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Supplementary Information

Polymer photocatalysts with plasma-enhanced activity

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General methods: All reagents were obtained from Sigma-Aldrich, TCI, ABCR, or Fluorochem and used as received. Polymer P35[1] was synthesized using synthetic routes previously published. Water for the hydrogen evolution experiments was purified using an ELGA LabWater system with a Purelab Option S filtration and ion exchange column (ρ = 15 MΩ cm^{-1}) without pH level adjustment. Reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. ^{1}H NMR spectra were recorded at 400.13 MHz on a Bruker Avance 400 NMR spectrometer. CHN Analysis was performed on a Thermo EA1112 Flash CHNS-O Analyzer using standard microanalytical procedures. ICP-MS analysis was performed on a Perkin Elmer ICP MS NexION 2000 with equipped with a collision/reaction cell after a microwave digest of the materials in nitric acid (67-69%, trace metal analysis grade) in a microwave. The solutions were diluted with water before the measurement and the instrument was calibrated with Pd standards in aqueous solution and Y-89 as the internal standard. The mass peak at 106 m/z with He KED mode was used to calculate the amount of residual palladium in the samples. The UV-visible absorption spectra of the polymer networks were recorded on a Shimadzu UV-2550 UV-vis spectrometer as powders in the solid state. Imaging of the polymer morphology was achieved on a Hitachi S4800 Cold Field Emission SEM, with secondary electron, backscatter and transmission detectors after a coating with chromium. OTS treatment of the glass slides was performed with *n*-octadecyltrichlorosilane using a previously reported procedure.[2] Polymers were coated on these substrates by spin-coating chloroform solutions (3 mg mL^{-1}) at 3000 rpm for 30 seconds before drying at 60 °C for one hour. Drop-casting was performed by casting chloroform solutions (0.2 mL, 3 mg mL^{-1}) onto smooth or frosted glass substrates (Griffiths and Nielsen Ltd, 26 × 16 mm) at room temperature. The solvent was left to slowly evaporate before drying at 60 °C for one hour. Water contact angles were measured on a drop-shape analysis apparatus (Krüss DSA100). The contact angles were fitted using the Young–Laplace equation. Wetting envelopes were determined using water and diiodomethane. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS Ultra DLD instrument. The chamber pressure during the measurements was 5×10^{-9} Torr. Wide energy range survey scans were collected at pass energy of 80 eV in hybrid slot lens mode and a step size of 0.5 eV. High-resolution data on the C 1s and O 1s photoelectron peaks was collected at pass energy 20 eV over energy ranges suitable for each peak, and collection times of 5 min, step sizes of 0.1 eV. The charge neutraliser filament was used to prevent the sample charging over the irradiated area. The X-ray source was a monochromated Al Kα emission, run at 10 mA and 12 kV (120 W). The energy range for each ‘pass energy’ (resolution) was calibrated using the Kratos Cu

$2p_{3/2}$, Ag $3d_{5/2}$ and Au $4f_{7/2}$ three-point calibration method. The transmission function was calibrated using a clean gold sample method for all lens modes and the Kratos transmission generator software within Vision II. The data were processed with CASAXPS (Version 2.3.17). The high-resolution data was charge corrected to the reference C 1s signal at 284.8 eV. Photoelectron spectroscopy in air (PESA) measurements were recorded using a Riken Keiki PESA spectrometer (Model AC-2). Samples for PESA were prepared on glass substrates.

Plasma treatment: A purpose build, vacuum-based, RF plasma system was used to treat the samples. It consists of a 30-litre stainless steel vacuum vessel housing a horizontally orientated parallel plate electrode system, pumped to base pressures of less than 0.1 Pa by a combined turbo molecular (65 L s^{-1}, Edwards EXT70) and rotary (12 m^3 h^{-1} Pfeiffer, DUO 10MC) pump set. In plasma operation, samples were placed on the lower grounded electrode and 99.99% pure argon gas was fed to the chamber via a flow controller (50 sccm range, MKS Instruments), maintaining a constant working pressure of 1.33 Pa (10 mTorr), measured by a Pirani pressure gauge (APG-MP B, Edwards Vacuum). The plasma was maintained between the electrodes at a nominal power of 10 W using a RF power supply (Coaxial Power Systems) operating at 13.56 Hz with minimal reflected power. The samples were accessed to the vessel via a removable flange and treated for a range of times from 5 to 60 minutes. All samples were tested for their photocatalytic performance or measurements were performed within 48 hours after treatment.

Hydrogen evolution measurements: A reactor was charged with the photocatalyst, water/scavenger mixtures, sealed with a septum, and degassed thoroughly by N_2 bubbling for 30 minutes. The reaction mixture was illuminated with a 300 W Newport Xe light-source (Model: 6258, Ozone free) for the time specified at a fixed distance under atmospheric pressure. The Xe-light source was cooled by water circulating through a metal jacket. Gas samples were taken with a gas-tight syringe and run on a Bruker 450-GC gas chromatograph equipped with a Molecular Sieve 13X 60-80 mesh 1.5 m × ⅛” × 2 mm *ss* column at 50 °C with an argon flow of 40 mL min^{-1}. Hydrogen was detected with a thermal conductivity detector, referencing against standard gases with known concentrations of hydrogen. Hydrogen dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen was neglected in the calculations. The rates were determined from a linear regression fit and the error is given as the standard deviation of the amount of hydrogen evolved. No hydrogen evolution was observed for a mixture of water/triethylamine under $\lambda > 420$ nm illumination in absence of a photocatalyst.

External quantum efficiency measurements: FS-Dodec was drop-casted from chloroform solution (0.2 mL, 3 mg mL^{-1}) onto frosted glass substrates (Griffiths and Nielsen Ltd, 26 × 16 mm) at room temperature. The solvent was left to slowly evaporate before drying at 60 °C for one hour. The coated slide was submerged in water, triethylamine, and methanol (1:1:1 vol. mixture, 8 mL), degassed with nitrogen for 30 minutes and irradiated with a $\lambda = 420$ nm LED (3.16 mW cm^{-2}) controlled by an IsoTech IPS303DD power supply. An area of 8 cm^2 was illuminated and the light intensity was measured with a ThorLabs S120VC photodiode power sensor controlled by a ThorLabs PM100D Power and Energy Meter Console. The external quantum efficiencies were estimated using the equation below:

$$EQE_{\lambda 420\,nm} = 2 \times \frac{moles\ of\ hydrogen\ evolved}{moles\ of\ incident\ photons} \times 100\%$$

The EQE at 420 nm was determined to be 0.5 ± 0.05% for a single slide. When three slides were stacked in a row held in place by a spacer the EQE at 420 nm was increased to 0.9 ± 0.06%.

Photocurrent measurements: Chronoamperometric measurements were carried out on an EC-Lab SP-200 (Bio-Logic Science Instruments SAS, France) in a three-electrode-cell system with an fluorine doped tin oxide (FTO) coated glass slide as the working electrode, $Ag/AgCl_2$ electrode (0.63 V vs standard hydrogen electrode) as the reference electrode, platinum wire as the counter electrode. Chloroform (5 mL) was mixed with the ground polymer (5 mg), ultrasonicated to dissolve the polymer and this solution (1.5 mL) was drop-casted onto an FTO glass working electrode (active area 1.5 cm^2). The sample was then dried under atmosphere for 10 minutes. Three-electrode-cell system was purged with N_2 for 30 minutes before measurement. The measurement was performed in an aqueous sodium sulfate solution (0.01 M) illuminating the back of the FTO working electrode with a xenon light source (300 W, $\lambda > 295$ nm).

