrodes were rinsed with demi water and ethanol and left to air dry before use.

Construction of dye-sensitised solar cells (DSSCs)

Sensitised TiO₂ photoanodes and Pt counter electrodes were sandwiched together using a hotmelt ionomer (60 µm, Meltonix polymer 1170-60, Solaronix, Switzerland) and a soldering iron (320°C, Weller, PU-81). The electrolyte (1.2 M LiTFSI, 1.0 M **TEMPO**, 0.1 M **TEMPO(BF₄)**) in MeCN) was introduced into the cells by vacuum backfilling. The outside of the cell was thoroughly cleaned by wiping the cell with a tissue moistened with EtOH before sealing with more Meltonix and a glass coverslip, using a soldering iron (320°C) to melt the polymer. The DSSCs were measured masked (0.07 cm²) by using a P211 potentiostat (Zahner TLS3, 100 mW cm⁻¹ LED lamp).

Illumination setup for of the dye-sensitised photoelectrochemical cells (DSPECs)

Photoreactor composed of 2 Teflon compartments is separated by a Nafion-177 membrane (FuelCellStore). The working compartment contained the photoanode (masked size 0.64 cm²) as a WE and an Ag/AgCl (leakless, eDAQ, ET069) RE and was filled with a solution of 1.2 M LiTFSI, in MeCN (3 mL). The counter electrode compartment containing a Pt electrodeposited on FTO was filled with a solution of MeCN with 1.2 M LiTFSI (3 mL). The top contains a large opening with a septum to add or remove electrolyte and/ or substrate or sample aliquots of the reaction mixture. Chronoamperometric photocurrent measurements at 0 V vs. Ag/AgCl were obtained using P211 potentiostat (Zahner). Chopped-light experiments were performed by 90s illumination and 90 s dark while using a LED light source (Zahner, TLS3, 100 mW cm⁻², Figure S7) for a period of 30 minutes. Benzyl alcohol (30 μL, 290 μmol) was added to the working compartment after 10 and 20 minutes. For long term photosynthesis experiments was the WEC was filled with a solution of 1.2 M LiTFSI, 1.0 M **TEMPO**, 0.1 M PhCH₂OH, and 19.65 mM chlorobenzene as an internal standard in MeCN (3 mL), and the counter electrode compartment was filled with a solution of MeCN with 1.2 M LiTFSI, 1.0 M AcOH and 19.65 mM chlorobenzene (3 mL). The photoanode was illuminated with an LED light source (Zahner, TLS3, 50 mW cm⁻², Figure S7) for a period of 32 hours. To monitor the reaction, GC samples were taken during the measurement and diluted in MeCN. The counter electrode compartment was attached to a Gas GC to measure H₂ evolution. An initial spike of benzaldehyde, due to store-bought compounds seen in all measurements, was subtracted for clarity. (Original data, Table S3). The integration of half the photocurrent determines the number of electrons to account for two electrons needed per oxidation reaction. The photocurrent is shown in Figure S6.

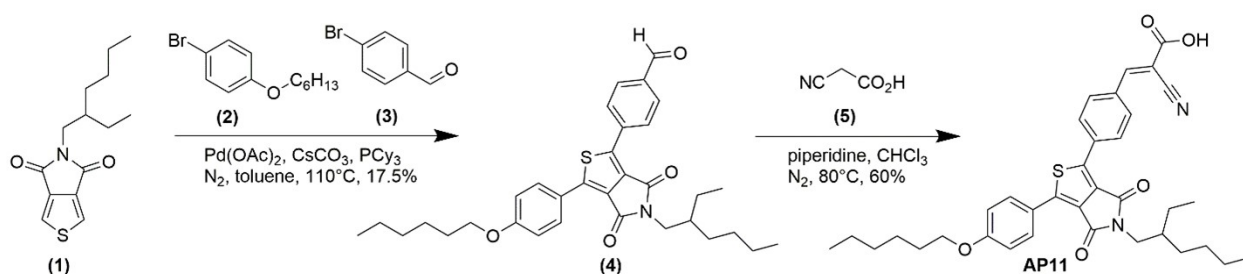
Discussion on the difference in the amount of (S-)TEMPO in hetero- or homogenous systems.

The immobilised **S-TEMPO** has 18 nmol cm⁻¹ at the surface, while experiments performed with homogenous **TEMPO**, a concentration of 1 M in the anolyte, is used (akin to DSSCs). However, a one-on-one comparison between “concentrations” heterogenous and homogenous systems cannot be made. It is noteworthy that the difference in the amount of **(S-)TEMPO** seems rather large. The immobilised **S-TEMPO** is assumed to stay in close proximity to the photosensitiser, yielding a high local concentration of redox-mediating catalyst at the surface. To ensure the concentration difference between the homo- and heterogeneous systems is not the leading cause of photocurrent enhancement, an experiment with lower **TEMPO** concentration is performed, and results are shown in Figure S18. We surmise that a higher concentration (1 M **TEMPO**) is necessary to establish an ideal to a steady state of **TEMPO^{0/+}** within the long-term DSPEC. With lower amounts of **TEMPO**, the device risks limitations in dye regeneration due to all **TEMPO** converted to **TEMPO⁺**.

Synthesis and Characterisation

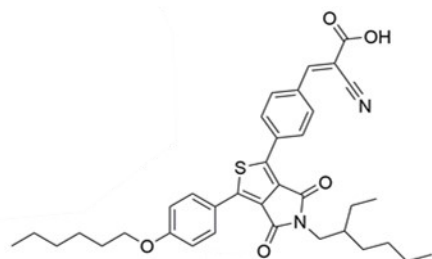
Materials and methods

All reagents and solvents were obtained from Sigma-Aldrich, Fluorochem, or VWR and used without purification unless described otherwise. DCM and toluene were dried in a solvent purification system. Column Reactions were performed under atmospheric conditions unless otherwise noted. Column chromatography was performed using silica gel (SiliCycle, SiliaFlash P60, 40–63 μm , 230–400 mesh) while fractions were analysed using TLC (TLC silica gel 60 F₂₅₄, Merck KGaA) visualised with 254/350 nm light. ¹H-NMR spectra were recorded on a Bruker AV400 spectrometer, with chemical shifts reported in ppm relative to tetramethylsilane by referencing the residual solvent signal. High-resolution mass spectrometry (HR-MS) was measured on an AccuTOF GC v 4g, JMS-T100GCV mass spectrometer (JEOL, Japan) equipped with field desorption (FD) emitter, Carbotec (Germany), FD 13 μm . Current rate 51.2 mA min⁻¹ over 1.2 min machine using FD as ionisation method.



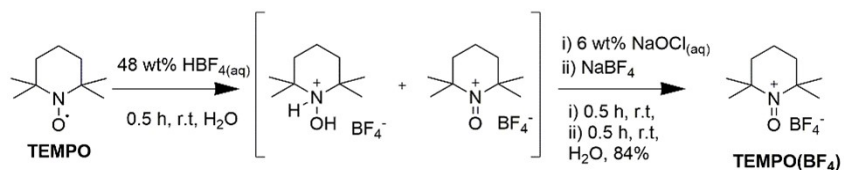
Scheme 1: Synthesis of AP11.²

Synthesis of AP11



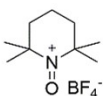
Following the literature procedure,² 5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**1**) (0.050 g, 0.19 mmol 1 eq), 1-bromo-4-(hexyloxy)benzene (**2**) (0.048 g, 0.19 mmol, 1 eq.), 4-bromobenzaldehyde (**3**) (0.034 g, 0.19 mmol, 1 eq.), were added to a flame-dried flask. Toluene (2 mL) was added, and the solution was bubbled with N₂. Then, Pd(OAc)₂ (4.2 mg, 0.019 mmol, 10 mol %), tricyclohexylphosphine (0.010 g, 0.035 mmol, 20 mol %), and Cs₂CO₃ (0.073 g, 0.22 mmol, 1.2 eq.) were added to the solution. The mixture was stirred for 16 hours at 110°C under an inert atmosphere. After cooling, H₂O (5 mL) was added to the mixture. The mixture was extracted with Et₂O (3 × 10 mL), and the organic layer was separated, dried (Na₂SO₄), and filtered. The solvent was removed with rotary evaporation, and the residue was purified via column chromatography (Silica) using 10% ethyl acetate/hexane as eluent collecting the 2nd fraction. The intermediate (4-

