Angewandte
Chemie

Hybrid Silica

A Better Understanding of the Self-Structuration of Bridged Silsesquioxanes**

Joël J. E. Moreau, Benoît P. Pichon,*
Michel Wong Chi Man, Catherine Bied, Hans Pritzkow,
Jean-Louis Bantignies, Philippe Dieudonné, and
Jean-Louis Sauvajol

Sol–gel chemistry represents an interesting field of research for designing hybrid organic–inorganic materials.[1–3] Solid materials with new properties have been prepared in this way and in this context, bridged silsesquioxanes[4,5] rapidly developed as potentially applicable hybrid materials in many areas of interest, such as in heterogeneous catalysis,[6,7] solid-phase extraction,[8] and nonlinear optics.[9] The challenge for materials chemists is to direct the organization of these solids for an optimal accessibility of the organic functionalities. In this currently expanding area, the surfactant-mediated route for the structuration of silica[10] has successfully been extended to bridged silsesquioxanes.[11] Periodic mesoporous hybrid silicas have been synthesized from silyl organics, $(RO)_3Si\text{-}R'\text{-}Si(OR)_3$ with R′ acting as organic bridging units. In all cases, external templating macromolecules or supramolecular assemblies were employed as the main structuring agent. Moreover, it has been shown that weak interactions between aromatic units in the solid could afford anisotropic nanostructured materials.[11a,12] We recently introduced a novel and general approach for the organization of these hybrids based on hydrogen-bonding interactions that are provided by urea groups within the organic bridging fragment.[13] We took advantage of the auto-association properties of these organic units to self-direct and structure the final solid material. Accordingly, we succeeded in preparing hybrids with interesting morphologies such as helical fibers,[13a] hollow tubes and spheres,[13b] and also layered sheets exhibiting long-distance ordered structure.[13c] It is interesting to note that in the absence of these self-associative groups, the hydrolysis and condensation of organotrialkoxysilanes always led to amorphous solid materials.[4,5] However, self-organized hybrids formed through a heterogeneous solid/liquid hydrolysis–condensation reaction.[13–15] The mechanism of the structuration of the solid and its relation to the nature of the supramolecular assemblies arising from the self-association of the molecular precursor was unclear.

On this basis, we explored the possibility of forming a soluble urea-derived molecule which could self-assemble and lead to an organized hybrid via a homogeneous hydrolysis–condensation reaction. In this paper, we describe the synthesis of a convenient soluble silylated diureidophenylene derivative and its conversion to a self-organized, ordered hybrid material in a homogeneous fashion.

Compound **1** was synthesized by the reaction of γ-isocyanatopropyltriethoxysilane with 1,4-diaminobenzene. When subjected to acid hydrolysis with HCl in a 1:1 volume mixture of THF and water, **1** completely dissolved, and after 0.5 h a white precipitate appeared. The mixture was kept under static conditions at 65 °C for 3.5 days to afford **BS1** (Scheme 1).

Elemental analysis and solid-state ^{13}C and ^{29}Si NMR studies showed that the solid material **BS1** consists of a highly condensed siloxane network with organic fragments covalently bonded to the silica network. The solid-state ^{29}Si NMR exhibits T^2 ($\approx 55\,\%$) and T^3 ($\approx 45\,\%$) units and no Q units, which indicates that approximately one uncondensed OH group per two silicon atoms remain in the solid network.

A scanning electron microscope (SEM) image shows **BS1** to consist of crystalline plates (Figure 1 a; 1.5–-16 µm long, 0.5–3 µm wide and 70–120 nm thick), which is confirmed by the observed light extinction of the crystallites in optical polarized microscopy. Transmission electron microscope

---

[*] Prof. Dr. J. J. E. Moreau, Dipl. Arb. B. P. Pichon,
Dr. M. Wong Chi Man, Dr. C. Bied
Hétérochimie Moléculaire et Macromoléculaire (UMR-CNRS 5076)
Ecole Nationale Supérieure de Chimie de Montpellier
8, rue de l'école normale, 34296 Montpellier cédex 5 (France)
Fax: (+33) 467-147-212
E-mail: jmoreau@cit.enscm.fr

