Monolithic Spiropyran-Based Porous Polysilsesquioxanes with Stimulus-Responsive Properties

Daniel Euchler, Caroline R. Ehgartner, Nicola Hüsing, and Andrea Feinle*

ABSTRACT: Dynamic materials comprising spiropyrans have emerged as one of the most interesting and promising class of stimulus-responsive materials. Spiropyrans are often embedded in polymer matrices; their covalent attachment into porous monolithic silsesquioxane frameworks, however, is virtually unexplored. We demonstrate that a silylated spiropyran derivative can be covalently incorporated into ultralight silsesquioxane-based bulk materials by a two-step co-condensation sol–gel approach without restricting its conformational freedom and thus its stimulus-responsive properties. UV–vis measurements prove the conversion of the colorless closed-ring form of the spiropyran molecule into its highly colored purple isomer or the yellow colored protonated structure thereof. The transformation can be triggered simply by irradiation of the spiropyran-containing silsesquioxane monolith with UV or visible light or by the pH value of the chemical environment. A strong dependence of the surface polarity and water wettability on the prevalent isomer was observed. The contact angle of a water droplet on the monolithic surface can be altered from 146° to 100° by irradiation of the monolith with UV light for 3 min. Additionally, the prepared materials possess high specific surface areas, low bulk densities, and porosities of up to 84%.

KEYWORDS: co-condensation, polysilsesquioxanes, porous materials, sol–gel chemistry, spiropyrans, stimulus-responsive materials

INTRODUCTION

Dynamic materials in which selected properties can be “switched on” and “off” more and more attract the attention of researchers, and the demand for novel stimulus-responsive materials is rising due to their broad applicability ranging from optical memory devices to holographic gratings or optical sensors. Stimulus-responsive organic molecules such as azobenzenes, stilbenes, diarylethenes, or fulgides are well-known and have long been the focus of interest. In the last few years, however, the class of spiropyrans (SPs) has become popular as well. SPs comprise an indoline and chromene moiety positioned perpendicular on either side of the spiro C–O bond. In the SP form, both parts are not in conjugation and the isomer mainly absorbs in the UV region, whereas the isomer undergoes a 6π-electrocyclic ring opening reaction by an external stimulus and forms a highly colored merocyanine (MC) product, which can be protonated to the yellow colored MCH+ isomer. In recent literature studies, a rising number of publications about the incorporation of SPs in diverse materials can be found. To name some recent examples, Sumaru et al. reported the possibility to use spiropyran-functionalized poly(N-isopropylacrylamide) (pNIPAAm) for the recognition of cyclodextrin, Cao et al. described the possibility to capture or release cells on or from spiropyran-modified Janus particles by UV or visible light irradiation, and several publications exploited the different colorations of SP for chemical drawing purposes or mechanochemical studies (e.g., in stress/strain sensing and damage reporting). Further examples for SP-based dynamic materials can be found in an excellent review recently given by R. Klajn.

Interestingly, little is known about the introduction of responsive entities in organofunctional polysilsesquioxanes, although these represent interesting and promising alternatives to the materials reported above. Compared to polymeric bulk materials, methyltrimethoxysilane (MTMS)-based polysilsesquioxanes possess high porosities, high specific surface areas, low densities, superhydrophobic surfaces, and outstanding mechanical properties. From these properties, several advantages occur: high porosities allow a diffusion-controlled mass transport into the materials, high specific surface areas ensure high accessibilities of embedded spiropyran moieties,

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and low densities allow the design of functional and lightweight materials. In our present study, the introduction of SPs as stimulus-responsive molecules in organic–inorganic hybrid carriers was investigated. SP was chosen as the preferred responsive entity, not only because a variety of different external stimuli can lead to its transformation into the MC isomer as reported above but also because of the great difference in the chemical and physical properties these isomers possess. Whereas the SP isomer is hydrophobic and transparent in the visible region, the MC isomer can be wetted by aqueous solutions and appears purple/red colored with a strong absorption peak at around 540 nm.37