Synthesis of FS-Dodec via Suzuki-Miyaura-type polycondensation. A flask was charged with 9,9-di-*n*-dodecyl-9*H*-fluorene-2,7-diyl-diboronic acid (591 mg, 1.0 mmol), 3,7-dibromodibenzo[*b*,*d*]thiophene sulfone (374 mg, 1.0 mmol), toluene (17.5 mL), Starks' catalyst (2 drops), and an aqueous solution of Na_2CO_3 (7.5 mL, 2 M). The mixture was degassed by bubbling with N_2 for 30 minutes, before $[Pd(PPh_3)_4]$ (17.5 mg) was added, and heated for 2 days at 110 °C. The mixtures were evaporated to dryness and washed with water. The crude polymer was then further purified by Soxhlet extraction with methanol, acetone, and ethyl acetate. The high molecular weight fraction of the polymer was recovered by Soxhlet extraction with chloroform. The chloroform was removed and the polymer redissolved in a minimal amount of chloroform, precipitated into a large access of methanol, filtered off and dried under reduced pressure giving the product as a dark green solid in 79% yield (561 mg). Anal. Calcd for **FS-Dodec** $(C_{49}H_{62}O_2S)_n$: C, 81.91; H, 8.74; S, 4.48%. Found: C, 81.97; H, 8.88; S, 4.29; Pd, 0.07%. ^{1}H NMR (400MHz, $CDCl_3$) 8.19 (2 H, s),7.83-8.03 (6 H, m) 7.61-7.72 (4 H, m), 2.12 (4 H, s, br), 1.03-1.32 (40 H, m), 0.84 (6 H, t, $J = 6.2$ Hz). Note: For the yield was calculated ignoring the presence of end functional groups whose nature is unclear.

General procedure for the synthesis of all materials via Suzuki-Miyaura-type polycondensation: A flask was charged with the monomers, *N*,*N*-dimethylformamide, and an aqueous solution of K_2CO_3 (2 M). The mixture was degassed by bubbling with N_2 for 30 minutes, before $[Pd(PPh_3)_4]$ was added, and heated to 150 °C for 2 days. The mixture was cooled to room temperature and poured into water. The precipitate was collected by filtration and washed with H_2O and methanol. Further purification of the polymers was carried out by Soxhlet extraction with chloroform to remove any low-molecular weight by-products and the product was dried under reduced pressure. Note: For all polymers the yields were calculated ignoring the presence of end functional groups whose nature is unclear.

Synthesis of P35-5%Fl: 2,7-Dibromo-9*H*-fluorenone (0.017 g, 0.05 mmol), 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (0.334 g, 0.95 mmol), 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b*,*d*]thiophene sulfone (0.468 mg, 1.00 mmol), *N*,*N*-dimethylformamide (25 mL), K_2CO_3 (2 M, 5 mL), and $[Pd(PPh_3)_4]$ (20 mg) were used in this polymerization. After work-up and Soxhlet the product was obtained as a yellow solid (404 mg, 92%). Anal. Calcd for $(C_{26.9}H_{17.7}S_2O_{2.05})_n$: C, 80.34; H, 4.48; S, 7.49%; Found C, 76; H, 4; S, 8%. Note: For the yield was calculated ignoring the presence of end functional groups whose nature is unclear.

Synthesis of P35-25%Fl: 2,7-Dibromo-9*H*-fluorenone (0.085 g, 0.25 mmol), 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (0.264 g, 0.75 mmol), 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b*,*d*]thiophene sulfone (0.468 mg, 1.00 mmol), *N*,*N*-dimethylformamide (25 mL), K_2CO_3 (2 M, 5 mL), and $[Pd(PPh_3)_4]$ (20 mg) were used in this polymerization. After work-up and Soxhlet the product was obtained as a yellow-orange solid (392 mg,90%). Anal. Calcd for $(C_{26.5}H_{16.5}S_2O_{2.25})_n$: C, 79.73; H, 4.19; S, 7.49%; Found C, 75; H, 4; S, 7%. Note: For the yield was calculated ignoring the presence of end functional groups whose nature is unclear.

Synthesis of P35-50%Fl: 2,7-Dibromo-9*H*-fluorenone (0.169 g, 0.50 mmol), 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (0.176 g, 0.50 mmol), 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b*,*d*]thiophene sulfone (0.468 mg, 1.00 mmol), *N*,*N*-dimethylformamide (25 mL), K_2CO_3 (2 M, 5 mL), and $[Pd(PPh_3)_4]$ (20 mg) were used in this polymerization. After work-up and Soxhlet the product was obtained as an orange solid (347 mg, 80%). Anal. Calcd for $(C_{26}H_{15}S_2O_{2.5})_n$: C, 78.97; H, 3.83; S, 7.49%; Found C, 74; H, 4; S, 8%. Note: For the yield was calculated ignoring the presence of end functional groups whose nature is unclear.

Removal of residual palladium from FS-Dodec:[3,4] FS-Dodec (9 mg) was dissolved in $CHCl_3$ (3 mL) and washed with an aqueous solution of sodium *N*,*N*-diethyldithiocarbamate (0.1 M, 2 × 3 mL). The organic phase was then washed with water (2 × 3 mL) and filtered over a plug of silica in a glass pipette. The silica was washed with additional $CHCl_3$ (3 mL) before removing the solvent under reduced pressure. ICP-MS analysis for palladium content was performed and a palladium content of 310 ppm was found present in the sample.

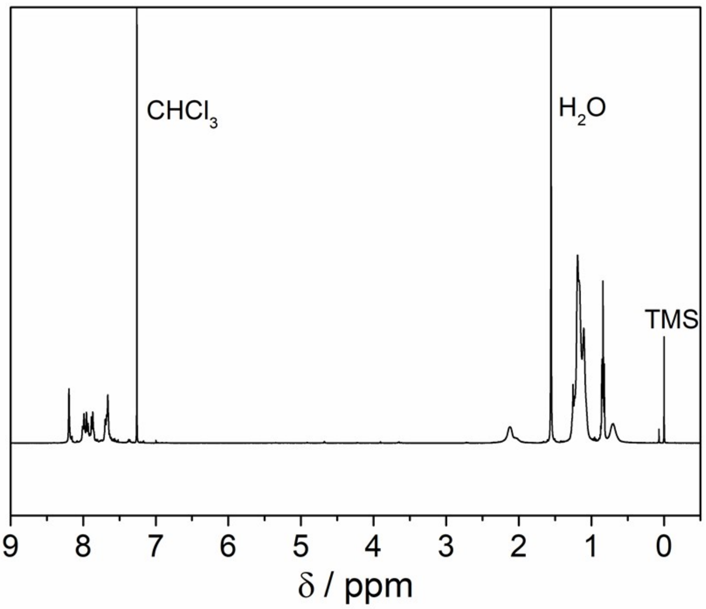

Figure S-1: ^1H NMR spectrum of the **FS-5Dodec** in $CDCl_3$.

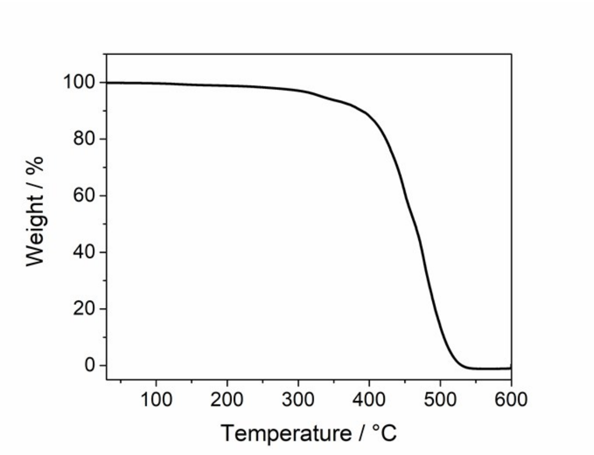

Figure S-2: TGA trace of **FS-5Dodec** powder heated at 10 °C min^{-1} under air.