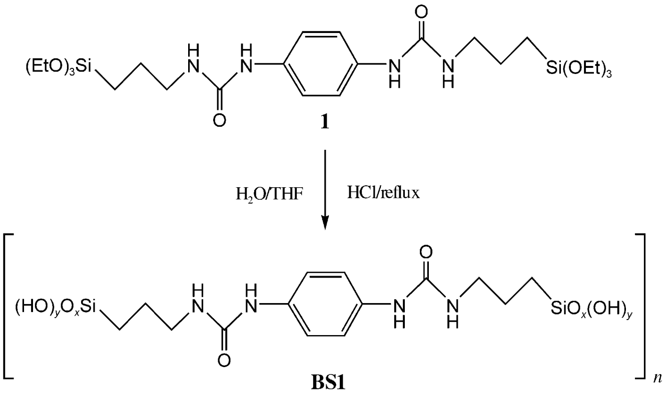
Dr. H. Pritzkow
Anorganisch-Chemisches Institut, Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

Dr. J.-L. Bantignies, Dr. P. Dieudonné, Dr. J.-L. Sauvajol
Groupe de Dynamique des Phases Condensées (UMR-CNRS 5581)
Université de Montpellier II, Place Eugène Bataillon, 34095
Montpellier cédex 5 (France)

[**] We gratefully acknowledge the "Ministère de la Recherche de France" through the ACI 2002 Nanosciences-Nanotechnologies and the CNRS for financial supports. We thank Prof. Dr. Pierre Delord and Dr. Martin In for helpful discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200352485



Scheme 1. Synthesis of compound **1** and of the lamellar-bridged silsesquioxane **BS1**.

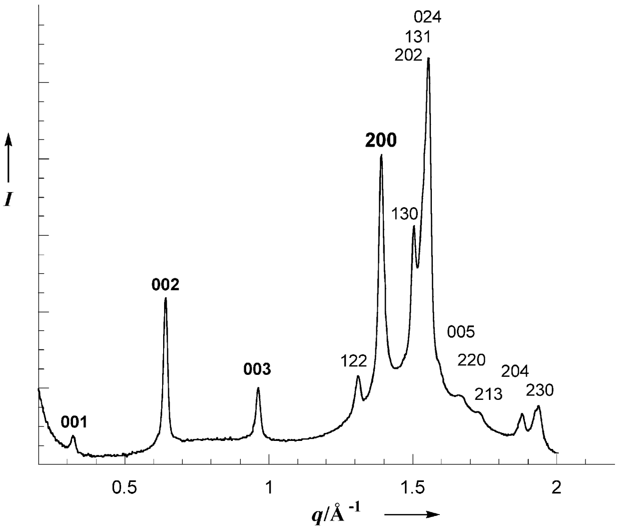


Figure 2. XRD profile of **BS1**.

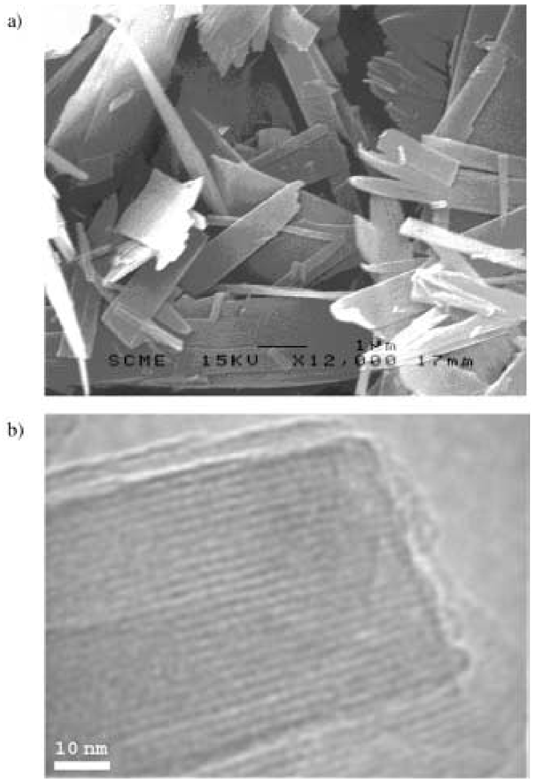


Figure 1. Electronic microscopy pictures of **BS1**; a) SEM image, and b) TEM image.

