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Self-Directed Assembly of Photoactive Hybrid Silicates Derived from an Azobenzene-Bridged Silsesquioxane

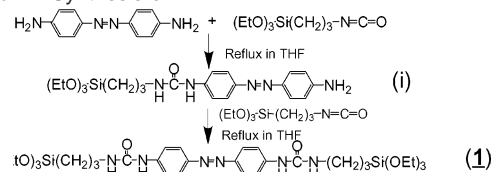
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Received August 2, 2002

Hybrid silicate materials derived from organo-bridged silsesquioxane precursors, $\text{RO}_3\text{-Si-R'-Si-OR}_3$, where R and R' are organic ligands, represent a remarkably diverse class of nanocomposites capable of forming both Si-O-Si and Si-C-Si bonds with molecular scale homogeneity. Recently, in an effort to better control structure and function, surfactant-directed self-assembly or self-directed assembly (SDA) has been used to synthesize hierarchical organo-bridged polysilsesquioxanes that exhibit order over multiple length scales.¹⁻⁷ For surfactant-directed self-assembly,¹⁻⁴ hydrophilic silicic acid moieties formed by alkoxide hydrolysis interfacially co-organize with hydrophilic surfactant headgroups to form periodically ordered hybrid mesophases. SDA exploits hydrogen-bonding, π - π , and/or hydrophobic interactions between the R' bridges to form generally mesoscopically ordered lamellar architectures that can exhibit well-defined ribbonlike or twisted helical morphologies on the macroscale.⁵⁻⁷ Significantly, using surfactant-directed self-assembly combined with SDA, Inagaki et al.² recently synthesized hybrid silicates with mesoscopically ordered pores and molecularly ordered walls.

Despite the recent success in self-assembly of hybrid silicates, the R' ligands, including methane, ethane, benzene, toluene, xylene, dimethoxybenzene, and thiophene,^{2-4,7} have had limited intrinsic functionalities, serving predominantly passive roles such as influencing the wetting characteristics or reducing the framework dielectric constant. Here we report the synthesis and self-directed assembly of a photoactive azobenzene-bridged silsesquioxane, 4,4'-bis(3-triethoxysilylpropylureido)azobenzene **1**. Hydrogen-bonding interactions between the three active centers of the bis-ureide groups ($-\text{NH}-\text{CO}-\text{NH}-$) combined with π - π interactions between the azobenzene groups serve to self-assemble **1** into a highly ordered lamellar mesostructure in which the *d*-spacing is optically controlled through photoisomerization of the azobenzene moiety before or after assembly.

Compound **1** was synthesized by addition of 0.98 g (4.6 mmol) of 4,4'-azodianiline to 2.35 g (9.5 mmol) of γ -isocyanatopropyltriethoxysilane in 12 mL of tetrahydrofuran (THF, water-free), see Scheme 1. After being refluxed for 24 h under room light, the supramolecular product (**1a**), a needlelike yellow precipitate, was filtered, washed with hexane, and vacuum-dried. The overall yield was ca. 90%, and the purity was quite high based on NMR and IR spectroscopic analyses (see Supporting Information). Thin films (sample **1b**) were prepared by dissolution of **1a** in THF (ca 5.7 mg/mL) followed by casting on a silicon substrate. Slower evaporation of this same solution produced a shiny yellow faceted solid (sample **1c**). Samples **1a-c** showed sheet, twisted rope, and ribbonlike structures on the macroscale similar to those observed

Scheme 1. Synthesis of **1**^a

^a Intermediate product (i) is highly soluble in THF, and **1** is weakly soluble in THF.

for bis-urea-bridged polysilsesquioxanes (see Supporting Information).⁵ Exposure of the solid samples to water vapor or acid or base catalysts promoted hydrolysis and condensation of the silicon alkoxide moieties to form hybrid siloxane networks.

