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1 Introduction

Photoresponsive materials have attracted increasing attention owing to their potential applications in smart devices.¹⁻⁷ Azobenzene is a typical photoresponsive molecule that undergoes photochemical conversion between trans and cis isomers, accompanied by large changes in the molecular shape and size.8 Azobenzene-containing photoresponsive organic polymers such as liquid crystal elastomers (LCEs),9 liquid crystal gels (LCGs)10 and polymer particles11 showing reversible size, shape or colour changes or bending-unbending motions under irradiation have been reported. Moreover, photoresponsive materials capable of various dynamic motions, such as directed motion,12 oscillation,13 rolling14 and inchworm movement,15 have been prepared. The requirements to achieve such unique properties are as follows: (1) azobenzene moieties should be arranged in order or selectively excited with polarized light to convert the molecular-level shape change or motions into the macroscopic scale and (2) free volume and mobility of azobenzene moieties

Synthesis of ordered photoresponsive azobenzene– siloxane hybrids by self-assembly[†]

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In this study, photoresponsive azobenzene-siloxane hybrids with lamellar structures were prepared by selfassembly using two types of alkoxysilane precursors, 4-[3-(triethoxysilyl)propoxy]azobenzene (P1) and 4-[3-(diethoxymethylsilyl)propoxy]azobenzene (P2). The films H1 and H2 were prepared by spin-coating hydrolyzed solutions of P1 and P2, respectively, on a glass substrate followed by heating to induce polycondensation. X-ray diffraction patterns revealed that H1 and H2 have lamellar structures with different d-spacings (3.20 nm and 2.37 nm, respectively), suggesting that the arrangements of the azobenzene moieties are different. These samples show slight but reversible changes in the d-spacings under photo-irradiation. Under UV irradiation, H1 shows a slight decrease in *d*-spacing, while H2 shows a slight increase. Such changes were caused by trans-cis isomerization of a part of the azobenzene moieties in the films, as confirmed by UV-vis absorption spectroscopy. These processes were reversible, with the d-spacings recovering their original values under visible light irradiation. Furthermore, P1 and P2 were co-hydrolyzed and polycondensed with tetraethoxysilane to give lamellar films (H1' and H2') showing a higher degree of trans-cis photoisomerization of the azobenzene moieties. Both H1' and H2' show increase in the *d*-spacings after soaking in various organic solvents. Possible structural models have been proposed to explain these photoresponsive properties of the azobenzene-siloxane nanohybrids, which will find potential applications as smart sensors and adsorbents in future.

> should be guaranteed to realize efficient photoisomerization. The aforementioned polymer-based materials have satisfied these requirements; for example, azobenzene moieties are unidirectionally aligned in the film by a rubbing procedure, and the flexibility of the polymer chains gives them adequate free volume and mobility.

> Silica-based inorganic-organic hybrid materials have been extensively studied because of their advantages of high thermal and chemical stabilities, good mechanical properties and high transparency.¹⁶ Azobenzene-silica hybrids could be a new class of photoresponsive smart materials. Ogawa et al.17 and Inoue et al.18 have reported the intercalation of azobenzene derivatives between layered inorganic crystals and demonstrated their interesting photoresponsive behaviours, such as photo-induced changes in the basal spacings and adsorption properties. On the other hand, self-assembly techniques in combination with sol-gel chemistry provide more diverse control over the structure, composition and morphology of silica-based hybrid materials.19-22 Azobenzene moieties are grafted to the inner wall of mesoporous silica either by co-condensation of azobenzenemodified alkoxysilane and tetraethoxysilane (TEOS) in the presence of a surfactant^{23,24} or by post-modification of mesoporous silica25 to achieve dynamic pore size changes and controlled release of small molecules. Periodic mesoporous organosilicas (PMOs) in which azobenzene moieties are embedded in the wall have also been prepared.26,27

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Furthermore, ordered azobenzene–silica hybrid materials can be prepared by surfactant-free self-assembly processes. Liu *et al.*²⁸ reported the self-assembly of bis-trialkoxysilylated azobenzene into a lamellar structure by intermolecular hydrogen bonding. Unfortunately, this lamellar hybrid shows no photoresponsive properties, probably owing to the low mobility and lack of free volume between azobenzene moieties.

