SUPPORTING INFORMATION

Multimodal analysis of POM/photosensitizer modified nanoporous block copolymers

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Experimental Procedures

Sodium perborate tetrahydrate and sodium persulfate were purchased from Sigma-Aldrich (St. Louis, MO, USA). Boric Acid, potassium chloride (KCl) and hexaammineruthenium (III) chloride ($[Ru(NH_3)_6]Cl_3$) were purchased from Merck, (Darmstadt, Germany). Tris(2,2'-bipyridyl)ruthenium(II)chloride, ($[Ru(bpy)_3]Cl_2$) was purchased from Acros Organics (Fair Lawn, NJ, USA). High purity water 18.1 MΩcm, Barnstead Nanopure – Thermo Fisher Scientific (Dubuque, IA, USA) was used for all solutions. Track-etched polycarbonate membranes (pore diameter: 2 µm) were purchased from Osmonic Inc. (Minnetonka, MN, USA). All chemicals and analytical grade solvents were purchased from Sigma-Aldrich Chemie GmbH (Munich, Germany). BlocBuilder MA was kindly donated by Sylvain Bourrigaud of Arkema and used as received. Styrene and 2-(dimethylamino)ethyl methacrylate and analytical grade solvents were purchased from Sigma-Aldrich Chemie GmbH (Munich, Germany). BlocBuilder MA was kindly donated by Sylvain Bourrigaud from Arkema (Colombes, France) and used as received.

Block copolymer synthesis

For the synthesis of the polystyrene (PS) polymer the initiator BlocBuilder MA (106 mg, 0.28 mmol) was dissolved in 32 mL styrene ([M]/[I]=1000). The oxygen was removed from the reaction mixture by three freeze-pump-thaw cycles and the reaction vessel was subsequently filled with argon. The reaction mixture was heated at 110 °C for 21 h. Afterwards, the mixture was cooled down in liquid nitrogen. The resulting polymer was precipitated twice in cold methanol (M_n= 31.700 g mol^{-1}, Đ=1.08).
In the second step, 1.2 g of the macroinitiator PS (M_n= 31.700 g mol^{-1}) were dissolved in a solution of 10 mL tetrahydrofuran (THF) and DMAEMA (2.86 mL, [M]/[I]=450). The reaction mixture was subsequently degassed by three freeze-pump thaw-cycles. Afterwards the reaction vessel was filled with argon and heated at 110°C for 1.5 h. The stabilizer of DMAEMA was removed by

passing through a short column of basic alumina. After the polymerization, the reaction mixture was cooled down to room temperature and precipitated three times in hexane (M_n= 42.900 g mol^{-1}, Đ=1.20).

Membrane fabrication

Membranes were prepared via the NIPS process as described previously:[1] films were cast onto glass substrates from 15 wt% block copolymer solution in THF/ N,N-dimethylformamide (DMF) (70/30 wt%) solvent mixtures using a 200 mm gate height doctor blade. The film casting was carried out in a climate chamber from Plas-Labs (Lansing, MI, USA) at controlled humidity (50%) and temperature (22 °C). After casting, the membrane was exposed to air for 30 s (so called "open time"), followed by fast immersion into a coagulation water bath. The membranes were lifted off from the glass substrates, and then stored in deionized water.

Functionalization of the block copolymer membrane

The functionalization of the membranes was carried out in deionized water. For every unit of DMAEMA in the block copolymer, a unit of WOC was added to the solution. $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ was prepared following the synthesis by Hill and co-workers.[2] Catalyst and photosensitizer immobilization were achieved in a facile two-step process. All steps were carried out in a round bottom flask having a round mesh (polyamide mesh-Nylon) to protect the membrane from damages through the magnetic stir bar. A round piece of membrane (ca. 450 mm^2) was immersed in 20 mL of a 0.64 mmol L^{-1} $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ x $27H_2O$ aqueous solution for 24 hours kept under stirring. The solution was then exchanged with deionized water and stirred for 24 hours to remove possible excess of the catalyst. Following, the membrane was immersed in an aqueous solution of the 1.2 mmol L^{-1} $[Ru(bpy)_3]Cl_2$ and kept under stirring for 24 hours. Another washing step in deionized water was carried out and the modified membrane was stored in ultrapure water prior to use.

Sample Preparation for (S)TEM/EDX analysis

The "WOCbranes" were embedded into EPON resin (Sigma-Aldrich Chemie GmbH, Munich, Germany) to avoid a possible reduction of the pore size during drying processes, avoiding thus morphological changes of the membrane. Embedding was performed following a protocol of Walter et al.[3] During this process, the water content of the wet membrane was substituted with propanol and EPON resin. For embedding, samples were incubated successively for one hour in 33%, 50% and 67% EPON resin in isopropanol, then overnight in 100% EPON and polymerized for 48 h at 60 °C. A Leica Ultracut UCT ultra microtome was used to prepare the ultrathin cross-sections (30 nm thickness for EDX mapping, 70 nm for TEM), which were then mounted on carbon-coated Formvar (Plano GmbH, Wetzlar, Germany) films on a 300-mesh cupper TEM grid.