(5-(2-ethylhexyl)-3-(4-(hexyloxy)phenyl)-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c] pyrrol-1-yl) benzaldehyde (**4**) was isolated as a yellow solid and used without further purification. The yellow solid (18 mg, 0.033 mmol, 1 eq.), cyanoacetic acid (**5**) (13 mg, 0.1 mmol 3 eq.), piperidine (few drops), and CHCl₃ (3 mL) were added to an oven-dried pressure tube. The pressure tube was sealed under N₂ and stirred at 80°C for 16 h, after which it was cooled to ambient temperature, acidified with acetic acid (~1.0 mL), and partitioned between Et₂O (5 mL) and H₂O (5 mL). The organic layer was separated, and the solvents were removed by rotary evaporation to afford a yellow solid, which was subjected to column chromatography (silica) with a mixture of 5% methanol/dichloromethane. The product **AP11** (E)-2-Cyano-3-(4-(5-(2-ethylhexyl)-3-(4-(hexyloxy)phenyl)-4,6-dioxo-5,6-dihydro-4H-thieno[3,4-c] pyrrol-1-yl)phenyl) acrylic acid was obtained as a yellow solid (12.4 mg, 0.020 mmol, 11%). ¹H NMR (400 MHz, CDCl₃) δ 8.38 – 8.30 (m, 3H), 8.14 (d, *J* = 8.5 Hz, 4H), 7.01 (d, *J* = 8.7 Hz, 2H), 4.09 – 4.01 (m, 2H), 3.61 (d, *J* = 7.4 Hz, 2H), 1.90 – 1.78 (m, 3H), 1.49 (d, *J* = 7.8 Hz, 2H), 1.40 – 1.33 (m, 10H), 1.00 – 0.88 (m, 11H). FD-MS *m/z* calcd [M⁺] for C₃₆H₄₀N₂O₅S: 612.2663 Found: 612.2654

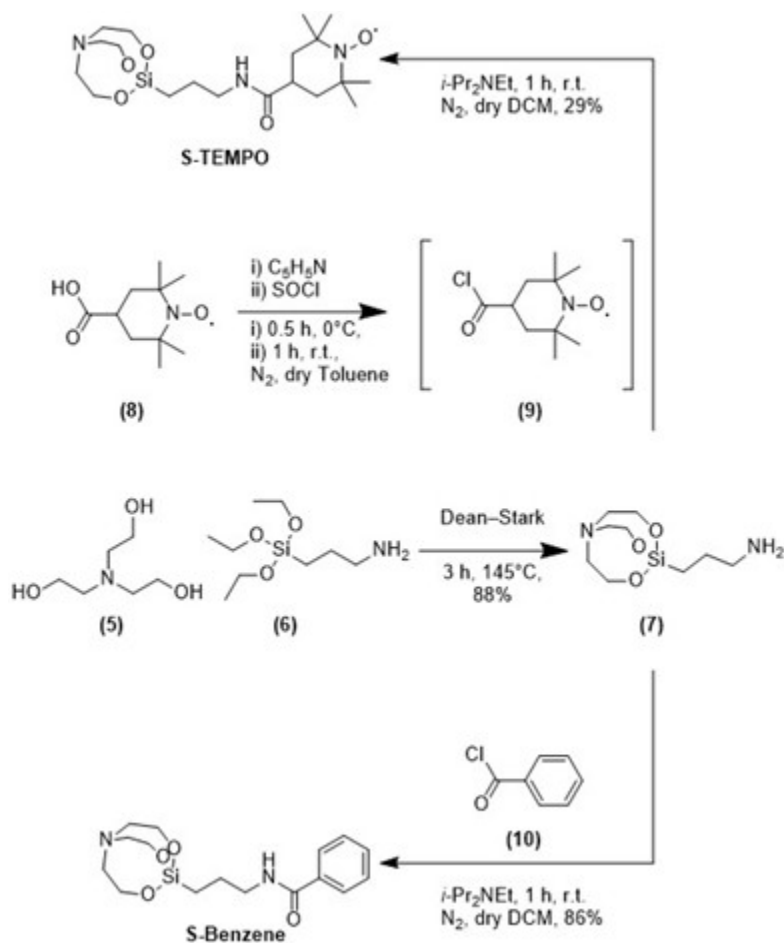


Scheme 2. Synthesis of TEMPO(BF₄).³

Synthesis of TEMPO(BF₄)

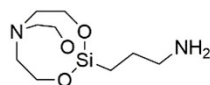


TEMPO(BF₄) was synthesised according to literature procedures.³ **TEMPO** (2,2,6,6-tetramethylpiperidine 1-oxyl, 0.53 g, 2.5 mmol, 1 eq.) and deionized water (1 mL) were added in a round bottom flask. The thick orange slurry was stirred vigorously with a large stir bar. HBF_{4(aq)} (48% w/v, 0.39 mL, 3 mmol, 1.14 eq.) was added while vigorously stirring the orange reaction mixture, causing a colour change to yellow. After 0.5 hours, NaOCl_(aq) (6% w/v, 1.39 mL, 1.25 mmol, 0.5 eq.) was dropwise added to reaction mixture dropwise over 0.5 hours. NaBF₄ (0.27 g, 2.5 mmol, 1 eq.) was added, and the mixture was stirred for 10 minutes, before cooling the mixture at 5°C overnight and filtered, to obtain the product **TEMPO(BF₄)** as a yellow solid (0.52 g, 2.1 mmol, 84%) ¹H NMR (400 MHz, CD₃CN) δ 2.48 (s, 4H), 2.26 – 2.14 (m, 1H), 1.85 – 1.34 (m, 12H).



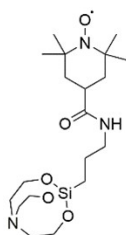
Scheme 3. Synthesis of **S-TEMPO** and **S-Benzene**.⁴

Synthesis of 3-aminopropylsilatrane



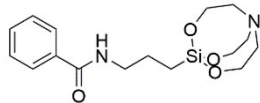
3-aminopropylsilatrane (**7**) was synthesised according to a literature procedure.⁴ Triethanolamine (**5**) (2.3 mL, 21.375 mmol, 1 eq.) and 3-aminopropyl(triethoxy)silane (**6**) (5.3 mL, 22.5 mmol, 1.05 eq.) combined in a round-bottomed flask fitted with a Dean-Stark apparatus under an N₂ flow and stirred. The mixture was heated from room temperature to 145°C and refluxed for 3 hours. Then, the reaction mixture was cooled to room temperature before refrigerating overnight at 4°C. The white solid was washed with hexane, filtered, dried under vacuum, obtaining the product (**7**) (4.4 g, 18 mmol, 88% yield). ¹H NMR (300 MHz, CDCl₃) δ 3.78 (t, *J* = 5.8 Hz, 6H), 2.82 (t, *J* = 5.8 Hz, 6H), 2.65 (t, *J* = 6.9 Hz, 2H), 1.54 (ddt, *J* = 11.5, 8.6, 7.0 Hz, 2H), 0.49 – 0.37 (m, 2H).). FD-MS *m/z* calcd [M⁺] for C₉H₂₀N₂O₃Si: 233.1221 Found: 233.1327.

Synthesis of S-TEMPO



S-TEMPO was synthesised according to a literature procedure.⁴ 4-carboxy-TEMPO (**8**) (100 mg, 0.5 mmol, 1 eq.) was dissolved in anhydrous toluene (5 mL), yielding an orange solution. Pyridine (0.1 mL, 1.2 mmol, 2.4 eq.) was added to the solution, and the mixture was cooled to 0°C and bubbled with N₂. SOCl₂ (0.06 mL, 0.75 mmol, 1.5 eq.) was added dropwise, and the solution turned red. The mixture was stirred at room temperature for 1 h, and a red precipitate was observed. The red-coloured liquid layer was separated and washed with anhydrous toluene (5 mL). The combined liquid fractions were concentrated in vacuo giving intermediate (**9**). The red solid was dissolved in anhydrous DCM (3 mL) and bubbled with N₂ giving a red solution. 3-aminopropylsilatrane (**7**) (140 mg, 0.6 mmol 1.2 eq) was added to a separate solution of anhydrous DCM (4 mL) whereafter *i*-Pr₂NEt (0.16 mL, 0.92 mmol, 1.8 eq) was added. The mixture was stirred and bubbled with N₂ until dissolved, giving a clear mixture. The red mixture containing (**9**) was added to the stirring solution. The red solution was stirred for 1 hour at room temperature under N₂ pressure. The reaction mixture was concentrated under N₂ flow, and a red/orange solid was precipitated from DCM by adding *n*-pentane. The solvent was removed with a syringe, and the orange solid was dried over N₂ flow. The resultant orange powder was redissolved in DCM (15 mL) washed 1% NaHCO_{3(aq)} (3 × 10 mL) and brine (10 mL). The organic layer was dried over MgSO₄ and filtered. The solvent was evaporated under reduced pressure giving the product **S-TEMPO** as an orange solid (60 mg, 0.14 mmol, 29%). DRIFT: σ (cm⁻¹): 2932, 2873, 1657, 1549, 1453, 1130, 1098, 765. FD-MS m/z calcd [M⁺] for C₁₉H₃₆N₃O₅Si: 414.2424 Found: 414.2441.