In this study, novel photoresponsive azobenzene–siloxane hybrid materials with lamellar structures have been prepared using triethoxysilyl- and diethoxysilyl-functionalized azobenzene precursors (denoted as **P1** and **P2**, respectively) by a surfactant-free self-assembly process (Scheme 1). Lamellar hybrid films (**H1** and **H2**) with different arrangements of azobenzene moieties were formed *via* self-assembly of hydrolyzed precursors, showing different photoresponsive properties, *i.e.* reversible but opposite changes in the *d*-spacings under UV/vis irradiation. Furthermore, co-condensation of these precursors with TEOS leads to lamellar hybrids (**H1**' and **H2**') exhibiting more efficient *trans-cis* isomerization of azobenzene moieties. The results of detailed structural characterization as well as the photoresponsive properties of these new types of ordered azobenzene–siloxane hybrid materials have been presented in this paper.

2 Experimental

Materials

The chemicals 4-phenylazophenol (98.0%), allyl bromide (>98.0%) and *N*,*N*-dimethylformamide (DMF, dehydrated, >99.5%) were purchased from Wako Pure Chemical Industries. Sodium hydride (NaH) (60% dispersion in paraffin liquid), triethoxysilane (>97.0%) and diethoxymethylsilane (>95.0%) were purchased from Tokyo Chemical Industry. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (Pt \sim 2%) was purchased from Sigma-Aldrich. All chemicals were used without further purification.

Synthesis of 4-allyloxy-azobenzene

In a 100 ml Schlenk flask, 4-phenylazophenol (1.98 g, 0.010 mol) was dissolved in DMF (25 ml). Activated NaH (1.80 g, 0.045 mol) dispersed in DMF (30 ml) was added to the flask. After stirring at room temperature for 2 h, allyl bromide (3.63 g, 0.030 mol) was added, and the mixture was stirred at 60 °C for one day under a nitrogen atmosphere. The product was extracted with ethyl acetate and washed with cold water. Evaporation of ethyl acetate gave a dark-red, crude solid product. Yellow crystals (1.65 g;



Scheme 1 Structures of diethoxysilyl- and triethoxysilyl-azobenzene precursors (**P1** and **P2**) and preparation of four types of lamellar, azobenzene–siloxane hybrid films by self-assembly with and without TEOS.

yield of 69%) were obtained after recrystallization from EtOH. ¹H NMR (δ , 270 MHz, CDCl₃): 4.62 (d, 2H, OCH₂CH=CH₂), 5.30–5.48 (d, 2H, OCH₂CH=CH₂), 6.01–6.15 (m, 1H, OCH₂CH= CH₂), 7.01–7.05 (d, 2H, ArH), 7.40–7.53 (m, 3H, ArH), 7.86–7.94 (m, 4H, ArH). ¹³C NMR (δ , 67.8 MHz, CDCl₃): 69.02, 114.94, 118.05, 122.54, 124.70, 129.01, 130.35, 132.73, 147.07, 152.76, 161.03.

Synthesis of 4-[3-(triethoxysilyl)propoxy]azobenzene (P1)