"WOCbrane" digestion

For quantification of Ru, Co, and W content of the membranes via GFAAS, six samples of a few mm^2 each were taken from two individual immobilization batches using a scalpel (for each batch n=3). Each membrane piece was transferred to a micro-centrifuge tube, and 100 µL of nitric acid (HNO_3, 63% AnalR Normapur, VWR International GmbH, Darmstadt, Germany) precleaned by subboiling distillation (dst1000, Salvillex Corporation, USA) were added for digestion. Subsequently, the samples were treated in an ultrasonic bath for 10 min at 40 °C followed by mixing for 60 s at 2500 rpm. Ultra-sonication and mixing steps were repeated two more times. After that, 1000 µL of ultrapure water (obtained from ultrapure water purification system Sartorius AG, Göttingen, Germany) were added and the resulting suspension was vortexed for another 60 s at 2500 rpm. All steps of this sample preparation procedure were performed in a laminar flow box (Susi Super Silent, Spetec GmbH, Erding, Germany) in order to minimize possible trace contamination. Micro-centrifuge tubes (VWR International GmbH, Darmstadt, Germany) and pipette tips (Brandt GmbH & Co KG, Wertheim, Deutschland) were precleaned by immersion in 10% subboiled HNO_3 for at least 24 h and subsequent storage in 0.5% subboiled aqueous HNO_3.

Instrumentation

Scanning electrochemical microscopy (SECM)

A custom-built SECM setup (software: G. Wittstock, University Oldenburg, Oldenburg, Germany) was used to study the O_2 evolution at "WOCbranes" using Pt UMEs. Approach curves were recorded in 5 mmol L^{-1} hexaammineruthenium (III) chloride/0.1 mol L^{-1} KCl solution. A customized electrochemical flow cell was designed that allowed purging of the WOCbrane with Ar. Photocatalytic studies were carried out in 5 mmol L^{-1} sodium persulfate in 100 mmol L^{-1} borate buffer solution (pH 8.05). To ensure a constant argon flow, a flow rate of 1 mL min^{-1} was applied using a mass flow controller (MFC) (Bronkhorst GmbH, Kamen, Germany). Track-etched polycarbonate membranes with a pore size of 2 µm and a pore density of 2x10^6 pores/cm^{2}were used as support for the soft membranes and allowing a uniform Ar stream. The photocatalytic measurements of membrane B were performed within two days after modification, and of membrane A within a time period of four days after modification. A 400-µm optical fiber (MT-28L01, Thorlabs GmbH, Bergkirchen, Germany) connected to a 21.8 mW blue LED (M470F3, Thorlabs GmbH) was attached to the tip holder and placed 1 cm above the membrane. All electronic devices were placed outside of the Faraday cage.

Pt microelectrodes (ME) were fabricated with an RG value of 30. A Pt wire (10 µm diameter, Goodfellow, Bad Nauheim, Germany) was melted into borosilicate glass (glass capillaries were purchased from Hilgenberg, Malsfeld, Germany). The electrodes were then polished using diamond lapping films (Allied High-Tech Products, Rancho Dominguez, CA, USA) and aluminum oxide suspensions (LECO, St. Joseph, MO, USA). The electrochemical characterization of the UME was performed in a three-electrode setup, with an Ag/AgCl/3M reference electrode (RE), a Pt counter electrode (CE) and the ME as working electrode in a 5 mmol L^{-1} hexaammineruthenium (III) chloride/0.1 mol L^{-1} KCl solution.

Nuclear magnetic resonance spectroscopy (NMR)
^{1}H-NMR spectra were measured on a 300 MHz Bruker AVANCE spectrometer using $CDCl_3$, as deuterated solvent at a temperature of 298 K. The solvent residual peak $CDCl_3$ was used as standard.

Size exclusion chromatography (SEC)
SEC measurements in THF were performed on an Agilent system equipped with G1310A pump, a G1362A refractive index detector, and both a PSS Gram30 and a PSS Gram1000 column in series. THF was applied as eluent at 1 mL min^{-1} flow rate and the column oven was set to 40 °C. For calibration PS standards were used.

Thermogravimetric analysis (TGA)
TGA was performed on a Perkin-Elmer-TGA 8000 instrument under airflow (20 mL min^{-1}) at a heating rate of 10 °C min^{-1}.

Scanning electron microscopy (SEM)
SEM was performed on a Zeiss (Oberkochen, Germany) (LEO) 1530 Gemini FESEM operating at 5 to 10 kV using an InLens detector. Previously, the samples were coated with gold (~5 nm) using a SCD005 sputtering device BAL-TEC (Balzers, Liechtenstein).

Transmission electron microscopy (TEM)
TEM investigations were carried out using JoelTEM 1400 with an accelerating voltage of 110 kV. EDX mapping was performed at a Hitachi S-5200 field emission scanning electron microscope (FESEM) equipped with a scanning transmission electron microscopy (STEM)-detector (Hitachi High-Tech Corp., Tokyo, Japan) and an EDAX Phoenix X-ray detector system with a 30 mm^2 SUTW window (AMETEK GmbH, Weiterstadt, Germany). Acceleration voltage of 30 kV and a current of 20 µA were used for the measurements.

Micro-X-ray fluorescence spectrometry (µXRF)
Element maps of W and Co in the loaded membranes were recorded using micro-X-ray fluorescence spectrometer M4 Tornado (Bruker Nano GmbH, Berlin, Germany). For this purpose, membranes were dried for 1 h at room temperature and placed on an Ultralene ® foil (SPEX Sample Prep, Metuchen, NJ, USA) stretched on 31 mm open-ended X-cells (SPEX Sample Prep). The X-cells were fixed in a custom-made holder attached to the M4 Tornado sample stage. The instrument is equipped with an Rh X-ray tube which was operated at maximum power (50 kV, 600 µA). The polychromatic beam is focused via poly capillary lenses to a spot size of approximately 25 µm. The dwell time per pixel was set to 10 ms. Detection of the fluorescence quants takes place at a XFlash 430-PA detector with an active area of 30 mm^2 and a resolution of <145 eV for Mn-Kα. Fiji software (1.53k 07/06/2021) was used for both data visualization via Fire lookup table and interpretation of the intensity distribution.

