

Electronic supplementary information (ESI)

Visible light-induced RAFT for asymmetric functionalization of silica mesopores

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Experimental

Chemicals. Pluronic® F127, 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, 98%, HPLC), ethanol (absolute EMPLURA®), Dichlormethane (anhydrous, ≥99.8%), 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine zinc (ZnTPP), (3-aminopropyl)triethoxysilane (APTES, ≥ 98%), Dimethylaminoethyl methacrylate (DMAEMA, 98%) and tetraethylorthosilicate (TEOS) (98%, reagent grade) have been purchased from Sigma-Aldrich/Merck. The monomer DMAEMA was destabilized over a γ -aluminium column before use. 2-(methacryloyloxy)ethyl phosphate (MEP, 90%, Sigma-Aldrich/Merck) was used as received. Toluene (anhydrous, 99.8%) was purchased from Alfa Aesar and dimethylsulfoxid (DMSO) (99%) from Grüssing GmbH.

Preparation of mesoporous silica thin films. The preparation of the mesoporous silica thin films was carried out using the sol-gel process. The amphiphilic triblock copolymer Pluronic® F127 was used as template and TEOS as inorganic precursor. Inspired by Dunphy et al.^[1] a dip-coating process were performed to produce mesoporous silicafilms with pore sizes of ~13 nm and film thicknesses of ~500-600 nm. For the dip-coat solution 9,8 mL TEOS were dissolved in 48,0 mL ethanol. Than 5,22 g Pluronic® F127 and 12,8 mL of a freshly prepared hydrochloric acid solution (0,05 M) were added. The solution was stirred for 1h at room temperature and stored in the freezer (-18°C) till use.

The formation of the mesoporous silica thin films was realized by the *Evaporation-Induced Self-Assembly* (EISA-process).^[2] Glass substrates, ITO-coated glass substrates and silicon wafers were washed with ethanol and dip-coated using a withdrawal speed of 2 mm/s under controlled environmental conditions in a climate-controlled chamber (40-50% rel. humidity, 25 °C). The films were stored under these conditions for at least 1h before the following temperature treatment was carried out: heat up to 60 °C in 10 min and hold the temperature for 60 min, then a temperature increase to 130 °C within 10 min, and holding the temperature at 130 °C for 60 min. Subsequently heating to 350 °C using a heating rate of 1 °C/min and keeping this temperature for 2h.

Surface grafting of DDMAT. For grafting the RAFT-agent DDMAT on the mesoporous silica film the DDMAT was modified with a silica-anchor according to the literature.^[3] Briefly, under nitrogen atmosphere 1 mmol DDMAT was dissolved in 50 mL dry dichloromethane (DCM). In another flask 1 mmol EDC HCl was dissolved in 10 mL dry DCM. Then the EDC HCl solution was added dropwise into the first flask. The solution was cooled and stirred at 0°C before 1 mmol APTES was added dropwise. The yellow/orange reaction solution was stirred for 2h at 0°C and after that for another 2h at room temperature. The solution was concentrated using a rotary evaporator (40°C). Thereafter a silica gel column chromatography (1:1 v/v EE and cyclohexene) was performed ($R_{f(\text{DDMAT-derivate})} = 0,92$). The grafting of the modified RAFT agent DDMAT and the following polymerization were carried out on mesoporous silica thin films being deposited on glass substrates, indium-tin-oxide (ITO)-coated glass

substrates or silicon (Si)-wafer substrates. To functionalize the mesoporous silica films a solution of 2.4 mmol L⁻¹ DDMAT-derivate (DDMAT with silica-anchor) in dry toluene was prepared and filled into a Schlenk flask, which contained substrates with mesoporous silicafilms under nitrogen atmosphere. The Schlenk flask was placed in a water bath (80°C) for 1h. Subsequently, the substrates were washed with toluene and ethanol.

PDMAEMA and PDMAEMA-*b*-PMEP functionalization of mesoporous silicafilms. Inspired by the group of Pester^[3] the polymer functionalization of the films were performed by a PET-RAFT using visible light. As photo catalyst ZnTPP and as solvent DMSO was used. To functionalize films with PDMAEMA-*b*-PMEP first the functionalization step with DMAEMA was performed for 2h followed by the polymerization of MEP. For the polymerization DDMAT-functionalized mesoporous silicafilms were placed in tubes containing a solution with the following molar ratios: [monomer]: [ZnTPP]: [DMSO (mL per mg ZnTPP)] = [500]: [0.025]: [10 mL]. The polymerization was initiated by visible light irradiation (LUMATEC Superlite 410, 400-700 nm filter, 38 mW cm⁻²) for 2h. After irradiation, the residual monomer was extracted in water for at least 10 min.

ATR-IR spectroscopy. IR spectra were recorded in the attenuated total reflection (ATR) mode using a Spectrum One Fourier transform infrared (FT-IR) spectrometer from PerkinElmer in the range from 4000-650 cm⁻¹. The mesoporous silica films were scratched off with a razor blade. The data were background-corrected from the software. Also the spectra were baseline corrected and normalized to the Si-O-Si asymmetric stretching vibrational band at ~1060 cm⁻¹ using OriginPro9.

Ellipsometry. The determination of refractive indices and film thicknesses were carried out by ellipsometry on silicon wafer substrates (Si-Mat, Kaufering, Germany, 100mm diameter, 525±25 µm thickness, type P/Bor, <100> orientation, CZ growth method, 2–5W resistivity, polished on 1 side) using the device nanofilm EP3-SE from the company ACCURION with a 658 nm laser. The mesoporous silicafilms were characterized before and after each functionalization step comparing three different positions each before and after functionalization. As software EP4-View and EP4-model (version 1.2.0) was used for measurement and model analysis. For the measurements an angle range of 38° -70° in 2° increments were used and was performed at three measuring points along the pulling direction of the dip coating and measured in *one-zone* mode (Si-wafer → SiO₂- oxide layer → SiO₂ mesoporous). With the program Regul'Hum (version 3.3) a relative humidity of 15 % was adjusted to exclude water condensation inside the mesopores. The calculation of pore fillings was carried out according to Bruggemann effective medium theory^[8,9] by using the refractive indices. For PDMAEMA a refractive index of 1.517^[4] was used, for all other organic molecules n=1.5 was assumed.

CO₂-plasma treatment. The CO₂-plasma treatment was performed with a Diener Electronic 20 Femto plasma system analogous to Krohm et al.^[5] and Babu et al.^[6] at a pressure of 0.3 mbar and a power of 20% (10 watts). The duration was 12 seconds.