Hydrosilylation of 4-allyloxy-azobenzene (0.704 g, 0.003 mol) with an excess amount of triethoxysilane (2.324 g, 0.015 mol) was performed in toluene (15 ml) in the presence of Pt as a catalyst (0.03 g, 3 imes 10⁻⁵ mol). The mixture was stirred at 70 °C for 24 h under a nitrogen atmosphere, and the solvent and unreacted triethoxysilane were removed in vacuo. P1 was obtained as a red liquid (1.09 g, 90% yield) after purification using gel permeation chromatography (GPC) with chloroform as the eluent. ¹H NMR (δ , 270 MHz, CDCl₃): 0.76–0.83 (t, 2H, OCH₂CH₂CH₂Si), 1.21-1.27 (t, 9H, SiOCH₂CH₃), 1.89-2.00 (m, 2H, OCH₂CH₂CH₂Si), 3.81-3.90 (m, 6H, SiOCH₂CH₃), 4.00-4.06 (t, 2H, OCH₂CH₂CH₂Si), 6.98-7.01 (t, 2H, ArH), 7.25-7.53 (m, 3H, ArH), 7.86–7.92 (t, 4H, ArH). ¹³C NMR (δ, 67.8 MHz, CDCl₃): 6.51, 18.32, 22.76, 58.47, 70.18, 114.72, 122.54, 124.76, 129.02, 130.29, 146.88, 152.82, 161.67. ²⁹Si NMR (δ, 53.45 MHz, CDCl₃): -45.6. ESI-MS: m/z: 403.2047 [M + H]⁺.

Synthesis of 4-[3-(diethoxymethylsilyl)propoxy]azobenzene (P2)

The chemical 4-allyloxy-azobenzene (0.483 g, 0.002 mol) dissolved in toluene (15 ml) was mixed with diethoxymethylsilane (1.34 g, 0.010 mol) and 0.02 g (2 × 10⁻⁵ mol) of Pt catalyst. The mixture was stirred at 70 °C for one day. A red liquid (0.69 g; yield of 93%) was obtained after solvent evaporation followed by purification using GPC. ¹H NMR (δ , 270 MHz, CDCl₃): 0.14–0.18 (s, 3H, SiCH₃), 0.74–0.80 (t, 2H, OCH₂CH₂CH₂Si), 1.20–1.25 (t, 6H, SiOCH₂CH₃), 1.85–1.64 (m, 2H, OCH₂CH₂CH₂Si), 3.74–3.83 (m, 4H, SiOCH₂CH₃), 3.99–4.04 (t, 2H, OCH₂CH₂CH₂Si), 6.98–7.01 (t, 2H, ArH), 7.25–7.52 (m, 3H, ArH), 7.86–7.94 (t, 4H, ArH). ¹³C NMR (δ , 67.8 MHz, CDCl₃): –4.87, 9.97, 18.42, 22.81, 58.19, 70.40, 114.71, 122.54, 124.75, 129.02, 130.28, 146.88, 152.80, 161.64. ²⁹Si NMR (δ , 53.45 MHz, CDCl₃): –5.2. ESI-MS: *m/z*: 373.1942 [M + H]⁺.

Preparation of azobenzene-siloxane hybrid films

An aqueous solution of HCl was added to THF solutions of **P1** and **P2**, and the mixtures (molar compositions of **P1** : THF : $H_2O : HCl = 1:50:15:0.03$ and **P2** : THF : $H_2O : HCl = 1:50:10:0.004$) were stirred at room temperature for 40 and 60 min, respectively. A portion of the mixtures was spin-coated on glass substrates to obtain thin films. Turbid, yellowish films (**H1** and **H2**) were obtained from **P1** and **P2** after heating at 120 and 60 °C, respectively, to induce polycondensation. Cast films were also prepared from **P1** and **P2** on glass substrates under similar conditions. They were pulverized and heated at 120 and 80 °C for solid-state NMR and MS characterizations.

H1' and H2' were prepared by co-hydrolysis and polycondensation of P1 and P2, respectively, with TEOS. TEOS was added to the previously stirred (~5 min) mixtures of P1 or P2, THF, HCl and H₂O. Further stirring was conducted for 1.5 h (for P1) and 3 h (for P2) before spin-coating on glass substrates. After heating at 120 °C, transparent, yellow films were obtained. Molar ratios of the mixtures for preparing H1' and H2' were P1 : TEOS : THF : H₂O : HCl = 1 : 4 : 50 : 19 : 0.05 and P2 : TEOS : THF : H₂O : HCl = 1 : 4 : 50 : 19 : 0.02, respectively.