Total reflection X-ray fluorescence spectrometry (TXRF)
Quantification of Co and W in the storage water of leaching experiments was performed using TXRF Picofox S2 high-efficiency module (Bruker Nano GmbH, Berlin, Germany). The Picofox S2 is equipped with a Mo X-ray tube, operated with a voltage of 50 kV and a current of 600 µA. 50 µL of each digest were diluted in 1000 µL of ultrapure water and mixed with 10 µL of Ti standard solution (100 mg L^{-1} in 2% HNO_3, Sigma Aldrich, Darmstadt, Germany) as internal standard. After thorough mixing for 60 s at 2500 rpm, 10 µL were applied to a siliconized (silicone solution, SERVA electrophoresis GmbH, Heidelberg, Germany) sample carrier (Bruker Nano GmbH, Berlin, Germany). For each sample three sample carriers were prepared and dried at 60°C for 30 min on a hot plate. The lifetime per sample carrier was set to 1000 seconds and three replicate measurements per sample carrier were performed (n=3).

High resolution-continuum source-graphite furnace atomic absorption spectrometry (HR-CS-GFAAS)
Simultaneous quantification of Ru and Co in the digested membranes was performed using HR-CS-GFAAS. A ContrAA 600 spectrometer (Analytik Jena GmbH, Germany) equipped with a graphite furnace atomization unit and solid sampling SSA 600 auto sampler was used. As purge and protective gas argon with a purity of 99.996% (MTI, Germany) was applied. For atomic absorption measurement a sector of 0.36 nm (200 Pixels) was selected, which includes both, the most sensitive line of Ru (349.895 nm) and a line of Co (349.668 nm). The pixel 38 (349.667 nm) and pixel 164 (349.895 nm) were evaluated by manually integration of the absorbance signal with the software OriginPro 2019b (OriginLab Corporation, USA).Three replicate measurements were performed by applying 10 µL of the digest onto a pyrolytic graphite-coated sample platform (Analytik Jena GmbH). Platforms are transferred automatically into the pyrolytic graphite-coated tube and the temperature program as shown in **Table S1** was started. Ru and Co concentration were determined using external calibration. For this purpose, a stock standard solution of 15 µg L^{-1} Ru and 0.7 mg L^{-1} Co was prepared by dilution of adequate volume of Ru/Co standard solution (1000 mg L^{-1} in 5% HCl, VWR International GmbH, Germany) in 0.5 mol L^{-1} subboiled aqueous HNO_3. Subsequently, different volumes of the stock standard solution were pipetted on the platform and the furnace program (Table S1) was started.

Table S1: Graphite furnace program.

Step	Temperature [°C]	Ramp [°C s^{-1}]	Hold [s]	Time [s]	Gas flow
Drying I	80	6	20	29.2	On
Drying II	90	3	20	23.3	On
Drying III	110	5	20	24.0	On
Pyrolysis I	350	50	15	19.8	On
Pyrolysis II	800	300	20	21.5	On
Pyrolysis II	1400	600	20	21	On
Gas adaption	1400	0	5	5.0	Off
Atomization	2500	1600	15	15.7	Off
Cleaning	2500	0	5	5	On

Results and Discussion

The *PS-b*-PDMAEMA diblock copolymer for the preparation of the membranes was synthesized in a two-step procedure. In the first step, the hydrophobic block was prepared via nitroxide-mediated polymerization (NMP) of styrene (**Figure S1**). This block forms the membrane scaffold and is therefore larger than the hydrophilic block. The resulting PS polymer has an average molar mass (M) of 31.700 g mol^{-1} and a polydispersity (Đ) of 1.08 (**Figure S2**). In the second step, the PS macroinitiator is used for the NMP of DMAEMA, which led to the final diblock copolymer PS_{304}-b-$PDMAEMA_{71}$ (Mn= 42.900 g mol^{-1}, Đ=1.20), the subscripts denote the number of repeating units of each monomer. The weight share of DMAEMA of the overall polymer is 26% and was calculated via nuclear magnetic resonance (NMR) measurements (**Figure S2a**)

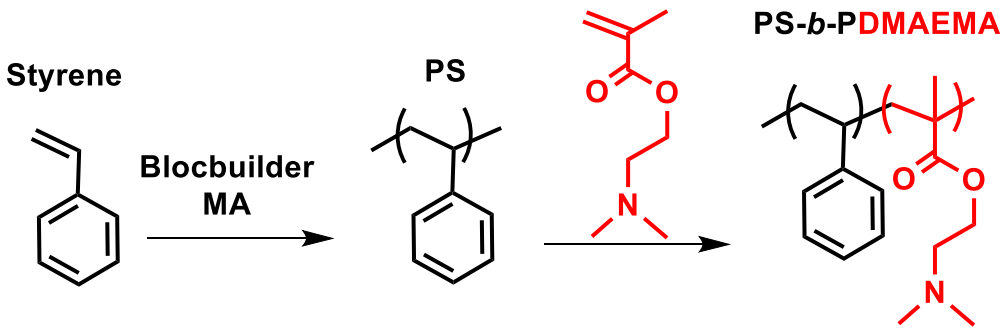

Figure S1: Stepwise synthesis of the diblock copolymer PS-*b*-PDMAEMA via NMP.

