One of the interesting possibilities for mesoporous polymer–silica hybrid materials is that pore parameters might be tunable physically by controlling the segmental motions of polymer chains. Thus, all the samples were subjected to thermal treatment at temperatures above the glass transition temperature of the polymethacrylate ($T_g \sim 110\,°C$). Upon thermal treatment, both the surface area and pore volume of the hybrid materials decreased significantly. For example, the S_{BET} and V_{pore} values for sample MSM-a52 decreased from 783 and 0.65 to 690 m^2g^{-1} and 0.57 cm^3g^{-1}, respectively, after heating at $130\,°C$ for 15 h. Such changes could be attributed to the diffusive segmental motions or relaxation of the polymer chains above T_g, leading to partial blockage of pores. This is also supported by the observation that control samples prepared without the polymer component exhibited little change in the pore parameters after the same thermal treatment. Further investigation is in progress to explore this phenomenon. Transparent and monolithic hybrid samples could be prepared with polymer contents up to 15 wt.-%. However, upon removal of DBTA, the materials were found to contain mainly micropores, which might be caused by the relatively high mobility of the polymer chains compared to the rigid silicate framework.

In summary, we have described the synthesis of polymethacrylate–silica hybrid mesoporous materials with pore diameters of 3–6 nm via the acid-catalyzed sol-gel reaction of TEOS with P(MMA-MSMA) in the presence of DBTA as the pore-forming agent. Removal of DBTA by solvent extraction affords hybrid materials with large surface areas (~800 m^2g^{-1}) and pore volumes (~0.7 cm^3g^{-1}) as well as relatively narrow pore size distributions. In the hybrid framework, the polymer chains are covalently bonded to the silicate matrix through the cross-condensation of the alkoxysilyl groups in both TEOS and P(MMA-MSMA). This synthesis protocol should be applicable to a broad range of other organic polymers and inorganic matrices as well as to the surfactant-templating pathway. The combination of mesoporosity with organic polymer functionality and hydrophobicity could give rise to promising new materials and applications for guest–host chemistry and biosensor devices.

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Fast Response Photochromic Mesostructures**

By *Gernot Wirnsberger*, *Brian J. Scott*, *Bradley F. Chmelka*, and *Galen D. Stucky**

Photochromic materials are a well-known class of compounds which change their color upon irradiation with light.[1] This interesting effect can be used in the development of optical waveguides and shutters, light modulators, optical storage media and delay generators as well as other optical solid state devices when these dyes are doped into appropriate matrices.[2–9] For certain applications, like an optical shutter, a fast response time is required. For this purpose, a wide range of chemically different matrices have been investigated for photochromic dyes. The matrix compositions ranged from purely organic ones, e.g., poly(methylmethacrylate) (PMMA),[10–12] to hybrid inorganic–organic composites (ormosils),[13,14] and finally to purely inorganic matrices, such as sol–gel derived silicates[15,16] and aluminosilicates.[17] For inorganic matrices, the thermal back-fading of the colored forms of the dyes towards their colorless forms is on the timescale of minutes to hours which excludes their use in certain applications. Another problem arises from the competition between direct and reverse photochromism that is often observed in inorganic matrices (direct photochromism is observed when colorless sam-

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ples become colored upon irradiation, whereas the opposite is true for reverse photochromism). However, when inorganic matrices are chemically modified to be more hydrophobic, only direct photochromism is observed. Further, the response time for the back-fading process has been shown to be very fast (rate constant of $k = 0.2$ s^{-1}) for a spirooxazine derivative occluded in an organically modified silicate (ormosil), equaling the response time of that dye in ethanol.[14] Also, in purely organic matrices like PMMA, the response time of a spirooxazine derivative can be significantly faster than in purely inorganic oxide based hosts (see Table 1).

Table 1. Photochromism and bleaching constants of spiropyrans and spirooxazines in selected matrices and solvents [10,12,14,16,31].