Synthesis of S-Benzene



The synthesis of **S-Benzene** was inspired by literature procedures.⁴ Benzoyl chloride (**10**) (0.12 mL, 0.72 mmol, 1 eq) was dissolved in anhydrous DCM (3 mL) and bubbled with N₂ affording a colourless solution. 3-aminopropylsilatrane (**7**) (140 mg, 0.6 mmol 1.2 eq) was added to a separate solution of anhydrous DCM (4 mL) whereafter *i*-Pr₂NEt (0.16 mL, 0.92 mmol, 1.8 eq) was added. The mixture was stirred and bubbled with N₂ until dissolved, giving a clear mixture. The benzoyl chloride solution was added to the stirring solution. The colourless solution was stirred for 1 hour at room temperature under N₂ pressure. The reaction mixture was concentrated under N₂ flow, and a white solid was precipitated from DCM by adding *n*-pentane. The supernatant solvent was removed with a syringe, and the white solid was dried over N₂ flow. The resultant white powder was redissolved in DCM (15 mL) washed with 1% NaHCO_{3(aq)} (3 × 10 mL) and brine (10 mL). The organic layer was dried over MgSO₄ and filtered. The solvent was evaporated under reduced pressure giving the product **S-Benzene** as a white solid (210 mg, 0.62 mmol, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.74 (m, 2H), 7.53 – 7.36 (m, 3H), 6.84 (s, 1H), 3.78 (t, J = 5.8 Hz, 6H), 3.47 (q, J = 6.3 Hz, 2H), 2.83 (t, J = 5.8 Hz, 6H), 1.86 – 1.74 (m, 2H), 0.65 – 0.46 (m, 2H). DRIFT: σ (cm⁻¹): 2974, 2949, 2857, 1638, 1549, 1130, 1089, 777, 714. ESI⁺-MS m/z calcd [M-H⁺] for C₁₆H₂₄N₂O₄Si: 337.1584 Found: 337.1579.

Figures and Tables

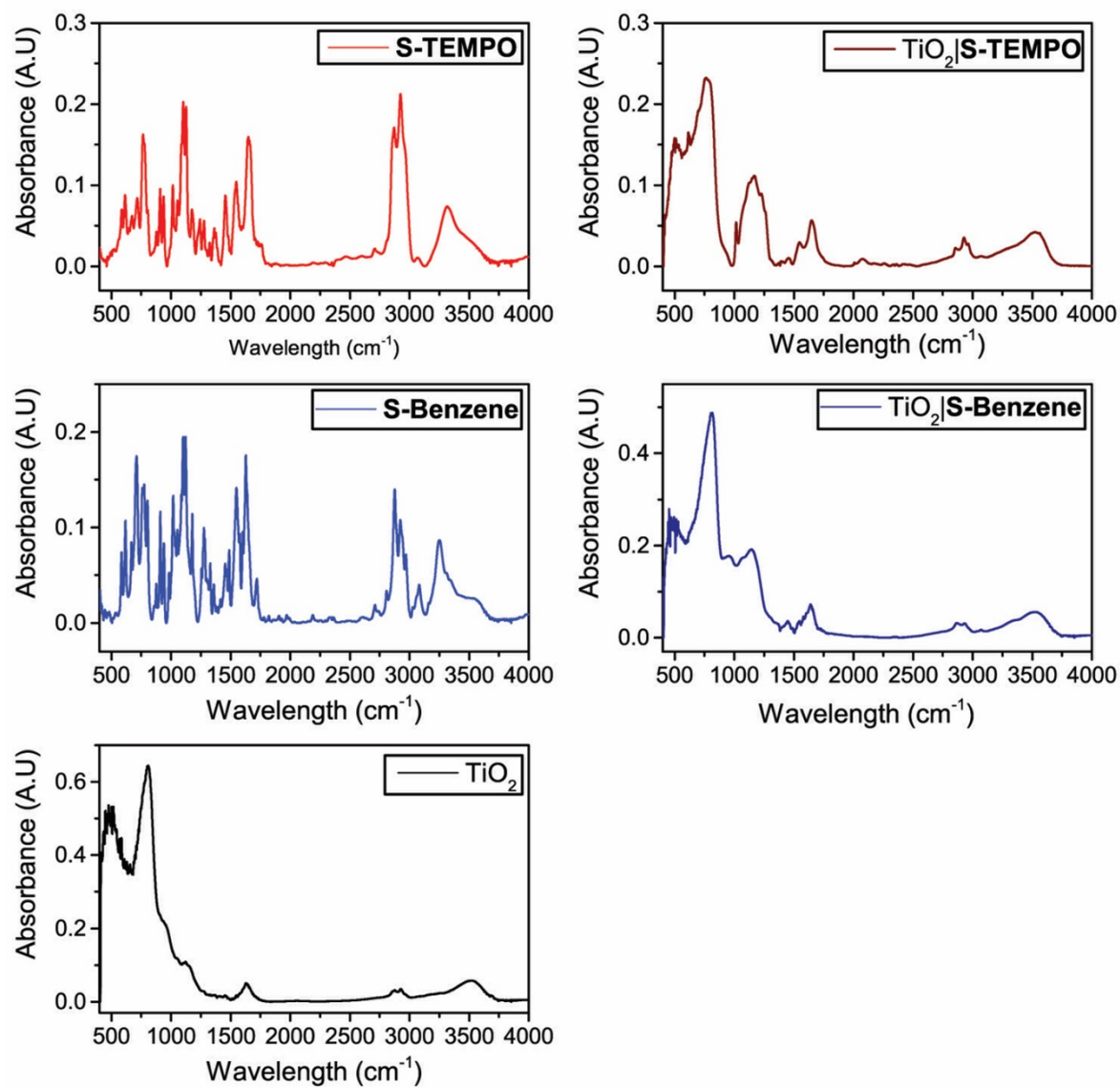


Figure S1. Full DRIFT spectra of **S-TEMPO** (red) and **S-Benzene** (light blue) free and on TiO₂ support (**S-TEMPO** = maroon, **S-Benzene** = marine) with unfunctionalised TiO₂ black).

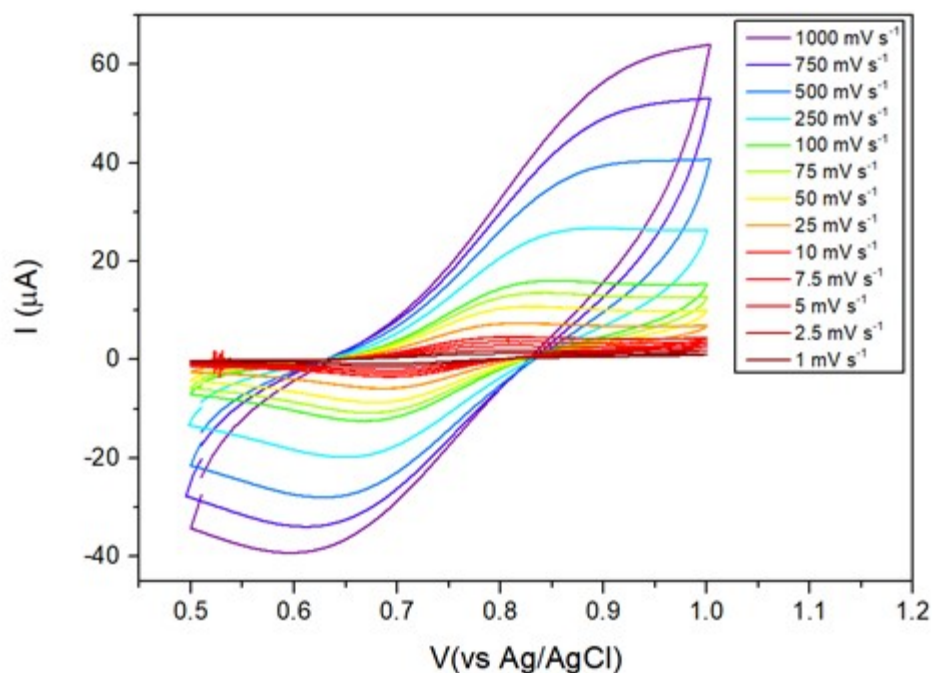


Figure S2. Cyclic voltammetry measurements with various scan rates of FTO|TiO₂|S-TEMPO as working electrode. Conditions: area TiO₂ = 0.19 cm², reference electrode = Ag/AgCl, counter electrode = Pt wire, electrolyte = 100 mM LiTFSI in MeCN

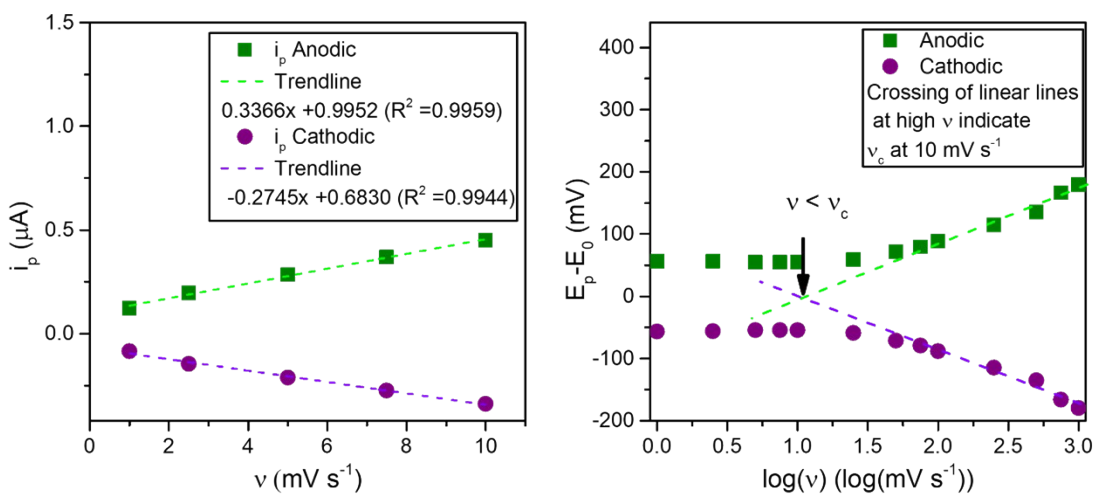


Figure S3. Data deduced of cyclic voltammetry measurements with various scan rates of FTO|TiO₂|S-TEMPO as working electrode Left) anodic (green) and cathodic peak (purple) peak current (i_p) plotted against the scan rate (v) and their linear trendlines Right) Trumpet plot of the difference in peak potential and half wave potential of anodic (green) and cathodic peak (purple) peak potentials plotted against the $\log(v)$. The cross-section of the linear lines of the variable scan rate (v) is considered the critical scan rate (v_c). Conditions: area TiO₂ = 0.19 cm², reference electrode = Ag/AgCl, counter electrode = Pt wire, electrolyte = 100 mM LiTFSI in MeCN