Thermogravimetric analysis (TGA). The TGA measurements were performed on the TGA 1 STARE System from Mettler Toledo with the software STARE Software, version 12.10b (Build 6401). For the

measurement 100 µl aluminium-crucibles were used. The Sample mass was between 0.66 mg and 1.15 mg. The following temperature treatment was carried out using an air flow of 30 mL/min: Heat up from 25°C to 100 °C in 10 K/min and hold the temperature for 15 min, heat up to 600°C in 10K/min. Determination of the grafting density and chain length were done by using the following equations 1-3. $W\%$ is the weight loss from TGA measurements, G_I is the grafting density of the RAFT agent DDMAT, G_P the polymer grafting density and S_{sp} the specific surface. [7]

$$G_I \left(\frac{\text{molecule}}{\text{nm}^2} \right) = \frac{\frac{W\%_{\text{silica} + \text{Initiator}}}{100 - W\%_{\text{silica} + \text{Initiator}}} - \frac{W\%_{\text{silica}}}{100 - W\%_{\text{silica}}}}{M_{\text{Initiator}} \cdot S_{sp}} \cdot N_A \quad (1)$$

$$G_I = G_P \quad (2)$$

$$M_P = \frac{\frac{W\%_{\text{silica} + \text{polymer}}}{100 - W\%_{\text{silica} + \text{polymer}}} - \frac{W\%_{\text{silica} + \text{Initiator}}}{100 - W\%_{\text{silica} + \text{Initiator}}}}{G_P \cdot S_{sp}} \cdot N_A \quad (3)$$

Cyclovoltammetry (CV). Cyclic voltammetry measurements for investigation of pore accessibility was performed at the Potentostat Autolab PGSTAT302N from Metrohm Autolab BV with the software Nova 2.0. 100 mM KCl solution was used as background electrolyte. As anionic probe molecule $[\text{Fe}(\text{CN})_6]^{4-/3-}$ an as cationic probe molecule $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ (each 1 mM in 100 mM KCl solution) were used. Furthermore, 0.06 vol% ethanol was added to the solution. The pH values were set using diluted hydrochloric acid or diluted sodium hydroxide solution. An Ag/AgCl-electrode (BASi, Typ RE-6) and a graphit electrode (Alfa Aesar) were used as reference electrode and the counter electrode, respectively. As working electrode, the ITO layer of the substrate was used (Delta Technologies, 4-8 Ω). The measured mesoporous film area was 0.21 cm². For each measurement a scan rate sequence of 200, 100, 25, 300, 500, and 200 mVs⁻¹ was measured in this order, while each scanrate was cycled three times. For evaluation the scanrate of 100 mVs⁻¹ was used. For all data it was made sure that the first and the last 200 mVs-1 scanrate show comparable scans.

X-ray Photoelectron Spectroscopy (XPS). XPS was measured on the SSX 100 ESCA Spectrometer from Surface Science Laboratories Inc. with a monochromatic Al K α X-ray source and a S-Probe geometry. The spectrometer is equipped with a flat specimen holder and the analyzer-horizontal is 35°. The X-ray spot size was 0.25 mm x 1.0 mm using an energy of 9 kV (10 mA). The overview spectra were measured using a pass energy of 150 eV, a neutralizer energy of 0.5 eV and a step size of 0.5 eV. The resolution was 0.16 eV. For binding spectra, the passing energy was 50 eV, the neutralizer energy 0.5 eV, step size 0.05 eV and the resolution 0.054 eV.

Scanning electron microscopy (SEM). The SEM measurements were performed on the device Philips XL30 FEG with a SE detector, operated on an accelerating voltage of 20 kV and a working distance of approx. 10 mm. Before SEM measurements the samples were fixed on the sample holder using conducting tape (copper) and coated with a 7 nm platinum/palladium layer using a Cression 208 HR Sputter Coater.

Transmission electron microscopy (TEM). TEM measurements were performed on a Philips FEI CM-20 transmission electron microscope with a resolution of 2.3 Å operating at an accelerating voltage of 200

kV. For sample preparation the mesoporous silica film were scratched off from the substrate, dispersed in ethanol and placed in the ultrasonic bath for 3 min. The dispersion was dropped on a TEM grid and dried under ambient conditions.

Time of Flight - Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS measurements were performed using an IONTOF TOF.SIMS⁵ NCS instrument in the negative ion polarity. Depth profiling analysis was done using 30 keV Bi₃⁺ primary ions, at a current of 0.12 pA and cycle time of 150 μs on an area of 200 x 200 μm². 10 keV Ar₁₅₀₀ gas cluster ions at a current of 10.33 nA were applied to an area of 400 x 400 μm² for sputter erosion.

Argon and Krypton adsorption measurements. Argon and krypton adsorption measurements were performed on an Autosorb iQ (5.29.21093) from Quantachrom with the software version 5.21. The device is equipped with a CyroSync which makes the performances of measurements at 87 K possible. Silica films which were scratched off of the carrier material as well as films on cover glasses were investigated. Argon measurements at 87 K over the whole pressure range from approximately 10⁻⁴ – 1 were performed for scratched off mesoporous silica films. Silica films on the cover glasses were investigated with a krypton 11 point BET at 77 K in a relative pressure range of 0.05 to 0.3. Before measuring, the both samples types were degassed at 80°C for 12 h at a high vacuum. The measured isotherms were evaluated based on the Brunauer-Emmet-Teller (BET) model using the program ASiQwinTM.

Pore functionalization – reproducibility

In Figure S1 the reproduction experiments of correlation of pore fillings (obtained by ellipsometry) and intensities of carbonyl-signals (obtained by ATR-IR-spectroscopy) which are related to Figure 2 in the manuscript are shown. By inserting functional groups or polymers, the refractive index increases. After polymerization of DMAEMA for 2h a significant increase of the refractive index can be observed (Figure S1 a, magenta to blue). After functionalization with PDMAEMA for 2h it was possible to reinitiate the RAFT and polymerize MEP on the same mesoporous film. In the film without CO₂ plasma treatment the thickness increases and only a small increase of the refractive index was observed (Figure S1 red to blue). With CO₂-plasma (Figure S1 b) treatment a smaller growth of film thickness is observed in the sample, compared to the film which is not treated.

The pore filling degrees are ~80 vol% after 2h (Figure S1c+d). For the film, which without plasma treatment a pore filling degree after copolymer functionalization of 100 % was obtained, which can result due to the assumption of the refractive index of 1.5 for PMEP and the copolymer, while calculation using the Bruggeman's effective medium approximation.^[8,9] The intensities of the carbonyl signals, obtained by ATR-IR spectroscopy, are comparable for mesoporous films with and without CO₂ plasma treatment.