Molecule	Matrix	Type of photochromism	Decay
spirooxazine	SBA-15 film	direct	$k = 0.15$ s^{-1}
	SiO$_2$	direct-reverse	$t_{0.5} = 2.3 \times 10^5$ s
	MeSiO$_{1.5}$	direct	$k_1 = 1.15 \times 10^{-2}$ s^{-1}
			$k_2 = 1.4 \times 10^{-3}$ s^{-1}
	MeHSiO$_2$–HSiO$_{1.5}$	direct	$k = 0.2$ s^{-1}
	PMMA	direct	$k_1 = 4 \times 10^{-2}$ s^{-1}
			$k_2 = 4 \times 10^{-3}$ s^{-1}
	EtOH	direct	$k = 0.2$ s^{-1}
spiropyran	SBA-15 film	direct	$k = 2.0 \times 10^{-4}$ s^{-1}
	SiO$_2$	direct, changes to reverse	$k_{direct} = 6.7 \times 10^{-5}$ s^{-1}
			$k_{reverse} = 1.7 \times 10^{-5}$ s^{-1}
	EtSiO$_2$	direct	$k = 1.7 \times 10^{-4}$ s^{-1}
	MeHSiO–HSiO$_{1.5}$	direct	$k = 5 \times 10^{-3}$ s^{-1}
	PMMA	direct	$k_1 = 7 \times 10^{-4}$ s^{-1}
			$k_2 = 1 \times 10^{-4}$ s^{-1}
	EtOH	direct	$k = 3.76 \times 10^{-4}$ s^{-1}
	benzene	direct	$k = 0.112$ s^{-1}
	polystyrene	direct	$t_{0.5} = 350$ s

Mesostructured materials, on the other hand, possess both inorganic and organic domains separated on the nanometer scale. This provides principally the possibility for a rational design of the dye-microenvironment together with the advantages of high processability and robustness of these nanohybrid materials. For these reasons, we explored block-copolymer/silica mesostructures as hosts for two often used representative photochromic dyes, namely 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-2(H)-indole], a spiropyran (SP), and 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphth[2,1-b][1,4]oxazine], a spirooxazine (SO) derivative. Their structures are given in Figure 1 together with one of the several reaction products upon illu-

Fig. 1. The structure of the photochromic dyes used and one of their corresponding open forms.

mination for each one of the dyes. Upon illumination with UV light the C–O bonds break, resulting in the colored merocyanine forms.[1] The open structures are best described in the zwitterionic form for the SP dye and the quinoidal form for the SO dye, respectively. Thin mesostructured films were deposited onto glass slides by dip-coating and investigated with a simple pump–probe setup. It is shown that the photochromic dyes are incorporated predominantly within the hydrophobic domain of the mesostructures and exhibit direct photochromism, with very fast response times in the case of SO. The decay time fits are mono-exponential for both dyes, indicating a homogeneous dye environment. Moreover, the occluded dyes exhibit direct photochromism even after months and for SO films show a slightly faster response when completely dried. These findings are important for the application of photochromic sol–gel derived materials in optical devices.

The mesostructured films were typically prepared by refluxing a composition of 2 g of the block-copolymer P123 [poly-(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide), (PEO)$_{20}$(PPO)$_{70}$(PEO)$_{20}$, Aldrich], 20.4 g ethanol (EtOH), 2.2 g H$_2$O, 0.1 g 2M HCl, and 7.0 g tetraethylorthosilicate (TEOS) for one hour. Afterwards the solutions were cooled to room temperature and either the SP or the SO dye (Aldrich) was mixed into the solution and the solution stirred until the dye had been dissolved completely. These solutions with a molar composition range of P123/EtOH/H$_2$O/HCl/TEOS/dye = 0.010:13.2:3.8:3 $\times$ 10^{-4}–6 $\times$ 10^{-4}:1:1.5 $\times$ 10^{-3}–3.5 $\times$ 10^{-3} were used for the deposition of films on cleaned glass slides. The glass slides were withdrawn from the solutions with a speed of about 1 cm s^{-1}. This results in relatively thick (several micrometers) crack-free films.