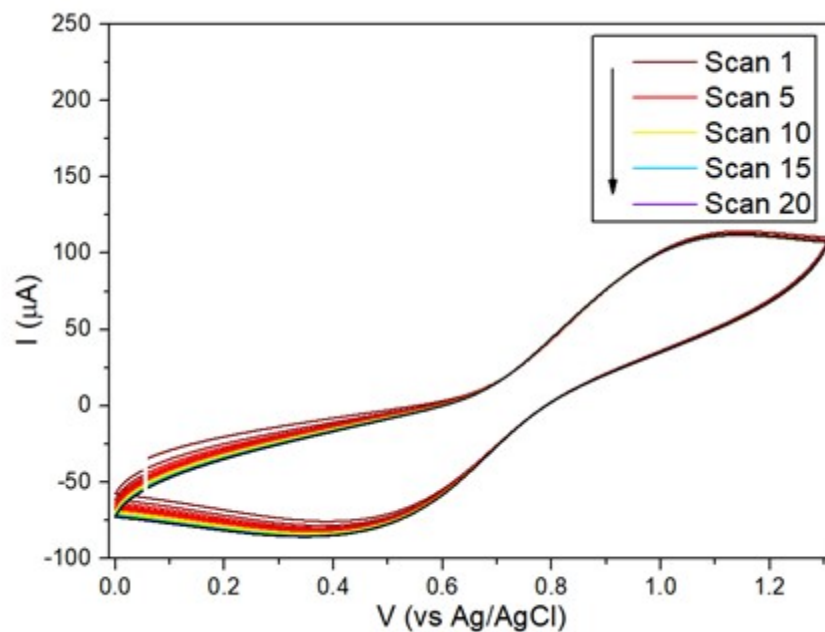


Figure S4. Multiple scans of cyclic voltammetry with of FTO|TiO₂|S-TEMPO as working electrode. Conditions: area TiO₂ = 0.19 cm², reference electrode = Ag/AgCl, counter electrode = Pt wire, electrolyte = 100 mM LiTFSI in MeCN scan rate 1 V s⁻¹

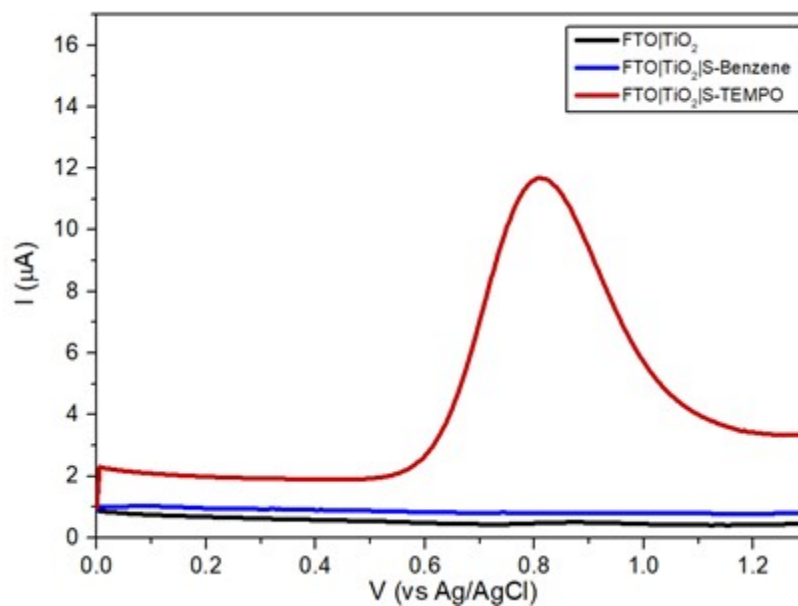


Figure S5. Differential pulse voltammetry with of FTO|TiO₂|S-TEMPO as a working electrode. Concentration was determined by

$$T = \frac{Q}{nFA}$$

using the integration of the current (Q) of FTO|TiO₂|S-TEMPO subtracted by FTO|TiO₂, $n=1$, F = Faraday constant, and A is area TiO₂ = 0.19 cm². Conditions: reference electrode = Ag/AgCl, counter electrode = Pt wire, electrolyte = 100 mM LiTFSI in MeCN

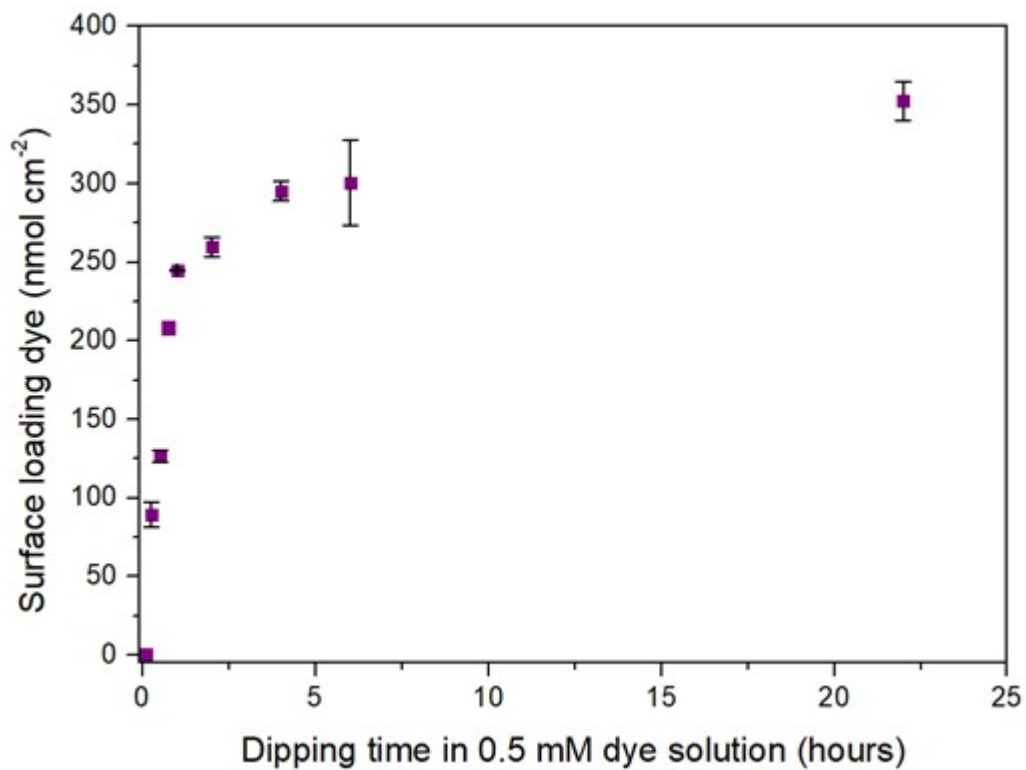


Figure S6. Dye leaching experiment with \varnothing 0.5 cm TiO₂ electrodes dipped for 24 hours in a DMF 1 % 1 M TBAOH (1 mL) in MeOH.

