SUPPORTING INFORMATION

Photochromic Spiropyran- and Spirooxazine-Homopolymers in Mesoporous Thin Films by Surface Initiated ROMP

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Synthesis and compound characterization

Reagents 2,3,3-trimethyl-3H-indol, 6-bromohexan1-ol, acetonitrile, dichloromethane, sodium hydroxide, diethyl ether, sodium sulfate, 2-hydroxy-5-nitrobenzaldehyde, ethanol, hexane, ethyl acetate, 5-norbornene-2-carboxylic acid (endo/exo-mixture, predominantly endo), 4-dimethylaminopyridine (DMAP), 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDC), and 1-nitroso-2-naphthol were purchased from Alfa Aesar. Potassium chloride, potassium ferricyanide (III), and *N*,*N*-dimethyl formamide were purchased from Merck Millipore. All chemicals were used as received unless otherwise noted. The N-Grubbs-Hoveyda-type catalyst was synthesized as described elsewhere.¹ All synthetic steps were performed under protective nitrogen atmosphere.

Synthesis of 1-(6-hydroxyhexyl)-2,3,3-trimethyl-3H-indole-1-ium bromide (2). 2,3,3trimethyl-3H-indol (1) (1.59 g, 10 mmol) and 2-bromhexanol (1 g, 11 mmol) are dissolved in 0.6 mL acetonitrile. The solvent amount is chosen based on the literature from J.M. Galvin et al. in order to increase Fischer-base yields.² The reaction mixture is stirred for 15 h at 85 °C under reflux. Afterwards the mixture is slowly cooled to ambient temperature and acetonitrile is removed under reduced pressure. The product is dried under high vacuum overnight. The obtained red oil is dissolved in 20 mL dichloromethane, extracted three times with H₂O (demin.) and directly used to be converted into the Fischer-base to subsequently synthesize the spiropyran alcohol (4).

Synthesis of 6-(3,3-dimethyl-2-methyleneindolin-1-yl)hexan-1-ol (3). The 1-(6-hydroxyhexyl)-2,3,3-trimethyl-3H-indol-1-ium bromide (2) is dissolved in H_2O (demin.) 35 mL and 0.1 M NaOH-solution 20 mL are added dropwise to form the Fischer-base. The basic solution becomes milky turbid. The suspension is stirred for 5 more minutes in order to precipitate the Fischer base (3) completely. The product is extracted three times in 30 mL diethyl ether. The color of the organic phase changes to yellow. To remove water from the

etheric solution, Na_2SO_4 (4 g) is added, stirred for 2 min, filtered and diethyl ether is removed under reduced pressure. The yellow product (**3**) is dried under high vacuum for 5 min. The remaining yellow oil (2.97 g, 11.4 mmol, ~66 %) is immediately converted into compound 6-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]-1'-yl)hexane-1-ol (**4**).

Synthesis of 6-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]-1'-yl)hexan-1-ol (SP-

OH) (4). 2-Hydroxy-5-nitrobenzaldehyde (7) 2 g (11.3 mmol) are added to a solution of 2,3,3-trimethylindoleninalcohol (3) 2.94 g (11.3 mmol) in 15 mL ethanol. The reaction mixture turns deeply red. The solution is stirred for 18 h at 85 °C under reflux. The solvent is removed under reduced pressure and the raw product (16) is fully dissolved in 10 mL hexane/ethyl acetate (5:1) at 53 °C. Under cooling to room temperature a red solid precipitates. This solid is recrystallized two times from 10 mL hexane/ethyl acetate (5:1) at 53 °C. ¹H-NMR reveales a mixture of 6-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]-1'-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]. yl)hexan-1-ol (4) and Using recrystallization from hexane/ethyl acetate (5:1) higher yields of spiropyran alcohol (4) as compared to purification with column chromatography, using hexane/ethyl acetate (5:1), are obtained. The spiropyran alcohol (4) is dried under high vacuum overnight. 1.80 g (4.4 mmol) of a pink solid (4) with a yield of 39 % are obtained for this reaction step.