For spectroscopic characterization, a simple pump–probe setup was used. It consisted of a tungsten lamp output as the probe and the UV lines of an Ar$^+$ ion laser as pump source. The tungsten lamp probe beam was strongly attenuated by neutral density filters, reduced in diameter by an iris and finally weakly focused onto an area with a diameter of ~500 μm^2. After passing the sample, the probe beam was directed towards the spectrometer by a mirror which was placed in the focal point of the collecting lens in front of the spectrometer. This off-focal-plane-setup was necessary in order to eliminate radiation from the strongly luminescent SP compound. The 351/365 nm lines of an Ar$^+$ ion laser were employed as the pump source and passed through a set of neutral density filters and used to illuminate the sample on an area of ~1 mm^2, making an angle with the probe beam of about 15°. The pump beam was adjusted to overlap concentrically with the smaller probe beam. The pump energy was varied for the two dyes; the SP-based compounds are much more susceptible to photodegradation and, hence, lower power levels were used. For the measurement of the transient absorption spectra, spectra of the background, of the probe only, pump only, and pump and probe were recorded.[18] Time-dependent response curves were obtained by following the signal at the wavelength of the maxima in the transient absorption spectra. Spectra of solu-
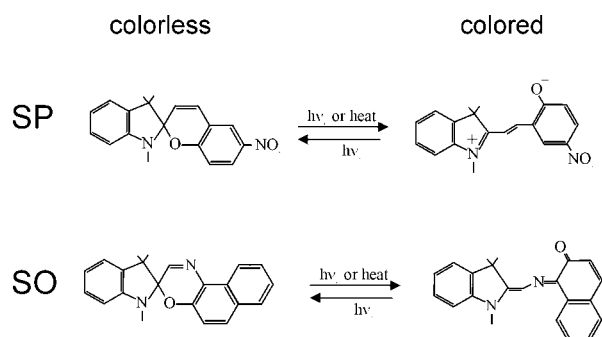
tions and of as-synthesized films were also taken on a Shimadzu UV-1610 spectrophotometer.

The solutions, from which the films were prepared are either deeply red (SP) or slightly green (SO). In EtOH the closed forms are stabilized; upon addition of HCl the solutions become colored indicative of the open forms.[19] However, when films were prepared by dip-coating they became completely colorless within several hours, suggesting a stabilization of the closed forms for both dyes.

It has been previously demonstrated that the dip-coating technique[20] itself results in optically clear films with high mesostructural ordering. This is evidenced by X-ray diffraction (XRD) (Fig. 2). The X-ray patterns show *h*00 reflections only, indicative of an alignment of hexagonally arranged chan-
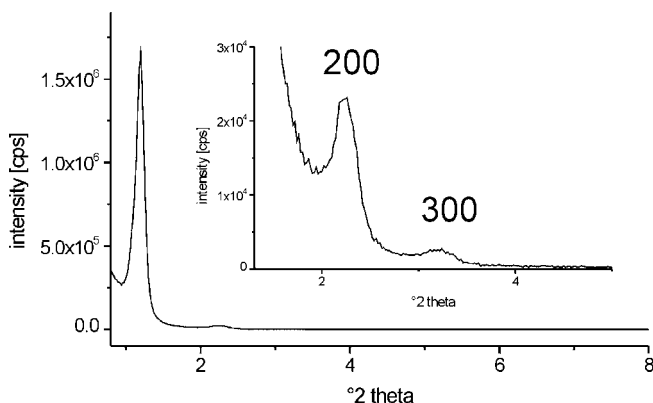
Fig. 2. X-ray pattern of a spiropyran-doped hexagonal (*p6mm*) mesostructured film.

nels parallel to the substrate plane, as commonly found for mesostructured films prepared by P123 block-copolymer templating under weakly acidic conditions (SBA-15 type materials).[21] The *p6mm* symmetry was confirmed by transmission electron microscopy (TEM) along different crystallographic axes. Although the mesostructural long-range order might be interesting for certain applications, in our case the organic/inorganic nanoseparation which defines the mesostructure itself is more important. The biphase nature on the nanometer scale provides chemically different environments for the dyes, or in other words, the chemical surrounding of the occluded species can be tuned depending on its preference for either of the two nanoseparated phases.