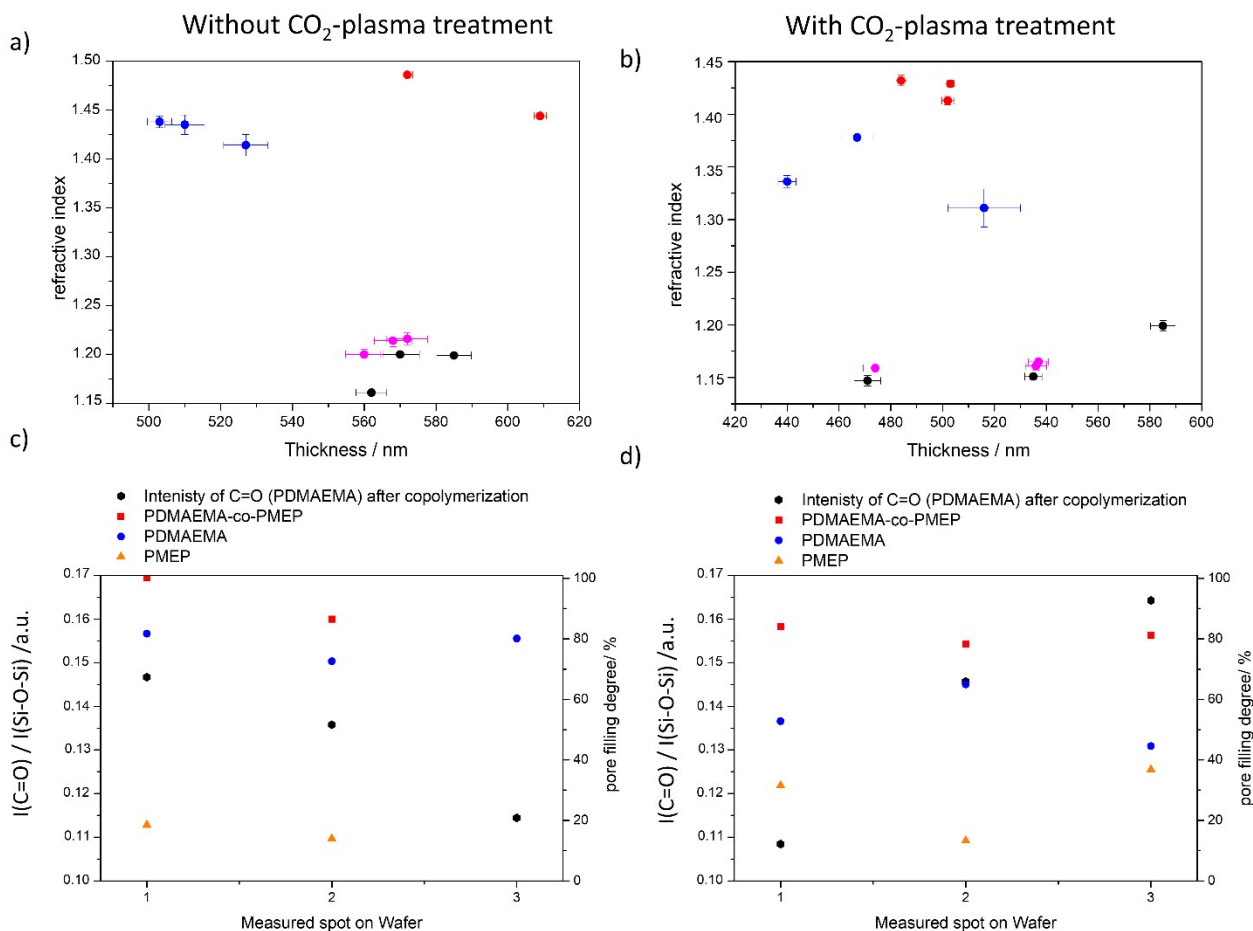


Figure S1. a+b) Results of the ellipsometry measurements: black=mesopores silicafilm, magenta=DDMAT-functionalized film, red=PDMAEMA-functionalized film, blue=PDMAEMA-*b*-PMEP functionalized film. c+d) Correlation between the pore filling degrees (from ellipsometry) and the carbonyl signal of the polymer (from ATR-IR-measurement). Shown are each one samples, which were measured on three different spots.

The correlation of pore fillings (obtained by ellipsometry) and intensities of carbonyl-signals (obtained by ATR-IR-spectroscopy) from Figure 2 in the manuscript is shown in Figure S2. Upon the first polymerization step using DMAEMA the intensity of the carbonyl band at $\sim 1725 \text{ cm}^{-1}$ in Si-O-Si valence vibration ($\sim 1060 \text{ cm}^{-1}$) normalized ATR-IR spectra increases up to 0.147 a.u. after 2h without CO₂ plasma treatment (Figure S3 b). The re-initiation with MEP results in a further intensity increase of the C=O vibrational band up to 0.165 a.u. (Figure S2a, black). CO₂ plasma treated films show lower C=O vibrational band intensities as compared to mesoporous films without CO₂ plasma treatment. For the 2h polymerization time using DMAEMA a C=O vibrational band intensity up to 0.114 a.u. is detected Figure S3a), which increases up to 0.140 upon re-initiation with MEP (Figure S2b, black; while reproducibility experiments intensity increases up to 0.164 a.u. Figure S3a).

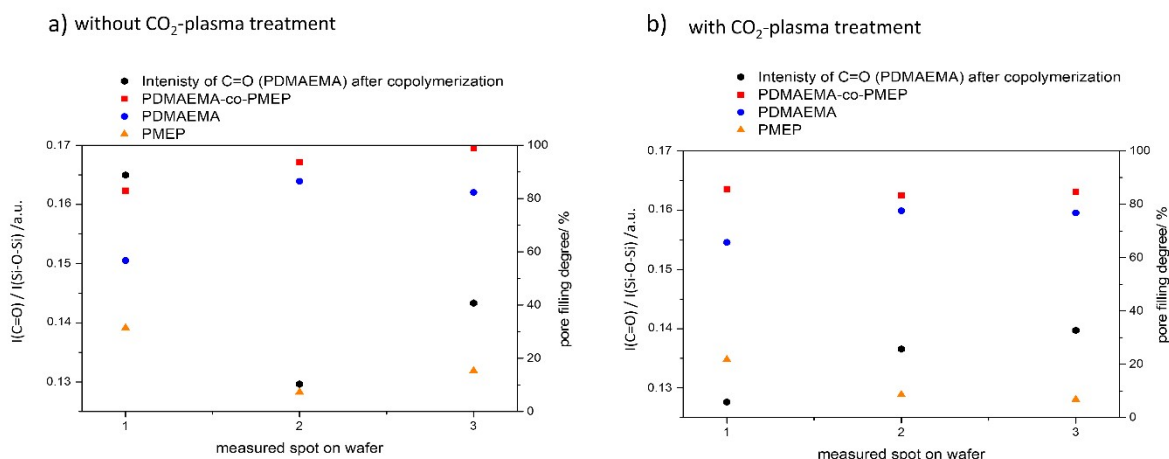


Figure S2. Correlation between the pore filling degrees (from ellipsometry) and the carbonyl signal of the polymer (from ATR-IR-measurement). Shown are each one samples, which were measured on three different spots. Data belongs to Figure 2 in the manuscript.

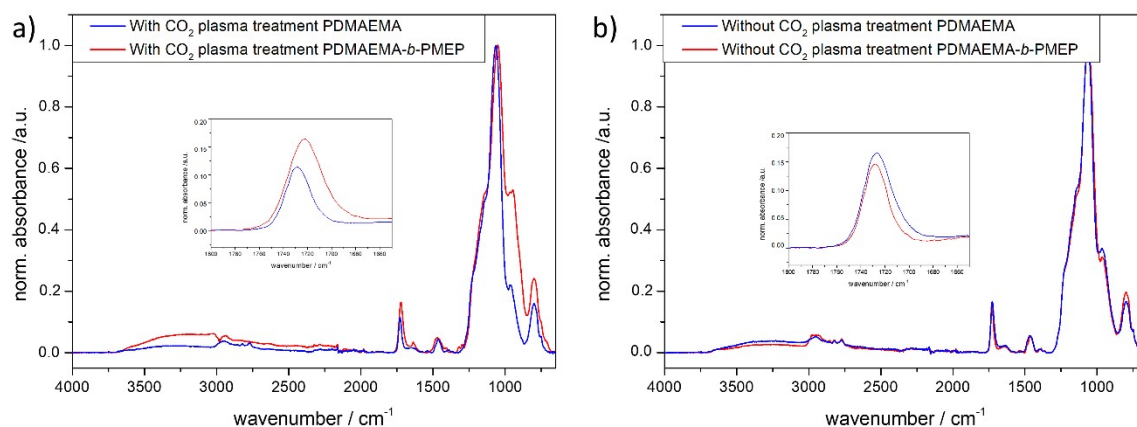


Figure S3. ATR-IR spectra of PDMAEMA (blue) and PDMAEMA-*b*-PMEP (red) functionalized films a) with and b) without CO₂-plasma treatment. Spectra are baseline corrected and normalized to Si-O-Si at approx. 1060 cm⁻¹.