(TEM) analysis (Figure 1 b) demonstrates the sheetlike structure of the solid with an interlamellar distance of ≈19.8 Å, which can be related to the length of the bridging organic unit as already reported for alkylene derivatives.[13c]

The X-ray powder diffraction pattern (XRD) of **BS1** exhibits sharp peaks that indicate a material with a long-range-ordered structure (Figure 2). Three orders of (00*l*) peaks are clearly assigned to the lamellar structure with *d* spacings (19.7 Å) in good agreement with the interlamellar distance observed from the TEM picture. This is the first time that a self-structured bridged silsesquioxane with long-range order is obtained in a homogeneous reaction from a solution of a completely dissolved molecular precursor. To clarify the mechanism of formation of the self-organized hybrids, we carried out a single-crystal X-ray structural study of **1**,[16] which allows an analysis of the organized hybrid **BS1** (Figure 3).

There are two independent centrosymmetric molecules in the cell, which are alternately bonded by intermolecular hydrogen bonds of the urea groups (N···O separations = 2.88–2.91 Å) forming sheets along the *a* axis (Figure 3 a). The phenylene groups of neighboring molecules in the sheet are not coplanar (angle between the planes = 35.9°). The sheets adopt a herringbone packing motif in the direction of the *b* axis (Figure 3 b).

The main observation that helps to interpret the lamellar structure of **BS1** is seen in Figure 3 a: The intermolecular distance between two neighboring urea groups (4.5 Å) is consistent with the (200) peak found in the XRD profile of **BS1**. Taking into account the regular repetition of the two twisted phenylene units, a periodicity twice that length (9.0 Å) is observed and can clearly be assigned to hydrogen-bonding interactions between the urea groups.

We applied an X-ray profile-matching procedure (Full-Prof/WinPlotr software), to determine the structure of **BS1**. The results show that the diffraction spectrum of **BS1** fits with an orthorhombic crystal lattice with the following parameters: $a = 9.05$, $b = 14.06$, $c = 19.7$ Å. The *a* values are very close for both solids indicating that the periodicity in **1**, related to the hydrogen bonding between molecules, should be maintained in **BS1**. Moreover, the structure of **BS1** is characterized by a smaller volume than that of **1**. This is consistent with a closer packing of molecules in the *bc* plane with the loss of EtO groups by condensation and is presumably favored by siloxane-bond formation during polycondensation. The **BS1** lamellar distance observed across the crystal thickness in the TEM (Figure 1 b) is of the same order of magnitude as *c*. This value appears to be associated to the lamellar character of this solid. These results indicate that the polycondensation of **1** in