The films themselves are completely transparent in the visible range, with transmissions of ~97–100 %, indicative that both dyes are present in their closed form. We also note that the transmission for films doped with either of the dyes does not decrease within the time of several weeks. Typical spectra of the films during UV exposure are depicted in Figure 3. The SO-doped composite films shows an absorption maximum at ~620 nm together with a weaker second maximum at ~584 nm as observed previously in ormosils.[10] In contrast, the SP-doped materials only show one broad absorption in the visible range with a maximum at around 527 nm. The band maximum position for the transient spectrum was found to be similar to that of SP in EtOH[22] which varies with concentration be-
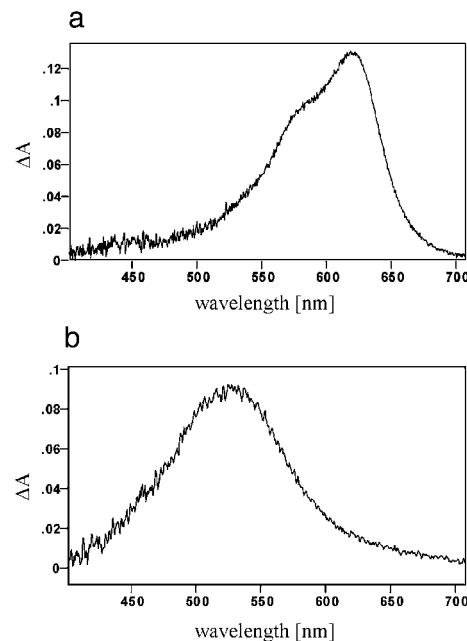
Fig. 3. Absorption spectra of the colored forms of a) SO-doped and b) SP-doped SBA-15 films.

tween 550 nm (4×10^{-5} M) and 532 nm (10^{-2} M). For comparison, in apolar solvents like benzene, the band maximum is at 596 nm with a second, weaker band at 555 nm. Hence, the transient absorption spectrum is reminiscent of a rather polar microenvironment; however, from the observation that the SP dye exhibits direct photochromism in the mesostructured silica but not when occluded in non-mesostructured, dried silica glasses, we conclude that the SP dye is incorporated within the organic nanophase, most probably in the more polar poly(ethylene oxide) (PEO) sequence of the block copolymers.

Visual inspection of the coloration/decoloration kinetics by simply irradiating light with an UV lamp on the thin films shows that the dyes exhibit different decoloration kinetics. The SO-doped mesostructured films undergo a very fast thermal fading becoming colorless, again, to the eye within a few seconds after exposure. A typical set of time-dependent spectral data for several coloration/decoloration cycles is given in Figure 4. From the bleaching curves we extracted rate constants of $k = 0.15$ s^{-1} for samples that were three weeks old.
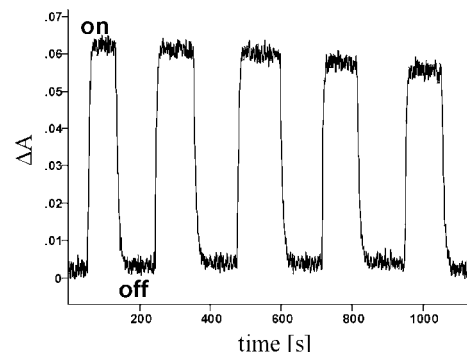
Fig. 4. Time-dependent photocoloration and -bleaching for SO-doped SBA-15 films. A small amount of photodecomposition during the exposure time is evident.

This very fast response compares well to that observed for the same dye in ethanol ($k = 0.2$ s^{-1})[22] and to that in sol–gel matrices prepared by hydrolysis of organosilanes, which exhibit the fastest response ($k = 0.2$ s^{-1}) reported so far for solid-state matrices.[14] In contrast, in purely inorganic oxide sol–gel materials, the response time is orders of magnitude lower (see Table 1 for some representative rate constants, a more comprehensive listing can be found elsewhere[14]).