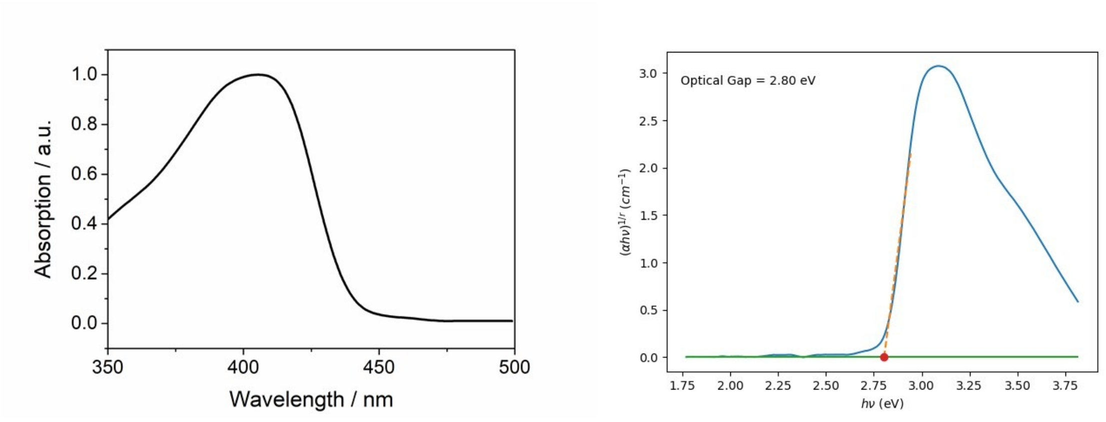

Figure S-3: UV-Vis spectrum of **FS-5Dodec** spin-coated from chloroform solution onto OTS-treated glass (left) and Tauc plot with estimated optical gap (right).

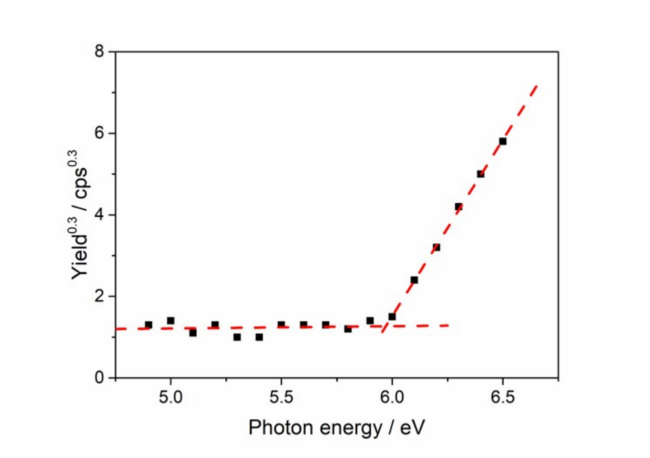

Figure S-4: PESA spectrum of FS-5Dodec on glass recorded on a Riken Keiki PESA spectrometer (Model AC-2) with a power number of 0.33 and a light intensity of 90 nW. The inferred ionisation potentials vs. SHE was calculated to be + 1.53 eV [E_{HOMO}(PESA) – 4.44 eV]. The LUMO was estimated to be -3.2 eV (E_{LUMO} = E_{HOMO}(PESA) + E_g).

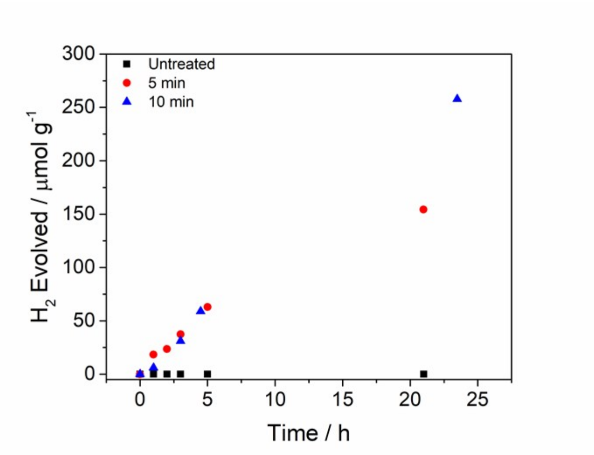

Figure S-5: Photocatalytic performance of Ar-plasma treated **FS-5Dodec** thin-films spin-coated on OTS-treated glass under visible light illumination. Plasma treatment conditions: 10 minutes Ar-plasma, 10 W, 10 mTorr. Photocatalysis conditions: 5 vol. % triethylamine in water, λ > 420 nm, 300 W Xe light source.

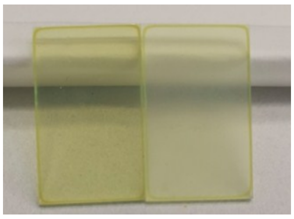

Figure S-6: Photographs of polymer films on a smooth, OTS treated glass slide (left) and on frosted glass (right).

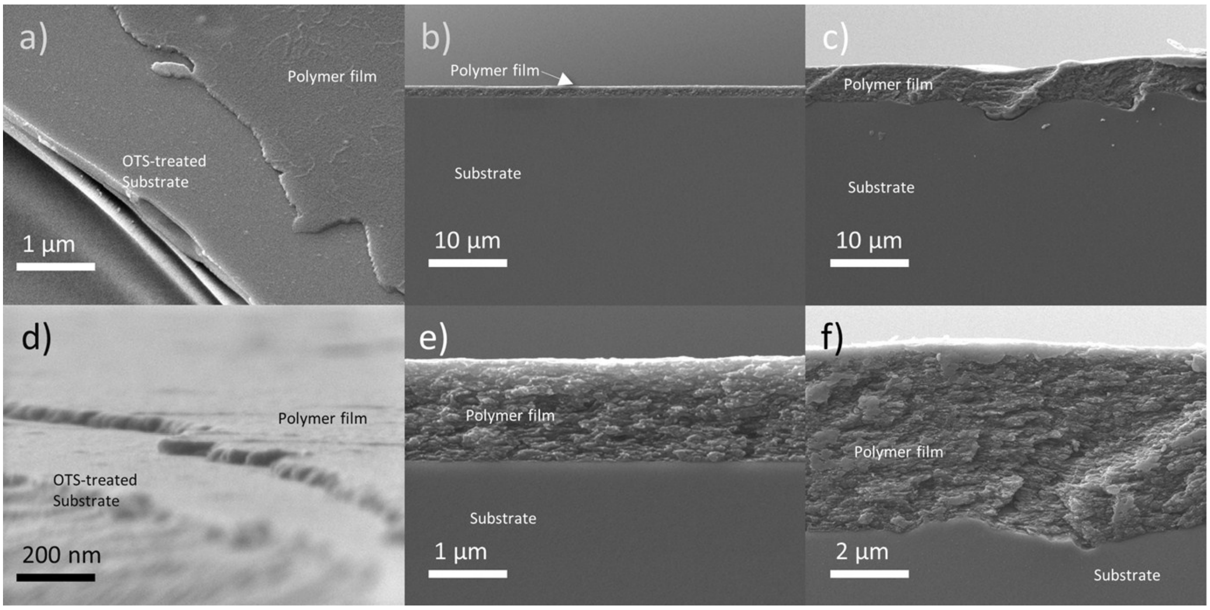

Figure S-7: SEM images of polymer films spin-coated onto a smooth, OTS treated glass slide (a, d), on a smooth, OTS treated glass slide (b, e) and on frosted glass (c, f). The thicknesses are approximately 20-30 nm for the spin-coated film, approximately 1.3 µm for the film on a smooth, OTS treated glass slide and between 4-6 µm for the polymer film on the frosted glass slide. Please not that snapping of the coated glass slide resulted in delamination of the film from the OTS-treated substrate due to it being very thin.

