



Supporting Information

Laser Writing of Block-Copolymer Images into Mesopores Using SBDC-Initiated Visible-Light-Induced Polymerization

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Supporting Information and experimental procedures

The role of SBDC to polymer functionalize the mesoporous silica films was demonstrated by irradiation of unmodified silica films without SBDC in presence of DMAEMA with and without ZnTPP as photo catalyst. Without SBDC no polymer functionalization was observable in ATR-IR measurements (Figure S1).

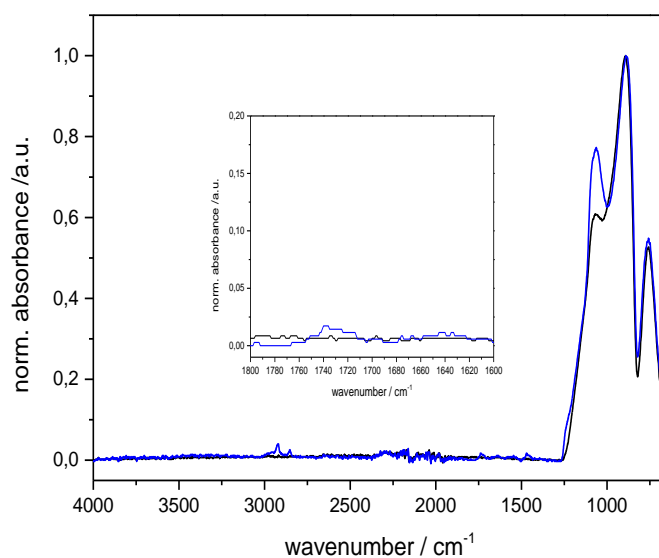


Figure S1: ATR-IR measurement of unmodified silica films which were irradiated analog to polymer functionalization at 38 mW/cm² for 60 min with 400-700 nm with (blue) and without (black) the photo catalyst ZnTPP. The measurement was carried out on top of the substrate, the spectra are baseline corrected and normalized to Si-OH vibrational band at approx. 905 cm⁻¹. Films were only rinsed with DMSO and ethanol after irradiation and not extracted in solvent.

To prove the possibility to use visible light of the wavelength 405 nm to initiate the polymerization without photo catalyst, DMAEMA were polymerized in mesoporous silica films for 10 min using two different irradiation intensities of 23 and 90 mW cm^{-2} at 405 nm. Each experiment was performed twice showing similar results. After irradiation the films were washed and extracted to remove unbound monomer. For both energies the maximal intensity of the carbonyl vibrational band is approximately 0.14 a.u. (Figure S2), which is consistent with experiments using the 400-700 nm and 365 nm (Figure 2). The results clearly show a polymer formation using SBDC functionalized films under visible light irradiation (405 nm) without additional photo catalyst.

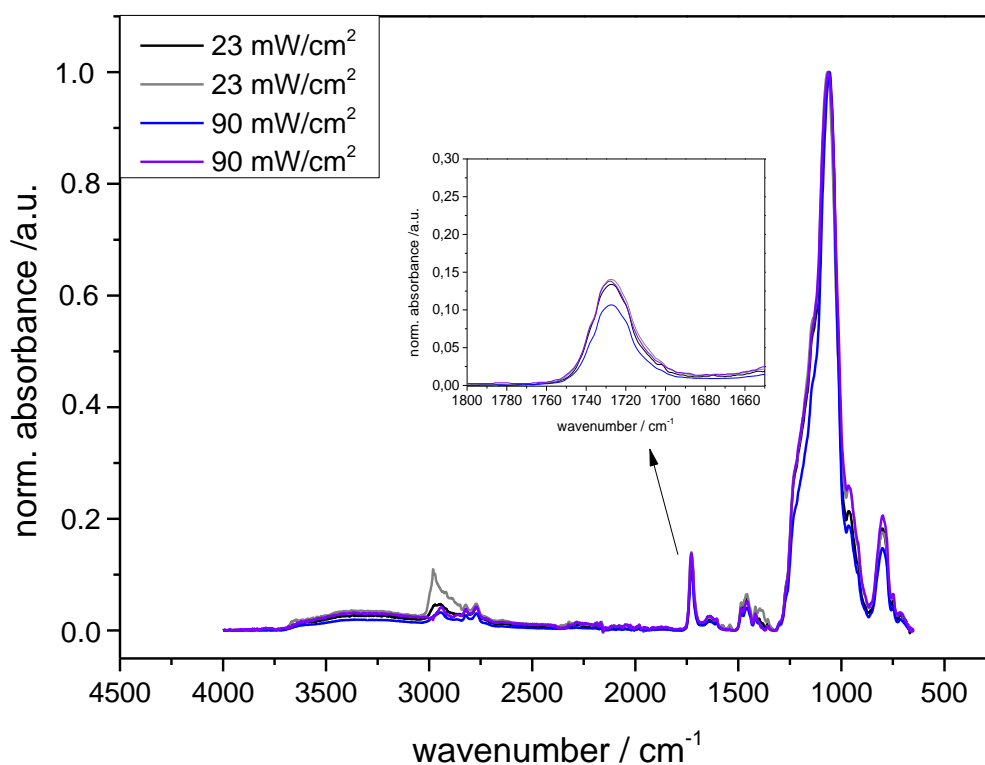


Figure S2: ATR-IR spectra of DMAEMA functionalized silica films. For polymerization 405 nm without additional photo catalyst at 23 and 90 mW cm^{-2} . For ATR-IR measurements the mesoporous film was scratched off the substrate and the spectra were baseline corrected and normalized to Si-O-Si vibrational band at 1060 cm^{-1} .