In the mesostructured materials investigated here, the SO is located within the organic part of the composite based on the conclusions that the response is very fast, which has been previously observed only in organically modified sol–gel materials. Secondly, in pure silicates, upon drying the materials became colored and began to exhibit reverse photochromism. We investigated samples which have been stored at ambient conditions for varying times after their synthesis and did not find any indication for reverse photochromism. Instead, another interesting feature was evident from the fits of the bleaching curves for the SO-doped materials. Fresh samples, which had been stored for about 40 h, showed a slightly slower response ($k = 0.094$ s^{-1}) when compared with 3 weeks old samples ($k = 0.15$ s^{-1}). This is in contrast to sol–gel glasses, where during aging the matrix environment becomes more restricted and the open molecular forms become stabilized by contacts with the pore walls (e.g., by hydrogen bonding).[16,17] In our case, the increased rate of photobleaching might indicate ongoing hydrolysis and condensation within the inorganic silica and at the block-copolymer/silica interface. This reduces the number of sites available for the open forms of the SO to stabilize and hence results in faster bleaching kinetics. We also note that the thermal bleaching, regardless of the film age, could always be fit by single exponential decay with r^2 values >0.993.[23] This is indicative of a homogenous dye environment and agrees well with the suggestion that the photochromic species are located predominantly within the organic part of the biphase composites.

SP-doped materials show a much slower thermal bleaching. Figure 5 depicts a typical cycle obtained upon exposing the film to UV light and subsequent bleaching. The difference in the temporal behavior of SP in comparison to SO lies in the chemical nature of the open forms of these dyes. For SO, the open form is best described as a quinoidal structure (Fig. 1),
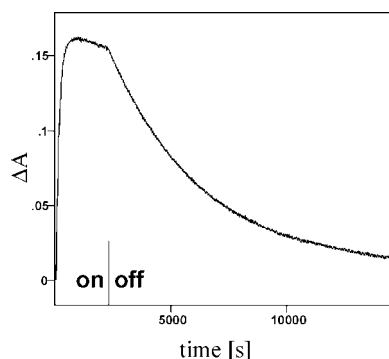
whereas for SP the C–O bond cleavage leads to different zwitterionic isomers or quinoidal structures.[24] Although we suggest that the SP molecule is predominantly located in the organic part of the composites, the open form might be stabilized by interaction at the silica/block-copolymer interface. The thermal fading ($k = 2.0 \times 10^{-4}$ s^{-1}, monoexponential) is similar in to that observed in EtOH and faster than in SiO$_2$ sol–gel glasses (Table 1). We also note that the thermal bleaching is nearly fully reversible for this photochromic dye (Fig. 5), in contrast to the behavior in organically modified silicates.[14] The slower thermal fading of SP in SBA-15 type films compared to apolar solvents may be accounted by several factors, namely the increased polarity of the PEO/PPO (where PPO = poly(propylene oxide)) segments against apolar solvents and the possible stabilization of the open form at the interface. Moreover, in solids the dye experiences an enhanced microviscosity, as demonstrated by the fact the lowering of the thermal fading in an apolar polystyrene matrix (see Table 1).[22]

In summary, we have shown that mesostructured materials are excellent hosts for photochromic dyes. Both dyes investigated, a spiropyran and a spirooxazine derivative, show direct photochromism, becoming colored upon UV illumination and bleaching thermally back to their colorless closed forms. The response times of SO-doped materials are very fast, being in the range of the best values reported so far for solid state composites. The materials show long-term stability with no obvious competition between direct and reverse photochromism with increasing time. As these silica/block-copolymer materials can also be processed easily in any desired shape, including fibers,[25] thin films,[21] monoliths,[26] waveguide structures,[27] and optical coatings,[28] photochromic mesostructures are promising candidates for application in this field, e.g., as optical shutters and light modulators.[29] A further extension might be the use of dyes which do not thermally bleach, but can be switched by two different beams in the UV and visible range of the spectrum.[30]

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Fig. 5. Time-dependent photocoloration and -bleaching for SP-doped SBA-15 films. The decay during exposure is due to photodecomposition.