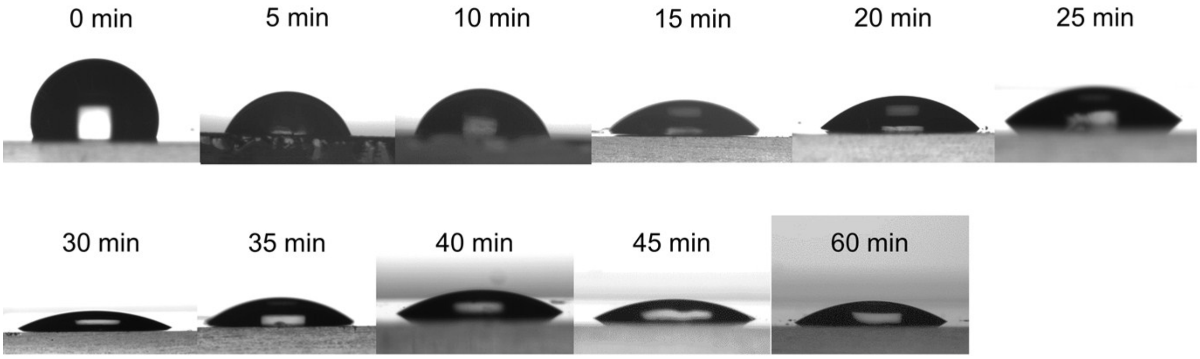

Figure S-8: Water drops on films of **FS-5Dodec** on OTS-treated glass after given treatment time with Ar plasma (Conditions: Ar plasma, 10 mTorr, 10 W).

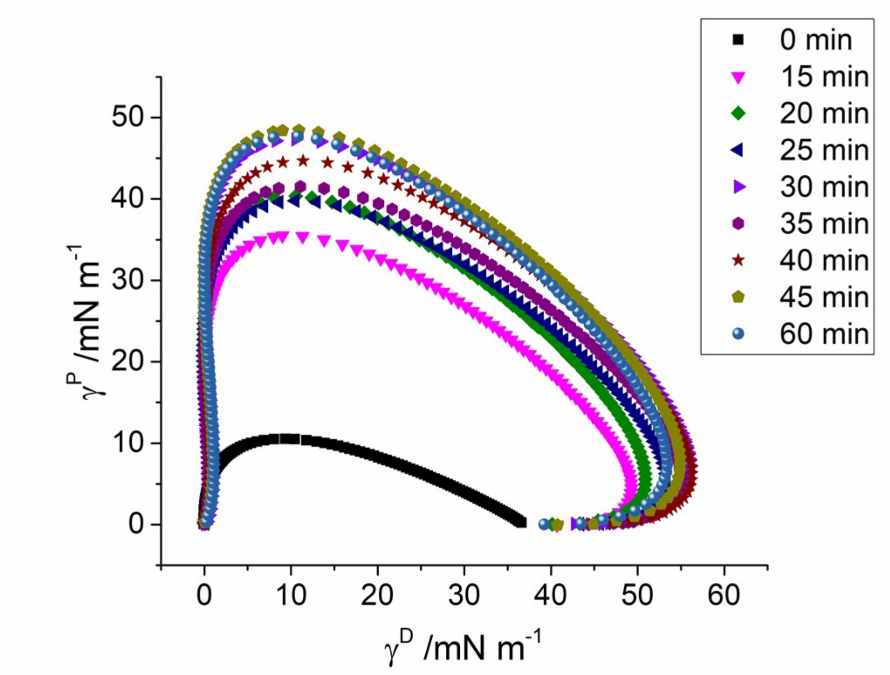

Figure S-9: Wetting envelopes of untreated and plasma treated polymer films on glass with their polar and disperse fractions determined using water and diiodomethane.

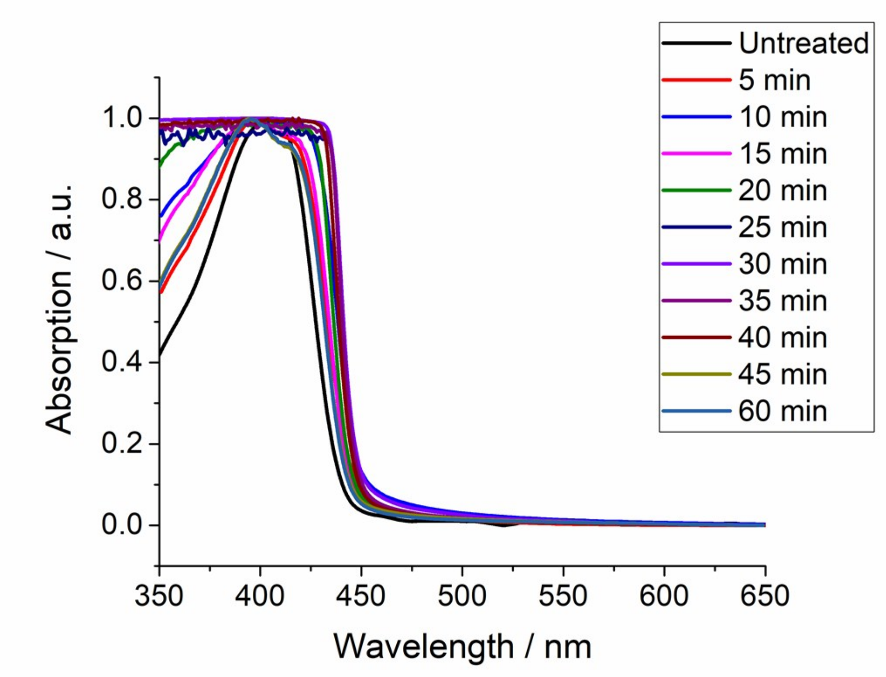

Figure S-10: UV-visible absorption spectra of untreated and plasma treated polymer films on glass.

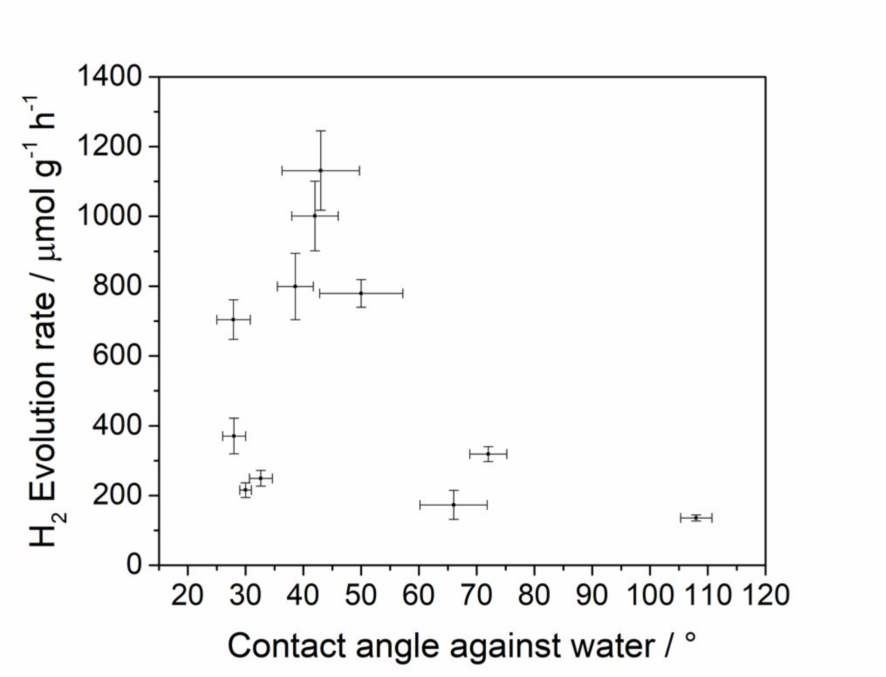

Figure S-11: Photocatalytic performance of Ar-plasma treated **FS-5Dodec** films drop-casted on glass under visible light illumination. Photocatalysis conditions: 5 vol. % triethylamine in water, λ > 420 nm, 300 W Xe light source.