## EXPERIMENTAL SECTION

### Materials

2-(3′,3′-Dimethyl-6-nitrosipino[2H-1-benzopyran-2,2′-indoline]-1-yl)ethanol (97% purity) was purchased from abcr (Germany). 3-(Triethoxysilyl)propylisocyanate (95%), methyltrime-thoxyxilane (98%, MTMS), Pluronic F-127, urea, acetic acid (29.98%), hydrochloric acid (37%,aq. HCl), and anhydrous dimethylformamide (99.8%, DMF) were obtained from Sigma-Aldrich. Methanol (technical grade) was purchased from VWR International. All chemicals were used without further purification.

### Characterization

FT-IR spectra were obtained by using a Vertex 70 spectrometer equipped with a PLATINUM-ATR unit (Bruker) with a 4 cm⁻¹ resolution. Absorption/reflection spectra were recorded with a PerkinElmer UV–vis–NIR spectrophotometer (Lambda 750) equipped with a 66 mm integration sphere and converted in the range from 200 to 800 nm by the Kubelka–Munk function. 1H NMR spectra were obtained using a 600 MHz Bruker Avance III HD spectrometer equipped with a 1H/13C/15N/31P quadruple-resonance probe at 298 K. Bulk densities (ρb) were calculated from the heights, diameters, and masses of cylindrical monoliths. Skeletal densities (ρs) were determined by helium pycnometry on a Micromeritics AccuPyc II 1340 at 25 °C. The porosity P was calculated by P = [1 – ρb/ρs]/100. Nitrogen adsorption–desorption measurements were carried out at −196 °C on a Micrometrics ASAP 2420. For size distributions calculations were performed by using the Barret–Joyner–Halenda method (BJH).18 The specific surface area was calculated by the Brunauer, Emmett, and Teller 5-point method in the relative pressure range of 0.05–0.39. Prior to the measurement, the samples were degassed in vacuum for 12 h at 300 °C. Transmission electron micrographs (TEM) were recorded with a JEOL JEM F200 TEM using a TVIPS F2162 k by 2k CMOS camera, and the diameters of 150 selected particles were measured in each sample to determine the average particle size distribution. Scanning electron microscopy (SEM) was performed on a Zeiss ULTRA Plus operating at 5 kV accelerating voltage with an InLens detector. Uniaxial compression–decompression tests were performed on a ZwickRoell RetroLine universal testing machine equipped with a 2.5 kN load cell. The samples were compressed up to 60% with a compression rate of 1 mm min⁻¹. The Young’s modulus E was calculated between a strain of 1 and 20% by using the equation E = [F/A]/[h/k0], with F being the force applied, A the area or cross section of the cylindrical monolith, k0 the height of the sample before, and h the height of the sample after compression. The gel fraction of the samples was determined with Gel (%) = M/Gel with M0 as the weight of the ambiently dried sample and Mf the weight of the supercritical dried samples after extraction of the soluble parts.

Contact angles were determined using a DSA10L device (Krüss Ltd., Germany) with an integrated DSA10 control unit. The volume of the water droplet was set to 3 μL. Prior to the measurement, the samples were irradiated with visible light for 10 min to ensure conversion of MC isomers into their SP form. Images were taken in 10 s time intervals, and the contact angle was determined using the TRACKERMAN software. As a UV radiation source, a 10 mW laser pointer with a beam diameter of 0.3 cm and light emission at a wavelength of 405 nm or a germicidal hand lamp with a light emission at 365 and 405 nm (16 W) was used.