In Table S1 and Table S2 the ellipsometry measurements from the replication experiment are listed. In Table S3 and Table S4 the ellipsometry measurements referring to the results shown in Figure 2 are listed. For calculation of pore filling with PMEPE the pore filling degrees in general from “SiO₂-mesop. + DDMAT-derivate + PDMAEMA “are used.

Table S1. Ellipsometry results from PDMAEMA-*b*-PMEP functionalization of mesop. silicafilms at 38 mW/cm² without CO₂-plasma treatment. Reproducibility-experiment.

| Not CO ₂ -plasma treated | Layer | Position | n | $\Delta_n \pm$ | d nm | $\Delta_d \pm$ nm | RMSE | Pore filling in general % | Pore filling with PDMAEMA % | Pore filling with PMEPA % | V _{pore} (porosity) % |
|-------------------------------------|--|----------|-------|----------------|---------|----------------------|-------|------------------------------|--------------------------------|------------------------------|-----------------------------------|
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ -mesop. | 1 | 1.161 | 0.004 | 562 | 4.3 | 2.096 | | | | 63.30 |
| | | 2 | 1.200 | 0.005 | 570 | 5.4 | 2.838 | | | | 54.89 |
| | | 3 | 1.199 | 0.005 | 585 | 4.8 | 2.512 | | | | 55.11 |
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate | 1 | 1.200 | 0.005 | 560 | 5.2 | 2.740 | 12.3 | | | |
| | | 2 | 1.214 | 0.006 | 568 | 5.2 | 2.989 | 5.05 | | | |
| | | 3 | 1.216 | 0.006 | 572 | 5.7 | 3.147 | 6.10 | | | |
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate+PDMAEMA | 1 | 1.438 | 0.006 | 503 | 3.4 | 1.011 | 82.73 | 81.73 | | |
| | | 2 | 1.414 | 0.011 | 527 | 6.2 | 1.481 | 73.52 | 72.60 | | |
| | | 3 | 1.435 | 0.010 | 510 | 5.5 | 1.432 | 80.73 | 80.13 | | |
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate+PDMAEMA+PMEP | 1 | 1.486 | 0.002 | 572 | 1.5 | 0.414 | 100.22 | | | 18.49 |
| | | 2 | 1.444 | 0.003 | 609 | 1.7 | 0.735 | 86.53 | | | 13.93 |

Table S2. Ellipsometry results from PDMAEMA-*b*-PMEP functionalization of mesop. silicafilms at 38 mW/cm² with CO₂-plasma treatment. Reproducibility -experiment.

| CO ₂ - plasma treated | Layer | Position | n | $\Delta n \pm$ | d nm | $\Delta d \pm$ nm | RMSE | Pore filling in general % | Pore filling with PDMAE MA % | Pore filling with PMEP % | V _{pore} (porosit y) % |
|--|--|----------|-------|----------------|---------|----------------------|--------|------------------------------------|---|--------------------------------------|--|
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ - mesop. | 1 | 1.147 | 0.005 | 471 | 5.1 | 1.118 | | | | 66.34 |
| | | 2 | 1.151 | 0.003 | 535 | 3.3 | 1.473 | | | | 65.47 |
| | | 3 | 1.199 | 0.005 | 585 | 4.8 | 2.512 | | | | 55.11 |
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ - mesop. +DDMAT- derivate | 1 | 1.159 | 0.004 | 474 | 4.6 | 1.229 | 3.65 | | | |
| | | 2 | 1.161 | 0.004 | 536 | 4.1 | 1.935 | 3.08 | | | |
| | | 3 | 1.165 | 0.004 | 537 | 3.9 | 1.921 | - | | | |
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ - mesop. +DDMAT- derivate+P DMAEMA | 1 | 1.336 | 0.006 | 440 | 3.5 | 2.690 | 54.26 | 52.81 | | |
| | | 2 | 1.378 | 0.002 | 467 | 6.2 | 3.949 | 65.79 | 64.97 | | |
| | | 3 | 1.311 | 0.018 | 516 | 14.0 | 10.055 | 38.55 | 44.54 | | |
| | SiOx-layer | 1 | | | 5.6 | 0.0 | 0.134 | | | | |
| | SiO ₂ - mesop. +DDMAT- derivate+P DMAEMA+ PMEP | 1 | 1.432 | 0.005 | 484 | 2.0 | 1.544 | 84.0 | | 31.48 | |
| | | 2 | 1.413 | 0.004 | 502 | 2.3 | 0.980 | 78.26 | | 13.29 | |
| | | 3 | 1.429 | 0.003 | 503 | 1.4 | 0.473 | 81.26 | | 36.72 | |

Table S3. Ellipsometry results from PDMAEMA-*b*-PMEP functionalization of mesop. silicafilms at 38 mW/cm² without CO₂-plasma treatment.

| Not CO ₂ -plasma treated | Layer | Position | n | $\Delta n \pm$ | d nm | $\Delta d \pm$ nm | RMSE | Pore filling in general % | Pore filling with PDMAEMA % | Pore filling with PMEPEP % | V _{pore} (porosity) % |
|-------------------------------------|--|----------|-------|----------------|---------|----------------------|-------|------------------------------|--------------------------------|-------------------------------|-----------------------------------|
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop. | 1 | 1.201 | 0.006 | 545 | 5.3 | 2.769 | | | | 54.68 |
| | | 2 | 1.191 | 0.005 | 546 | 5.1 | 2.647 | | | | 56.82 |
| | | 3 | 1.174 | 0.004 | 544 | 4.5 | 2.255 | | | | 60.48 |
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate | 1 | 1.161 | 0.003 | 488 | 3.9 | 1.122 | - | | | |
| | | 2 | 1.176 | 0.005 | 546 | 4.8 | 2.442 | - | | | |
| | | 3 | 1.230 | 0.016 | 500 | 7.9 | 4.612 | 18.23 | | | |
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate+PDMAEMA+PMEPEP | 1 | 1.350 | 0.005 | 440 | 2.9 | 2.503 | 51.52 | 56.70 | | |
| | | 2 | 1.451 | 0.001 | 499 | 0.8 | 0.203 | 86.29 | 86.45 | | |
| | | 3 | 1.442 | 0.001 | 496 | 0.3 | 0.092 | 83.67 | 82.28 | | |
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate+PDMAEMA+PMEPEP | 1 | 1.434 | 0.002 | 552 | 1.4 | 0.288 | 82.95 | | 31.43 | |
| | | 2 | 1.464 | 0.002 | 553 | 1.2 | 1.464 | 93.58 | | 7.29 | |
| | | 3 | 1.481 | 0.003 | 523 | 1.5 | 1.481 | 98.98 | | 15.34 | |

Table S4. Ellipsometry results from PDMAEMA-*b*-PMEP functionalization of mesop. silicafilms at 38 mW/cm² with CO₂-plasma treatment.