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Molecular Batteries: Harnessing Fe(CN)6 3– Electroactivity in Hybrid Polyaniline–Hexacyanoferrate Electrodes**

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Recent progress on hybrid organic–inorganic materials has concerned mainly the development of structural materials based on hybrid silicon–carbon networks.[1–3] There is another category of materials that can also benefit from the synergy offered by the hybrid concept. In functional hybrid materials, for instance, the emphasis in not put on the improvement of mechanical properties but on harnessing useful chemical properties of the components. The combination of dissimilar compounds offers an opportunity to find complementary and synergic behavior in these materials.[4]

This approach has guided our recent work on the design of functional hybrid materials based on conducting organic polymers (COPs) and electroactive inorganic species.[4–15] The hybrid materials have the polymeric nature and good conductivity of COPs, and the added electroactivity of the inorganic species.[4–6,10–12] This concept offers a way to harness the electroactivity of molecular species, putting them to work in a solid polymeric matrix, leading to hybrid materials that could be useful as electrodes for plastic batteries. Among the hybrids with molecular anions, those based on polyoxometalates were first studied as models due to the structural and chemical connection of heteropolyanions with metal-oxide clusters.[16,17] Thus, the synthesis, characterization, and electrochemical properties of polypyrrole/$PMo_{12}O_{40}$[5] and polyaniline/$PMo_{12}O_{40}$[10] hybrid materials were first reported. When heteropolyanions such as phosphomolybdate $[PMo_{12}O_{40}]^{3-}$ are used as doping species, they are anchored into polyaniline (PAni) or polypyrrole (PPy) thanks to their large size and charge, which results in a cation-insertion mechanism during reduction of the hybrid.[4,5,8,10] Thus, contrary to conventional p-doped COPs, these materials are lithium-insertion cathodes and can be used in source–sink reversible lithium cells. Nevertheless, these polyoxometalate anions present a very large electrochemical equivalent weight and a limited capacity to accept electrons reversibly. In contrast, hexacyanoferrate anions have a low molecular weight and can exchange reversibly in solution one electron per iron atom, resulting in a very favorable electrochemical equivalent weight.

We have previously reported the synthesis of PPy/HCF hybrid materials[11] but found only moderate specific charge values possibly due to the formation of oxygenated groups (carbonyl, hydroxyl) in the polypyrrole chain.[15]

Following the same strategy of using ferricyanide as an effective electroactive component, but trying to avoid the problems arising from the use of PPy as a COP in the hybrids, we have performed and report here the synthesis and characterization of PAni/HCF hybrids and have studied their electrochemical properties and performance as cathodes in reversible lithium cells. PAni is a conducting polymer whose behavior as a cathode in lithium batteries has been reported with many counterions;[18–22] but to our knowledge, never in combination with electroactive inorganic anions to form hybrids. In the present communication we show the excellent behavior of PAni/HCF hybrids as cathodes in rechargeable lithium batteries, not only with respect to their cyclability but also to their high specific charge and efficiency.

The chemical synthesis of PAni/HCF was carried out at 0 °C (preferred) and at room temperature for comparison. In order to avoid the presence of any other anions in the reaction medium, which could compete with the hexacyanoferrate for the doping of polyaniline, $H_3Fe(CN)_6$ prepared from $K_3Fe(CN)_6$ was used as acid and oxidizing agent.

It is important to note that it is not necessary to carry out any crosslinking after the synthesis of PAni/HCF hybrids prepared under these conditions.[23]

The Fourier transform infrared (FTIR) spectrum of a representative PAni/HCF polymer prepared chemically is shown in Figure 1. The presence of a band at 2050 cm^{-1} assigned to the –CN stretching confirms that HCF has been incorporated into the polymer. The low intensity of the HCF band is due to the high background corresponding to the tail of a charge-transfer band from the polymer. Samples prepared at different temperatures and times present essentially the same IR spectrum, the main difference between them being the yield obtained,

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