### Synthesis of a Spiropyran-Derived Si Precursor

The synthesis was carried out according to the protocol of Allouche et al.20 2-(3′,3′-Dimethyl-6-nitrosipino[2H-1-benzopyran-2,2′-indoline]-1′-yl)ethanol (0.14 mmol, 1.0 equiv) and 3-(triethoxysilyl)-propylisocyanate (0.14 mmol, 1.0 equiv) were dissolved in 1 mL of dry DMF. The solution was heated in argon at 80 °C and kept at this temperature under stirring for 12 h. After cooling to room temperature, the as-prepared solution with a concentration of spiropyran derivatives of 0.084 mmol mL⁻¹ was protected from light and used without further purification. If not used directly, the solution was stored under argon and protected from light to prevent oxidation and side reactions.

1H NMR (600 MHz, CDCl3, 25 °C, TMS), yield 60%, δ = 7.97 (m, 1H), 7.15 (td, J = 1.2, 7.6 Hz, 1H), 7.06 (dd, J = 1.0, 6.9 Hz, 1H), 6.87 (t, J = 10.3 Hz, 1H), 6.85 (d, J = 7.3 Hz, 1H), 6.72 (d, J = 9.0 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 5.86 (d, J = 10.1 Hz, 1H), 3.82–3.78 (m, 1H), 3.80 (q, J = 6.9 Hz, 6H), 3.67 (dt, J = 6.9, 7.1 Hz, 1H), 3.42 (ddd, J = 6.1, 7.6, 13.4 Hz, 1H), 3.30 (dt, J = 5.5, 14.9 Hz, 1H), 3.27 (t, J = 6.7 Hz, 2H), 1.71 (quint, J = 6.6 Hz, 2H), 1.26 (s, 3H), 1.21 (t, J = 6.9 Hz, 9H), 1.16 (s, 3H), 0.65 (t, J = 8.3 Hz, 2H).

IR (ATR) ν = 2928 (m, C–H), 2860 (m, C–H), 1661 (s, amide-C, TMS), yield 60%, δ = 10.3 (s, C=O), 7.97 (m, C=O), 1385 (s, C=O), 1352 (m, C=O), 1265 (m, C=H), 1089 (s, C–O), 658 (m, C=O) cm⁻¹.

### Preparation of Spiropyran-Modified Polysilsesquioxanes

Starting compositions for each sample are listed in Table 1.

| sample name | V (MTMS) (mL) | V (SP-DMF) (μL) | n (SP)/n (MTMS) |
|-------------|--------------|----------------|-----------------|
| SP0-MTMS    | 2.5          | 0              | 20:1            |
| SP1-MTMS    | 2.5          | 25.0           | 10:1            |
| SP2-MTMS    | 2.5          | 50.0           | 5:1             |
| SP3-MTMS    | 2.5          | 75.0           | 3:1             |
| SP4-MTMS    | 2.5          | 125.0          | 1.0:1           |
| SP10-MTMS   | 2.5          | 250.0          | 20:1            |
| SP20-MTMS   | 2.5          | 500.0          | 10:1            |

- The functional porous polydimethylsiloxane monoliths were prepared via a co-condensation approach of methyldimethylsiloxane (MTMS) and spiropyran-derived propyltriethoxysilane. The surfactant Pluronic F127 (M = 12.6 kDa), urea (0.25 g, 4.2 mmol), and aqueous acetic acid (3.5 mL, 10 mM) were mixed in a polystyrene container and stirred for 5 min at room temperature. MTMS (2.5 mL, 18 mmol) and the respective amount (1 to 20 vol %, volume percentage based on the volume of MTMS) of the spiropyran derivative containing DMF solution (SP-DMF) were added under vigorous stirring at ambient temperature. The mixture was stirred for 30 min, and subsequently, the obtained sol was transferred into a polypropylene container, sealed, and placed in a ventilated oven at 60 °C to induce gelation. The wet gel was kept at this temperature for 4 days for aging. After 4 days, the sample was removed from the polypropylene vessel, immersed in an excess amount of methanol (MeOH), and again kept at 60 °C. The solvent was exchanged four times after 8 h soaking intervals to remove the surfactant and unreacted chemicals. After the extraction process, the wet gels were placed in an autoclave and sealed, and the autoclave was filled with liquid carbon dioxide (CO₂). The vessel was heated to 60 °C and pressurized to 100 bar. Under continuous flow conditions, the MeOH/CO₂ mixture was released repeatedly until supercritical CO₂ was left solely. The depressurization rate was 1 MPa min⁻¹.