¹H-NMR (300 MHz, CDCl₃) δ (ppm): 8.04 – 7.98 (20&18, m, 2H,), 7.16 (2, pt, J = 7.7 Hz, 1H), 7.05 (6, pd, 1H), 6.86 (15&1, t, 2H), 6.71 (17, d, J = 10.1 Hz, 1H, H_{Ar}), 6.53 (3, d, J = 7.8 Hz, 1H), 5.85 (16, d, J = 10.4 Hz, 1H, C=CH), 3.61 (26, pt, 2H, CH₂COH), 3.22 – 3.05 (21, m, 2H, CH₂N), 1.60 – 1.45 (22&25, m, 4 H, CH₂), 1.32 – 1.26 (23&24, m, 4H, CH₂), 1.16 (10&11, s, 6H, CH₃). R_f = 0.32 (hexane/ethyl acetate 5:1).

Synthesis of 6-(3',3'-dimethyl-6-nitrospiro[chromen-2,2'-indolin]-1'-yl)hexyl bicyclo[2.2.1]hept-5-en-2-carboxylate (SP-Nb) (5). 5-norbornene-2-carboxylic acid (0.62 g (4.48 mmol, 1 eq) predominantly endo), 4-dimethylaminopyridine (DMAP), 0.27 g (2.24 mmol, 0.5 eq), 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDC) 1.03 g (5.38 mmol, 1.2 eq) are added to the SP-OH (4) (1.83 g, 4.48 mmol, 1 eq) and the reaction mixture is dissolved in 17 mL dichloromethane under nitrogen atmosphere at room temperature and stirred overnight. The raw product is completely dissolved in dichloromethane and the present EDC is extracted with H₂O (demi.) three times. The solvent is removed under reduced pressure and the dry product is purified by column chromatography using a hexane/ethyl acetate/dichloromethane (8:1:1) solvent mixture ($R_{f1} = 0.49$, $R_{f2} = 0.42$, endo-exo mixture). A pale-pink solid (5) 1.8 g (3.4 mmol) with a yield of 76 % for this reaction step is obtained.



¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.04 – 8.00 (20&18, m, 2H), 7.17 (2, pt, 1H,³ $J_{2,3}$ = 7.6 Hz), 7.09 (6, pd, 1H,³J = 7.4 Hz), 6.92 (15, pd, 1H,³ $J_{15,16}$ = 10.4 Hz); 6.87 (1, 1H, pt, ³ $J_{1,6}$ = 7.4 Hz) 6.77 (17, d, ³J = 9.75 Hz, 1H, H_{Ar}), 6.58 (3, d, J = 7.8 Hz, 1H, H_{Ar}), 6.19-6.16 (33, m, 0.3 H endo); 6.16-6.09 (33 and 32, exo?); 5.92-5.89 (32 endo?); 5.88 (16, d, 1H, ³ $J_{16,15}$ = 10.4 Hz) 4.15 – 4.04 (26, m, 2H, 1.4 H exo?), 4.04-3.96 (26,m 0.68 H endo?) 3.25 – 3.11 (21, m, 2H, endo and exo), 3.01–2.90 (31&30, m, 2H, CH), 2.21–1.89 (34, m, 2H, (Nb) CH₂), 1.69 – 1.53 (22&25, m, 4H, CH₂), 1.50 (35, d, 1H, CH), 1.34 (23&24&36, m, 6H, CH₂), 1.28 (10, s, 3H, CH₃), 1.18 (11, s, 3H, CH₃). MS (EI) m/z 528. R_{f1} = 0.49 , R_{f2} = 0.42 - endo/exo-mixture (hexane/ethylacetate 5:1).

Synthesis of 6-(3,3-dimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazin]-1-yl)hexan-1ol (6): After the Fischer-base (3) (3.79 g, 14.6 mmol) has been synthesized from 1-(6hydroxyhexyl)-2,3,3-trimethyl-3H-indol-1-ium bromide (2) (66 % yield), (3) is dried under high vacuum for a few minutes. Subsequently, 1-nitroso-2-naphthol 1 eq (3.3 g, 19.1 mmol) is added and both reagents are dissolved in 15 mL ethanol (abs.). The reaction mixture is stirred under reflux at 80 °C overnight. The solvent is removed under reduced pressure and the raw product is purified by column chromatography in a hexane/ethyl acetate/dichloromethane-mixture 5:1:0.5 (R_f = 0.25). Recrystallization from hexane yields a green crystalline product after drying overnight under high vacuum with a yield of 30 % (2 g, 4 mmol).



¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.60 (22, d, 1H, H_{Ar}), 7.77 (14&19, t, 2H, H_{Ar}), 7.66 (16, d, 1H, H_{Ar}), 7.60 (21, m, 2H, H_{Ar}), 7.41 (20, t, 1H, H_{Ar}), 7.22 (2, t, 1H, H_{Ar}), 7.08 (3, d, 1H, H_{Ar}), 7.03 (15, d, 1H, H_{Ar}), 6.90 (1, t, 1H, H_{Ar}), 6.62 (6, d, 1H, H_{Ar}), 3.56 (30, t, 2H, HO-CH₂), 3.28 – 3.15 (25, m, 2H, =N-CH₂), 1.93–1.51 (26&29, m, 4H, CH₂), 1.38 (23&24, s, 6H, CH₃), 1.34 – 1.26 (27&28, m, 4H, CH₂). MS (EI) m/z 414. R_f=0.25 (hexane/ethyl acetate/dichloromethane 5:1:0.5).

Synthesis of 6-(3,3-dimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazin]-1-yl)hexyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (SPO-Nb) (7). EDC (1 eq, 0.554 g, 2.89 mmol), DMAP 0.177 g (1.45 mmol, 1 eq), 5-norbornene-2-carboxylic acid 0.4 g (2.89 mmol, 1 eq) are dissolved in 8 mL dry dichloromethane and added to the dry spirooxazine alcohol (SPO-OH) (5) (1.2 g, 2.89 mmol, 1 eq) dissolved in 8 mL of dry dichloromethane. The reaction mixture is stirred at ambient temperature under nitrogen atmosphere overnight. After 21 h 50 mL dichloromethane are added to dissolve the precipitate. The present EDC is removed by extracting the solution three times with H₂O (demi.). The solvent is removed under reduced pressure and the raw product is purified by column chromatography using hexane/ethyl acetate (5:1) (R_{f1} = 0.75, R_{f2} = 0.71 - endo/exo-mixture). 1.24 g (1.66 mmol) of an orange-yellow oil (7) are obtained corresponding to a yield of 80 %.



¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.47 (24, d, 1H, H_{Ar}), 7.62 (14, s, 1H, -CH=N-), 7.59 (21, d, 1H, H_{Ar}), 7.47 (18, d, 1H, H_{Ar}), 7.42 (23, pt, 1H, H_{Ar}), 7.23 (22, pt, 1H, H_{Ar}), 7.05 (1, pt, 1H, H_{Ar}), 6.91 (3, d, 1H, H_{Ar}), 6.86 (17, d, 1H, H_{Ar}), 6.73 (2, t, 1H, H_{Ar}), 6.46 (6, d, 1H, H_{Ar}), 6.25 – 5.70 (36&37, m, 2H, -HC=CH-), 3.99 – 3.71 (30, m, 2H, CH₂-OCO), 3.20–2.90 (25 and 35/39, m, 2H, CH₂-N), 2.89 – 2.68 (35&34, m, 2H, CH), 2.06 – 1.76 (38, m, 1H, CH), 1.73 – 1.60 (38 oder 40, m, 1H, CH₂), 1.59–1.46 (26, m, 2H, CH₂), 1.41–1.36 (40, m, 2H, CH₂), 1.33 – 1.26 (29 and 40, m, 2H, CH₂), 1.20 (15&16, s, 6H, CH₃), 1.17–1.10 (27&28, m, 4H, CH₂).

Further remarks on the monomer synthesis. For both, SP-Nb (6) and SPO-Nb (7), the formation of the SP/ SPO core represents the yield limiting step. For SPO-Nb low yields are obtained. This is due to several reasons: The main one is the low reactivity of the nitrosogroup due to the low electrophilicity of the nitrogen atom. Furthermore, difficulties associated with the chromatographic isolation are observed also reported in the literature.³ One challenge in the purification via column chromatography is the affinity of spiro-compounds to silanol-groups.⁴ To circumvent loss of material we developed recrystallization strategies for SP-OH (4) and SPO-OH (5). Column chromatography was used for the more hydrophobic SP-Nb (6) and SPO-Nb (7) compounds with higher R_{f} -values, to obtain the final ROMP-monomers.