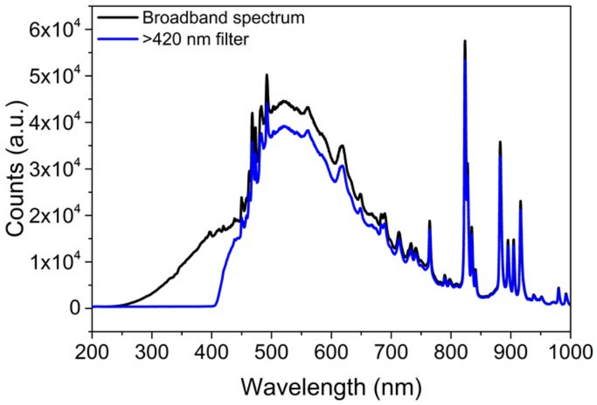

Figure S-12: Output of the Xe-light source used in this study.

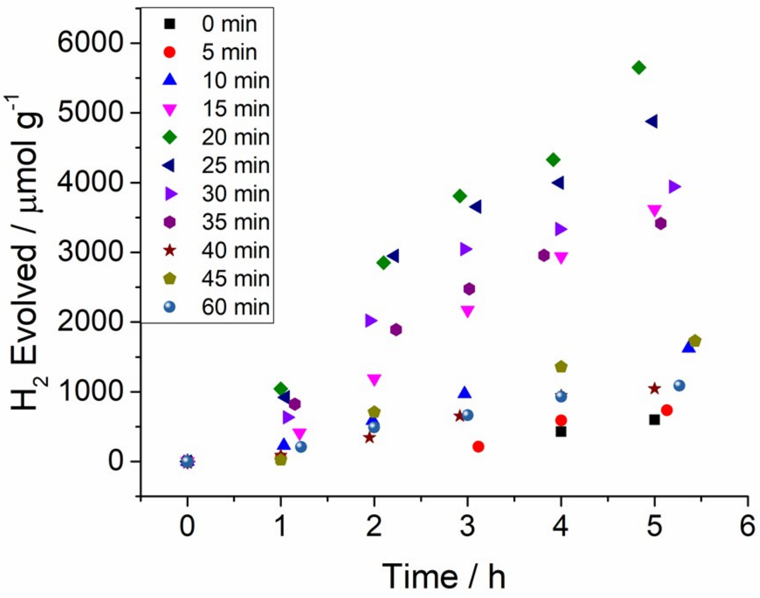

Figure S-13: Photocatalytic hydrogen evolution production under visible light. Conditions: Drop-cast films on glass, 5 vol. % triethylamine in water, λ > 420 nm, 300 W Xe light-source.

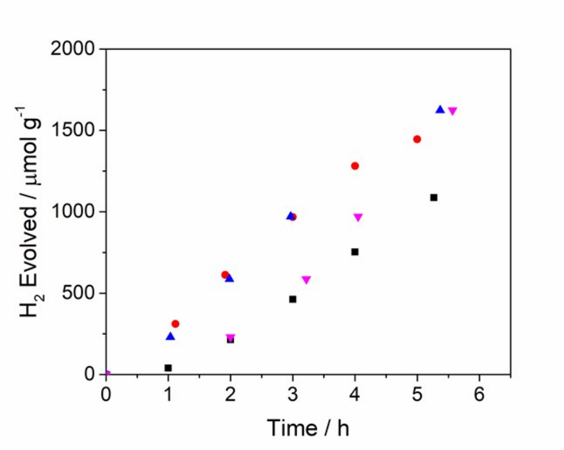

Figure S-14: Photocatalytic performance of Ar-plasma treated **FS-5Dodec** films drop-casted on glass under visible light illumination. Plasma treatment conditions: 10 minutes Ar-plasma, 10 W, 10 mTorr. Photocatalysis conditions: 5 vol. % triethylamine in water, λ > 420 nm, 300 W Xe light source. Average HER = 315.8 ± 52.6 µmol^{-1} g^{-1} h^{-1}.

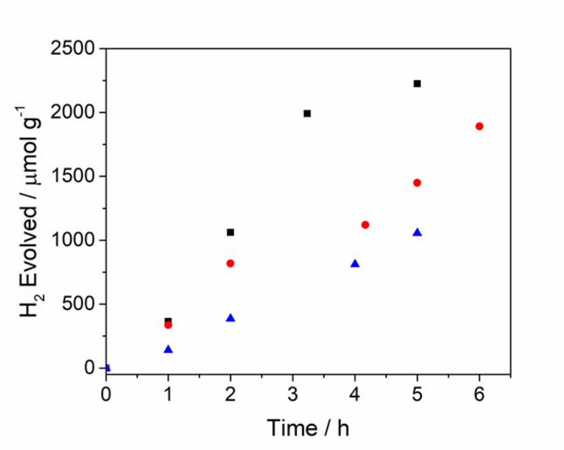

Figure S-15: Photocatalytic performance of N_2/O_2-plasma treated **FS-5Dodec** films drop-casted on glass under visible light illumination. Plasma treatment conditions: 10 minutes O_2/N_2 plasma, 11 W 60 mTorr, 15 minutes. Photocatalysis conditions: 5 vol. % triethylamine in water, λ > 420 nm, 300 W Xe light source. Average HER = 325.2 ± 106.0 µmol^{-1} g^{-1} h^{-1}.

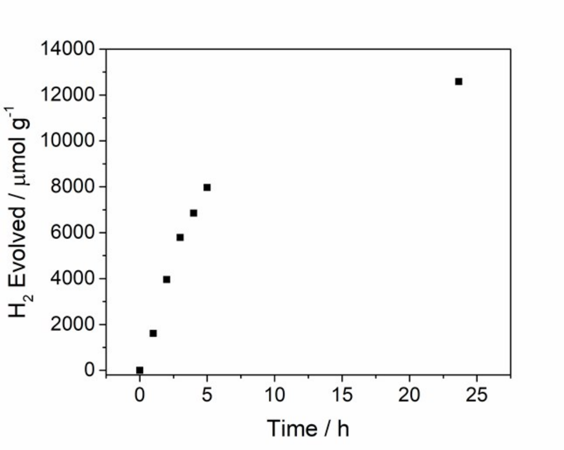

Figure S-16: Photocatalytic performance of Ar-plasma treated **FS-5Dodec** film drop-casted on glass under visible light illumination. Plasma treatment conditions: 20 minutes Ar-plasma, 10 W, 10 mTorr. Photocatalysis conditions: 5 vol. % triethylamine in water, λ > 420 nm, 300 W Xe light source.