### Table 1. Required Amounts for the Preparation of SP0-MTMS, SPx-MTMS Monoliths with x Giving the vol % of SP-DMF (vol % Based on the Amount of MTMS), and the Corresponding Molar Ratio of SP to MTMS

- The derived Si Precursor. The synthesis was carried out according to the protocol of Allouche et al.20 2-(3′,3′-Dimethyl-6-nitrosipino[2H-1-benzopyran-2,2′-indoline]-1′-yl)ethanol (0.14 mmol, 1.0 equiv) and 3-(triethoxysilyl)-propylisocyanate (0.14 mmol, 1.0 equiv) were dissolved in 1 mL of dry DMF. The solution was heated in argon at 80 °C and kept at this temperature under stirring for 12 h. After cooling to room temperature, the as-prepared solution with a concentration of spiropyran derivatives of 0.084 mmol mL⁻¹ was protected from light and used without further purification. If not used directly, the solution was stored under argon and protected from light to prevent oxidation and side reactions.

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RESULTS

Synthesis. To enable a covalent attachment of spiropyran to a polysilsesquioxane network using sol−gel chemistry, the photo-responsive molecule \(N\)-hydroxyethyl-spiropyran was modified with hydrolyzable alkoxy groups by reaction with 3-(triethoxysilyl)propylisocyanate in DMF following a protocol published by Allouche et al. (Figure 1).\(^{25}\) A yield of 60\% was determined by \(^1\)H NMR spectroscopy. Longer reaction times did not result in higher yields. FT-IR spectroscopy additionally confirmed the reaction by a decreasing intensity of the peak of the isocyanato group at 2265 cm\(^{-1}\) and the formation of two new peaks at 1661 cm\(^{-1}\) for amide 1 and 1503 cm\(^{-1}\) for amide 2 vibration.

Spiropyran-functionalized methyltrimethoxysilane (SPx-MTMS) monoliths were prepared in a two-step sol−gel process in the presence of acetic acid, urea, and the triblock copolymer Pluronic F127 (EO\(_{108}\)PO\(_{70}\)EO\(_{108}\)) as a surfactant to avoid macroscopic phase separation between the developing hydrophobic methylsilsesquioxane network and the polar environment. The alkoxy groups of MTMS and SP were hydrolyzed in aqueous acetic acid in the first step followed by initiation of condensation reactions by heating the mixture to 60 °C. The elevated temperature caused decomposition of urea to carbon dioxide and ammonia and raised the pH value to pH = 11. The basic environment favored condensation reaction of the hydrolyzed silanes, and gelation of the sol occurred after 1 h.

The percentage of SP-DMF in MTMS was varied from 0 to 20 vol \% based on the volume of MTMS. At values above 10 vol \%, partial precipitation of the spiropyran derivative in the precursor solution was observed, leading to undefined amounts of attached SP in the network structure. Therefore, the upper limit was set to 10 vol \%, and monoliths prepared with higher concentrations of SP were not studied further. The nomenclature of the investigated samples was the following:

- SP0-MTMS: no addition of SP (reference material).
- SPx-MTMS: addition of \(x\) vol \% SP-DMF based on the volume of MTMS \((x = 1, 2, 3, 5,\) and \(10)\).

The color of the SPx-MTMS samples changed during preparation: the dark purple colored SP-DMF solution converted into a reddish-orange one after its addition to the precursor solution and turned into a colorless state after the removal of the solvent.