Preparation of powder samples from P1 and P2

An aqueous solution of HCl was added to the EtOH solutions of **P1** and **P2**. The molar ratios of the mixtures were **P1**: EtOH : H_2O : HCl = 1 : 75 : 38 : 0.02 and **P2** : EtOH : H_2O : HCl = 1 : 100 : 10 : 0.02. Under stirring at room temperature for several hours, yellow precipitates were formed. The precipitates were collected by filtration and heated at 120 °C for 4 h to induce polycondensation.

Characterization

Liquid-state ¹H-, ¹³C- and ²⁹Si-NMR spectra were recorded on a JEOL JNM-270 spectrometer at 270, 67.8 and 53.45 MHz, respectively, using CDCl₃ as the solvent and tetramethylsilane as the internal reference. Solid-state ¹³C and ²⁹Si CP/MAS NMR spectra were recorded using a JEOL CMX-300 spectrometer at resonance frequencies of 75.57 and 59.7 MHz, respectively. Xray diffraction (XRD) patterns were obtained using a RIGAKU UltimaIV diffractometer with Cu Ka radiation. Fourier transform infrared (FTIR) spectra were recorded using a JASCO FT/ IR-6100 spectrometer by the KBr pellet technique. UV/vis absorption spectra were recorded using a JASCO V-670 instrument. Morphologies of the samples were observed on a fieldemission scanning electron microscope (FE-SEM, Hitachi S-900) with an accelerating voltage of 6 kV. Before the observation, the samples were sputter-coated with Pt. Transmission electron microscopy (TEM) observations were conducted on a JEOL JEM-2000EXII at an accelerating voltage of 200 kV. Sample films were pulverized from the substrates, dispersed in ethanol (for H1) or water (for H2) and dropped on microgrids (Cu mesh). A SUPERCURE-204S UV light source (San-ei electric) with the intensity in the range of 67-76 mW cm⁻² was used for UV and visible light irradiation of the samples. UV cut (HOYA L-420 nm) and UV pass (HOYA U-340 nm) filters were used.

3 Results and discussion

Characterizations of H1 and H2

XRD patterns of the thin films of **H1** and **H2** (Fig. 1) show lamellar-structured features with different *d*-spacings. **H1** exhibits a sharp peak corresponding to the *d*-spacing of 3.20 nm with higher order reflections, indicating highly uniform mesoscale periodicity. On the other hand, **H2** shows a different profile with a much smaller *d*-spacing of 2.37 nm. The macroscopic morphologies of these films are also different. FE-SEM images of the top surfaces of **H1** and **H2** are shown in Fig. 2. **H1** shows a wrinkled surface morphology, while **H2** has a rough Journal of Materials Chemistry C



Fig. 1 XRD patterns of azobenzene–siloxane hybrid films (a) H1 and (b) H2 prepared by hydrolysis and polycondensation of P1 and P2, respectively.



Fig. 2 FE-SEM images of the top surfaces of (a) H1 and (b) H2

surface consisting of stacked thin plates. The TEM image of **H1** (Fig. 3) clearly shows the lamellar structure with a periodicity of *ca.* 3.2 nm, which is consistent with the XRD result. Unfortunately, TEM observation of **H2** was unsuccessful because it was susceptible to electron beam damage.

H1 and H2 prepared as cast films show similar XRD patterns (Fig. S1 in the ESI[†]). Solid-state ¹³C and ²⁹Si CP/MAS NMR spectra of these samples after pulverization are shown in Fig. 4. The ¹³C CP/MAS NMR spectra show peaks assigned to azobenzene and propylene linkers. No peaks of ethoxy groups are observed, confirming complete hydrolysis of both precursors. The ²⁹Si CP/MAS NMR spectrum of H1 shows the peaks at -48, -56 and -66 ppm, corresponding to T¹ (CS*i*(OSi)(OH)₂), T² (CS*i*(OSi)₂(OH)) and T³ (CS*i*(OSi)₃), respectively, suggesting that condensation has proceeded. On the other hand, the ²⁹Si CP/MAS NMR spectrum of H2 shows a single D¹ peak at -13 ppm.