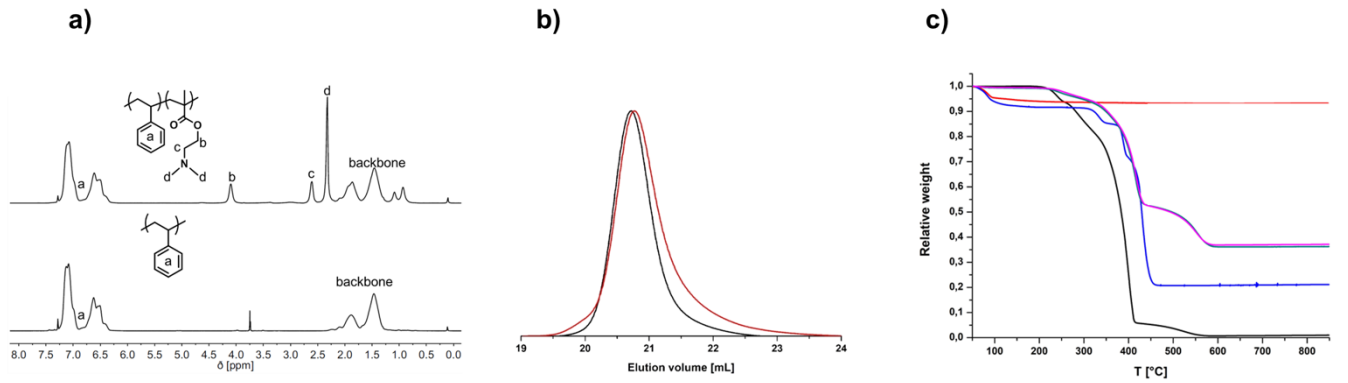

Figure S2: a) NMR of PS-*block*-poly(N,N-dimethylaminoethyl methacrylate); b) SEC of PS standard (black) and *PS-b*-PDMAEMA (red), THF was used for solvent; c) TGA graph of membrane before functionalization (black), pure $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ WOC (red), the pure $Ru(bpy)_3Cl_2$ photosensitizer (blue), the membrane functionalized with the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (green) and the membrane functionalized with both $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $Ru(bpy)_3^{2+}$ photosensitizer (magenta).

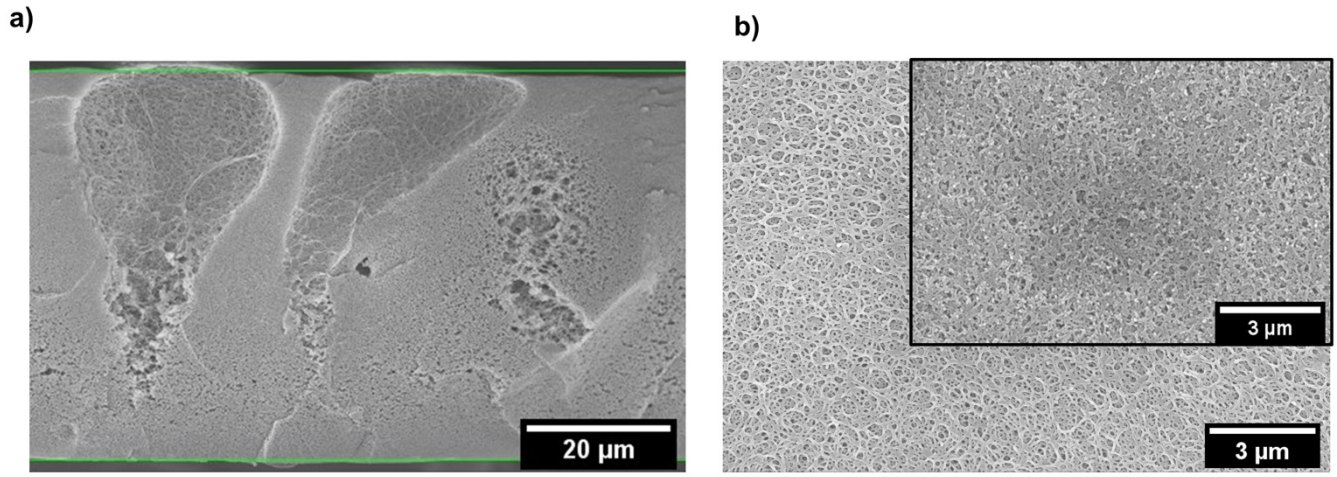

Figure S3: SEM image of pristine nanoporous block copolymer membrane; a) cross-section; b) top view of both sides of the membrane.