Ellipsometry was measured using mesoporous silica films without CO_2 plasma treatment^[1,2] and thus with possible polymer formation at the outer planar mesoporous film surface. For polymerization visible light (400-700 nm, 2.5 and 38 mW cm^{-2}) without ZnTPP as catalyst was used. Irradiation times between 10 min and 3h were investigated (Table S2 -Table S11).

Table S2: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 3h at 38 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2,8	0,0	0,131		
SiO ₂ -mesop.	1	1.151	0.003	572	3.5	1.711		
	2	1.162	0.003	586	3.8	1.879		
	3	1.171	0.004	593	4.1	1.993		
SiO ₂ -mesop.+ SBDC	1	1.289	0.005	529	4.3	3.130	42	
	2	1.293	0.005	542	4.2	2.856	41	
	3	1.325	0.007	530	5.2	3.537	49	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.441	0.001	528	0.8	0.009	84	79
	2	1.441	0.001	534	0.7	0.141	80	79
	3	1.430	0.001	554	0.9	0.178	80	69

Table S3: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 2 h at 38 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.152	0.002	535	2.4	1.103		
	2	1.155	0.003	563	3.1	1.550		
	3	1.158	0.003	564	3.1	1.554		
SiO ₂ -mesop.+ SBDC	1	1.264	0.006	517	4.3	2.832	34	
	2	1.274	0.005	528	4.3	2.979	36	
	3	1.272	0.004	535	3.7	2.564	35	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.447	0.001	545	0.8	0.156	86	83
	2	1.439	0.001	525	0.4	0.092	83	80
	3	1.444	0.001	523	0.6	0.132	85	82

Table S4: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 1 h at 38 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.167	0.003	581	3.6	1.776		
	2	1.175	0.004	581	3.8	1.870		
	3	1.180	0.004	589	4.0	1.991		
SiO ₂ -mesop.+ SBDC	1	1.281	0.005	543	4.0	2.788	36	
	2	1.275	0.005	548	4.1	2.755	33	
	3	1.300	0.004	555	3.9	2.302	40	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.329	0.017	565	11.8	3.201	50	24
	2	1.369	0.010	545	6.6	2.194	61	45
	3	1.375	0.009	570	6.3	1.192	62	42

Table S5: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 30 min at 38 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.159	0.003	570	3.4	1.680		
	2	1.167	0.003	577	3.6	1.809		
	3	1.177	0.004	587	4.0	1.964		
SiO ₂ -mesop.+ SBDC	1	1.271	0.005	534	3.8	2.632	35	
	2	1.289	0.005	539	3.9	2.710	39	
	3	1.325	0.005	535	4.3	2.743	48	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.389	0.004	500	2.5	1.489	68	56
	2	1.354	0.004	520	2.6	2.194	57	34
	3	1.433	0.002	563	1.3	0.278	81	71

Table S6: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 10 min at 38 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.155	0.002	547	2.8	1.363		
	2	1.166	0.004	578	3.9	1.926		
	3	1.176	0.004	585	4.1	2.019		
SiO ₂ -mesop.+ SBDC	1	1.272	0.005	520	4.2	2.893	36	
	2	1.275	0.005	536	4.3	2.969	35	
	3	1.275	0.005	550	4.2	2.807	32	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.337	0.006	503	4.1	3.440	54	31
	2	1.318	0.005	526	3.6	2.626	47	21
	3	1.284	0.005	543	4.2	2.885	34	4

Table S7: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 3 h at 2.5 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.161	0.003	571	3.4	1.694		
	2	1.172	0.003	579	3.7	1.863		
	3	1.169	0.003	580	3.7	1.833		
SiO ₂ -mesop.+ SBDC	1	1.292	0.005	525	4.2	3.121	41	
	2	1.299	0.005	530	3.9	2.869	41	
	3	1.299	0.005	535	4.3	3.023	42	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.458	0.001	534	0.8	0.172	89	88
	2	1.455	0.001	542	0.8	0.174	88	89
	3	1.460	0.002	556	1.5	0.327	89	89