Synthesis of mesoporous allylsilica films. Mesoporous allylsilica films are synthesized via a sol-gel approach using tetraethoxysilane (TEOS), allyltriethoxysilane and the template (Pluronic[®] F127). The precursor solution is produced with the following mixing ratios: 0.8 TEOS : 0.2 allyltriethoxysilane : 0.005 Pluronic F127® : 24 EtOH: 5.2 H₂O: 0.28 HCl. The

solution is stirred for 24 h at room temperature and subsequently used for dip-coating and evaporation induced self-assembly (EISA-) at 55-60 % relative humidity, 298 K, and a dip coating speed of 2 mms⁻¹. The films are deposited on ITO-coated glass- (4-8 Ohm), silicon wafer-, or glass substrates. After film deposition the coated substrates are stored at 50 % RH for 24 h, and subsequently heated for 24 h at 60 °C, for 24 h at 130 °C followed by an increase of temperature of 1 °C/min up to 200 °C for 2 h. The template is removed in acidic ethanol (0.01 M HCl) for 3 days. Each mesoporous thin film is washed with pure ethanol, dried and stored under ambient conditions.

Synthesis of Poly[6-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)hexyl 2,4divinylcyclopentanecarboxylate] (PSP) and Poly[6-(3,3-dimethylspiro[indoline-2,3'naphtho[2,1-b][1,4]oxazin]-1-yl)hexyl 2,4-divinylcyclopentanecarboxylate] (PSPO) in solution and of PSP and PSPO containing allylsilica films. For ring-opening metathesis polymerization in solution both monomers SPO-Nb (7) (285 mg, 0.533 mmol), SP-Nb (5) (349.5 mg, 0.661 mmol) and the N-Grubbs-Hoveyda-type catalyst [RuCl₂(SIMes)(2-(N,Nmethyl,phenyl)aminobenzylidene)] (Roman Savka, Prof. Plenio, TU Darmstadt)¹ (15 mg, 0.022 mmol) need to be dried under high vacuum for 7 h at room temperature. The solvent dichloromethane is dried overnight above molar sieve (pore size: 0.3 nm) and degassed by a pump-freeze-procedure. DCM is then added to the catalyst and to the monomer, respectively (added volumina: V_{cat} =15 mL, V_{SP} =10 mL, V_{SPO} =10 mL) resulting in a monomer and a catalyst stock solution.

Before polymerization the mesoporous allylsilica films are degassed and dried, using three consecutive nitrogen–vacuum cycles and heating to remove water traces. Subsequently, 3.5 mL of ruthenium catalyst stock solution in dichloromethane (0.04 M) are added to the mesoporous film and left at room temperature for 3.5 h. The films are washed three times with 5 mL of dry dichloromethane under nitrogen atmosphere in order to remove as much unbound ruthenium catalyst from the mesoporous films as possible without bringing them into contact with air. The above mentioned monomer solution of SP-Nb (**5**) (0.06 M) or SPO-Nb (**7**) (0.05 M) in dichloromethane is then added to initiate surface initiated ring-opening polymerization. The polymerization is carried out at room temperature and is quenched after 1.5 h using 10 drops of ethylvinylether. After polymerization the solution homopolymers PSP and PSPO, probably due to non-completely removed unbound catalyst, are precipitated in ethanol. The PSP- and PSPO-containing allylsilica thin films are extracted in dry acetone for 30 minutes at room temperature to remove non-covalently bound monomer or polymer.