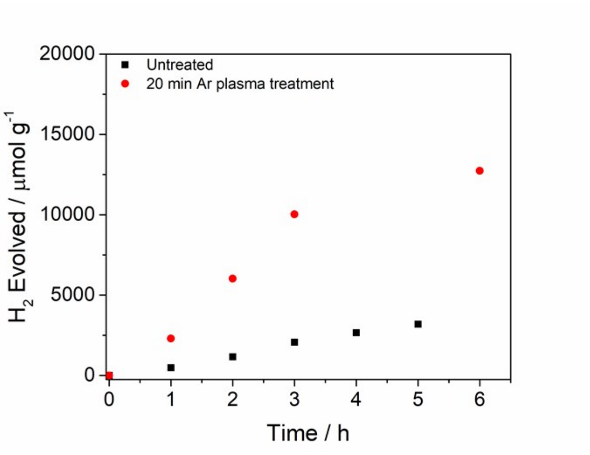

Figure S-17: Photocatalytic performance of **FS-5Dodec** film drop-casted on glass and after Ar-plasma treatment under visible light illumination. Plasma treatment conditions: 20 minutes Ar-plasma, 10 W, 10 mTorr. Photocatalysis conditions: triethylamine/methanol/water mixture (1:1:1), λ > 420 nm, 300 W Xe light source. HER (untreated) = 693 ± 38 µmol g^{-1} h^{-1}; HER (20 min Ar plasma) = 3861 ± 81 µmol g^{-1} h^{-1}.

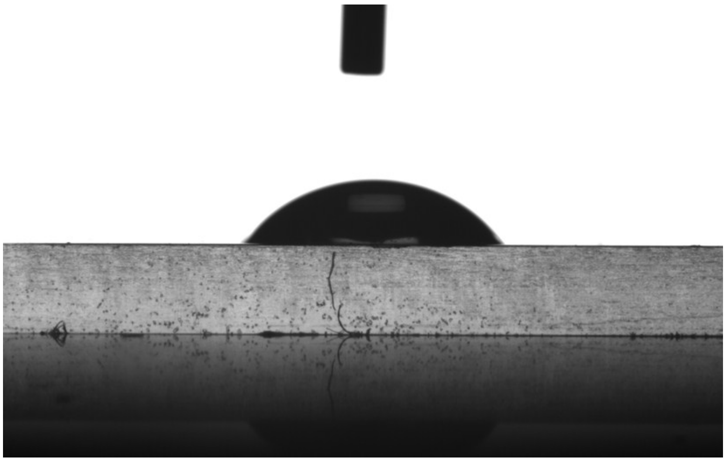

Figure S-18: Water drop on a film of **FS-5Dodec** on OTS-treated glass after 20 minutes treatment time with Ar plasma (Conditions: 10 mTorr, 10 W) and storage for one month under ambient conditions in the dark.

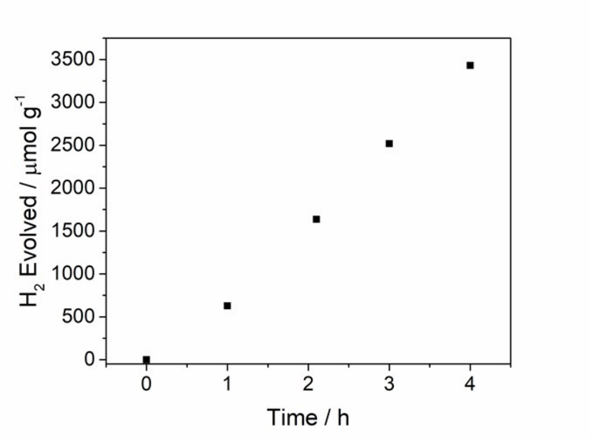

Figure S-19: Ar-plasma treated **FS-5Dodec** film drop-casted on glass after storage for one month under ambient conditions in the dark. Photocatalytic performance under visible light illumination in water/5 vol. % TEA. Plasma treatment conditions: 20 minutes Ar-plasma, 10 mTorr, 10 W. Photocatalysis conditions: Water, λ > 420 nm, 300 W Xe light source.

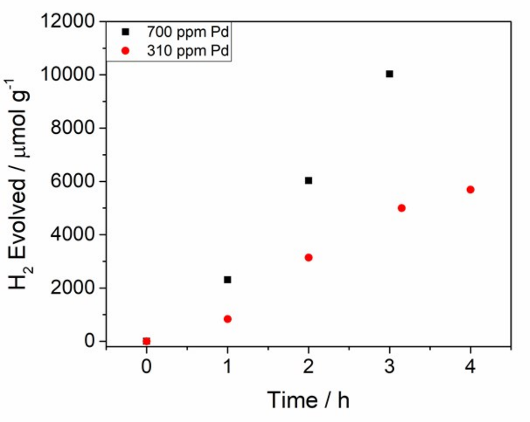

Figure S-20: Photocatalytic performance of **FS-5Dodec** film with 700 ppm and 310 ppm palladium as determined via ICP-MS drop-casted on glass and after Ar-plasma treatment under visible light illumination. Plasma treatment conditions: 20 minutes Ar-plasma, 10 W, 10 mTorr. Photocatalysis conditions: triethylamine/methanol/water mixture (1:1:1), λ > 420 nm, 300 W Xe light source. The linear hydrogen evolution rates were determined to be 3861.1 µmol g^{-1} h^{-1} for **FS-5Dodec** with 700 ppm Pd and to 1629 µmol g^{-1} h^{-1} for **FS-5Dodec** with 310 ppm Pd.

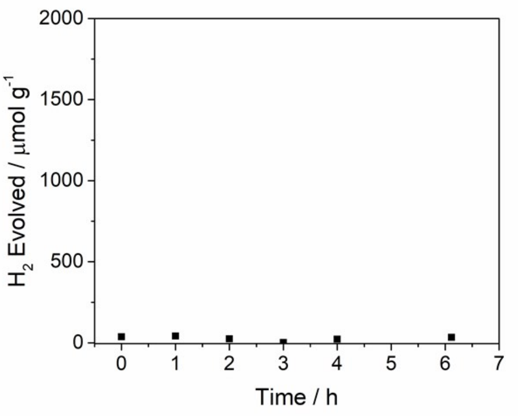

Figure S-21: Photocatalytic performance of Ar-plasma treated **FS-5Dodec** film drop-casted on glass under visible light illumination in water only. Plasma treatment conditions: 20 minutes Ar-plasma, 10 W, 10 mTorr. Photocatalysis conditions: Water, λ > 420 nm, 300 W Xe light source.

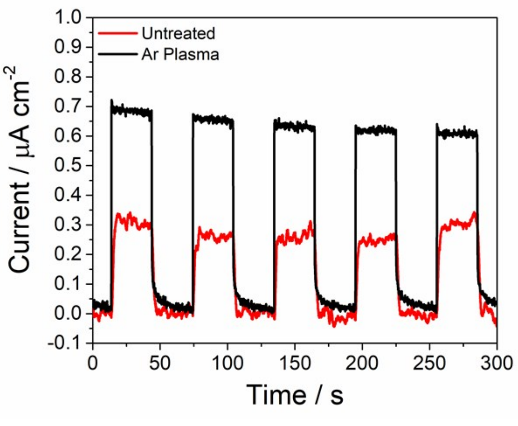

Figure S-22: Photocurrent measurements of **FS-5Dodec** before and after Ar plasma treatment (Ar plasma, 20 min, 10 W). Conditions: Broadband illumination (λ > 295 nm, Xe light source, on FTO-glass). The area illuminated was 1.5 cm^2 and a bias voltage of 0.63 V was used.

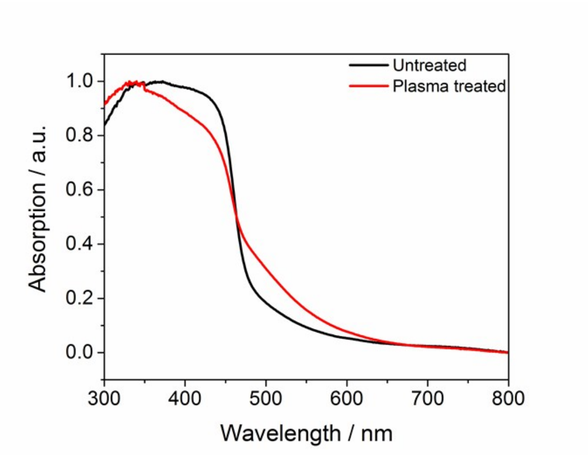

Figure S-23: UV-Vis spectra of **P35** before and after N_2/O_2 plasma treatment (Plasma treatment conditions: 10 minutes O_2/N_2 plasma, 11 W 60 mTorr, 15 minutes).