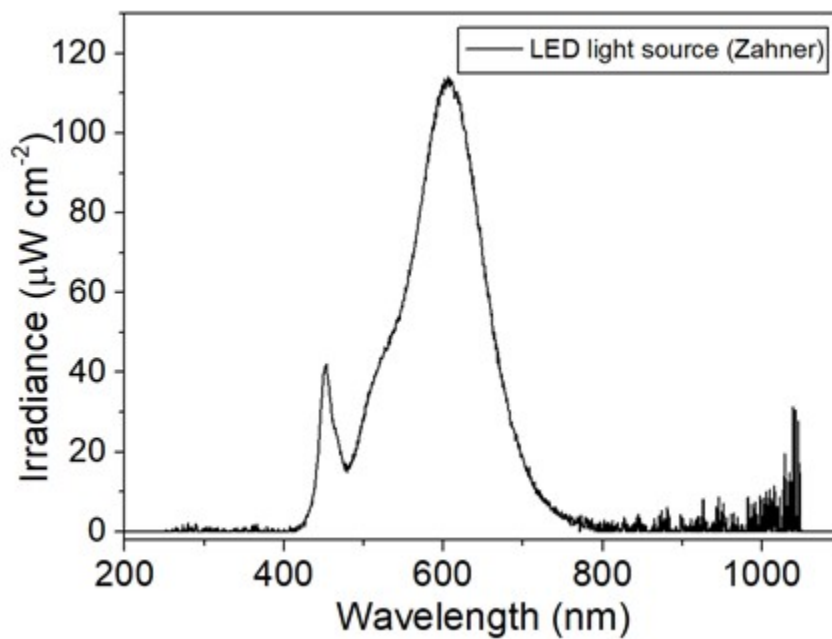


Figure S7. Reference spectra of used illumination source: LED light source (Zahner, TLS3, 50 mW cm⁻²)

Table S1. Data of **TEMPO**^{0/+}-based FTO|TiO₂|**AP11**_{0.5} sandwich DSSC devices with and without functionalisation over various amounts of dipping times with **S-TEMPO** and **S-Benzene** and the standard deviation in brackets (*N*=3). The DSSC consist of a WE (FTO|TiO₂|**AP11**_{0.5}) and a CE (FTO Pt electrodeposited) Electrolyte (1.2 M LiTFSI, 1.0 M **TEMPO** and 0.1 M **TEMPO**(BF₄) in MeCN), with a 0.07 cm² masked and a 4.71 μL volume.

Entry	Dipping (h)	Surface modification	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
1	1	None	1.75 (± 0.166)	0.426 (± 0.021)	0.43 (± 0.004)	3.33 (± 0.486)
2	5	None	1.75 (± 0.341)	0.433 (± 0.004)	0.45 (± 0.014)	3.42 (± 0.595)
3	21	None	1.74 (± 0.006)	0.454 (± 0.004)	0.46 (± 0.004)	3.43 (± 0.576)
4	1	S-Benzene	1.94 (± 0.091)	0.331 (± 0.016)	0.43 (± 0.004)	2.78 (± 0.234)
5	5	S-Benzene	2.13 (± 0.368)	0.400 (± 0.057)	0.45 (± 0.014)	3.78 (± 0.239)
6	21	S-Benzene	2.12 (± 0.030)	0.375 (± 0.050)	0.46 (± 0.004)	3.62 (± 0.496)
7	1	S-TEMPO	1.33 (± 0.438)	0.352 (± 0.023)	0.45 (± 0.007)	2.11 (± 0.797)
8	5	S-TEMPO	0.97 (± 0.117)	0.425 (± 0.018)	0.45 (± 0.002)	1.88 (± 0.498)
9	21	S-TEMPO	0.47 (± 0.016)	0.423 (± 0.28)	0.45 (± 0.001)	0.88 (± 0.087)

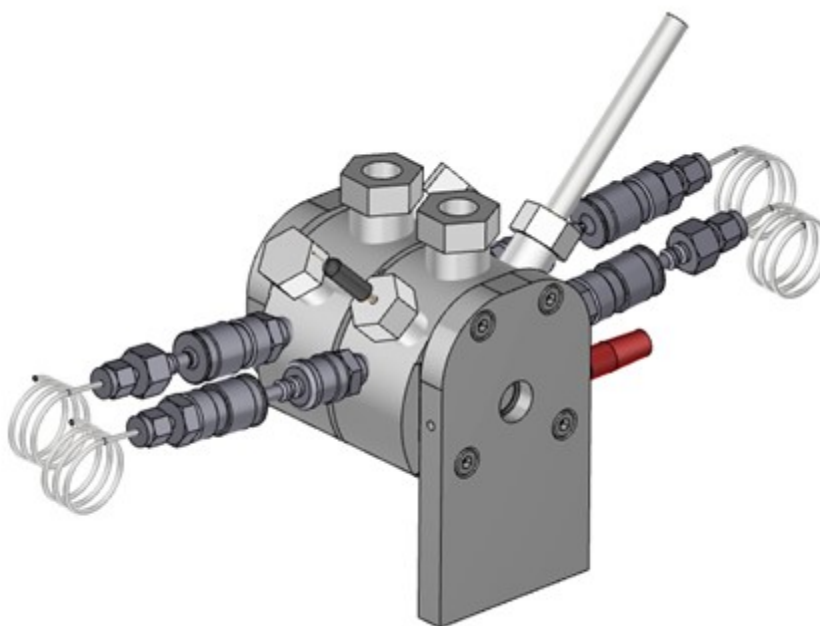


Figure S8. Image of photo-reactor

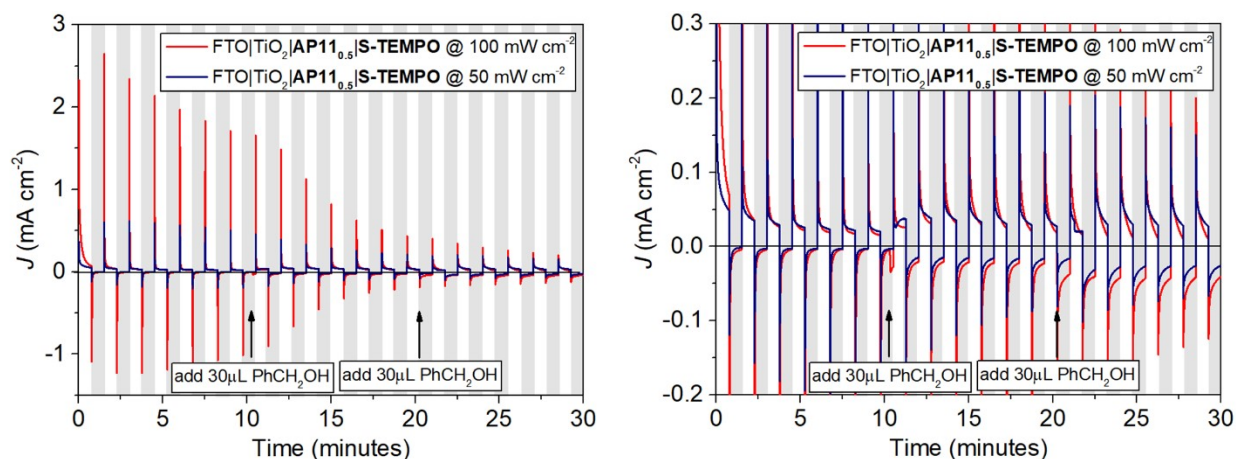


Figure S9. Chopped light experiments (full spectrum left, zoom right) at 100 (red) and 50 (blue) mW cm^{-2} with 45 seconds light on (white background) 45 seconds off (grey background). WE: $\text{FTO|TiO}_2|\text{AP11}_{0.5}|\text{S-TEMPO}$ General conditions: 1.2 M LiTFSI in MeCN (3 mL), 30 μL PhCH_2OH at 10 and 20 minutes, CE: FTO|Pt , 1.2 M LiTFSI 1.0 M AcOH in MeCN (3 mL), separated by Nafion-117 proton exchange membrane, RE: 0 V vs. Ag/AgCl

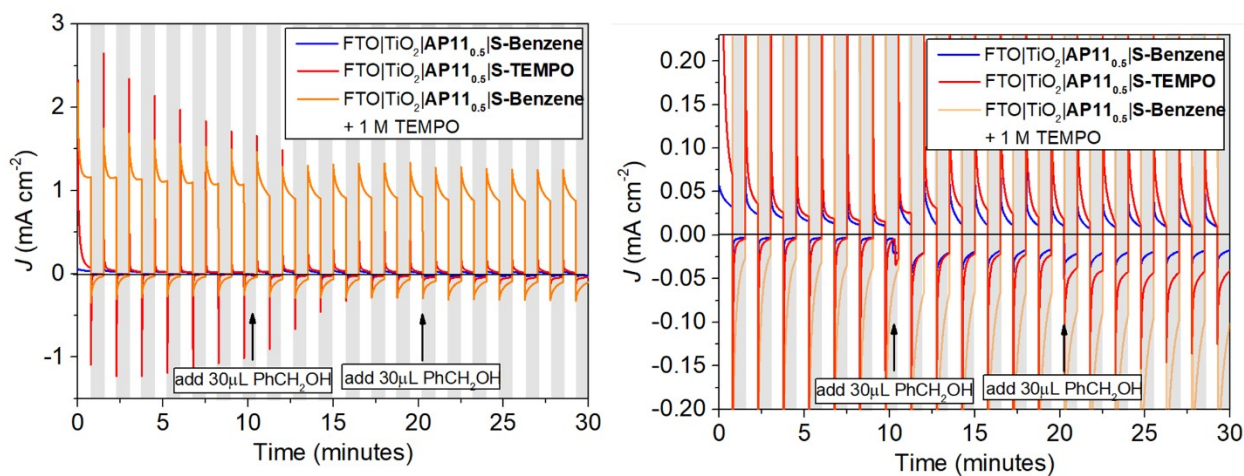


Figure S10. Chopped light experiments (full spectrum left, zoom right) at 100 mW cm^{-2} with 45 seconds light on (white background) 45 seconds off (grey background). WE: $\text{FTO|TiO}_2|\text{AP11}_{0.5}|\text{S-TEMPO}$ (red) or $\text{FTO|TiO}_2|\text{AP11}_{0.5}|\text{S-Benzene}$ (blue) and WE: or $\text{FTO|TiO}_2|\text{AP11}_{0.5}|\text{S-Benzene}$ (orange) + 1 M TEMPO in electrolyte. General conditions: 1.2 M LiTFSI in MeCN (3 mL), 30 μL PhCH_2OH at 10 and 20 minutes, CE: FTO|Pt in 1.2 M LiTFSI 1.0 M AcOH in MeCN (3 mL), separated by Nafion-117 proton exchange membrane, RE: 0 V vs. Ag/AgCl.