| Not CO ₂ - Plasma treated | Layer | Position | n | $\Delta n \pm$ | d nm | $\Delta d \pm$ nm | RMSE | Pore filling in general % | Pore filling with PDMAEMA % | Pore filling with PMEPEP % | V _{pore} (porosity) % |
|--------------------------------------|--|----------|-------|----------------|---------|----------------------|-------|------------------------------|--------------------------------|-------------------------------|-----------------------------------|
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop. | 1 | 1.203 | 0.005 | 536 | 4.9 | 2.611 | | | | 54.25 |
| | | 2 | 1.213 | 0.006 | 536 | 4.8 | 2.646 | | | | 52.11 |
| | | 3 | 1.202 | 0.005 | 541 | 4.9 | 2.588 | | | | 54.46 |
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate | 1 | 1.185 | 0.004 | 535 | 4.1 | 2.150 | - | | | |
| | | 2 | 1.194 | 0.065 | 536 | 5.0 | 2.667 | - | | | |
| | | 3 | 1.225 | 0.016 | 500 | 7.6 | 4.374 | 8.34 | | | |
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate+PDMAEMA | 1 | 1.387 | 0.002 | 478 | 1.1 | 0.928 | 64.00 | 65.69 | | |
| | | 2 | 1.425 | 0.001 | 489 | 0.7 | 0.355 | 76.63 | 77.55 | | |
| | | 3 | 1.427 | 0.001 | 484 | 0.6 | 0.321 | 77.87 | 76.74 | | |
| | SiOx-layer | 1 | | | 6.7 | 0.0 | 0.105 | | | | |
| | SiO ₂ -mesop.+DDMAT-derivate+PDMAEMA+PMEPEP | 1 | 1.442 | 0.005 | 495 | 2.6 | 0.875 | 85.74 | | 21.74 | |
| | | 2 | 1.436 | 0.006 | 512 | 3.1 | 0.747 | 83.24 | | 8.61 | |
| | | 3 | 1.439 | 0.003 | 505 | 1.7 | 0.455 | 84.70 | | 6.83 | |

Asymmetric functionalization and characterization by TOF-SIMS

ToF-SIMS measurements were used to confirm the asymmetric functionalization of the mesoporous silicafilms. In Figure S4 the data without normalization of the ToF-SIMS measurement from a PDMAEMA-*b*-PMEP functionalized film is shown. The high intensity of PO₃⁻ at the beginning of the sputtering, compared to the intensity of PO₃⁻ after removing the topmost layer prove the asymmetric pore functionalization.

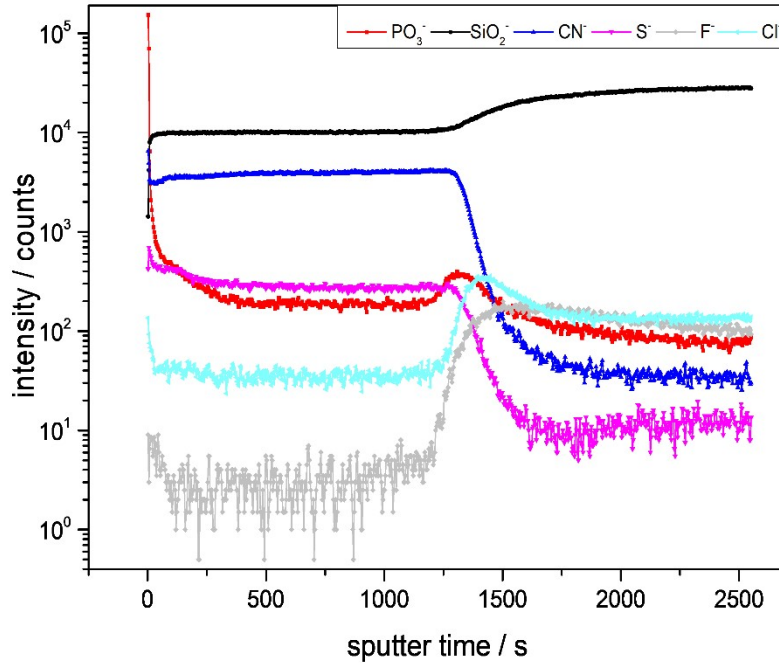


Figure S4. ToF-SIMS depth profiling measurements of PDMAEMA-*b*-PMEP-functionalized film.

Asymmetric functionalization and characterization by XPS

In XPS measurements nitrogen, indicating the presence of DDMAT-derivate and PDMAEMA, was detected in all XP-spectra, except for the unmodified mesoporous silica. After PMEPE functionalization phosphor was additionally detected (Figure S4 g + Table S5). The values of the XPS and ToF-SIMS measurements (Figure 3a) indicate that despite the small mass loss from the TGA (Figure 3c), a ratio of more than one MEP monomer per chain was obtained.

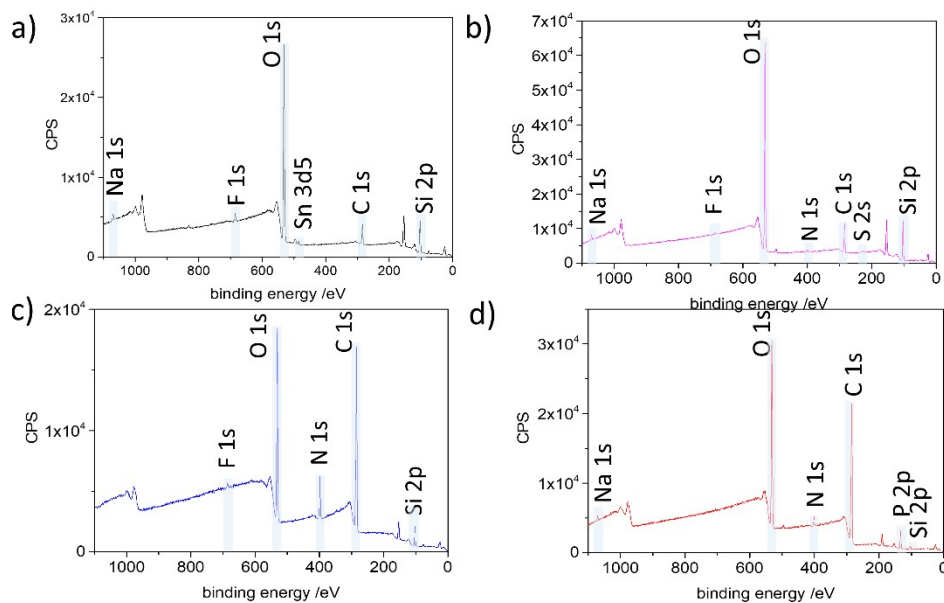


Figure S5. XPS spectra of mesoporous silicafilm (a, black), mesoporous silicafilm functionalized with the RAFT agent DDMAT-derivate (b, magenta), PAEMA-functionalized mesoporous silicafilm (c, blue) and PDMAEMA-co-PMEP-functionalized mesoporous silicafilm (d, red).