Fig. 3 TEM image of H1.



Fig. 4 Solid-state ¹³C CP/MAS NMR (left) and ²⁹Si CP/MAS NMR (right) spectra of (a) H1 and (b) H2.

This sample is soluble in organic solvents such as THF, and electrospray ionization mass spectrometry (ESI-MS) revealed the formation of dimers (main peaks: 615.2459: $[M + H]^+$, 637.2278: $[M + Na]^+$). Thus, **H2** is a type of molecular assembly, probably stabilized by intermolecular hydrogen bonding between silanol groups.

It is inferred that lamellar structures are formed by evaporation-induced self-assembly of hydrolyzed P1 and P2 monomers during spin-coating. After hydrolysis, ethoxyl groups of the precursors are converted to silanol groups (Si-OH). The hydrophobic interactions between the amphiphilic hydrolyzed monomers could be a driving force for self-assembly. Also, $\pi - \pi$ interactions between benzene rings may be effective for the formation of the lamellar structures. Subsequent heat treatment promoted polycondensation of the silanol groups while maintaining the lamellar structure. The *d*-spacings slightly decreased from 3.39 to 3.20 nm (H1) and from 2.59 to 2.37 nm (H2) upon heating. Heat-induced polycondensation was confirmed by FTIR spectroscopy (Fig. S2 in the ESI[†]). Before heating, peaks assigned to Si-OH vibrations at ca. 900 cm⁻¹ and the stretching vibration of hydrogen bonded SiO-H at 3280 cm⁻¹ are observed. After heating, the intensity of these bands decreased considerably, and the intensity of the band corresponding to Si-O-Si vibration at ca. 1020 cm⁻¹ increased.

Similar lamellar hybrids were also obtained as powders by hydrolysis in an EtOH solution. Layered, plate-like morphologies are clearly observed by FE-SEM (Fig. S3 in the ESI†). The XRD patterns of these powder samples show peaks characteristic of lamellar structures (Fig. S4 in the ESI†), similar to those of the film samples **H1** and **H2**. Their *d*-spacings are slightly different from those of the film samples, which may be due to the different reaction conditions. The additional broad peaks at $19-24^{\circ}$ (d = 0.37-0.47 nm) might be arising from the stacking of the azobenzene moieties by π - π interactions. These peaks are



Fig. 5 UV-vis absorption spectra of **H1** (left) and **H2** (right): (a, red) before irradiation, (b, blue) after UV irradiation for 5 min and (c, green) after subsequent visible light irradiation for 5 min.

barely visible for the films, possibly because their lamellar structures are oriented parallel to the substrate.

Photoresponsive properties of H1 and H2

Azobenzene molecules can undergo reversible *trans–cis* isomerization under UV/vis light irradiation and show a change in the molecular length from 0.90 to 0.55 nm. This process is facile in solution because of the high mobility of azobenzene. However, in the solid state, the mobility of azobenzene decreases considerably, especially when both phenyl groups are covalently bonded to polymer networks,²⁹ which might induce severe interference in photoisomerization.

In the systems presented here, even after the formation of siloxane networks, one end of the azobenzene moieties is still free to move. The UV-vis absorption spectra of H1 and H2 after UV/vis irradiation are shown in Fig. 5. Before irradiation (Fig. 5a), the thermally more stable trans isomer of azobenzene is plentiful in the films, showing a strong absorption at ca. 340 nm owing to π - π * transitions.⁸ After 5 min of UV irradiation (Fig. 5b), the intensity of the 340 nm peak decreases, while that of a small peak at ca. 440 nm attributed to the forbidden n- π^* transition of the metastable *cis* isomer increases, indicating partial trans to cis photoisomerization. No further change was observed when the irradiation time was prolonged. After a subsequent 5 min of visible light irradiation (Fig. 5c), the reverse cis to trans process occurred, which is confirmed by the recovery of the 340 nm peak and the decrease in the intensity of the 440 nm peak. Repeated UV/vis irradiation cycles induce the same changes in the UV-vis spectra.