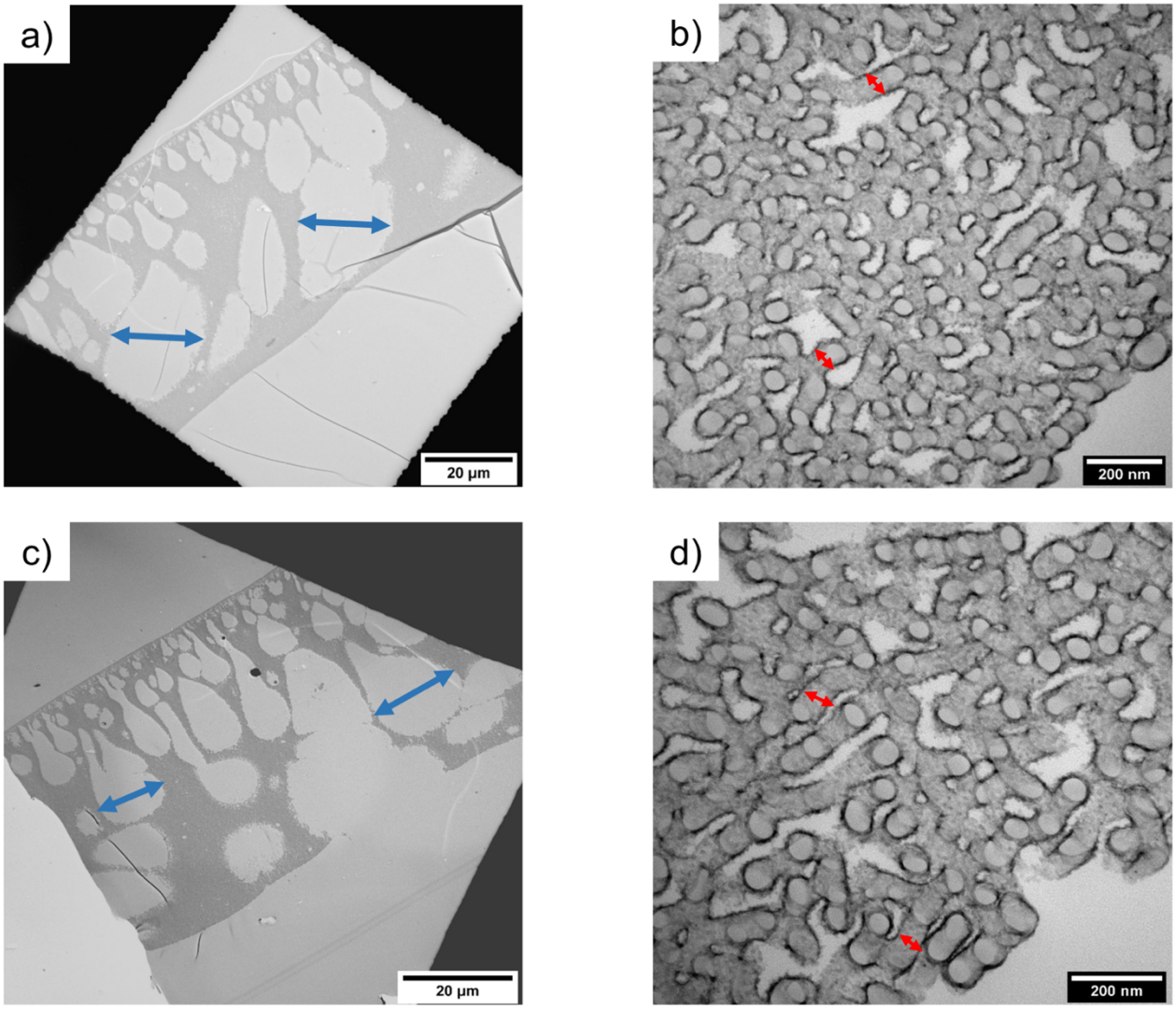

Figure S2: TEM image of EPON-embedded nanoporous block copolymer. a) Cross-section of modified nanoporous block copolymer; b) zoomed view of nanoporous block copolymer; c) cross-section of nanoporous block copolymer (after illumination); d) zoomed view of nanoporous block copolymer (after illumination).

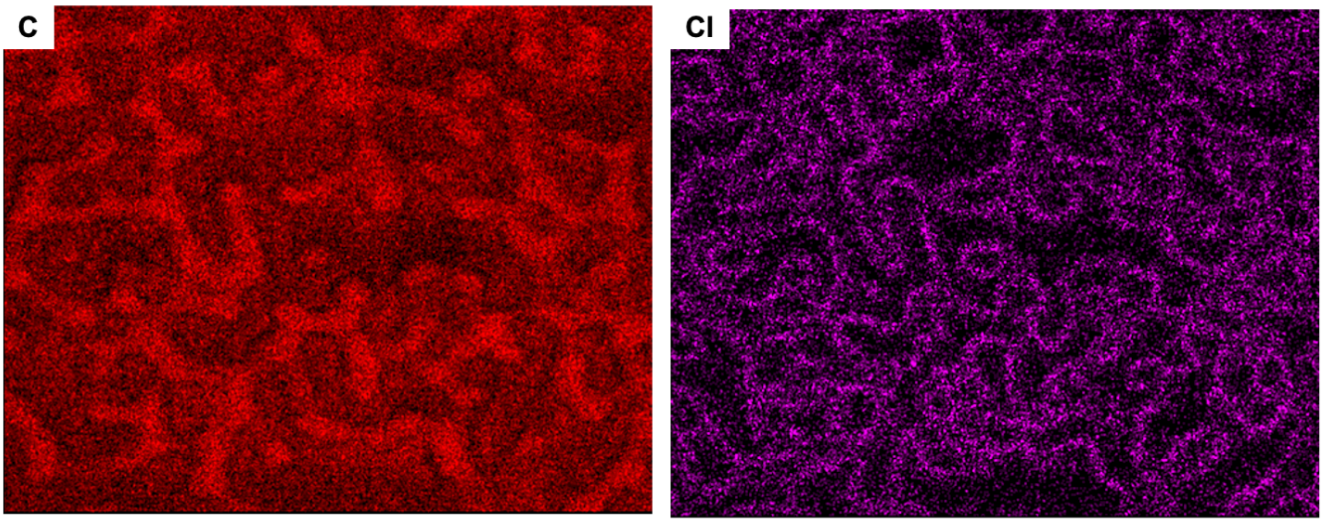

Figure S5: STEM/EDX mappings of the elemental distribution of carbon (C) and chlorine (Cl) of the modified block copolymer

