Supporting Information

POMbranes: Polyoxometalate-functionalized Block

Copolymer Membranes for Oxidation Catalysis

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1. Block copolymer characterization



Figure S1: Size exclusion chromatography (SEC) traces (solvent: $CHCl_3/TEA/IPA = 94/4/2$, polystyrene calibration) of the diblock copolymer $S_{68}D_{32}$ used for POM heterogenization. The block copolymer exhibits a monomodal distribution with a low polydispersity index.

2. POM-immobilization



Figure S2: POM-immobilization on the block copolymer $S_{68}D_{32}$: A) photographs of membrane color change from colorless (pristine membrane) to yellow (POMbrane) after POM immobilization; B) Decrease of supernatant coloration during POM immobilization on $S_{68}D_{32}$; C) $S_{68}D_{32}$ -V₂ in H₂O top view.



Figure S3: Transmission electron microscopy micrographs of micelles of pristine $S_{68}D_{32}$ (A, D), $S_{68}D_{32}$ and $H_5[PV_2Mo_{10}O_{40}]$ in the presence of H_2O_2 (B, E), $S_{68}D_{32}$ and $H_5[PV_2Mo_{10}O_{40}]$ formed under aqueous conditions(C,F). Block copolymer concentration was kept at 1 mg/mL for all samples.

The addition of POM to the block copolymer results in the formation of core-corona micelles were the core consists of hydrophobic polystyrene and the corona of hydrophilic DMAEMA-POM aggregates. Due to electrostatic repulsion between negatively charged POM units, POM-block copolymer micelles (B,C,E,F) show less tendency to agglomerate in comparison with pristine $S_{68}D_{32}$ (A,D).



Figure S4: DLS CONTIN plots for $S_{68}D_{32}$ -POM(V₂) in the absence and presence of H_2O_2 .

A	Spectrum A O Na Si P S V Cu Cu Mo Sn	Mass % 50.57 1.74 0.64 1.62 2.29 5.28 0.27 37.47 0.12
в	Spectrum B O Na Si P S V Br Mo	Mass % 63.47 2.74 1.10 1.15 2.13 3.36 0.03 26.03

Figure S5: EDX spectra of the $S_{68}D_{32}$ - V_2 surface (A) and cross-section (B). Both top view and cross-section of the hybrid membrane contain between 26 to 37 wt. % POM

3. UV-Vis determination of POM uptake by S₆₈D₃₂ membrane

Procedure: 7.7 mg of $S_{68}D_{32}$ was immersed in 15 mL of an aqueous solution containing 5.3 mg (3.0 mmol) of $H_5[PV_2Mo_{10}O_4]x12H_2O$ for 12 h. Afterwards, 1 mL solution was withdrawn by syringe and analyzed by UV-Vis spectroscopy. The final solution concentration of the POM was determined from the linear regression graph shown below.



Figure S6: Linear regression allowing the calculation of the $H_5[PV_2Mo_{10}O_{40}]$ concentration in the supernatant after POM uptake by $S_{68}D_{32}$.

 Determined POM wt. % in S₆₈D₃₂ :

 by UV-Vis:
 29.9%

 by TGA:
 31.4%

Both methods used for the determination of the POM content are in good agreement. The \sim 30 wt. % of POM loading corresponds to 40 % protonation of DMAEMA units.

4. Catalysis

Catalysis setup:

1. Batch conditions

Typical catalytic oxidation under batch conditions was performed in a 50 mL round-bottom flask equipped with a magnetic stir bar, which was separated from the catalyst/membrane by a rigid polyamide membrane to avoid mechanical damage (Figure S7A). Recycling experiments were performed by removal of the supernatant solution, followed by washing the membrane with distilled water (2 x 15mL) and CH₃CN (1 x 15 mL), followed by the addition of a new set of reagents.