The photoresponsive properties of **H1** and **H2** were further investigated by studying their structural changes under UV/vis irradiation. Fig. 6 (left) shows the XRD patterns of **H1** (a) before



Fig. 6 Variations in the XRD patterns (left) and *d*-spacings (right) of **H1** upon photo-irradiation: (a) before irradiation, (b) after the first cycle and (c) after the second cycle of UV (solid) and visible (dash) light irradiation.



Fig. 7 Variations of XRD patterns (left) and *d*-spacing (right) of **H2** upon photoirradiation: (a) before irradiation, (b) after the first cycle and (c) after the second cycle of UV (solid line) and visible (dashed line) light irradiation.

irradiation, (b) after the first cycle and (c) the second cycle of UV (solid line) and visible light (dashed line) irradiation. Reversible d-spacing changes are observed for each cycle. After UV irradiation, the intensity of the peak decreased, accompanying a slight decrease in the *d*-spacing. When visible light was subsequently applied, the position of the peak was almost recovered. This process could be repeated for several cycles. The variation in the *d*-spacing of H1 in these processes is shown in Fig. 6 (right), showing a *ca.* 0.05 nm decrease under UV irradiation. Interestingly, the phenomena observed for H2 were contrary. Reversible changes in the *d*-spacing of H2 under two cycles of UV/vis irradiation are shown in Fig. 7. After UV irradiation, the (001) and (003) peaks shifted to lower angles and partially (first cycle) and fully (after second cycle) recovered after visible light irradiation. There is an increase of ca. 0.03 nm in the d-spacing under UV irradiation.

Although the fluctuation ranges are very small, to the best of our knowledge, this is the first report on the reversible change in the *d*-spacings of self-assembled organosiloxane materials. By utilizing precursors with different numbers of alkoxy groups, different tendencies of *d*-spacing changes (decreasing or increasing) are observed. Such photoresponsive behaviour is thought to be caused by reversible partial *trans-cis* photoisomerization of azobenzene moieties, as evidenced by the UVvis spectra (Fig. 5). This result is in contrast to a previous report in which *trans* to *cis* isomerization is severely inhibited owing to extensive hydrogen bonding interactions.

Structural models of H1 and H2

To explain the differences in the structures and photoresponsive properties of H1 and H2, structural models are proposed (Fig. 8). Lamellar films consist of inorganic siloxane layers and organic azobenzene layers. The azobenzene groups should be in bilayer arrangements because the *d*-spacings are larger than the molecular lengths of hydrolyzed P1 and P2. The different *d*-spacings for H1 (3.20 nm) and H2 (2.37 nm) can be explained by the different tilt angles of the azobenzene moieties relative to the siloxane layers. The angles are calculated to be about 90 and 40° for H1 and H2, respectively. Such a difference is presumably due to the steric influence of the methyl group attached to the Si atoms and/or due to the difference in the number of Si–OH groups in the hydrolyzed P1 and P2.

The photo-induced changes in the *d*-spacings are much smaller than those expected from *trans-cis* isomerization of

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Fig. 8 Possible structural models of (a) H1 and (b) H2 formed by self-assembly and polycondensation of P1 and P2, respectively.

single azobenzene molecules (\sim 0.45 nm). It was speculated that photoisomerization of a part of azobenzene moieties triggers a slight change in the overall tilt angles in the lamellar hybrids. For H1, *trans* to *cis* isomerization of azobenzene induced a decrease in the tilt angle relative to the siloxane layers. On the other hand, because of the smaller tilt angle of azobenzene in H2 before irradiation, the formation of the *cis* isomers may increase the tilt angle under UV irradiation.