Table S8: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 2 h at 2.5 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.178	0.004	594	4.3	2.115		
	2	1.181	0.004	607	4.2	2.035		
	3	1.176	0.004	599	4.2	2.042		
SiO ₂ -mesop.+ SBDC	1	1.307	0.004	552	3.7	2.194	42	
	2	1.307	0.005	556	3.9	2.102	42	
	3	1.294	0.005	556	4.5	2.747	39	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.425	0.002	546	1.2	0.239	78	69
	2	1.392	0.005	542	3.0	0.729	68	50
	3	1.389	0.004	535	2.5	0.748	67	51

Table S9: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 1 h at 2.5 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.174	0.004	593	4.1	2.015		
	2	1.182	0.004	613	4.2	2.077		
	3	1.185	0.004	610	4.2	2.087		
SiO ₂ -mesop.+ SBDC	1	1.303	0.004	550	3.7	2.310	42	
	2	1.324	0.003	558	2.6	1.228	47	
	3	1.316	0.004	556	2.9	1.511	44	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.405	0.003	559	1.8	0.340	72	58
	2	1.394	0.002	556	1.5	0.291	68	46
	3	1.374	0.005	570	3.0	0.575	62	36

Table S10: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 30 min at 2.5 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEM A / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.181	0.004	602	4.1	2.026		
	2	1.183	0.004	605	4.2	2.071		
	3	1.183	0.004	605	4.2	2.047		
SiO ₂ -mesop.+ SBDC	1	1.331	0.004	546	3.5	1.794	50	
	2	1.337	0.004	547	3.3	1.592	51	
	3	1.325	0.005	550	3.3	1.967	48	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.352	0.004	550	2.9	1.012	55	15
	2	1.340	0.004	546	2.6	1.246	51	2
	3	1.321	0.003	559	2.1	1.030	45	-

Table S11: Ellipsometry measurements from Iniferter initiated polymerization with SBDC using an irradiation time of 10 min at 2.5 mW cm⁻².

Layer	Position	n	$\Delta n \pm$	d/ nm	$\Delta d \pm$ /nm	RMSE	Pore filling degree / vol%	Pore filling degree of PDMAEMA / vol%
SiOx-Layer	1			2.8	0.0	0.131		
SiO ₂ -mesop.	1	1.161	0.003	574	3.4	1.714		
	2	1.171	0.003	584	3.8	1.875		
	3	1.179	0.004	593	4.0	1.993		
SiO ₂ -mesop.+ SBDC	1	1.298	0.006	528	4.9	3.591	43	
	2	1.302	0.005	542	4.6	3.081	42	
	3	1.315	0.005	545	4.5	2.697	45	
SiO ₂ -mesop.+ SBDC - PDMAEMA	1	1.304	0.006	524	4.5	3.355	43	3
	2	1.312	0.005	534	3.9	2.684	44	6
	3	1.317	0.004	541	3.3	2.039	44	1

The presence of the photo catalyst inside the mesopores can be proven by UV/Vis-spectra. SBDC-functionalized silica films were incubated in a solution of monomer dissolved in DMSO, as well as in a solution of monomer and ZnTPP dissolved in DMSO, before the film was dried with pressured air and analyzed by UV/Vis. The spectra of the film, which was incubated in a solution containing ZnTPP clearly shows a peak at approx. 430 nm, originating from ZnTPP (Figure S3).

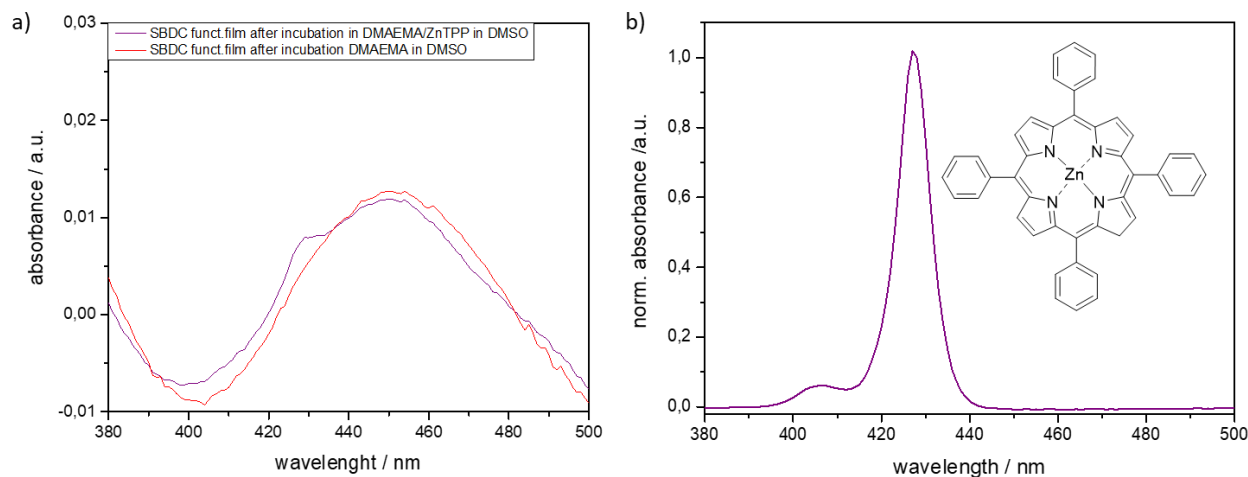


Figure S3: a) UV/Vis spectra of SBDC film after incubation in monomer and dye solution. b) UV/Vis of ZnTPP in DMSO, spectrum is baseline corrected and normalized.