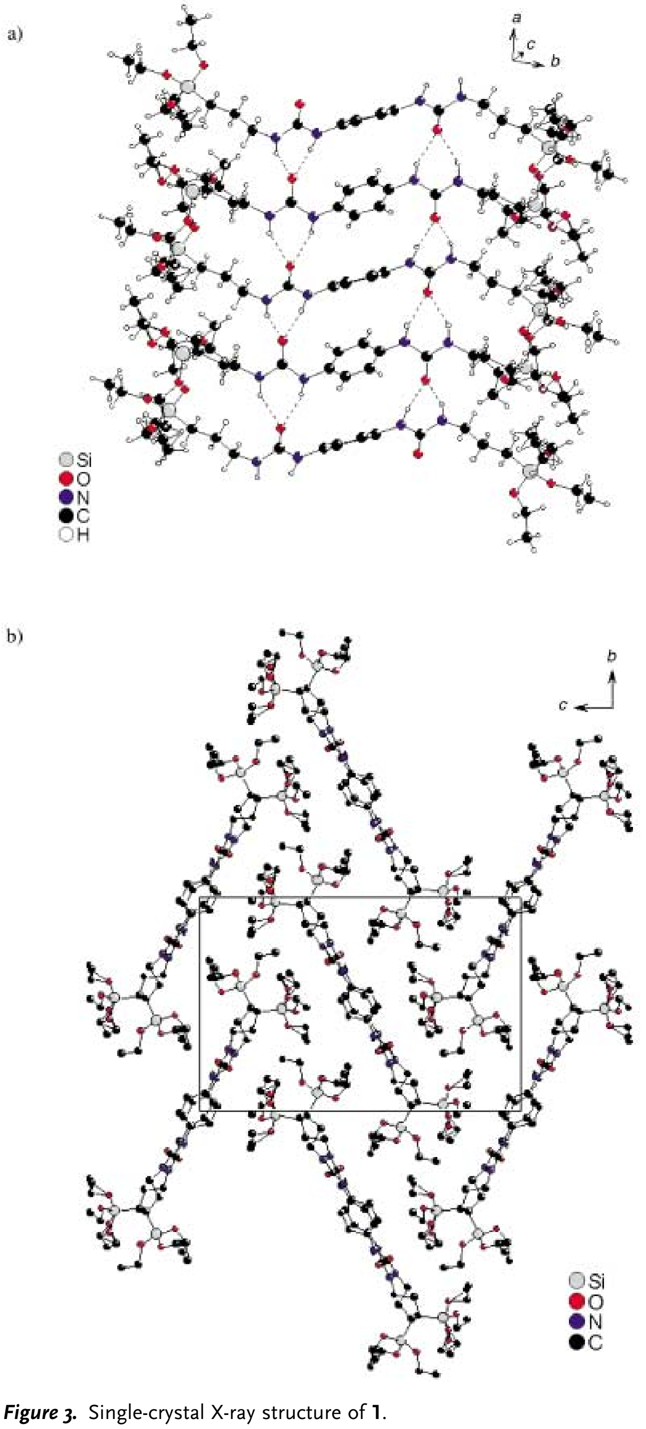


Figure 3. Single-crystal X-ray structure of **1**.

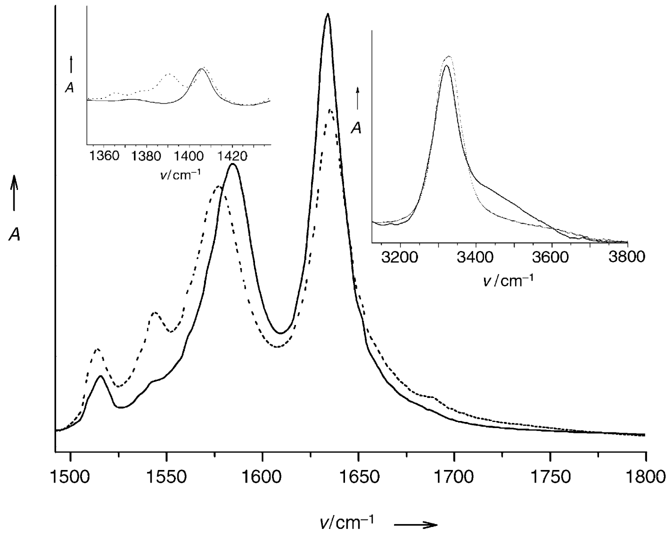


Figure 4. IR spectra of **1** (----) and **BS1** (——).

THF/water induces the formation of a crystalline solid **BS1** with structural similarities which can be explained by the self-assembly of the molecules through hydrogen bonds for both cases.