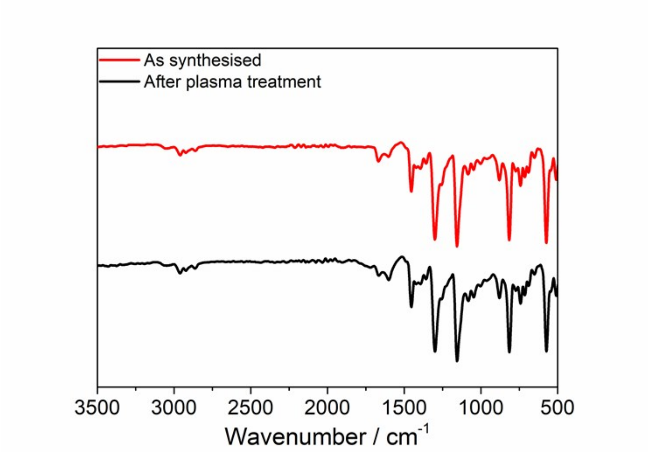

Figure S-24: FT-IR spectra of **P35** before and after N_2/O_2 plasma treatment (Plasma treatment conditions: 10 minutes O_2/N_2 plasma, 11 W 60 mTorr, 15 minutes).

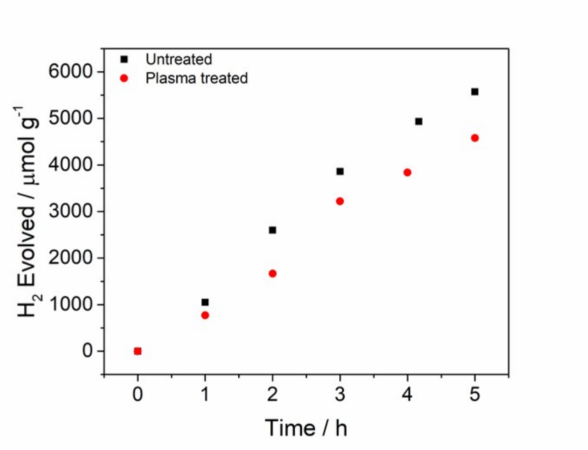

Figure S-25: Photocatalytic performance of **P35** and after N_2/O_2 plasma treatment under visible light illumination. Plasma treatment conditions: 10 minutes O_2/N_2 plasma, 11 W 60 mTorr, 15 minutes. Photocatalysis conditions: triethylamine/methanol/water mixture (1:1:1), $\lambda > 420$ nm, 300 W Xe light source.

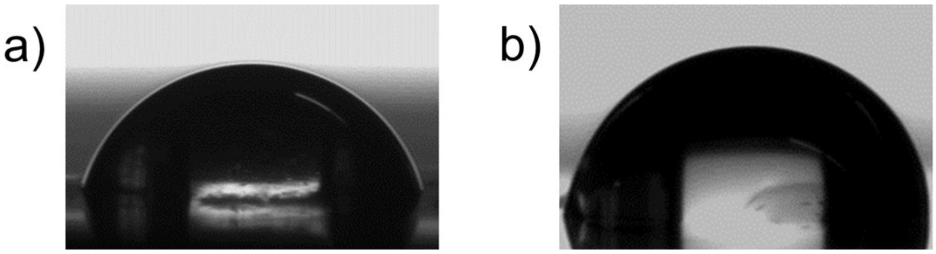

Figure S-26: Water drops on pallets of **P35** (a) before and (b) after N_2/O_2 plasma treatment (Plasma treatment conditions: 10 minutes O_2/N_2 plasma, 11 W 60 mTorr, 15 minutes).

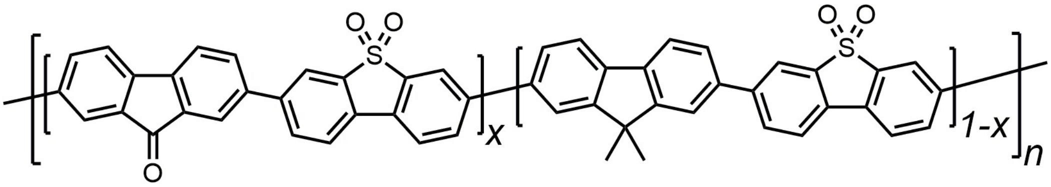

Figure S-27: Chemical structures of the **P35X%Fl** polymers.

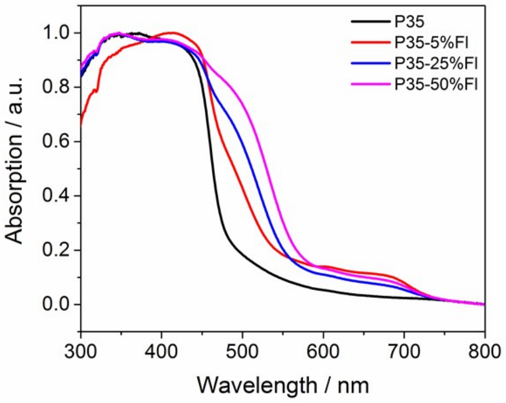

Figure S-28: UV-Vis spectra of **P35** and co-polymers of **P35 with fluorenone**.

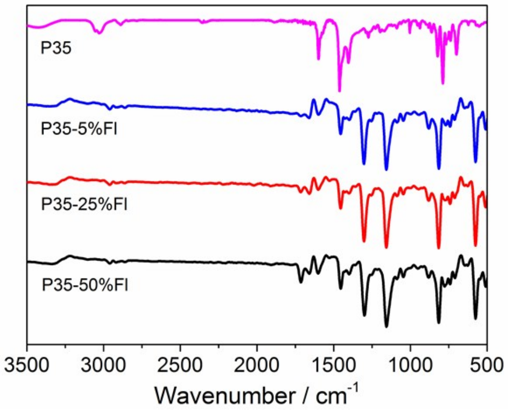

Figure S-29: FT-IR spectra of **P35** and co-polymers of **P35 with fluorenone**.

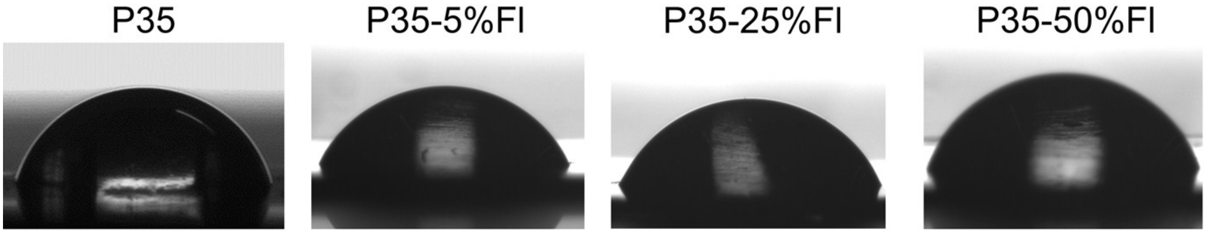

Figure S-30: Water drops on films of **P35** and the **P35 fluorenone co-polymers**. Contact angles were measured to be 77 ± 3° for P35, 72 ± 3° for P35-5%Fl, 78 ± 1° for P35-25%Fl, and 83 ± 2° for P35-50%Fl. Small differences could originate in grain-sizes on the surface of the pressed pallets.