Table S5. Results of XPS-measurements.

| Sample | C | O | N | S | P | Cl | F | Si | Sn | Na | Ratio Si:N | Ratio Si:P |
|---|-------|-------|------|------|------|-----|------|-------|------|------|------------|------------|
| | at% | at% | at% | at% | at% | at% | at% | at% | at% | at% | | |
| Mesoporous silicafilm | 11.73 | 64.05 | | | | | 1.33 | 20.75 | 0.16 | 1.99 | | |
| Mesoporous silicafilm + DDMAT | 18.41 | 55.74 | 0.74 | 0.66 | | | 0.3 | 22.7 | | 1.5 | 1:0.03 | |
| Mesoporous silicafilm + DDMAT +PDMAEMA | 58.72 | 28.6 | 6.89 | | | | 0.56 | 5.19 | | | 1:1.33 | |
| Mesoporous silicafilm + DDMAT + PDMAEMA- <i>b</i> -PMEP | 58.72 | 33.91 | 1.63 | | 4.01 | | | 0.94 | | 0.80 | 1:1.78 | 1:4.44 |

Asymmetric functionalization and characterization by TGA and gas adsorption

Using the mass loss from TGA measurements chain lengths were calculated according to literature.^[7] Therefore the specific surface area of the used mesoporous silicafilms was determined using gas adsorption. Argon gas adsorptions (87 K, pressure range 10^{-4} -1) and krypton adsorption (77K, in a relative pressure range of 0.05-0.3) were recorded and evaluated using the Brunauer-Emmet-Teller (BET) model. Argon gas adsorption experiments were performed using scratched off mesoporous silicafilms and reveal a specific surface area of $293 \text{ m}^2 \text{ g}^{-1}$ ($r=0.99997$). Using mesoporous silicafilms on cover glasses, which were prepared from the same dip coat solution on the same day under identical conditions a specific surface area of around $770 \text{ m}^2 \text{ g}^{-1}$ was determined, using krypton adsorption due to the higher sensitivity of krypton adsorption as compared to argon adsorption for the low material amount in thin films. The specific surface area was estimated considering the mass of the coating introduced into the cell. Specifically, the specific surface area was determined to be 763 ($r=0.9998$) and $784 \text{ m}^2 \text{ g}^{-1}$ ($r=0.9998$) for mesoporous films on cover glasses in two different measurements of two different samples with identical sample preparation. These values were deduced considering the determined surface of the material (1.526 and $1.568 \text{ m}^2 \text{ g}^{-1}$) and a mass of the coating of 0.2 wt% of the entire substrate with mesoporous film. Due to the sample preparation of scratching off mesoporous silicafilms, the specific surface area, determined using argon adsorption experiments must probably be considered more critically although both sample preparation methods have their advantages and disadvantages.

Asymmetric functionalization and characterization of pore accessibility using cyclic voltammetry

As mentioned in the manuscript we observed that water was not able to imbibe into the mesopores under the applied experimental conditions, reliable molecular transport characterization from aqueous solution was measured after addition of ethanol (0.06vol%, Figure 4, Figure S6, Figure S7).

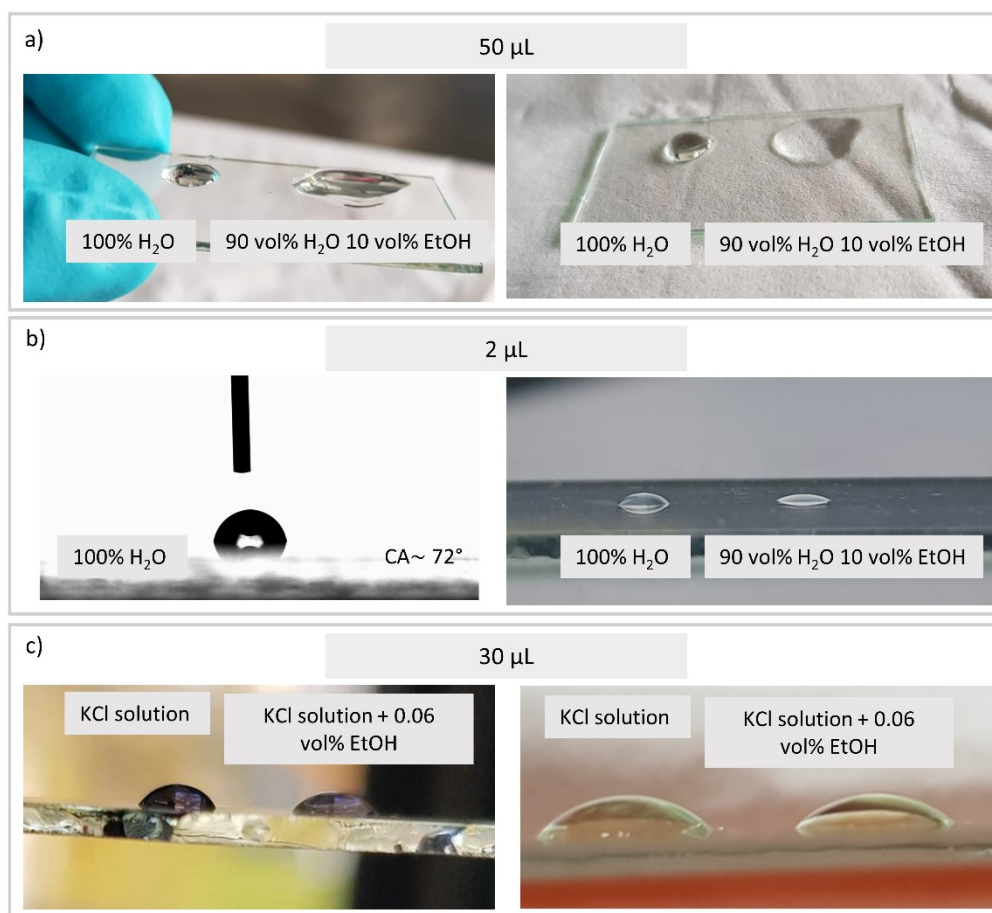


Figure S6. Reduction of the surface tension and contact angle of water on PDMAEMA-*b*-PMEP functionalized mesoporous silicafilms using a small amount of ethanol. b) static (2 µL) contact angle measurement.

Cyclic voltammetry measurements were used to analyze the pore accessibility of anionic and cationic probe molecules. As expected, the unmodified mesoporous silicafilms (Figure S7a) show pH-dependent ionic pore accessibility due to the silanol groups which are negatively charged at basic pH-values whereas the pore wall is neutral at acidic pH. Consequently, anionic and cationic probe molecules enter the mesoporous silica to a similar extent at acidic pH (Figure S7a, dotted lines). Anions are electrostatically excluded while cations are preconcentrated at basic pH (Figure S7a, line). After the DDMAT initiator functionalization, parts of the silanol groups are functionalized, the pore filling slightly increases up to around 18 vol% and the mesoporous film contact angle increases. These changes in surface chemistry result into a reduced peak current density, which is especially pronounced for cation preconcentration at basic pH (Figure S7 a, b blue line). Due to the remaining silanol groups the pH-influence on the ionic pore accessibility is maintained. The detected peak current densities at acidic pH in addition indicate that DDMAT is not hindering pore accessibility for the detected model ions and pore blocking can be excluded.