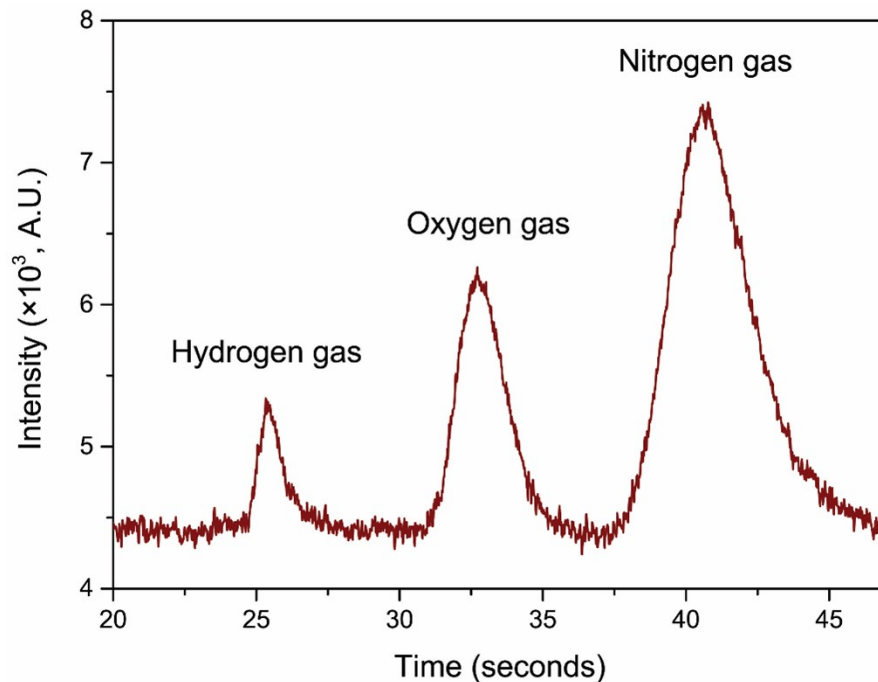


Figure S11. Light-driven qualitative hydrogen production in the homogeneous **TEMPO**-based DSPEC. The WE electrode compartment is filled with 0.1 M benzyl alcohol, 1.2 M LiTFSI, 1.0 M **TEMPO**, and 19.65 mM chlorobenzene in MeCN (3 mL) and is consisting of an FTO|TiO₂|**AP11** WE masked 0.64 cm² and an Ag/AgCl (leakless, eDAQ, ET069) RE. The CE compartment is separated by a Nafion-177 membrane (FuelCellStore) and is filled with 1.0 M AcOH, 19.65 mM chlorobenzene, and 1.2 M LiTFSI in MeCN (3 mL) and consist of a CE Pt electrodeposited on FTO. O₂ and N₂ are introduced during the injection. Chronoamperometric photocurrent measurements at 0 V vs. Ag/AgCl were obtained using P211 potentiostat (Zahner), with both compartments stirring. The photoanode was illuminated with a LED light source (Zahner, TLS3, 50 mW cm⁻², Figure 7), for a period of 32 hours. Gas Chromatography analysis was performed with a CompactGC (Interscience) equipped with a 5Å molecular sieve column (20 m length, 3.2 mm internal diameter). The column oven temperature was set at 34°C and a 2 mL min⁻¹ flow.

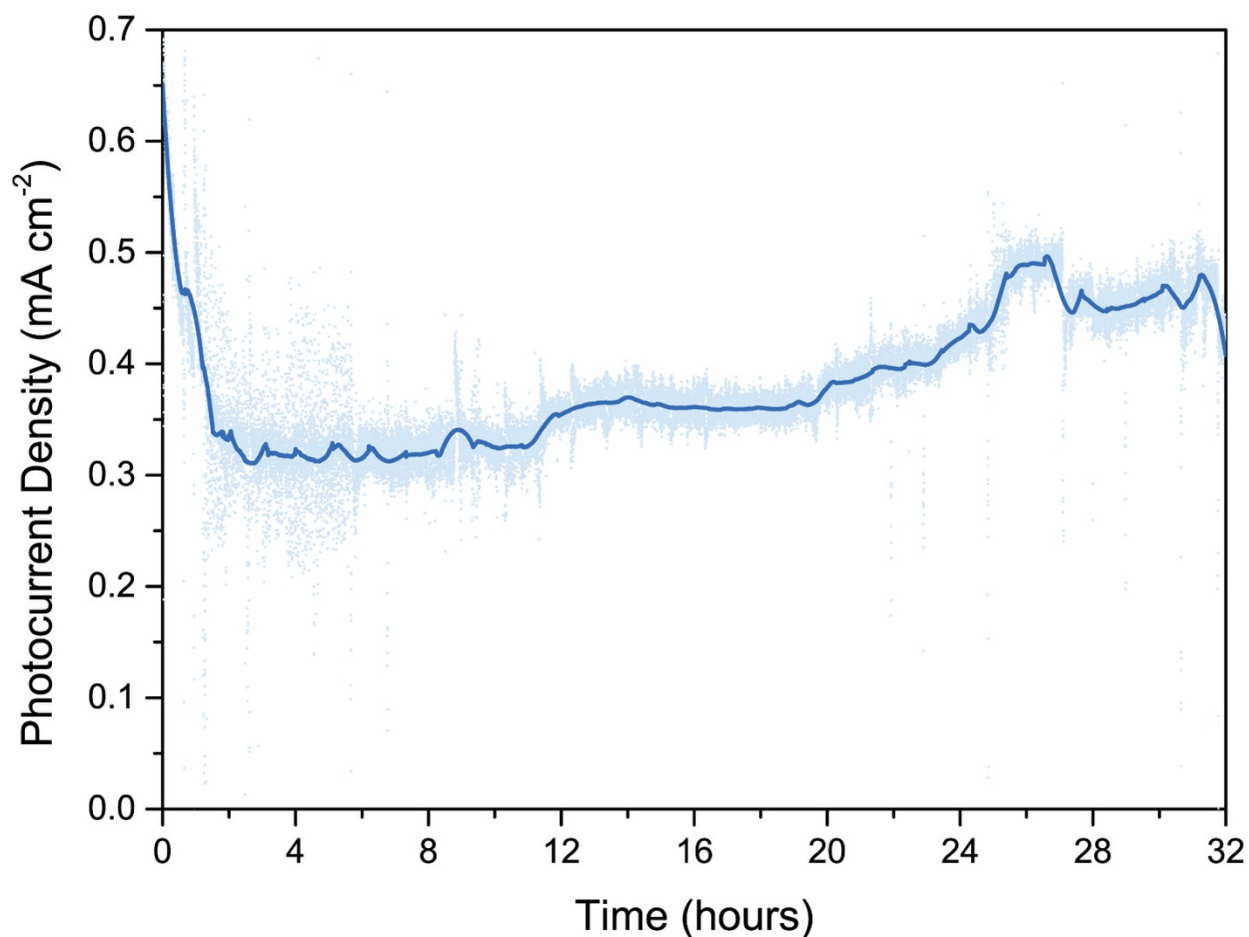


Figure S12. Photocurrent of homogeneous **TEMPO**-based DSPEC. The WE electrode compartment is filled with 0.1 M benzyl alcohol, 1.2 M LiTFSI, 1.0 M **TEMPO**, and 19.65 mM chlorobenzene in MeCN (3 mL) and is consisting of an FTO|TiO₂|**AP11** WE masked 0.64 cm² and an Ag/AgCl (leakless, eDAQ, ET069) RE. The CE compartment is separated by a Nafion-177 membrane (FuelCellStore) and is filled with 1.0 M AcOH, 19.65 mM chlorobenzene, and 1.2 M LiTFSI in MeCN (3 mL) and consist of a Pt electrodeposited on FTO CE. Chronoamperometric photocurrent measurements at 0 V vs. Ag/AgCl were obtained using P211 potentiostat (Zahner), with both compartments stirring. The photoanode was illuminated with a LED light source (Zahner, TLS3, 50 mW cm⁻², Figure 7) for a period of 32 hours. The light was turned on after 10 seconds giving a spike in photocurrent due to the capacitance effect.⁵ In the first phase of two hours, the system has to equilibrate because protons are generated at one side and consumed at the other side of the membrane, after which the photocurrent generates an average of 0.4 mA cm⁻² (*N*=3). Variations in photocurrent are caused due to multi reasons: The proton concentration influences the catalytic rate and therefore photocurrent and affects the level of the conduction band of TiO₂ as previously observed in water splitting DSPECs.⁶ Efforts were made to look more into the origin of photocurrent variations. Stirring seems to have a significant influence on photocurrent stability. Unstirred reactions show a slow decay of photocurrent. However, after sample taking (and therefore mixing the anolyte of the system), a spike in photocurrent is seen. The stirring, however, gives a noisy signal since measurements were taken every 0.2 seconds. (light blue) and were not seen during unstirred measurements and measurements is a time interval of 10 seconds. Therefore an average is given of 10 seconds shown (dark blue line). We included this noisy signal to show the significant variations in photocurrent due to the many influencing factors (concentration differences, sample taking starting, etc.) of the whole cell.