PSPO: ¹H NMR (500 MHz, CDCl₃): 8.55 (34, d, 1H, H_{Ar}), 7.72 (14&31, s, 2H, C=CH), 7.63 (16, d, 1H, H_{Ar}), 7.55 (33, d, 1H, H_{Ar}), 7.37 (32, t, 1H, H_{Ar}), 7.18 (2, t, 1H, H_{Ar}), 7.05 (1, t, 1H, H_{Ar}), 6.99 (6, d, 1H, H_{Ar}), 6.85 (15, d, 1H, H_{Ar}), 6.56 (3, d, 1H, H_{Ar}), 5.49–5.15 (39, 41, 26, m, 4 H, RCOO-CH₂, C=CH), 4.05–3.85 (21, m, 2H, N-CH₂), 3.76–3.68 (35, m, 2, H, CH), 3.21–3.09 (30, m, 2H, CH, 2.82–2.65 (38, m, 2H, CH), 2.46–2.36 (37, m, 2H, CH), 2.01–1.88 (22, 25, m, 4H, CH₂), 1.77–1.67 (36, m, 2H, CH₂), 1.32 (19, 20, s, 6 H, CH₃), 1.26–1.21 (23, m, 2H, CH₂), 1.20–1.17 (24, m, 2H, CH₂).



PSP: ¹H NMR (500 MHz, CDCl₃): 7.90 (16a, 18a, s, 2H, H_{Ar}), 7.20–7.14 (15a, m, 1H, H_{Ar}), 7.05 (1, t, 1H, H_{Ar}), 6.98 (4, d, 1H, H_{Ar}), 6.84 (3, d, 1H, H_{Ar}), 6.73 (17a, d, 1H, H_{Ar}), 6.65 (2, d, 1H, C=CH), 6.46 (14a, d, 1H, C=CH), 5.35–5.12 (18&19&6, m, 6H, C=CH & RCOO-CH₂), 3.98–3.80 (11a, m, 2H, =N-CH), 3.65–3.49 (15, m, 1H, CH-COO-R), 3.15–2.85 (22, m, 2H, CH₂), 2.82–2.64 (21, m, 2H, CH₂), 2.45–2.38 (20, m, 1H, CH), 1.85–1.47 (34&7&9&10&8a, m, 9H, CH₂), 1.23–1.07 (12&13, s, 6 H, s CH₃).

Table S1: Molecular weight and polydispersity of PSP and PSPO determined by gel permeation chromatography (GPC). The polymer generated in solution in the presence of catalyst modified mesoporous thin films was analyzed. In case the mesoporous films were plasma treated before catalyst binding this is indicated.

Sample	M _w	M _n	PDI
PSP	6.68·10 ⁴ g/mol	4.16·10 ⁴ g/mol	1.61
PSP (plasma)	3.15·10 ⁴ g/mol	2.27·10 ⁴ g/mol	1.39
PSPO	1.37·10 ⁴ g/mol	1.14·10 ⁴ g/mol	1.20
PSPO (plasma)	1.49·10 ⁴ g/mol	1.22·10 ⁴ g/mol	1.22

GPC-measurements are performed by Heike Herbert (group of Prof. Biesalski, TU Darmstadt). The polymer is dissolved in DMF as mobile phase with 3g/l LiCl added for GPC-measurements. The measurements are performed at ambient temperature, a flow rate 0.5 mL/min with a Hewlett-Packard Agilent 1200 Series GPS, with two coupled columns in series (PSS GRAM VS 3a und PSS GRAM AS 3b). The device is equipped with a refractive index detector (1200 Agilent RID 35 Grad). Calibration is performed against PMMA (PSS, Mainz Germany).

Estimation of the molar extinction coefficients by NMR spectroscopy: A further comparison of UV/VIS measurements and NMR experiments requires the extinction coefficients of the SP-Nb, SPO-Nb and their corresponding merocyanine forms. To obtain those extinction coefficients, molar fractions of SP-Nb and MC_{SP-Nb} as well as SPO-Nb and MC_{SPO-Nb} in thermal equilibrium at ambient temperature are estimated from NMR samples with different concentrations. As those ratios seem to be independent from the sample concentration it is legitimate to expect that they are valid also at the low concentration required for UV/VIS. For the MC_{SP-Nb} a fraction of about about 99 % SP-Nb and 0.8 to 1.2 % MC_{SP-Nb} is measured at 296.8 K. For the MC_{SPO-Nb} a fraction determination is hardly possible as the equilibrium fraction of the MC form is rather small and signal crowding impedes integration. A rough approximation gives 99.2 % SPO-Nb and 0.8 % MC_{SPO-Nb} . The estimated ϵ values are 2 795 828 L·m/Mol for the MC_{SP-Nb} , 895 620 L·m /Mol for the SP-Nb 180 000L·m /Mol for MC_{SPO-Nb} and 508 000 L·m /Mol SPO-Nb.