We investigated the reversible photo and thermal isomerization behavior of a dilute molecular dispersion of **1** (0.05 mg of **1a**/mL of ethanol prepared at room temperature under ambient lighting conditions), using UV/visible spectroscopy (Figure 1). From the absorption band at 378 nm (the π - π^* transition of the trans isomer), we determined the solution to consist of ca. 78% trans isomer ($\epsilon_{\text{max}} = 2.38 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).⁸ UV irradiation with a Hg arc lamp ($\lambda_{\text{max}} = 350 \text{ nm}$) decreased the intensity of the 378 nm band and slightly increased the intensity of the 470 nm band attributed to the cis isomer; a photostationary state (spectrum 1b, ca. 52% trans) was reached within ca. 10 min. Exposure to room light or heat caused the reverse isomerization (cis \rightarrow trans). For example, from the photostationary state (spectrum 1b), room light exposure increased the intensity of the 378 nm absorption band (spectra 1c-e) progressively, reaching a second photostationary state after 20 min. Alternatively, heat treatment (60 °C, for 5 min in the dark) caused the intensity of the 378 nm absorption band to exceed that of the as-prepared solution (spectrum 1f, ca. 87% trans). These results demonstrate the facile photoisomerization characteristics of the molecular form of **1**.

Low angle X-ray diffraction (XRD) was used to characterize the mesoscale structures of the supramolecular solid samples and their sensitivity to light. Figure 2 shows the XRD patterns of samples **1a-c** along with that of a sample (**1d**) prepared exactly as **1c**, but exposed to UV light during the evaporation step. The XRD patterns of **1a-c** are indicative of lamellar structures with *d*-spacings of 1.9 (**1a**) or 2.2 nm (**1b,c**), which we attribute to those of the cis and trans isomers (Figure 1 inset), respectively. Molecular models of the cis and trans isomers (using CS Chem3D Pro) estimate the molecular lengths to be ca. 2.8 and 3.1 nm, respectively, indicating that the bis-urea azobenzene units pack at angles of 48° (cis) or 45° (trans) relative to the plane of the lamellae. The XRD pattern of **1d** has *d*-spacings of 1.9 and 2.3 nm attributed to the presence of comparable populations of both isomers arranged into ordered subdomains. The absence of two distinct sets of (00*l*) peaks

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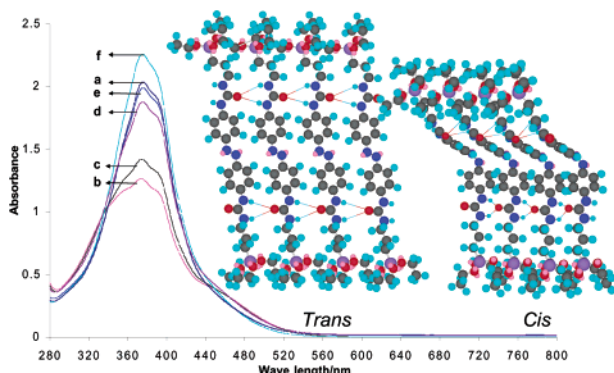


Figure 1. UV-vis absorption spectra of (a) **1a** in EtOH (0.05 g/L); (b) after UV irradiation for 10 min; (c–e) after room light exposure of (b) for 3, 10, and 20 min; (f) after heating (b) to 60 °C for 5 min. Inset: Supramolecular structures formed by SDA in trans or cis forms. Atomic legend: gray (C), dark blue (N), red (O), purple (Si), green (H).

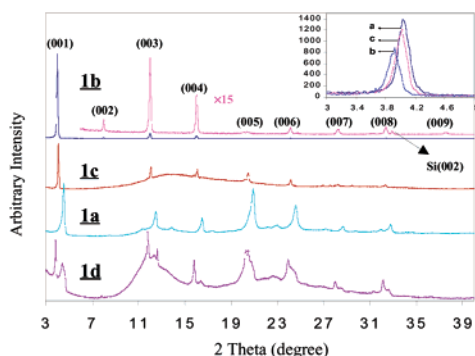


Figure 2. X-ray diffraction (XRD) patterns of the samples **1a**, **1b**, **1c**, and **1d**. Inset is XRD of **1b** film which shows a reversible *d*-spacing change due to light exposure ((a) as prepared; (b) after UV light exposure for 1 h; (c) after room light exposure of (b) for 2 days).

in samples **1a–c** suggests that these samples consist of a single domain type that presumably accommodates the presence of any minor amount of the opposite isomer by disordering or alteration of the packing angle.