Regeneration experiments were performed by removing the membrane, rinsing with distilled water (2 x 15mL) and CH₃CN (1 x 15 mL), followed by vacuum-drying (10⁻⁶ mbar for 4 h). Then, new aliquots of the reagents were added and catalysis was performed under standard conditions.

Anthracene oxidation:

13.5 mg of membrane (0.005 mmol of cat), anthracene (25 mg, 0.14 mmol) and CH_3CN (6 ml) were placed in the batch setup. Then, 0.5 mL of 30 wt. % aqueous H_2O_2 (4.8 mmol) were added. The reaction was performed at 40°C. Conversion was followed by GC-*MS*.

THT oxidation:

13.5 mg of membrane (0.005 mmol of cat), 119 μ L of THT (1.35 mmol) and 6 mL of CH₃CN were placed in the reaction setup. 280 μ L of 30 wt. % aqueous H₂O₂ (2.74 mmol) were added. The reaction was performed at 20°C. Conversion was followed by GC-MS using chlorobenzene as internal standard.

2. Flow conditions

Catalysis under flow conditions was carried out using an Amicon 8010 ultrafiltration cell under 0.3 bar of transmembrane pressure. The setup of the ultrafiltration cell is shown in Figure S7B. A solution containing 1.19 mL of THT (13.5 mmol) and 2.8 mL of 30 wt. % aqueous H_2O_2 (27.4 mmol) in 60 ml of CH₃CN was pumped through 13.5 mg of membrane (0.005 mmol of cat). Conversion was followed by GC-MS using chlorobenzene as internal standard.



Figure S7: Setup for catalytic oxidation under batch (A) and flow (B) conditions.



Schematic representation of Anthracene oxidation mechanism through a 2-step process. In the first step, the electron transfer from substrate to POM takes place, reducing V⁵⁺ to V⁴⁺. In the second step oxygen transfer from POM to substrate occurs. The POM is oxidized back to the native state by H_2O_2 . The mechanistic scheme was taken from J. Am. Chem. Soc. **2001**, *123*, 8531-8542.



Figure S8: Anthracene oxidation with $S_{68}D_{32}$ - V_2 . Catalysis performed under batch conditions with a catalyst loading of 4 mol % (based on V), 22 mM of anthracene (0.14 mmol) and 750 mM (4.8 mmol) of 30 wt. % aqueous H_2O_2 at 40°C in 6 mL of CH₃CN.



Figure S9: Change of the reaction mixture composition during 9,10-dihydroanthracene oxidation with $S_{68}D_{32}$ - V_2 as a function of time. Catalysis is performed under batch conditions with a catalyst loading of 4 mol % (based on V), 22 mM (0.14 mmol) of anthracene and 750 mM (4.8 mmol) of 30 wt. % aqueous H_2O_2 at 40°C in 6 mL of CH₃CN. The graphic shows that an unusually large amount of anthrone was accumulated during heterogeneous oxidation (maximum 13 % at t = 20 h). Under homogeneous conditions, the formation of anthrone was not observed.



Figure S10: SEM micrographs of the POM-functionalized membrane after catalysis A) Back view; B) cross-section; C) top view; D) top view in higher magnification. As shown in C and D, partial membrane degradation can be observed.



Figure S11: TEM micrographs of supernatant after catalytic anthracene oxidation. Residual pieces of membrane and core-corona block copolymer micelles were found in the solution.



Figure S12: UV-Vis comparison of supernatant solution after catalysis with POM standard solutions in CH_3CN that corresponds to expected level of POM leaching. Less than 1 wt. % of POM leaching is observed after cycle V.



Figure S13: EDX spectra of the $S_{68}D_{32}$ - V_2 surface (A) and cross-section (B) after cycle VI of THT oxidation. The Mo and V content on the surface and on the cross-section of the membrane before and after catalysis are comparable within experimental error, suggesting that no significant POM leaching is taking place under these conditions. This is in agreement with the UV-Vis spectroscopy described above (Figure S12).