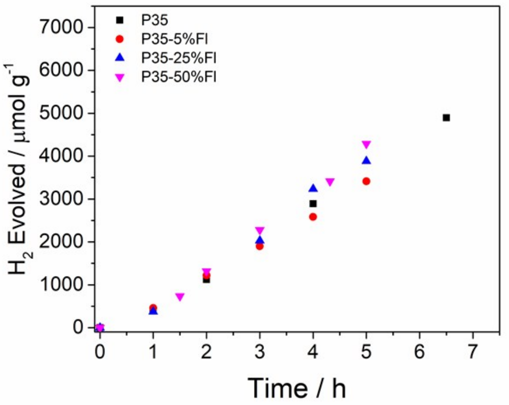

Figure S-31: Photocatalytic hydrogen evolution of **P35** and **co-polymers of P35** with fluorenone from water/methanol/triethylamine mixtures (1:1:1) under visible light (25 mg photocatalyst in 25 mL, λ > 420 nm filter, 300 W Xe light source).

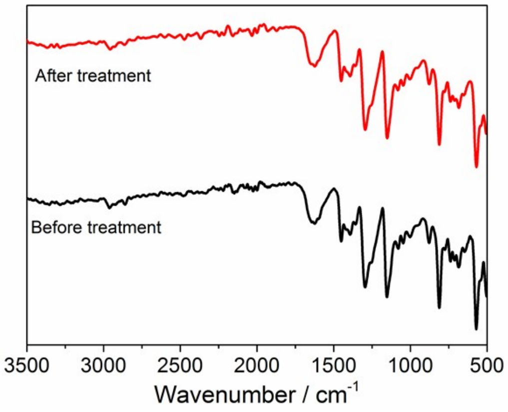

Figure S-32: FT-IR spectra of **FS-5Dodec** before and after Ar plasma treatment (Conditions: Ar plasma, 10 mTorr, 10 W, 20 min).

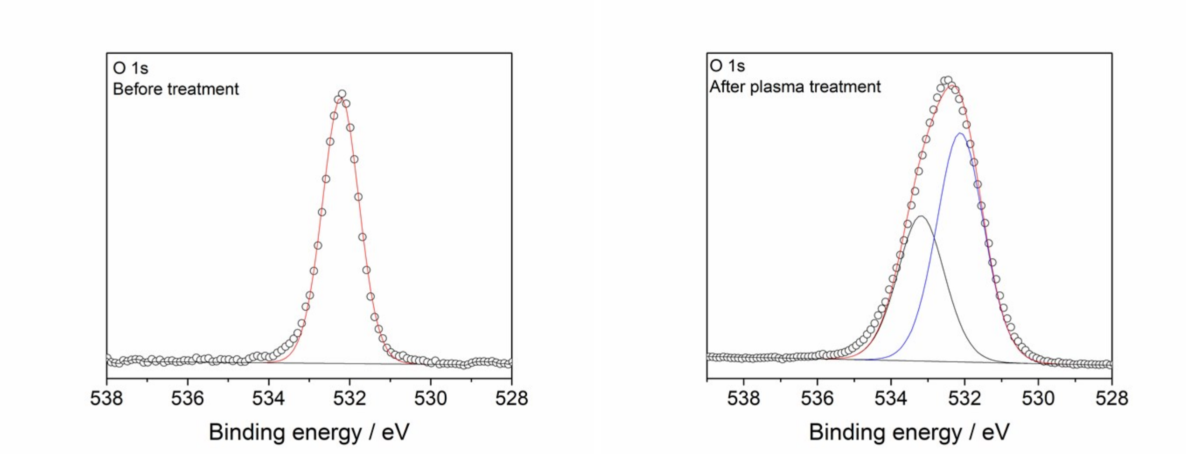

Figure S-33: Fits for the XPS spectra in the O1s region before and after plasma treatment.

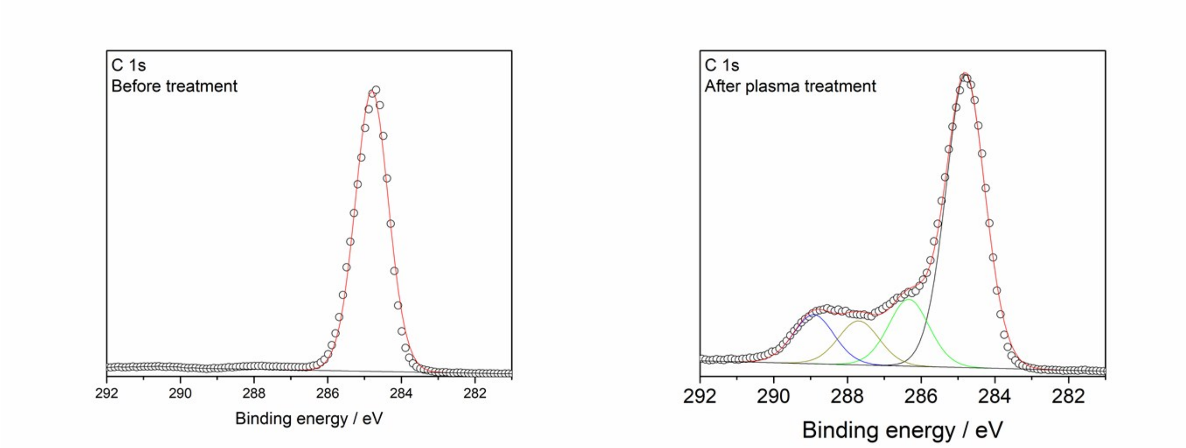

Figure S-34: Fits for the XPS spectra in the C1s region before and after plasma treatment.

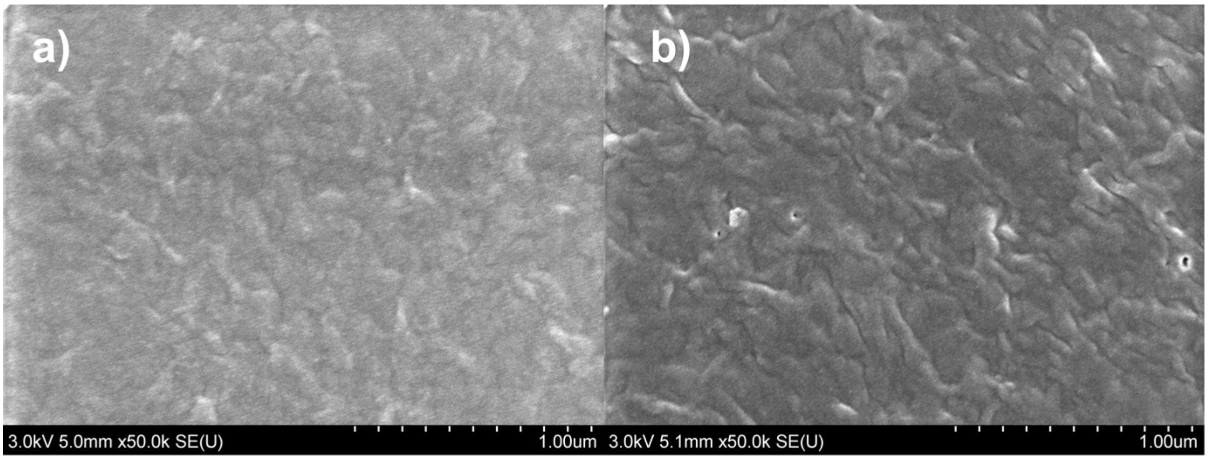

Figure S-35: SEM images of **FS-5Dodec** before and after Ar plasma treatment (Conditions: Ar plasma, 10 mTorr, 10 W, 20 min).

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