The results of the ellipsometry measurements from PDMAEMA-co-PMETAC functionalized silicafilms are listed in Table S12-S14.

Table S12: Results of ellipsometry measurements from PDMAEMA-co-PMMETAC functionalized silica films

Layer		Position 1	Position 2	Position 3
Oxide layer of Si-Wafer	d / nm	3.9 ± 0.00		
	$RMSE$	0.135		
Mesop. silica	d / nm	500.5 ± 3.6	540.1 ± 3.6	506.1 ± 6.0
	n	1.115 ± 0.003	1.160 ± 0.003	1.217 ± 0.007
	$RMSE$	1.258	1.729	3.440
	$V_{\text{pore}} / \%$	73	64	51
SBDC funct. film	d / nm	492.1 ± 3.3	511.0 ± 3.6	537.4 ± 4.6
	n	1.229 ± 0.004	1.273 ± 0.005	1.420 ± 0.008
	$RMSE$	1.982	2.459	0.932
	Pore filling degree / %	31	35	77
PDMAEMA funct. film	d / nm	476.7 ± 2.9	507.3 ± 3.3	505.7 ± 3.3
	n	1.256 ± 0.004	1.291 ± 0.005	1.284 ± 0.005
	$RMSE$	1.838	2.477	2.371
	Pore filling degree / %	37	39	25

PDMAEMA-co- PMETAC funct. film	<i>d</i> / nm	443.9 ± 0.5	474.0 ± 0.6	599.9 ± 10.7
	<i>n</i>	1.458 ± 0.001	1.439 ± 0.001	1.345 ± 0.015
	<i>RMSE</i>	0.552	0.346	1.870
	Pore filling degree / %	92	86	49

Table S13: Results of ellipsometry measurements from PDMAEMA-co-PMETAC functionalized silica films. Reproduction experiment 1.

Layer		Position 1	Position 2	Position 3
Oxide layer of Si-Wafer	<i>d</i> / nm	7.7 ± 0.1		
	<i>RMSE</i>	0.315		
Mesop. silica	<i>d</i> / nm	522.9 ± 4.1	526.4 ± 3.7	538.6 ± 4.4
	<i>n</i>	1.238 ± 0.005	1.261 ± 0.005	1.261 ± 0.005
	<i>RMSE</i>	2.434	2.435	2.863
	<i>V</i> _{pore} / %	47	42	42
SBDC funct. film	<i>d</i> / nm	517.5 ± 4.4	508.0 ± 3,9	516.4 ± 3.4
	<i>n</i>	1.275 ± 0.006	1.291 ± 0.005	1.347 ± 0.005
	<i>RMSE</i>	3.062	2.879	2.235
	Pore filling degree / %	15	14	40
PDMAEMA funct. film	<i>d</i> / nm	500.8 ± 3.6	518.5 ± 3.4	526.2 ± 2.5
	<i>n</i>	1.299 ± 0.005	1.315 ± 0.004	1.350 ± 0.003
	<i>RMSE</i>	2,769	2,588	1,354
	Pore filling degree / %	25	24	40
PDMAEMA-co- PMETAC funct. film	<i>d</i> / nm	505.5 ± 2.6	517.7 ± 0.9	518.4 ± 0.8
	<i>n</i>	1.489 ± 0.005	1.470 ± 0.002	1.452 ± 0.001
	<i>RMSE</i>	0.546	0.182	0.159
	Pore filling degree / %	104	97	88

Table S14: Results of ellipsometry measurements from PDMAEMA-co-PMETAC functionalized silica films. Reproduction experiment 2. Because of the inhomogeneous film only two positions were measured.

Layer		Position 1	Position 2
Oxide layer of Si-Wafer	d / nm	7.7 ± 0.1	
	$RMSE$	0.315	
Mesop. silica	d / nm	510.0 ± 4.6	549.6 ± 4.0
	n	1.275 ± 0.006	1.277 ± 0.004
	$RMSE$	3.139	2.668
	$V_{\text{pore}} / \%$	39	39
SBDC funct. film	d / nm	520.1 ± 3.5	523.6 ± 2.9
	n	1.314 ± 0.004	1.353 ± 0.004
	$RMSE$	2.609	1.644
	Pore filling degree / %	19	38
PDMAEMA funct. film	d / nm	513.4 ± 3.3	519.7 ± 2.0
	n	1.333 ± 0.004	1.377 ± 0.003
	$RMSE$	2.503	0.938
	Pore filling degree / %	28	49
PDMAEMA-co-PMETAC funct. film	d / nm	507.0 ± 0.7	552.3 ± 0.5
	n	1.461 ± 0.001	1.475 ± 0.001
	$RMSE$	0.151	1.118
	Pore filling degree / %	100	100

Re-initiation of PDMAEMA functionalized silica films using METAC were carried out at pH 6 and pH 9. We observed a 1.7 times higher polymer amount at pH 9 at which PDMAEMA is expected to be neutrally charged as compared to pH 6 using 10 minutes polymerization time at 38 mW/cm² irradiation intensity (Figure S4).