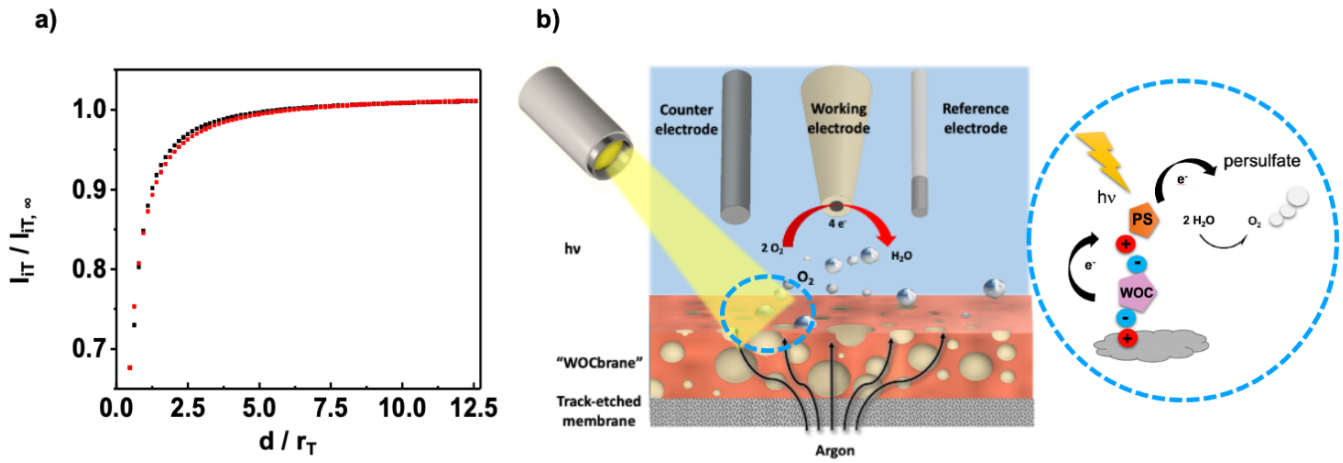

Figure S6: a) Exemplary SECM approach curve recorded with a Pt microelectrode in 5 mmol L^{-1} hexaammineruthenium (III) chloride / 0.1 mol L^{-1} KCl solution. Et_{ip} = -300 mV vs. QRE with a scan velocity 1 µm s^{-1}; black dotted line is the experimental curve showing negative feedback current; red dotted line is the theoretical approach curve using the fitting approach of Amphlett and Denuault[4]; b) Schematic of the track-etched membrane supported setup and the light-driven catalytic oxygen evolution under irradiation.

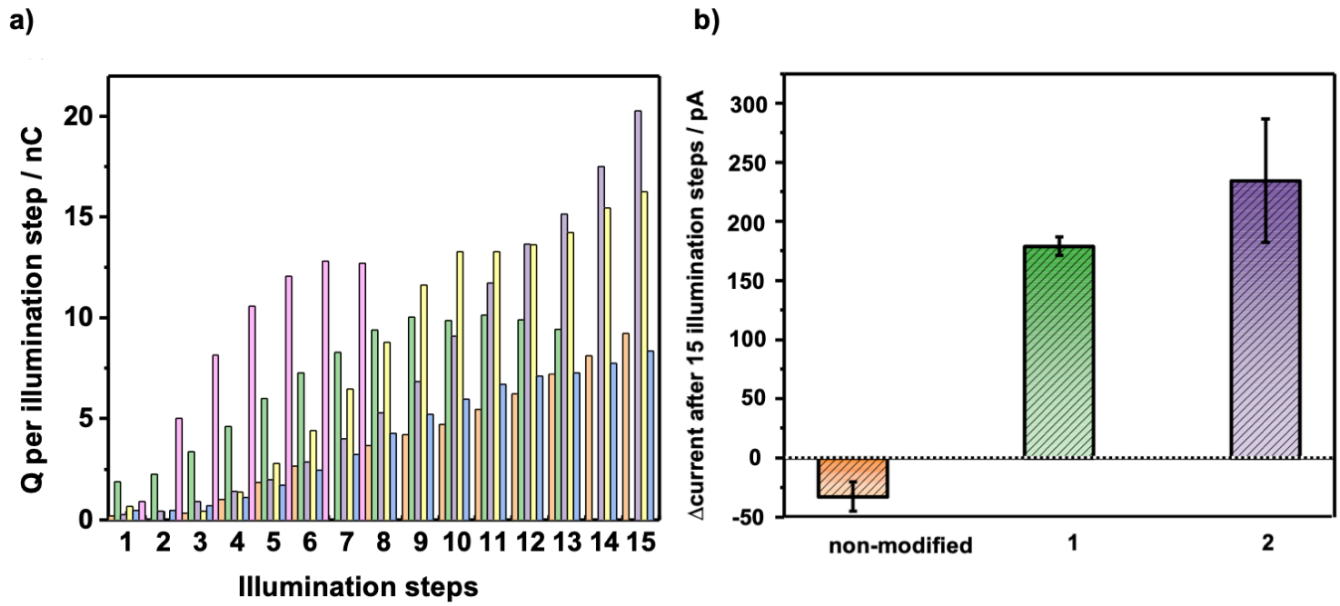

Figure S7: a) Charge evolution during 15 individual irradiation steps (60 sec) measured at 6 individual WOCbranes from two immobilization batches. b) overall current change measured at non-modified block copolymer membrane (orange, n = 4) and at WOCbranes from two immobilization batches (green, n =2; purple, n = 4).