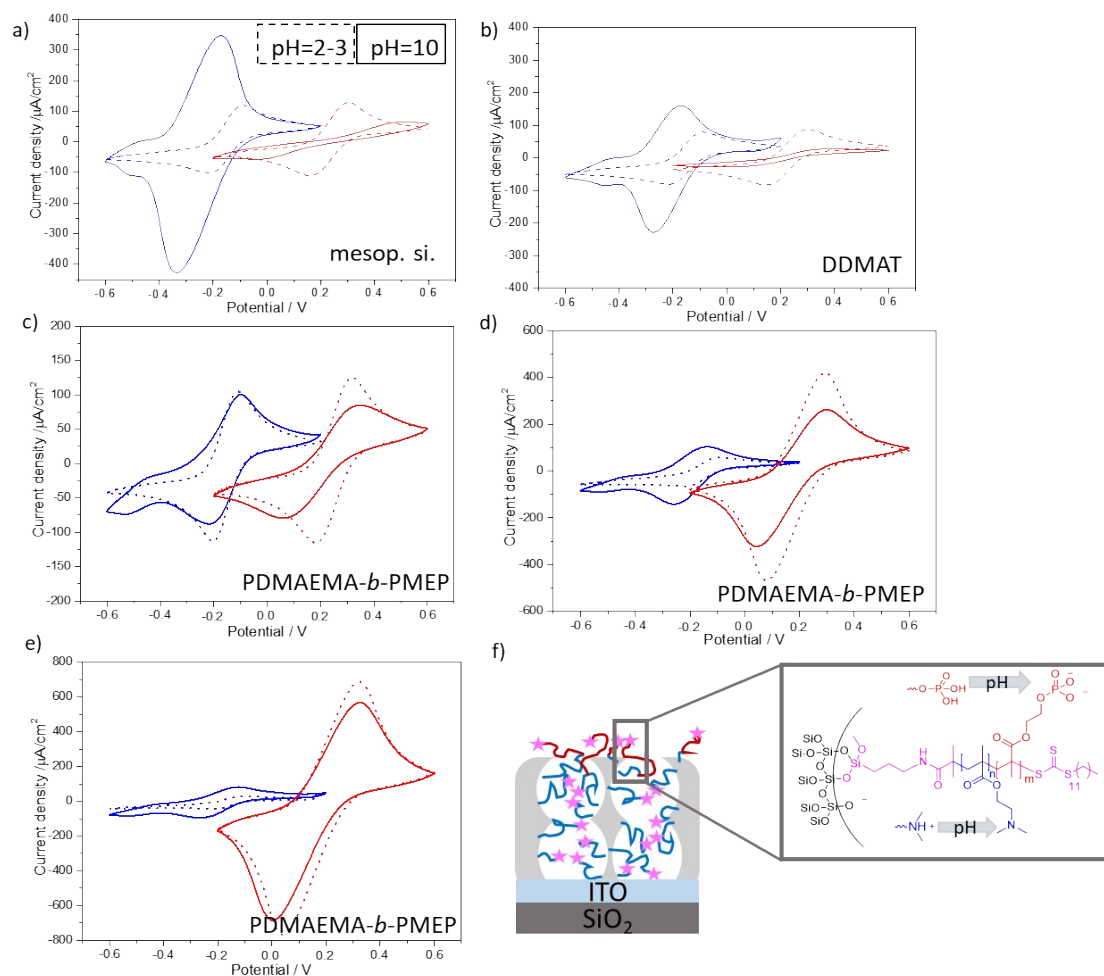


Figure S7. CV measurements (100mVs^{-1}) of a) unfunctionalized, b) DDMAT functionalized mesoporous silica film using 0.06 vol% of ethanol. c-e) Reproducibility-experiments of CV measurement of PDMAEMA-*b*-PMEP functionalized silica film using 0.06 vol% of ethanol. Shown are measurements using different samples. f) Schematic illustration of the porous silica film in dependence of the pH-value. blue) $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ as probe molecule; red) $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as probe molecule at concentration of 1 mM in 100 mM KCl electrolyte solution.

Film characterization by SEM and TEM measurements

The mesoporous silicafilms were characterized using SEM (Figure S8) and TEM (Figure S9). The SEM and TEM measurements clearly show that the mesoporous film remains intact in terms of layer thickness and mesoporous structure after polymer functionalization.

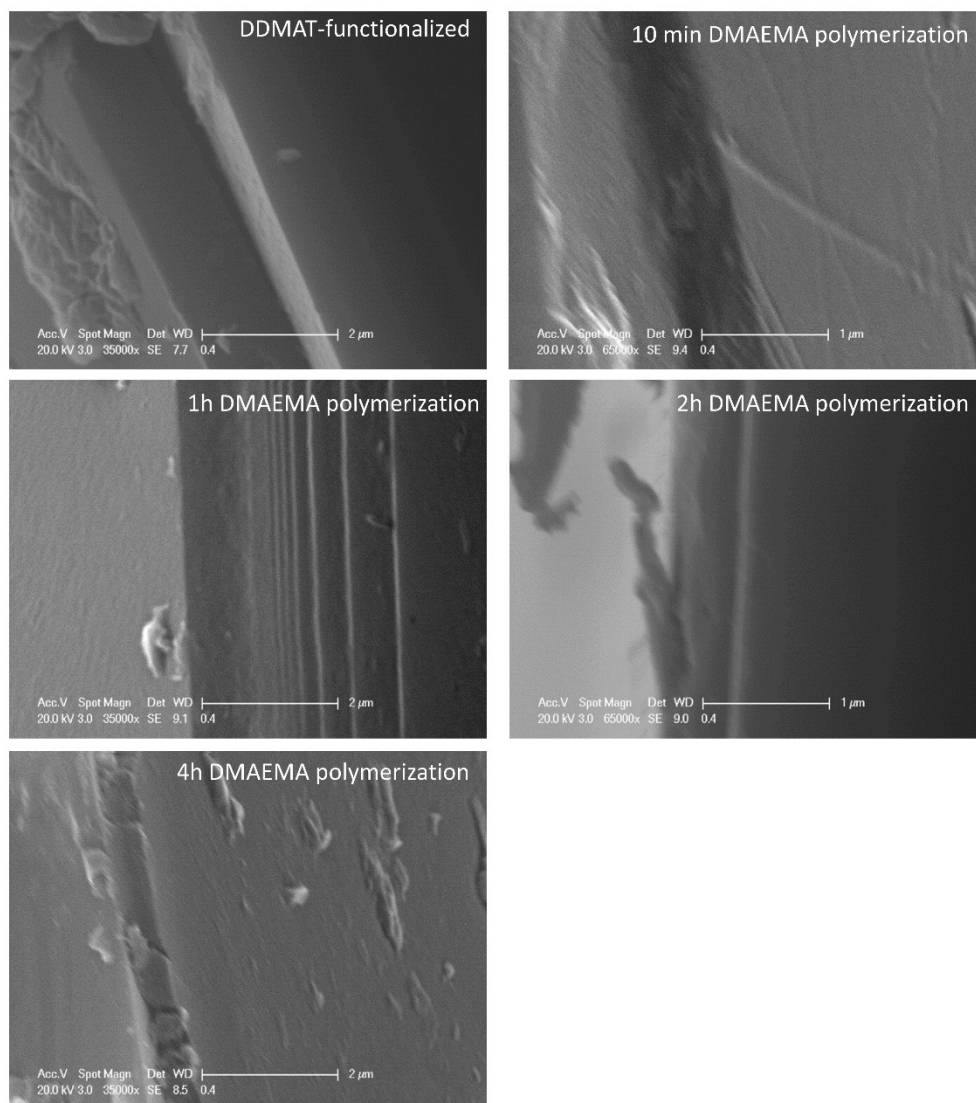


Figure S8. SEM measurements of DDMAT-functionalized mesoporous silicafilms after different polymerization times using DMAEMA.