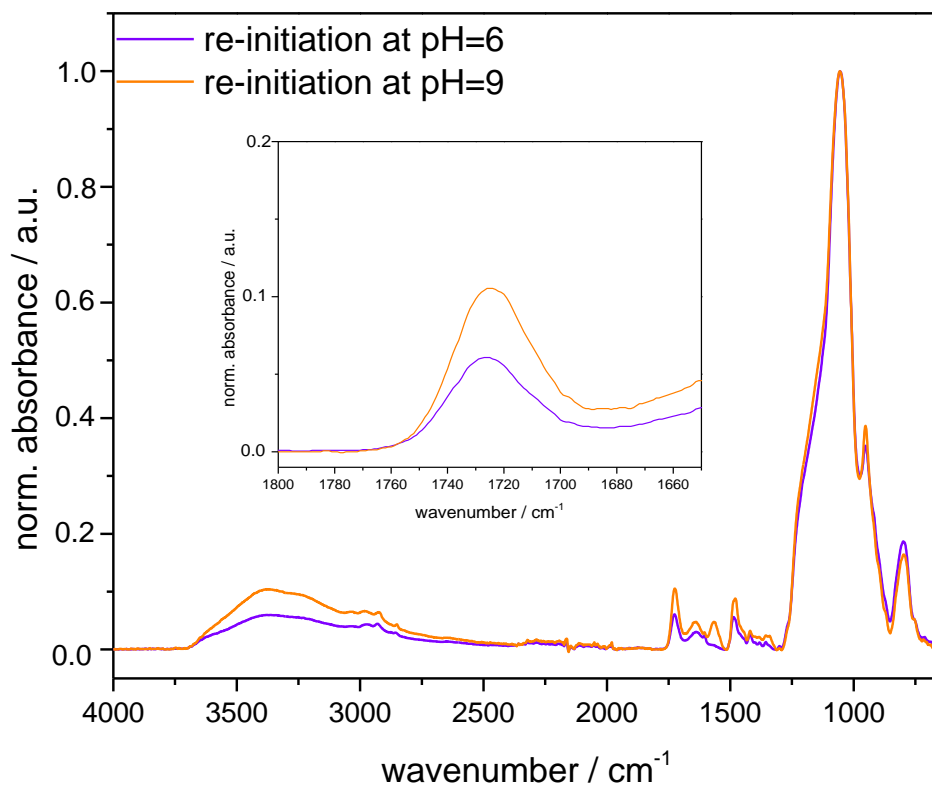


Figure S4: ATR-IR- Spectra of PDMAEMA-b-PMETAC functionalized silica films, using pH=6 (purple) or pH 9 (orange) for re-initiation. The films were scratched off from the substrate for the measurement, the spectra are baseline corrected and normalized to Si-O-Si vibrational band at approx. 1050 cm⁻¹.

The synthesized SBDC was analyzed by ¹H-NMR spectroscopy (Figure S5) and mass spectroscopy (MS, Figure S6). The obtained data are in accordance with literature.^[3]