Table S2. Calculated O_2-concentration of WOC/photosensitizer-embedded nanoporous block copolymer membrane after 15 illumination steps. 6 different samples from two batches were investigated.

O_2-concentration [µmol L^{-1}]					
Membrane 1.1	Membrane 1.2	Membrane 2.1	Membrane 2.2	Membrane 3.3	Membrane 3.4
163.37	291.72	351.13	386.15	198.25	196.48

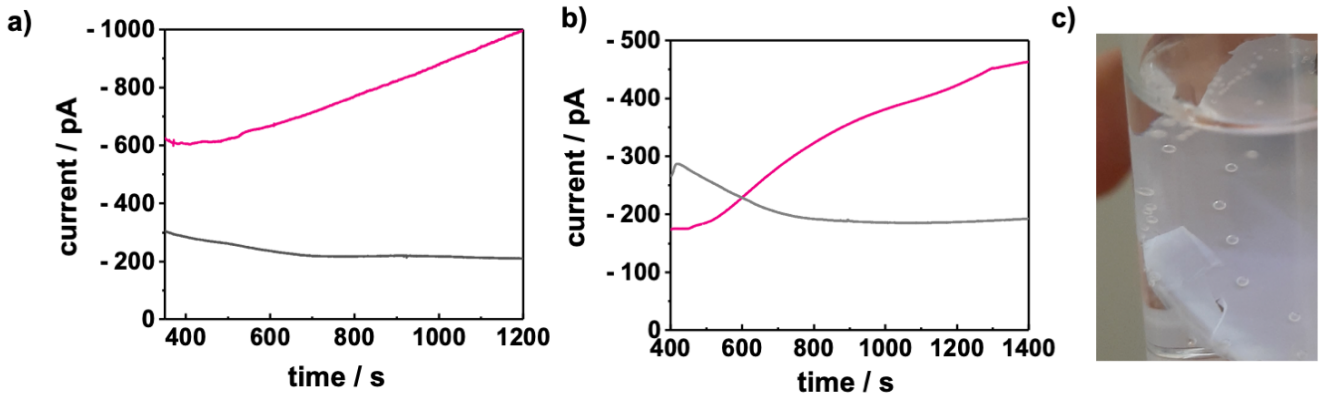

Figure S8: a) i-t curve revealing the O_2 reduction current recorded at the SECM tip when a non-modified membrane was purged with air (magenta) of Ar (grey); b) i-t curve showing the O_2 reduction current recorded at the SECM tip at a WOCbrane (magenta) and non-modified membrane (grey) in 1 mmol L^{-1} $[Ru(bpy)_3]^{2+}$, 5 mmol L^{-1} $Na_2S_2O_8$ /100 mM borate buffer solution under irradiation. d) Photograph of oxygen bubbles at the surface of WOCbrane after illumination in 5 mM $Na_2S_2O_8$/100 mM borate buffer solution.

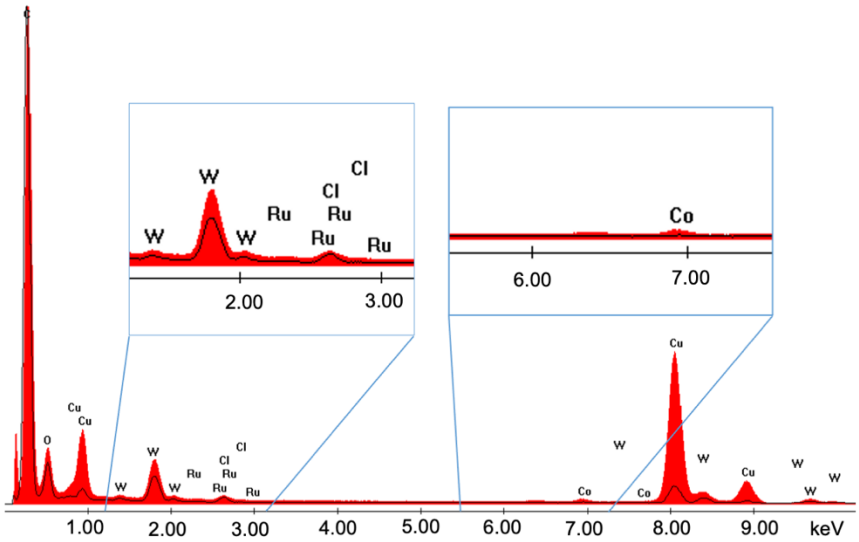

Figure S9: EDX spectra (red) of a non-illuminated WOCbrane and after 30 min of illumination (black line); intensity normalized to C peak. It should be noted that the Cu signal in the EDX spectra is due to the Cu TEM grid. Electrons scattered in the sampled membrane may hit the Cu grid producing Cu X-ray signals. The number of scattered electrons correlates with the density of the sampled volume and therefore the concentration of W.