Calculation of substrate and product based on GC analysis

In long-term experiments, concentrations (mM) and amounts (mmol) of benzyl alcohol and benzaldehyde are determined as follows: Samples were taken of the reaction mixture containing a maximum amount of 100 mM of substrate and product and 19.65 mM Chlorobenzene as an internal standard to account for potential evaporation of MeCN during the reaction. The obtained samples are diluted in MeCN to yield concentrations between 0 and 25 mM. A calibration curve (Figure S14) for benzyl alcohol and benzaldehyde were determined within these ranges giving a response factor of 341590 for benzyl alcohol and 463846 for benzaldehyde. The amount of dilution is determined by using an internal standard of chlorobenzene (19.65 mM) yielding the dilution factor using the formula:

$$\text{Dilution factor} = \frac{19.65 \text{ mM}}{\frac{\text{Area}_{\text{Chlorobenzene}}}{378482}} \quad \text{with 378482 the area of 19.65 mM chlorobenzene undiluted. We}$$

calculated the concentration by the following formula:

$$\text{Dilution factor} \times \frac{\text{Area}_{\text{PhCH}_2\text{OH or PhCHO}}}{\text{Response factor}_{\text{PhCH}_2\text{OH or PhCHO}}}$$

At $t=0$ an initial amount of product (oxidised substrate) is found since we used store-bought chemicals. This amount is subtracted to look into the light-driven generation of benzaldehyde to determine faradaic efficiencies.

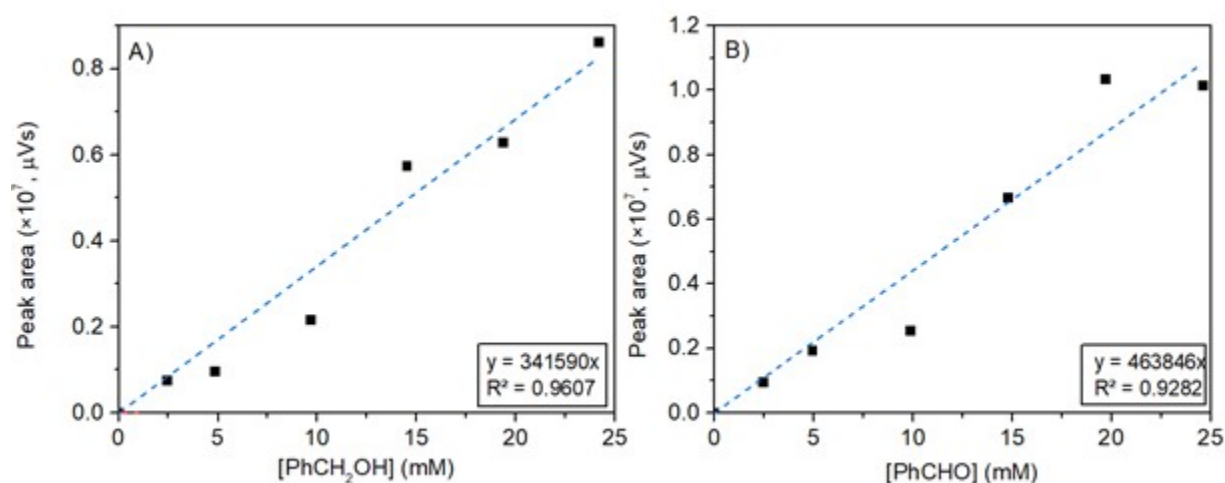


Figure S13. Calibration curves benzyl alcohol (PhCH_2OH) and benzaldehyde (PhCHO) for GC: A) Area of GC PhCH_2OH vs. $[\text{PhCH}_2\text{OH}]$, B) Area of GC PhCHO vs. $[\text{PhCHO}]$.

Table S2. Original GC data of light-driven benzyl alcohol conversion homogeneous **TEMPO** based DSPEC ($N=3$). The WE electrode compartment is filled with 0.1 M benzyl alcohol, 1.2 M LiTFSI, 1.0 M **TEMPO**, and 19.65 mM chlorobenzene in MeCN (3 mL) and is consisting of an FTO|TiO₂|**AP11** WE masked 0.64 cm² and an Ag/AgCl (leakless, eDAQ, ET069) RE. The CE compartment is separated by a Nafion-177 membrane (FuelCellStore) and is filled with 1.0 M AcOH, 19.65 mM chlorobenzene, and 1.2 M LiTFSI in MeCN (3 mL) and consist of a Pt electrodeposited on FTO CE. Chronoamperometric photocurrent measurements at 0 V vs. Ag/AgCl were obtained using P211 potentiostat (Zahner), with both compartments stirring. The photoanode was illuminated with a LED light source (Zahner, TLS3, 50 mW cm⁻², Figure 7) for a period of 32 hours. Samples were diluted before measuring.

Time (hours)	Benzaldehyde (Area)	Benzyl alcohol (Area)	Benzaldehyde (mM)	Benzyl alcohol (mM)	Chlorobenzene (Area)	Chlorobenzene (mM)	Dilution Factor	Sample #
0	175923	1007781	12.48	97.06	226075	19.65	32.90	1
0	181095	935220	13.46	94.36	215806	19.65	34.47	2
0	179086	973540	13.81	101.96	207906	19.65	35.77	3
1	209957	1263130	12.29	100.43	273853	19.65	27.16	1
1	172081	1005251	12.55	99.54	219890	19.65	33.83	2
1	159368	1003831	11.30	96.69	226055	19.65	32.90	3
2.6	213706	1200355	11.99	91.47	285745	19.65	26.03	1
2.6	194530	1062485	11.87	88.06	262702	19.65	28.31	2
2.6	194757	969723	14.08	95.21	221760	19.65	33.54	3
4.5	246363	1186852	12.08	79.05	326927	19.65	22.75	1
4.5	246563	973851	17.33	92.92	228199	19.65	32.59	2
4.5	247841	962294	17.43	91.88	228043	19.65	32.62	3
5.5	313082	1135917	19.01	93.65	264117	19.65	28.16	1
5.5	285109	959113	18.70	85.41	244524	19.65	30.42	2
5.5	320887	1127165	18.43	87.89	279257	19.65	26.63	3
6.75	283832	872557	20.51	85.64	221859	19.65	33.52	1
6.75	301281	928453	20.49	85.74	235778	19.65	31.55	2
6.75	311418	981043	20.17	86.28	247574	19.65	30.04	3
22	463145	653350	38.62	73.97	192313	19.65	38.68	1
22	549234	749234	39.01	72.25	225787	19.65	32.94	2
22	564373	778434	38.96	72.98	232258	19.65	32.02	3
23	580646	772916	39.71	71.78	234459	19.65	31.72	1
23	615638	818502	43.93	79.30	224742	19.65	33.09	2
23	583408	764876	40.21	71.58	232656	19.65	31.97	3
25	562882	692909	44.60	74.55	202375	19.65	36.75	1
25	517569	614925	42.20	68.08	196664	19.65	37.82	2
25	679052	792359	42.44	67.25	256560	19.65	28.99	3
27	666974	695496	47.24	66.89	226390	19.65	32.85	1
27	712348	729009	45.48	63.21	251142	19.65	29.62	2
27	618671	627994	45.97	63.36	215816	19.65	34.46	3
29	757841	712910	48.96	62.54	248190	19.65	29.97	1
29	678383	630798	50.82	64.16	214063	19.65	34.75	2
29	790579	737382	48.15	60.99	263263	19.65	28.25	3
31	707611	581380	51.05	56.95	222271	19.65	33.46	1
31	806602	690681	50.36	58.56	256828	19.65	28.96	2
31	742453	609614	53.52	59.67	222461	19.65	33.43	3
32	808955	620874	54.71	57.02	237085	19.65	31.37	1
32	790175	623052	53.14	56.90	238436	19.65	31.19	2
32	755211	607914	53.24	58.20	227446	19.65	32.70	3