Structural Analysis. The influence of the SP modification on the structural properties of SP-modified polysilsesquioxane monoliths was investigated by nitrogen sorption analysis, helium pycnometry, TEM, and uniaxial compression/decompression measurements.

Photographic images of all monoliths can be found in the Supporting Information (Figure S1). Their specific surface areas (SSAs) were calculated from data obtained by nitrogen sorption analysis (Figure 2). SP0-MTMS had a SSA of 600 m\(^2\) g\(^{-1}\), whereas SPx-MTMS with \(x\) between 1 and 10 displayed lower values with 545 ± 5 m\(^2\) g\(^{-1}\) (Figure 2a). The incorporation of SP also had little effects on the determined bulk densities and calculated porosities (Figure 2b). The reference sample SP0-MTMS had a bulk density of 0.23 g cm\(^{-3}\) and a porosity of 83\%, and SPx-MTMS (with \(x = 1–10)\) had bulk densities between 0.22 and 0.24 g cm\(^{-3}\) and porosities between 81 and 84\%. The gel fractions of the samples SP0-MTMS, SP5-MTMS, and SP10-MTMS were determined to be 55\% (SP0-MTMS), 57\% (SP5-MTMS), and 54\% (SP10-MTMS).

The adsorption−desorption isotherms obtained from nitrogen sorption measurements reveal that all samples possess type IV isotherms with a capillary condensation of nitrogen occurring at a relative pressure of around 0.6 \(p/p_0\) (Figure S2). Pore size distributions were calculated from the adsorption branch using the BJH method (Figure S2).\(^{40}\) For all samples, a mean pore diameter between 48 and 57 nm was determined with SP10-MTMS having the lowest and SP0-MTMS having the highest pore diameter.

The morphology of the three-dimensional network structure was determined by transmission electron microscopy (Figure

![Figure 1. Silylation of \(N\)-hydroxyethyl-spiropyran with 3-(triethoxysilyl)propylisocyanate.](image)

![Figure 2. (a) Specific surface area and (b) bulk density and porosity of SP0-MTMS and SPx-MTMS (\(x = 1, 2, 3, 5,\) and 10).](image)
3). All samples displayed a continuous fibrous network of globular aggregated particles with mean particle sizes of 9.4 ± 1.1 nm; no difference has been observed between the reference sample SP0-MTMS and selected SPx-MTMS (x = 5 and 10) monoliths. Additionally, high adsorbed volumes of nitrogen at low relative pressures in the nitrogen sorption measurement (Figure S2) and high-magnification transmission electron micrographs demonstrated a certain degree of microporosity in the globular particles (Figure S3).

To compare the influence of the SP attachment on the mechanical properties of the MTMS monoliths, uniaxial compression–decompression tests up to 60% strain were performed for the samples SP0-MTMS and SP10-MTMS (Figure 4). For both samples, comparable Young’s moduli of 3.03 MPa for SP0-MTMS and 3.15 MPa for SP10-MTMS were calculated (Figure 4a). No fractures were observed, and both samples sprang back to 98% of their initial height after decompression. Additionally, the mechanical property of the stimulus-responsive sample SP10-MTMS was measured prior to and after UV light irradiation to investigate the impact of the presence of the SP or MC isomer, respectively (Figure 4b). The calculated Young’s modulus of 3.13 MPa for the SP10-MTMS sample after UV light irradiation was almost identical with the Young’s modulus (3.15 MPa) of the same sample.
prior to UV light irradiation and still reached a comparable value after a second conversion of the SP into the MC form (Figure S4).