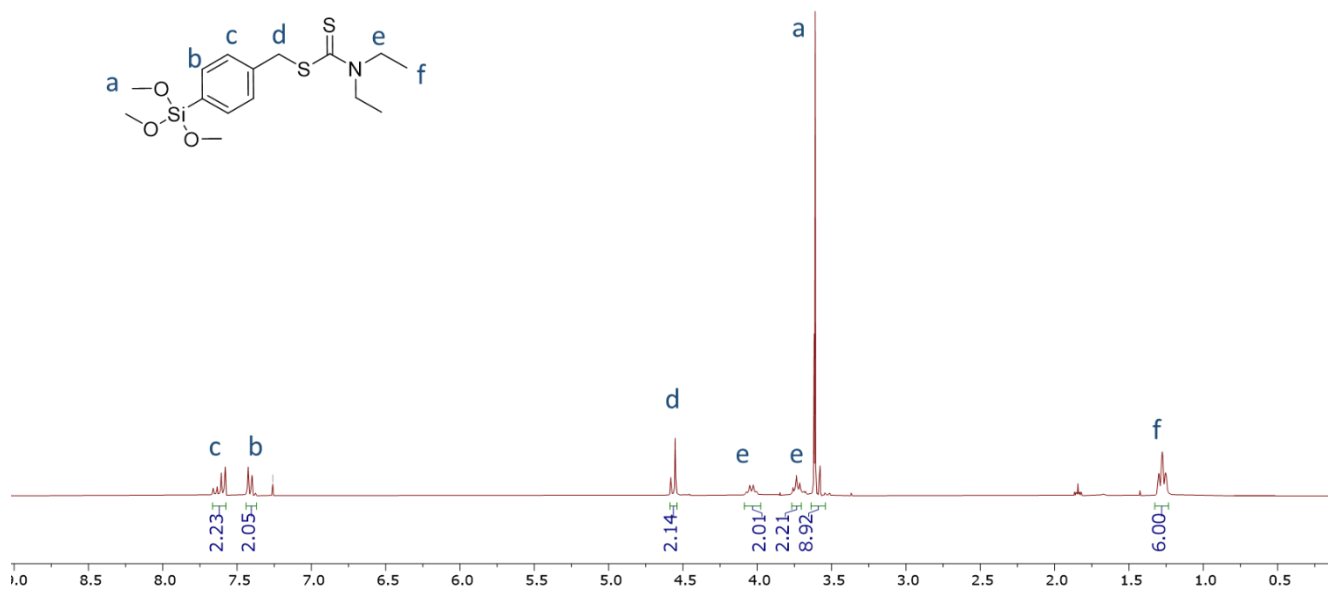


Figure S5: $^1\text{H-NMR}$ spectra (300 MHz) of SBDC in CDCl_3 .

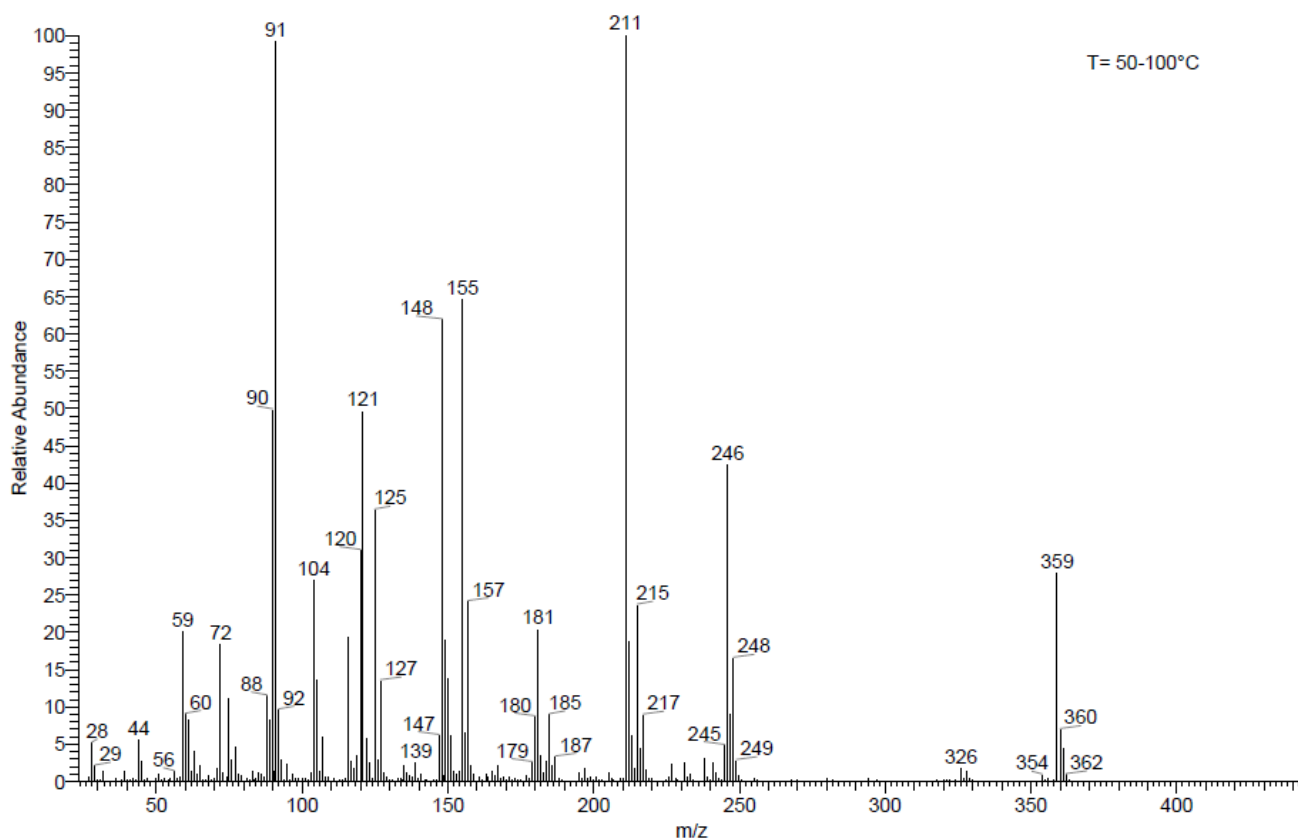


Figure S6: Electron ionization mass spectra of SBDC. The found molecular ion peak of $m/z=359$ clearly demonstrate the successful synthesis of SBDC.