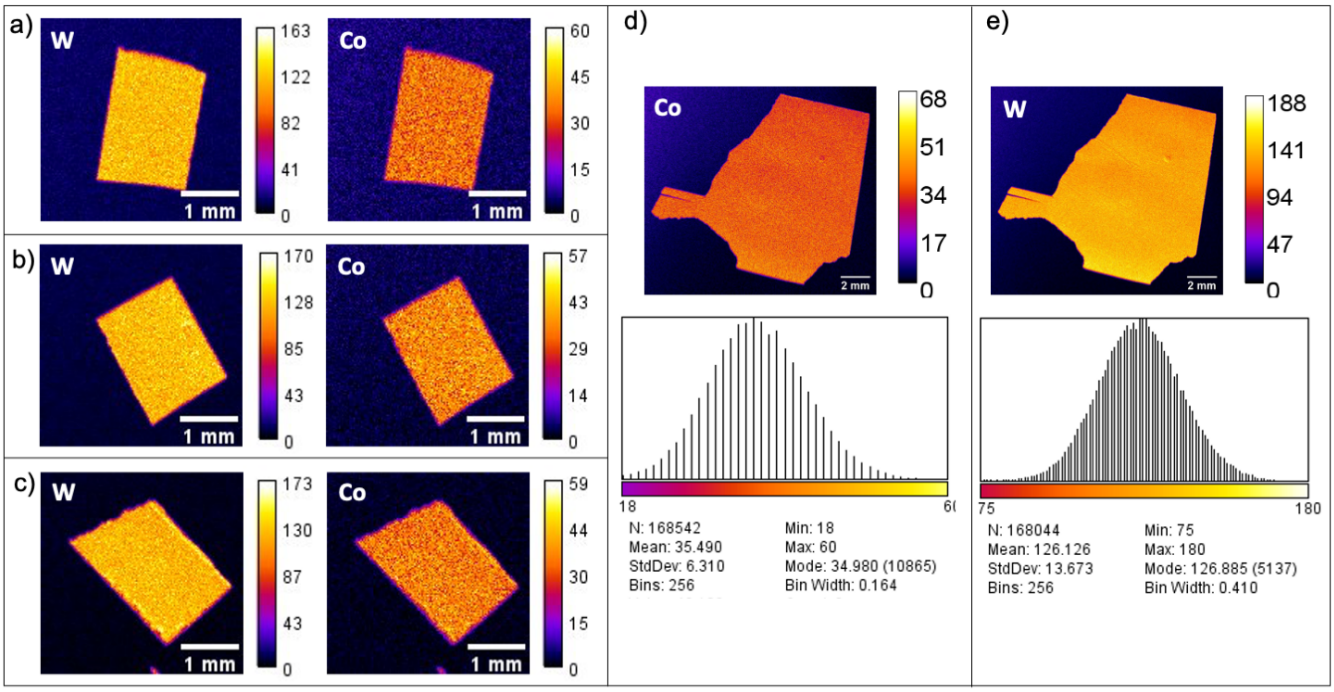

Figure S10: Element maps for cobalt and tungsten of smaller pieces of a WOCbrane C. a) Sample C1, size: 3.04mm^2; b) sample C2, size: 3.42 mm^2; c) sample C3, size: 5.66 mm^2; d/e) Sample C: Co/W intensity distribution)

Table S3. Concentrations of Co and Ru as found by GFAAS measurement in digests of pieces of membrane C. (Uncertainties given as ± one standard deviation with n=4 for concentrations and combined uncertainty for ratio.)

Sample	Size [mm^2]	Concentration found by GFAAS [nmol mm^{-2}]	
		Co	Ru
3.1	3.82	8.8 ± 0.6	< LOD
3.2	5.89	3.8 ± 0.2	< LOD
3.3	5.03	8.4 ± 0.6	< LOD
4.4	5.36	8.3 ± 0.4	< LOD

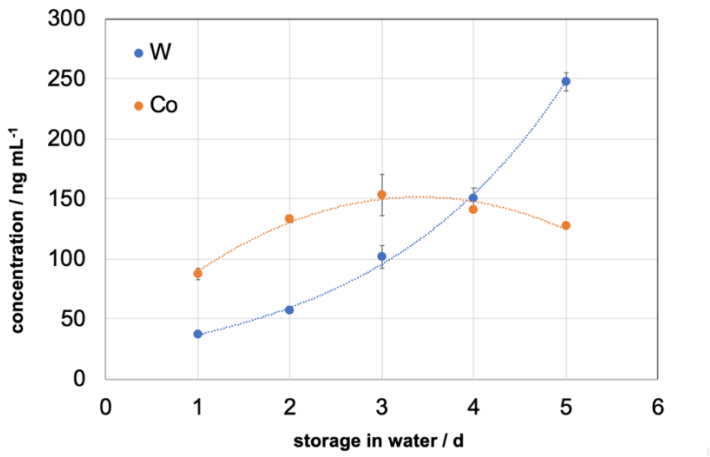

Figure S11: Leaching experiments over 5 days of a WOCbrane. Measurements of W and Co content of the storage water were performed *via* TXRF.

References

[1] F. Schacher, M. Ulbricht, A. H. E. Müller, *Adv. Funct. Mater.* **2009**, *19*, 1040–1045.
[2] Q. Yin, J. M. Tan, C. Besson, Y. V Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle, C. L. Hill, *Science* **2010**, *328*, 342–345.
[3] P. Walther, A. Ziegler, *J. Microsc.* **2002**, *208*, 3–10.
[4] J. L. Amphlett, G. Denuault, *J. Phys. Chem. B* **1998**, *102*, 9946–9951.

Author Contributions

Julian Kund performed the *in-situ* SECM experiments and wrote the draft manuscript. Jan Kruse fabricated the block copolymer membrane, carried out the TGA, SEC and NMR analysis and wrote part of the draft manuscript. Ivan Trentin performed the membrane functionalization. Gregor Neusser, Clarissa Read and Ulrich Rupp performed the TEM and STEM/EDX analysis. Andreas Gruber carried out the µ-XRF experiments and data analysis. Dominik Blaimer performed the HR-CS-GFAAS measurements. Christine Kranz, Felix Schacher, Carsten Streb and Kerstin Leopold designed and supervised the experiments and revised the manuscript. All authors have read and agreed to the version of the manuscript.