**Stimulus-Responsive Behavior.** The ability of the transparent closed-ring SP to convert into the highly colored MC isomer and its protonated yellow MCH⁺ form was investigated using UV−vis spectroscopy. Pictures of SP10-MTMS comprising the different isomers, their chemical structures, and corresponding UV−vis spectra are shown in Figure 5. Starting from SP10-MTMS with SP in the closed-ring form (i), the conversion and ring opening reaction of SP into its MC isomer was induced by irradiation of the monolith with UV light (16 W). Image (ii) in Figure 5a was taken after an irradiation time of 3 min. Corresponding UV−vis spectra of the sample prior to and after irradiation with UV light are shown in Figure 5b. The closed SP form absorbed light mainly in the range between 200 and 450 nm and thus appeared colorless. Additionally, a weak peak at a wavelength of 568 nm was observed indicating the presence of a small amount of MC isomers. The intensity of this peak increased after irradiation with UV light due to a shift of the SP-MC equilibrium toward the latter. Note that no further increase in the peak intensity was observed after longer irradiation times. The MC isomer can further be converted into a yellow colored protonated form by dropping a one molar methanolic solution of hydrochloric acid onto the surface of SP10-MTMS. The transformation of the purple MC into its protonated yellow colored MCH⁺ form occurred immediately at spots in direct contact with the hydrochloric acid solution; further conversion throughout the whole sample was observed after keeping the sample in the dark for more than one hour (image (iii), Figure 5a). UV−vis measurements prove this conversion by a shift of the absorption maximum from 568 to 421 nm. Back reaction of the MC or MCH⁺ into the closed-ring SP isomer was initiated by exposure of the monolith to visible light or by heat treatment at 80 °C. The kinetics of the MCH⁺ to SP conversion was significantly lower than the kinetics of the MC to SP conversion and was completed after several hours, while the MC to SP conversion occurred within minutes. The conversion of one form into the other can be repeated several times without destruction of the polysilsesquioxane matrix.

To investigate the influence of visible light on the conversion kinetics of the MC into the SP isomer, the UV-irradiated sample SP10-MTMS was broken into two parts. One was kept in the dark (Figure S5), whereas the other was irradiated with visible light (1.9 W) from a distance of 10 cm (Figure 6a). UV−vis spectra were taken after specific time intervals to follow the back reaction. The conversion of the SP into the MC isomer was determined to be a second-order reaction with a shift of the absorption maximum from 568 to 552 nm with progressing reaction. Distinct differences were observed between the back reaction rate of the two samples: irradiation with visible light allowed the MC isomer to transform into the SP isomer within 45 min, whereas even after days, no full recovery was observed for the sample that was kept in the dark.

The repeatability of the conversion of SP into MC isomers was investigated by irradiation of the SP10-MTMS sample with visible light for 60 min, subsequent irradiation with UV light for 3 min, and following the intensity changes of the absorption peak at 568 nm. The peak intensity dropped to 35%
of the initial intensity within the first three cycles but then remained constant (Figure 6b).

Besides changes in color, the conversion of one isomer into the other is known to influence the water wettability of SP-coated surfaces. Contact angle measurements were performed on SP10-MTMS to investigate the dependence of its water wettability on the presence of either the SP or the MC isomer of the photo-responsive molecule. For this, the contact angle of a water droplet was measured prior to and after irradiation of the monolith with UV light. A contact angle of 146° was determined prior to irradiation but the angle decreased to 100° after an irradiation time of 3 min (Figure 7). A repeatability study showed an increase in the contact angle from 100° to 107° after the second conversion cycle of the SP into the MC isomer and from 107° to 112° after the third. After 10 min of UV irradiation, the water was completely absorbed by the material. Note that no change in the contact angle was observed for SP0-MTMS after an irradiation time of 3 min, and the droplet was still present after 10 min of UV light irradiation.

The possibility to convert the SP into the MC isomer in selected areas of the sample is shown in Figure 8 for SP10-MTMS. "Writing" on the surface of cylindrical samples can be done with a UV laser pointer (Figure 8a). Patterns were obtained by placing a photomask on the surface of a flat round shaped 3 mm-high SP10-MTMS sample and irradiation from the top with UV light for 3 min (Figure 8b). The pattern was also present on the bottom side of the sample albeit slightly weaker. Erasing of the patterns was realized by irradiation with a hand lamp emitting light in the visible region. Similar demonstrations of “writing without ink” by using spiropyran embedded in PDMS were reported by Brown et al.