The occurrence of *d*-spacing changes for these hybrid films suggests the flexible properties of the networks, which not only enables the photoisomerization of azobenzene moieties but also changes the lamellar periodicities. This is inherently different from that of azobenzene-grafted mesoporous silica and similar to the organic polymer-based azobenzene-containing films or elastomers.

Structure and properties of H1' and H2'

Co-condensation of TEOS with **P1** and **P2** gave films (**H1**' and **H2**') with high transparency. The FE-SEM images of these films show uniform surface morphologies (Fig. S5 in the ESI[†]); these are quite different from the rough morphologies of the films prepared without TEOS (*cf.* Fig. 2). Their XRD patterns (Fig. 9a) show sharp peaks with different *d*-spacings (2.79 and 3.80 nm for **H1**' and **H2**', respectively). The larger *d*-spacing of **H2**' compared to **H2** (2.37 nm) can be reasonably explained by the increased thickness of the siloxane layers by TEOS incorporation. In contrast, the smaller *d*-spacing of **H1**' compared to **H1** (3.20 nm) strongly suggests that the arrangement of azobenzene was changed from a bilayer to an interdigitated monolayer, possibly owing to the increase of the lateral distance between hydrolyzed **H1** molecules by co-condensation with TEOS. UV-vis



Fig. 9 XRD patterns of H1' (left) and H2' (right): (a) before and (b) after swelling with dioxane.



Fig. 10 UV-vis absorption spectra of **H1**' and **H2**' (a, red) before irradiation, (b, blue) after 2 min of UV light irradiation and (c, green) after a subsequent 2 min of visible light irradiation.

absorption spectra of these films (Fig. 10) show higher degrees of *trans–cis* isomerization of azobenzene moieties under UV/vis irradiation.

Another influence of adding TEOS is that the materials swell when exposed to organic solvents. XRD patterns of H1' and H2' were measured after soaking in dioxane for 1 h (Fig. 9b). Both samples have maintained the lamellar structures but show large increases (0.54 and 0.45 nm) in d-spacings. Efficient trans-cis isomerizations were still observed for these swollen films (Fig. S6 in the ESI[†]). The films shrank after drying, as confirmed by the recovery of the *d*-spacings to the original values (data not shown). A similar increase in the *d*-spacings was observed when soaked in DMF; however, only a minor *d*-spacing increase (0.17 nm for H1') is observed in toluene. It is likely that hydrogen bonding between solvent molecules and silanol groups on the siloxane layers plays a crucial role in swelling. It should be noted that H1 shows only a small d-spacing increase (0.11 nm) in dioxane, and H2 is dissolved in dioxane. By cocondensation with TEOS, the change of the arrangement of interlayer organic moieties may facilitate the intercalation of solvent molecules.

XRD patterns after UV/vis irradiation were recorded to examine the photoresponsive properties of **H1**' and **H2**' before and after swelling. Although these films show higher degrees of photoisomerization compared to **H1** and **H2**, no significant shift of the XRD peaks was observed upon UV/vis irradiation (data not shown). It is likely that the photo-induced change of the interlayer distance is affected by the rigidity of siloxane layers or the density as well as the arrangement of azobenzene moieties in the organic layers. Further investigation is in progress to understand more in detail.

4 Conclusions

Alkoxysilyl-functionalized azobenzenes were used to produce photoresponsive organosiloxanes having a lamellar structure using a self-assembly process. The arrangement of the azobenzene moieties between the siloxane layers can be tailored by varying the number of alkoxy groups and by co-condensation with tetraalkoxysilane, leading to different photoresponsive behaviours, *i.e.* different degrees of *trans-cis* photoisomerization as well as change in lamellar periodicity under UV/vis irradiation. Furthermore, the swelling behaviours of lamellar structures in organic solvents were demonstrated. The present study offers a facile approach to fabricate a new class of azobenzene-based photoresponsive materials with highly organized structures. Further design of such self-assembled hybrid materials is important in order to realize smart materials showing drastic changes in the structure and shape in response to irradiation.

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