Determination of molar ratios of MC forms depending on the applied light flux: To validate the comparison between high energy irradiation UV/VIS and NMR spectroscopy measurements at lower light flux, a UV/VIS experiment with irradiation comparable to the NMR conditions was carried out. This enabled a direct comparison of the data obtained as photo flux is comparable. Here, a comparable rate constant k_{Vis} (SP-Nb) is obtained for UV/VIS and NMR spectroscopy. By using the obtained extinction coefficient for SP-Nb for this UV/VIS measurement as fraction of about 12 % MC_{SP-Nb} can be calculated within a PSS. This fraction was also observed by *in situ* irradiation NMR spectroscopy at 300 K. With this it can be shown, that fractions of SP-Nb and the corresponding MC_{SP-Nb} are not depending on the total concentration of the sample.

Overview on photochromic and acidochromic behavior of spiropyran and spirooxazine derivatives.



Figure S1: Scheme depicting the possible photochromic interconversions for spiropyran- and spirooxazine derivatives. This is an extension to the scheme shown in Figure 2.



Figure S2: IR spectra after UV-irradiation (magenta) and VIS irradiation (black) for PSP in solution (left) and PSP grafted to a mesoporous silica film (right). Only very minor changes could be observed at ambient conditions, which is in accordance with a low ratio of interconverted merocyanine species.

Sample	UV-Irradiation time / min	UV-energy density J/cm²	Vis-Irradiation time / min	Vis-energy density J/cm²	Cycles
SPO-Nb (Fig. 8a)	5.10	3.61	-		10
SP-Nb (Fig. 8b)	5.05	3.58	5.40	9.91	5
PSPO (Fig. 8c)	2.10	1.49	-		8
PSP (Fig. 8d)	3.93	2.78	6.05	11.11	4
PSPO & allylsilica (Fig. 8e)	0.67	0.47	-		2
PSP & allylsilica (Fig. 8f)	2.49	1.76	2.55	4.68	3
PSPO & allylsilica (Fig. 8g) (plasma)	0.95	0.67	-		3
PSP & allylsilica (Fig. 8h) (plasma)	2.21	1.56	3.00	5.51	3

Table S2: Values of total UV-irradiation time and energy in photostability experiments (corresponding to Figure 8 in the main text).

a) mesoporous silica + PSPO

300 200 0,00 0,25 0,50 0,75 1,00 1,25 1,50 distance / mm

c) mesoporous silica + PSPO

before polymerization	position 2	position 3				
d (20%allyIsilica)	169.0 nm ± 0.2 nm	169.9 nm ± 0.1 nm				
n (20%allyIsilica)	1.371 ± 0.001	1.367 ± 0.000				
RMSE	1.428	0.958				
after polymerization	position 2	position 3				
d (polymer/surface)	62.7 nm ± 0.7 nm	62.4 nm ± 1.0 nm				
n (allylsilica+PSPO)	1.395 ± 0.011	1.383 ± 0.017				
RMSE	2.017	3.413				

400

300

200

100

0.00

layer thickness / nm

d) mesoporous silica (plasma) + PSPO

before polymerization	position 1	position 2	position 3
d (20% allyIsilica)	166.8 nm ± 0.4 nm	169.9 nm ± 0.6 nm	180.0 nm ± 0.1 nm
n (20% allyIsilica)	1.364 ± 0.002	1.360 ± 0.002	1.374 ± 0.001
RMSE	1.965	2.496	0.369
	111 A	111 A	111 A
after polymerization	position 1	position 2	position 3
d (allylsilica+PSPO)	162.3 nm ± 0.7 nm	157.4 nm ± 0.3 nm	164.8 nm ± 0.3 nm
n (allylsilica+PSPO)	1.388 ± 0.002	1.392 ± 0.001	1.392 ± 0.001
RMSE	4.288	2.525	2.349