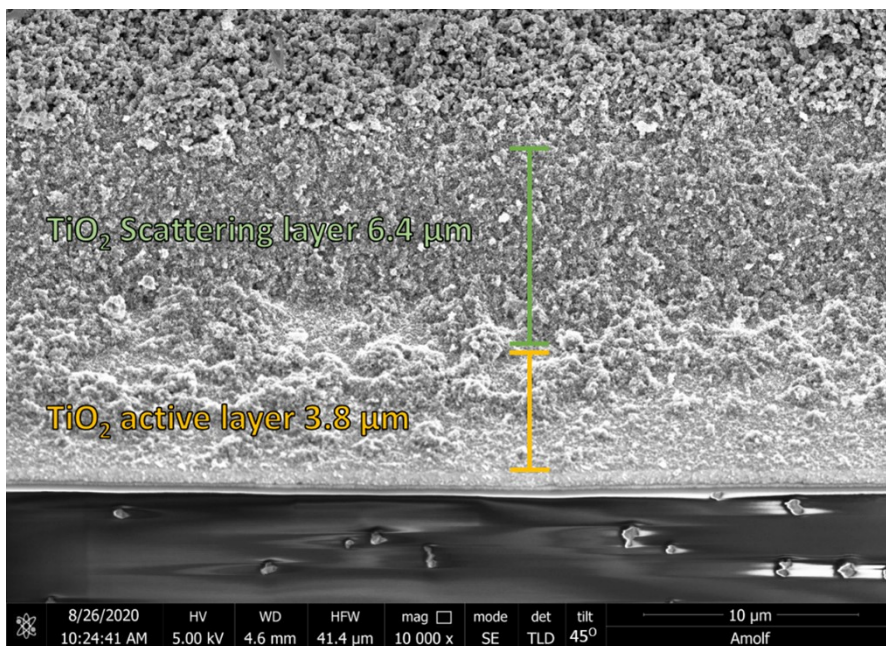


Figure S14: SEM imaging of FTO|TiO₂|AP11 measured under a 45° tilt. High-resolution scanning electron microscopy (SEM) images were acquired using an FEI Verios 460 with an acceleration voltage and current of 5 kV and 100 pA, respectively. Energy dispersive spectroscopy (EDS) elemental maps were obtained in the same instrument using an Oxford Xmax 80 mm² Silicon Drift Detector with 15 kV acceleration voltage and 1.5 nA current.

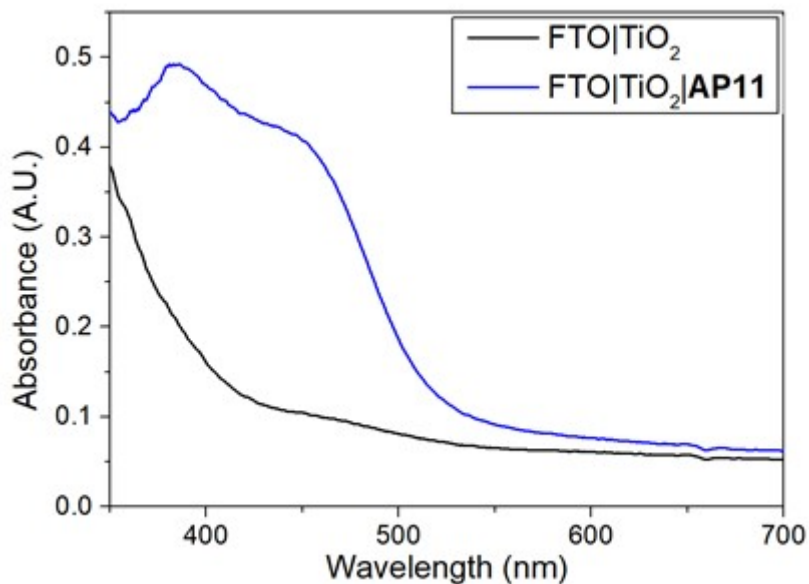


Figure S15: Optical properties of FTO|TiO₂, and FTO|TiO₂|AP11 measured with UV-Vis (Zahner).

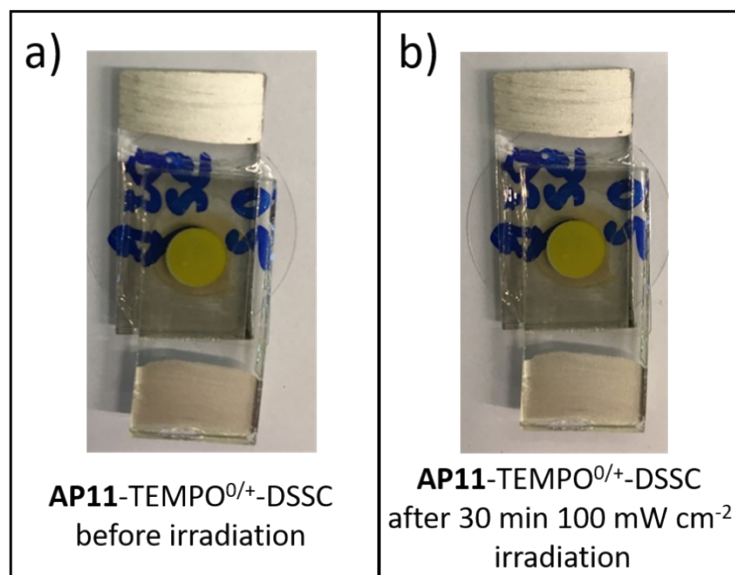


Figure S16: **AP11-TEMPO^{0/+}-DSSC** a) before irradiation and b) after irradiation for 30 minutes with a 100 mW cm⁻² LED light.

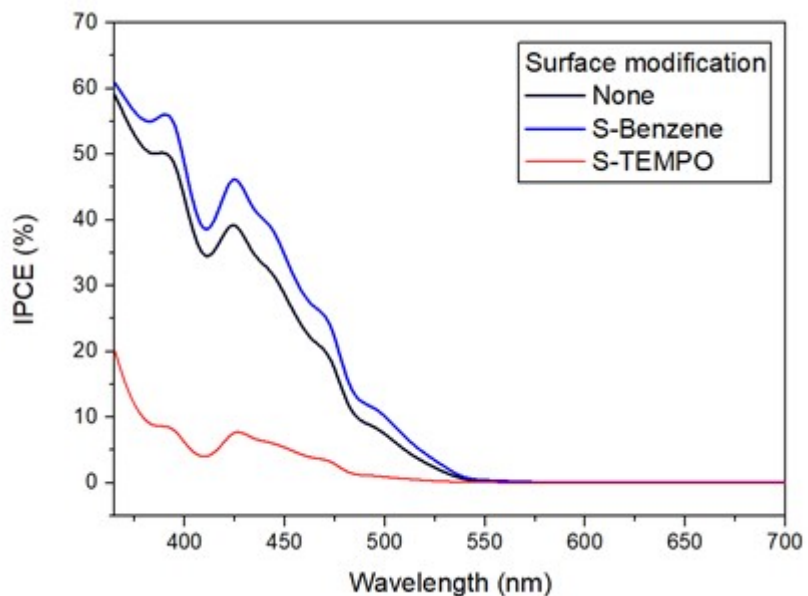


Figure S17 IPCE of **TEMPO^{0/+}-based FTO|TiO₂|AP11_{0.5}** sandwich DSSC devices with and without functionalisation over 21 hours of dipping time with **S-TEMPO** and **S-Benzene** and the standard deviation in brackets ($N=3$). The DSSC consist of a WE (FTO|TiO₂|**AP11_{0.5}**) and a CE (FTO Pt electrodeposited) Electrolyte (1.2 M LiTFSI, 1.0 M **TEMPO** and 0.1 M **TEMPO(BF₄)** in MeCN), with a 0.07 cm² masked and a 4.71 μ L volume.

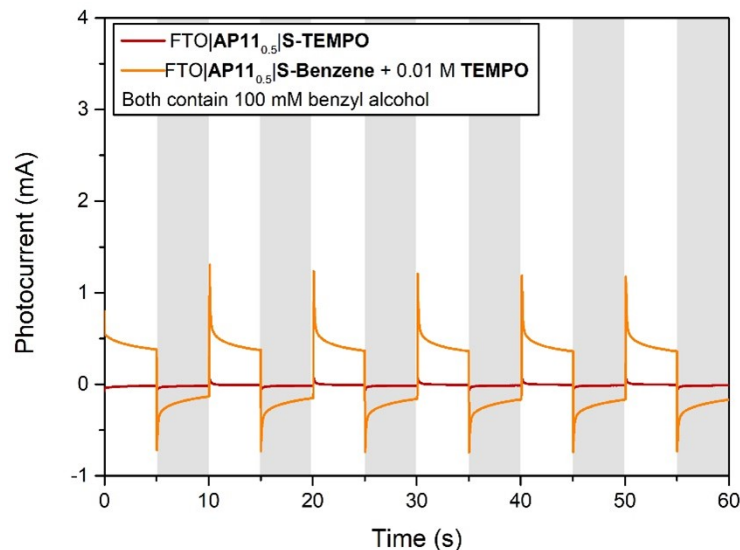


Figure S18. Chopped light experiments (at 100 mW cm^{-2} with 5 seconds light on (white background) 5 seconds off (grey background)). WE: FTO|TiO₂|AP11_{0.5}|S-TEMPO (red) or FTO|TiO₂|AP11_{0.5}|S-Benzene (orange) + 0.01 M TEMPO in electrolyte. General conditions: 1.2 M LiTFSI in MeCN (3 mL), 100m mM PhCH₂OH, CE: FTO|Pt in 1.2 M LiTFSI 1.0 M AcOH in MeCN (3 mL), separated by Nafion-117 proton exchange membrane, RE: 0 V vs. Ag/AgCl.

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