**DISCUSSION**

The results illustrate that SP can be successfully incorporated into a MTMS framework by a two-step co-condensation sol–gel approach. The color changes observed during the preparation of the monoliths can be explained by the different chemical environments. The more polar the environment, the more of the MC isomer is present. The wet gels are thus reddish-orange colored, whereas the equilibrium is shifted toward the SP isomer after drying of the gels due to the removal of the polar solvent and the presence of methyl groups in the host matrix. The prepared SPx-MTMS monoliths are therefore transparent and almost colorless. A slight purple hue, however, was observed for samples containing more than 5 vol % SP-DMF. This can be attributed to the interaction of adjacent zwitterionic MC isomers and stabilization of the responsive molecules in their open form at high concentrations, which inhibits full conversion of purple MC into colorless SP isomers even when an external stimulus is applied.

The reference sample SP0-MTMS was prepared following a protocol of Kanamori et al. Identical results regarding the SSA (597 m² g⁻¹), bulk density (0.24 g cm⁻³), and porosity (83%) were obtained. Comparison of SP0-MTMS with SPx-MTMS monoliths shows that the addition of a solution of SP in DMF (ε = 0.084 mmol mL⁻¹) at concentrations of up to 10 vol % has no significant influence on the structural properties. In all investigated samples, high SSAs, narrow pore size distributions, and narrow hysteresis loops were detected. The homogeneity of the samples can be confirmed by scanning electron (Figure S6) and transmission electron micrographs (Figure 3 and Figure S3), which show a globular network of aggregated, microporous 9.4 ± 1.1 nm-sized particles. Partial precipitation of SP in the precursor solution, however, was observed for samples containing 20 vol % SP-DMF due to π-stacking of the aromatic rings and their low solubility in the polar environment. The similar stress-strain curves of the reference sample SP0-MTMS and the stimulus-responsive sample SP10-MTMS additionally prove the low impact of the SP attachment on the properties of the porous framework. SP10-MTMS was slightly harder compared to SP0-MTMS, which can be attributed to π-stacking of the aromatic rings of the spiropyran isomers. Multiple conversions of the SP into the MC isomer were shown to have no influence on the mechanical properties of the sample and prove the high stability of the porous polysilsesquioxane framework.

The stimulus-responsive behavior of SPx-MTMS monoliths was followed by UV–vis measurements. An absorption peak at a wavelength of 568 nm was observed in the UV–vis spectrum of the sample SP10-MTMS after UV light irradiation and was still weakly present after irradiation with visible light, illustrating that both isomers are always in equilibrium. Conversion of the MC isomer into its protonated, yellow colored MCH⁺ form was obtained by dropwise addition of hydrochloric acid on top of the sample SP10-MTMS and proven by the presence of an intense absorption peak at a wavelength of 422 nm in the UV–vis spectrum. The peak shift from 568 nm (MC) to 422 nm (MCH⁺) is caused by a change of the electronic structure and the absorption behavior of the molecule after protonation. Note that the addition of 10 μL of hydrochloric acid on single spots on the surface is enough to protonate MC isomers throughout the whole sample; no absorption in the range of 568 nm was observed after the sample was kept in the dark for one hour. This can either be caused by capillary forces of the porous structure, which enhances the diffusion of hydrochloric acid throughout the monolithic network, or by intermolecular proton transfer reactions.