Figure S3: Characterization of mesoporous PSPO-modified silica films with and without plasma treatment. a, b) Profilometer measurements showing film thickness and surface roughness for PSPO modified mesoporous silica films without (a) and with (b) plasma treatment. c, d) Refractive index and film thickness as obtained by fitting ellipsometry data using a one-layer model at three different positions on one substrate before and after polymerization for PSPO modified mesoporous silica films without (c) and with (d) plasma treatment. The CO₂ plasma experiments were performed by D.J. Babu in the group of Prof. J.J. Schneider at TU Darmstadt following the experimental details given in: D. J. Babu, S. Yadav, T. Heinlein, G. Cherkashinin, J. J. Schneider, *J. Phys. Chem. C*, 2014, **118**, 12028-12034.⁵

In general, these data proof the polymerization based on increasing film thickness, refractive index and surface roughness upon polymerization without plasma treatment. The plasma treatment results in a slightly reduced film thickness and a very smooth external surface. Together with the simultaneous refractive index increase upon polymerization this proves the applicability of the plasma treatment. The experimental conditions for profiler, ellipsometry and AFM measurements are summarized below.

b) mesoporous silica (plasma) + PSPO

1.25 1.50

0.25 0.50 0.75 1.00

distance / mm

Profiler. The topography of mesoporous films in dry state is examined using a profiler Dektak XT (Bruker). The vertical resolution is 1 Å, horizontal resolution 120 000 measuring points, with a stylus force of 1 mg. For each measurement a "hills & valleys"-profile has been chosen.

Ellipsometry. The dry thickness of the surface-attached films on silicon wafers is measured using a Nanofilm EP3 imaging ellipsometer. One zone angle of incidence (AOI) variation measurements are captured between AOIs of 40° and 80° with a 658 nm laser. The apparent film thickness is calculated from the measured angles Ψ and Δ using the EP4 analysis software supplied with the instrument. The fitting parameters for the silicon oxide layer thickness (d(SiOx) = 2.5 nm is measured separately prior to polymer film immobilization) and the refractive index of the polymer layer (npolymer = 1.5) are held constant. To determine the porosity from the refractive indices, the Brueggemann effective medium approximation is used.⁶



Figure S4: Equilibrium UV-VIS absorption at 568 nm for a) PSP in DMF solution and b) grafted to a mesoporous film in contact with DMF at ambient conditions after VIS-irradiation. It is clearly visible that at ambient conditions a certain fraction of PSP is interconverted into the MC form. The ratio MC:SP in Figure S8a is 0.04 % relative to the absorption value of the fourth UV/VIS-irradiation cycle (M_w =3,15·10⁴ g/mol) in DMF. For PSP containing silica films without plasma treatment (Figure S8b) the absorption intensity in the thermal equilibrium at 568 nm is 9 % of the intensity after UV-switching.

Remark to Figure 7e in the manuscript. The kinetic data in Figure 7e were smoothened to exclude the effect of the UV-irradiation lamp. Data smoothing is perfomed using the Savitzky-Golay filter in OriginPro 8.6 (OriginLab®, Northampton, USA), to increase the signal-to-noise ratio for measured plasma treated PSP- and PSPO-containing allylsilica films.⁷ The resulting rate constants were not affected by this smoothing process.



Figure S5: Temperature-dependent absorption changes (black points) and the corresponding first order rate law fitting (red line) for SPO-Nb in DMF upon thermal relaxation at a) 240 K, b) 250 K, c) 260 K measured using NMR spectroscopy corresponding to Figure 5. d) shows the extracted Arrhenius type behavior.

For the SPO-Nb thermal fading of the open form at different temperatures can be described by mono exponential functions (Figure S5). Thermal fading rates of the SPO-Nb correspond to an Arrhenius like behavior (Figure S5) as expected for a unimolecular reaction. For the SP-Nb monomer a description of the thermal fading with a mono exponential function is valid for 300 K and 280 K, too. At lower temperatures thermal fading occurs on the timescale of several hours up to days.

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