The similarity of the structure of **1** with that of **BS1** can also be shown from their IR spectra (Figure 4). For comparison, they are normalized on one of the stretching ($\tilde{\nu}_{CC}$ = 1410 cm^{-1}) bands of the ring (left inset) as the number of rings is the same in both samples (note that the position of this band is the same for both compounds). Both samples are dominated by the amide modes, which are very sensitive to H-bonding (δ_{NH}, ν_{CO}, ν_{NH}).[17] The stretching frequencies ν_{CO} and ν_{NH}, centered at 1634 cm^{-1} and 3326 cm^{-1}, respectively, are at the same position for **1** and **BS1** (right inset) indicating that the strength of the H-bonding is similar. In contrast, the slight shift in the δ_{NH} mode around 1585 cm^{-1} is mainly related to structural differences between both samples.

Whereas in previous reports[13–15] organized solids were obtained upon hydrolysis of the precursor in the solid state, we have shown here for the first time that a highly crystalline hybrid material can be obtained upon hydrolysis of a completely solubilized precursor in solution. Its formation is due to the self-assembly properties of the molecular precursor, which direct the formation of the hybrid three-dimensional network. During the course of the reaction, the polycondensates organize via self-assembly of urea groups leading to a nanostructured hybrid material **BS1** in lamellar form. Relationships drawn from the single-crystal X-ray structural study of the crystalline molecular precursor allow significant progress in the interpretation of the structure of the resulting hybrid silica. The development of this method for the preparation of other hybrid silicas with new functionalities and targeted properties is currently in progress.

Experimental Section

1: 1,4-diaminobenzene (560 mg, 5.18 mmol) was dissolved in CH_2Cl_2 (40 mL) under a nitrogen atmosphere in a Schlenk tube. γ-Isocyanatopropyltriethoxysilane (2.69 mg, 10.9 mmol) was slowly added at room temperature and the mixture was stirred overnight. The solvent was evaporated and the white precipitate obtained was washed with pentane. The solution was filtered and the white solid was dried in vacuo.

Yield: 2.75 g, 88 %; m.p. 190 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 1577(δ_{NH}), 1636 (ν_{CO}), 3322 cm^{-1} (ν_{NH}); ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 0.59 (t, 4H; CH_2Si), 1.20 (t, 9H; CH_3), 1.51 (qt, 4H; CH_2), 3.14 (m, 4H; NCH_2), 3.80 (qd, 12H; OCH_2), 6.44 (s, 4H; H_{ar}), 6.49 (m, 2H; NH), 7.60 ppm (m, 2H; NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.8 (CH_2Si), 18.3 (CH_3), 23.8 (CH_2), 42.9 (CH_2N), 58.3 (CH_2O), 124.3 and 134.0

(C_{ar}), 157.8 ppm (CO); ^{29}Si (50 MHz, $CDCl_3$): $\delta = -45.4$ ppm; MS (FAB): m/z (%): 602 (25) [M^+]; elemental analysis calcd (%) for $C_{26}H_{50}N_4O_8Si_2$: C 51.80, H 8.37, N 8.82; found: C 51.51, H 8.16, N 8.82.

BS1: Compound **1** (125 mg, 0.21 mmol) was dissolved in THF (1.4 mL) and water (1.4 mL) from which a white precipitate appeared. A solution of HCl (1M, 41.5 μL) was added and the mixture was heated to reflux. After 5 min complete solubilization was observed. Precipitation occurred after 0.5 h. The mixture was filtered after 3.5 days and the solid was washed with water and ethanol prior to vacuum drying for 12 h. **BS1** was obtained as a white powder. IR (KBr): $\tilde{\nu} = 1585$ (δ_{NH}), 1635 ($\tilde{\nu}_{CO}$) and 3329 cm^{-1} ($\tilde{\nu}_{NH}$); ^{13}C CPMAS NMR: $\delta = 13.8$, 25.0, 44.3, 125.3, 134.1, 158.6 ppm; ^{29}Si CPMAS NMR: $\delta = -57.1$, -66.2 ppm (T^2 and T^3 units).

Received: July 28, 2003 [Z52485]

Keywords: hydrogen bonds · nanostructures · organic–inorganic hybrid composites · self-assembly · silsesquioxanes

---

[1] C. Sanchez, F. Ribot, *New J. Chem.* **1994**, *18*, 1007–1047.