Back conversion of both MC and MCH⁺ into the closed-ring SP isomers was shown to require irradiation of the monoliths with visible light. However, even the sample that was protected from light showed partial back conversion, which is driven by the presence of methyl groups stabilizing the SP isomer. A
further shift of the equilibrium toward the SP isomer, however, was not obtained because the cyclization of the spiro center occurs statistically and can only be accelerated by light or heat. The observed shift of the absorption maximum from 568 to 552 nm with increasing time intervals is a consequence of the decreasing polarity of the matrix during the back reaction. This phenomenon is known as “dark evolution” and commonly observed in stimulus-responsive materials. The drop of the intensity of the absorption peak to 35% of the initial intensity after the first three cycles as well as the increasing contact angle during the repeatability studies is a consequence of oxidation reactions on the MC isomer inside the porous network. In more detail, the butadiene bridge conjugated to the carbonyl group in the open MC form is susceptible for oxidative and radical attacks and results in diminishing photochromism and permanent darkening. No crack formation in the monoliths was observed during the kinetics studies, proving that the stimulus-responsive molecule has sufficient degrees of freedom to perform conformational changes.

In addition to color changes, irradiation of SPx-MTMS monoliths with UV light leads to an altered water wettability. SP in its closed-ring form is hydrophobic, whereas the zwitterionic form of the MC isomer is hydrophilic, leading to an increasing polarity of the monolith surface. In addition, the altered surface polarity changes the water absorption ability of the monolith. The porous network of the monolith is now accessible for water, whereas it was repelled from the sample prior to UV light irradiation.

Overall, the transformation of the stimulus-responsive molecule into its isomers occurs with comparable rates and with the same efficiency as in other polymeric materials. The distinctive feature of the porous host materials compared to other polymer matrices can be found in their field of application. Polymeric materials are mainly used as photocatalytic HCl gas sensors or as dry adhesives. The unique properties of the porous MTMS matrix award the SP-containing material some additional features. First, the bulk density of the responsive material is lower compared to other polymers due to the porous framework. Second, the pores give the material a high specific surface area and additionally facilitate diffusion from the exterior into the bulk. Reactions or adsorption processes can thus occur not only at the outer surface but also within the bulk, which enhances the reaction efficiency. Additionally, the sol–gel process allows the preparation of SP-containing polysilsesquioxanes in desired sizes and shapes under mild reaction conditions. The combination of highly porous polysilsesquioxanes with stimulus-responsive molecules thus has high potential to open new and very promising application areas for smart materials, e.g., in the field of porous membranes for controlled phase separation processes.

**CONCLUSION**

The preparation of spiropyran-embedded porous polymethylsilsesquioxanes can be successfully performed by a two-step sol–gel processing route involving co-condensation of MTMS with silylated spiropyran. The stimulus responsiveness of the spiropyran remains intact even after its covalent attachment onto the polysilsesquioxane matrix and can turn from a transparent, closed-ring SP form into a highly colored purple MC or yellow MCH+ form and vice versa. Reaction dynamics highly depend on the polarity of the chemical environment, the concentration of the photo-responsive molecules in the host matrix, and the presence of a light source. The unique properties of the host material, high specific surface areas, high porosities, and high mechanical strength remain largely unchanged after the incorporation of SP. The water wettability of the superhydrophobic material, however, can be altered by transformation of one isomer into the other, making this material highly interesting for a broad range of novel applications, e.g., for phase separation processes.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c14987.

Images, nitrogen sorption data, TEM and SEM images, and compression–decompression tests of the prepared samples (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Andrea Feinle — Chemistry and Physics of Materials, Paris-Lodron University Salzburg, 5020 Salzburg, Austria; Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario L8S 4M1, Canada; orcid.org/0000-0002-6691-7386; Email: andrea.feinle@sbg.ac.at

**Authors**

Daniel Euchler — Chemistry and Physics of Materials, Paris-Lodron University Salzburg, 5020 Salzburg, Austria

Caroline R. Elghartner — Chemistry and Physics of Materials, Paris-Lodron University Salzburg, 5020 Salzburg, Austria

Nicola Hüsing — Chemistry and Physics of Materials, Paris-Lodron University Salzburg, 5020 Salzburg, Austria; orcid.org/0000-0003-2274-9777

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c14987

**Author Contributions**

All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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