All samples showed at least eight orders of (00*l*) peaks, indicating highly uniform mesoscale periodicity. Scherrer analyses⁹ indicated that the domain sizes decreased from 90 to 49 nm in the order **1c**(trans) > **1d**(trans) > **1b**(trans) > **1a**(cis), reflecting that slow evaporation (**1c,d**) enables better ordering than fast evaporation (**1b**) or precipitation from concentrated solution (**1a**). Taking into account the electron density of the silane- and azobenzene-containing sublayers, the lower relative intensity of the (002) reflections as compared to the (001) or (003) reflections indicates that the two sublayers are of comparable thickness. Hydrolysis and condensation due to exposure of these samples to ambient humidity caused only slight changes in the *d*-spacings and peak widths, while exposure to a basic catalyst (ammonia vapor) caused greater disorder (we observed only four orders of 00*l* peaks) along with some peak broadening.

Alternating exposure of the thin film sample (**1b**) to UV and room light (Figure 2 inset) transduced a small reversible change in the *d*-spacing from 2.20 (predominantly trans isomer) to 2.25 nm after UV exposure. This dimensional change is in sense opposite to that expected from modeling (Figure 1 inset) and from sample **1d** where UV-induced trans–cis isomerization causes a reduced *d*-spacing. However, we also observed an increased *d*-spacing for the trans isomer in **1d**, which self-assembled during UV exposure. Because the corresponding UV–vis spectra show a reversible shift in overall intensity but no change in the relative intensities of the

378 and 470 nm bands, we conclude that due to extensive H-bonding interactions, trans ↔ cis isomerization is severely inhibited in the supramolecular solids – the small, reversible changes in *d*-spacing perhaps reflecting an optically induced change in bond angle or orientation for the trans isomer as occurs in the rotation or inversion mechanistic pathway.¹⁰ This result indicates that realization of the full potential of transduction of optical excitation into work (for applications in nanomechanical devices¹¹) will require **1** to be sufficiently dilute or chemically modified to prevent extensive hydrogen bonding.¹² We note that dilution of **1** in a trimethylsilylated xerogel where hydrogen bonding is avoided allowed facile isomerization as determined by UV–vis spectroscopy (see Supporting Information).

Because the pendant intermediate (i) is highly soluble in THF and the bridged molecule **1** is weakly soluble (Scheme 1), the primarily cis product **1a** forms at very high concentration and elevated temperature by exceeding the solubility limit. In contrast, trans solids **1b–d** form from very dilute solution. This difference may reflect an enhanced stability of the cis isomer at high concentration and elevated temperature due to noncovalent bonding interactions. Alternatively, the cis product **1a** may be homogeneously nucleated, whereas products **1b–d** may be heterogeneously nucleated at the solid–liquid or liquid–vapor interfaces during slow evaporation.¹³ In support of this latter hypothesis, amphiphilic azobenzene-containing moieties interfacially organized on a water surface form principally the trans isomer.¹⁴

Overall, photoactive bridged silsesquioxanes represent a new class of precursors that as molecules are of interest for optomechanical actuation and as solids provide a means of photocontrol of the supramolecular structure and properties.

Acknowledgment. This work was supported by DOE-BES, AFOSR, NSF, and SNL's LDRD programs. Sandia National Laboratories (SNL) is a Lockheed Martin Co., under Department of Energy Contract DE-AC04-94AL85000.

Supporting Information Available: ²⁹Si, ¹³C, ¹H NMR, and FTIR data of **1**. SEM images of samples (**1a–c**). UV–vis spectra of xerogel thin film derivatized with **1** and hexamethyldisilazane (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA027991W