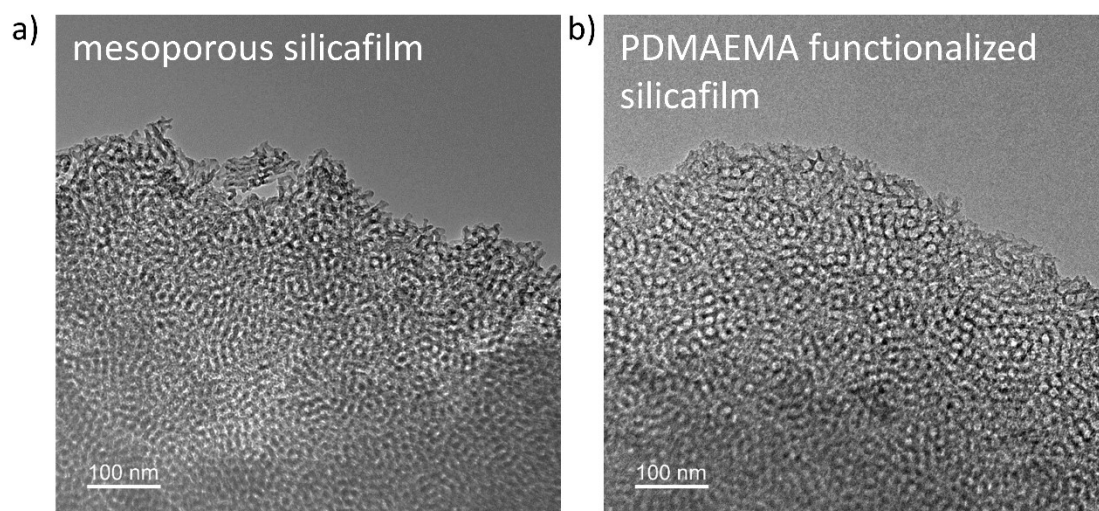
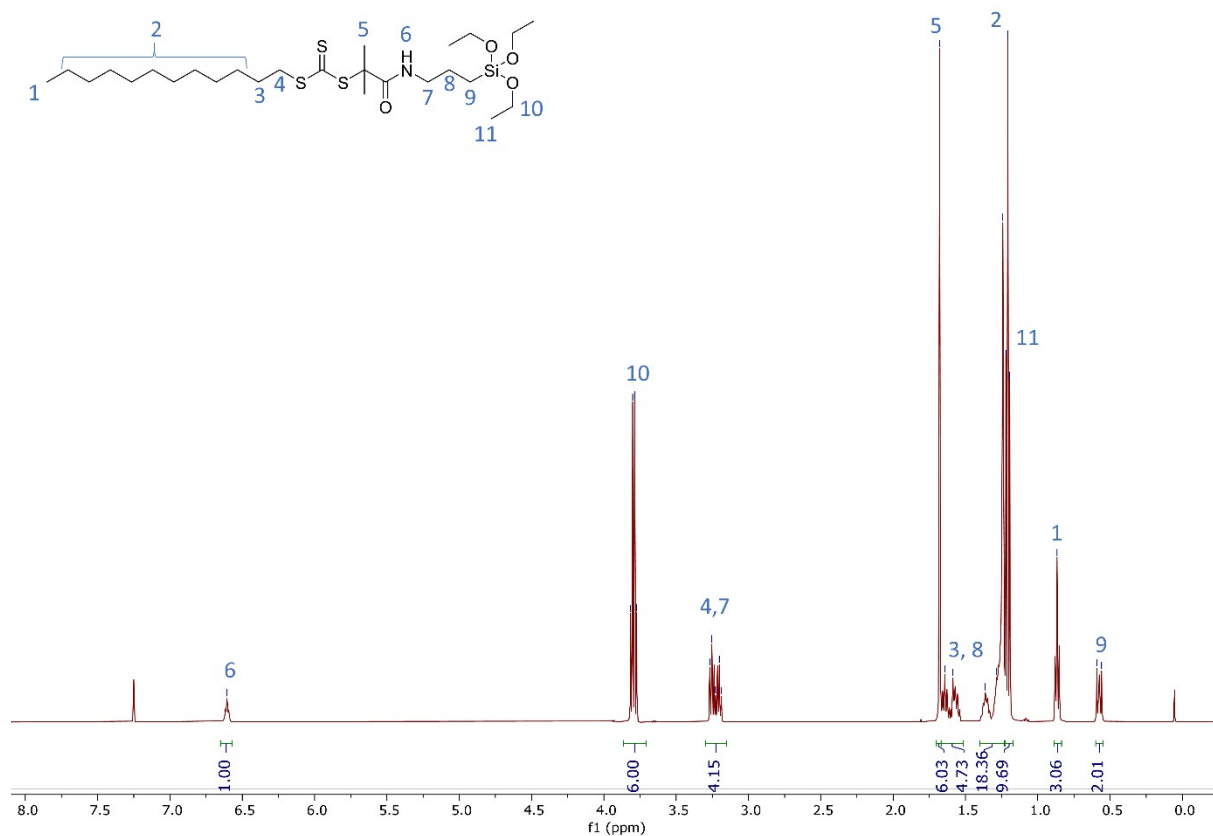


Figure S9. TEM measurements of a mesoporous silicafilm, functionalized with PDMAEMA using an irradiation time of 2h and 38mW cm^{-2} .

The preparation of the RAFT-agent DDMAT-derivate was analyzed by $^1\text{H-NMR}$ spectroscopy (Figure



S10). The obtained data are in accordance with literature. [3]

Figure S10. $^1\text{H-NMR}$ (300 MHz) of DDMAT-derivate in CDCl_3 .

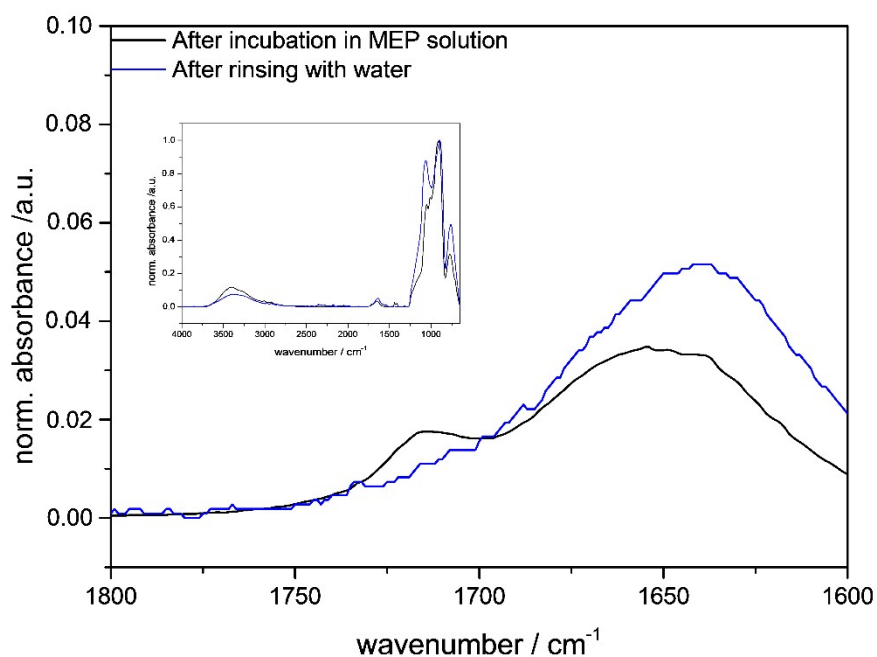


Figure S11. ATR-IR spectra of a DDMAT-functionalized silica film after incubation in MEP-DMSO solution for one hour (black) and after subsequent rinsing with water (blue). Measured on the glass substrate. Spectra are baseline corrected and normalized to Si-OH at approx. 905 cm^{-1} . It is clearly visible that the monomer can be extracted if not covalently bound to the mesoporous film.

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