The spectra of the lamp (400-700 nm) used for polymerization is shown in Figure S8.

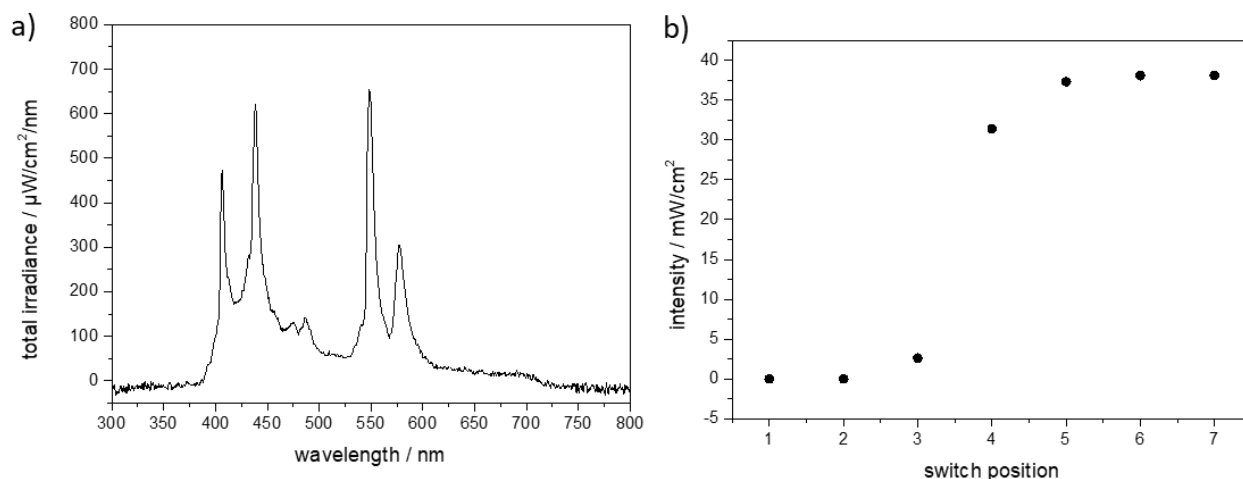


Figure S8: a) Spectra of the lamp (Lumatec Lamp Superlite 400). b) Possible intensities using lamp at 400-700 nm (Lumatec Lamp Superlite 400) irradiation.

Experimental section

Chemicals

Pluronic® F127, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (98%, HPLC), ethanol (absolute EMPLURA®), dichloromethane (DCM, anhydrous, $\geq 99.8\%$), 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine zinc (ZnTPP), dimethylaminoethyl methacrylate (DMAEMA, 98%), [2-(methacryloyloxy)-ethyl]-trimethylammoniumchloride (METAC, 80%wt in water), tetraethylorthosilicate (TEOS) (98%, reagent grade), tetrahydrofuran (THF, anhydrous, $\geq 99.9\%$), sodium *N,N*-diethyldithiocarbamate trihydrate (STC, ACS reagent) and *p*-(chloromethyl)-phenyltrimethoxysilane have been purchased from Sigma-Aldrich/Merck. The monomer DMAEMA was destabilized over a γ -aluminium column before use. Toluene (anhydrous, 99.8%) was purchased from Alfa Aesar and DMSO (99%) from Grüssing GmbH. Alexa Fluor 488 (A30629) was purchased from ThermoFisher Scientific. ATTO647N was purchased from ATTO-TEC GmbH.

Preparation of mesoporous silica thin films

The preparation of the mesoporous silica thin films was carried out using the sol-gel process and evaporation induced self-assembly. The amphiphilic triblock copolymer Pluronic® F127 was used as template and tetraethylorthosilicate (TEOS) as inorganic precursor. Inspired by Dunphy et al.^[4] dip-coating was performed to produce mesoporous silica films with expected pore sizes of ~ 16 nm and film thickness of ~ 500 -600 nm. For the dip-coat solution 9.8 mL TEOS were dissolved in 48.0 mL ethanol. Then 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 is realized by the *Evaporation-Induced Self-Assembly* (EISA-process).^[5] 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.

Synthesis of the photoiniferter SBDC

The synthesis of *N,N*-(Diethylamino)dithiocarbamoyl-benzyl(trimethoxy)silane (SBDC) was performed according to literature.^[3] In an excess of hot methanol sodium *N,N*-diethyldithiocarbamate was dissolved to remove impurities. After drying the sodium *N,N*-diethyldithiocarbamate (1.51 g, 8.81 mmol) was dissolved in dry THF (10 mL) and under a nitrogen atmosphere added dropwise to a solution of *p*-(chloromethyl)-phenyltrimethoxysilane (1.93 mL, 8.76 mmol) in dry THF (10 mL). After stirring for two hours at room temperature, the mixture was filtered to remove the sodium chloride and dried under reduced pressure to remove the THF.