[2] D. Avnir, *Acc. Chem. Res.* **1995**, *28*, 328–334.

[3] a) *Organic/inorganic Hybrid Materials*, *MRS Symp. Vol. 628* (Eds.: R. M. Laine, C. Sanchez, C. J. Brinker, E. Giannelis), **2000**; b) *Organic/inorganic Hybrid Materials*, *MRS Symp. Vol. 726* (Eds.: R. M. Laine, C. Sanchez, C. J. Brinker, E. Giannelis), **2002.**

[4] K. J. Shea, D. A. Loy, O. W. Webster, *J. Am. Chem. Soc.* **1992**, *114*, 6700–6710.

[5] R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. Wong Chi Man, *Chem. Mater.* **1992**, *4*, 1217–1224.

[6] U. Schubert, *New J. Chem.* **1994**, *18*, 1049–1058.

[7] A. Adima, J. J. E. Moreau, M. Wong Chi Man, *Chirality* **2000**, *12*, 411–420.

[8] J.-C. Broudic, O. Conocar, J. J. E. Moreau, D. Meyer, M. Wong Chi Man, *J. Mater. Chem.* **1999**, *9*, 2283–2285.

[9] B. Lebeau, S. Brasselet, J. Zyss, C. Sanchez, *Chem. Mater.* **1997**, *9*, 1012–1021.

[10] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartulli, J. S. Beck, *Nature* **1992**, *359*, 710–712.

[11] a) S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304–307; b) B. J. Melde, B. T. Holland, C. F. Blanford, A. Stein, *Chem. Mater.* **1999**, *11*, 3302–3308; c) T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867–871; d) A. Sayari, S. Hamoudi, Y. Yang, I. L. Moudrakovski, J. R. Ripmeester, *Chem. Mater.* **2000**, *12*, 3857–3863; e) Y. Lu, H. Fan, N. Doke, D. A. Loy, R. A. Assink, D. A. LaVan, C. J. Brinker, *J. Am. Chem. Soc.* **2000**, *122*, 5258–5261.

[12] B. Boury, R. J. P. Corriu, *Chem. Commun.* **2002**, 795–802.

[13] a) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, *J. Am. Chem. Soc.* **2001**, *123*, 1509–1510; b) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, *Chem. Eur. J.* **2003**, *9*, 1594–1999; c) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, J.-L. Bantignies, P. Dieudonné, J.-L. Sauvajol, *J. Am. Chem. Soc.* **2001**, *123*, 7957–7958.

[14] a) N. Liu, K. Yu, B. Smarsly, D. R. Dunphy, Y.-B. Jiang, C. J. Brinker, *J. Am. Chem. Soc.* **2002**, *124*, 14540–14541; b) N. Liu, D. R. Dunphy, M. A. Rodriguez, S. Singer, C. J. Brinker, *Chem. Commun.* **2003**, 1144–1145.

[15] H. Muramatsu, R. J. P. Corriu, B. Boury, *J. Am. Chem. Soc.* **2003**, *125*, 854–855.

[16] Crystal data for **1**: $C_{26}H_{50}N_4O_8Si_2$, $M_r = 602.88$, monoclinic, $P2_1/n$, $a = 9.037(1)$, $b = 15.502(2)$, $c = 23.387(3)$ Å, $\beta = 92.837(2)°$, $V = 3272.4$ Å^3, $\rho_{calcd} = 1.224$ g cm^{-3}. Data collection: CCDarea detector, $Mo_{K\alpha}$ radiation, $T = -170$ °C, 4690 unique reflections, 3362 observed ($I > 2\sigma 1$), $\Theta_{max} = 23.3°$. Structure solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL NT 5.1, Bruker-AXS 1998), 405 parameters, $R1 = 0.085$, $wR2 = 0.187$, with disorder of some of the ethoxy groups. CCDC-215379 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[17] G. Careri, U. Buontempo, F. Galluzzi, A. C. Scott, E. Gratton, E. Shyamsunder, *Phys. Rev. B* **1984**, *30*, 4689–4702.