Surface grafting of SBDC

To functionalize the mesoporous silica films a solution of 2.4 mmol L⁻¹ SBDC in dry toluene was prepared and filled into a Schlenk flask, which contained substrates with mesoporous silica films 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.

Polymer functionalization of mesoporous silica films

Inspired by the group of Pester 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.

For the polymerization DDMAT-functionalized mesoporous silica films were placed in tubes containing a solution with the following molar ratios with or without ZnTPP as photocatalyst: [monomer]: [ZnTPP]: [DMSO (mL per mg ZnTPP)] = [500]: [0.025]: [10 mL]. The polymerization was initiated by visible light (LUMATEC Superlite 410, 400-700 nm filter, 38 and 2.5 mW cm⁻² or Hoenle LED Cube 405 nm, 23.25 and 89.65 mW cm⁻²) or UV light (Bio-Link, 365 nm, 40W) irradiation. After irradiation, the residual monomer was extracted in water for at least 10 min. For re-initiation the procedure was performed analog. Polymerization of DMAEMA was always performed with destabilized DMAEMA, while METAC was used without prior destabilization.

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 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. For the analysis of the polymer quantity, only the C=O vibration at approximately 1720 cm⁻¹ in Si-O-Si normalized spectra was considered.

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. 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^[6] by using the refractive indices. For PDMAEMA a refractive index of 1.517^[7] 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.^[1] and Babu et al.^[2] at a pressure of 0.3 mbar and a power off 20% (10 watts). The duration was 12 seconds.

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 films 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.

UV/Vis spectroscopy

The UV/Vis spectroscopy was performed on the Agilent Cary 60 UV-Vis spectrophotometer. The investigated wavelength range was 350 nm to 800 nm. All measurements were performed in PMMA plastic cuvettes. For measurements on mesoporous films, the cuvettes were aligned perpendicular to the incident light beam using the Cary WinUV program (version 5.0.0.999). The spectra were baseline corrected using Origin Pro 9 software.

Cyclic voltammetry (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 [Fe(CN)₆]^{4-/3-} and as cationic probe molecule [Ru(NH₃)₆]^{2+/3+} (each 1 mM in 100 mM KCl solution) were used. The pH =10 were set using diluted sodium hydroxide solution. An Ag/AgCl-electrode (BASi, Typ RE-6) and a graphite 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.

¹H-NMR spectroscopy

¹H-NMR spectrum were recorded on a 300 MHz Avance II NMR Spektrometer (Bruker BioSpin GmbH) using CDCl₃ (99.8% D). The solvent residual peak was used as an internal reference. For analysis the software MestReNova (MestreLabResearch) was used. The spectrum was baseline corrected using a Bernstein polynomial fit. Furthermore, an automatic phase correction was performed.

Laser polymer writing

For laser polymer writing, a Nikon Eclipse Ti2-E (Nikon, Tokyo, Japan) equipped with a N-Storm module was used. A CFI Apo TIRF 60XC Oil (MRD01691) was used as objective. The setup was controlled using the NIS-Elements (version 5.20) software. To initiate the photopolymerization, the 405 nm illumination laser was used. A beam expander setting of “8x” in combination with the 60x objective resulted in a laser spot size of about 42 μm (1/e²) in diameter. Polymer “writing” was achieved by using the built-in macro function to loop over a list of xy-positions with the motorized sample stage and opening the laser illumination shutter for a specified time at each position. The list was created with a custom written Python script, translating the black pixel of a black and white pixel image into xy-positions. The distance between the xy-positions need to be specified by hand. This way a representation of the pixel image can be “printed” onto a sample.

The sample consisting of a mesoporous thin film prepared on a 2.5 mm diameter, 170 μm thick, No 1.5, round microscopy borosilicate cover glass (VWR International, Radnor, Pennsylvania, US). It was placed with the thin film facing upwards into a custom build stainless steel sample holder, which holds about 1 ml of polymerization solution (Monomer, ZnTPP, DMSO) on top of the sample.

Local polymerization visualization:

To visualize polymer functionalization with a fluorescence microscope, the polymer was stained with a fluorophore on the basis of electrostatic interactions. Alexa Fluor 488 was used as a negatively charged fluorophore to stain positively charged PMETAC whereas ATTO647N was used as a positively charged fluorophore to stain non-functionalized mesoporous film. The staining of the non-functionalized film was used as an indirect labeling of PDMAEMA, as the polymer functionalization prohibits ATTO647N staining, showing PDMAEMA functionalized areas as black. For staining, a solution of 1 mg/l fluorophore in water at pH 7 was applied to the sample for 10 minutes. Washing was performed for 20 minutes with water at pH 7 in between fluorophore staining and with water at pH 4 after the final staining step.

Images were acquired by confocal laser scanning microscopy, using the in-built “Navigator” tool of a Leica SP8 (Leica Microsystems, Wetzlar, Germany).

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