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# The Influence of Arylene and Alkylene Units on the Structuring of Urea-Based Bridged Silsesquioxanes

Benoît P. Pichon,<sup>\*[a,b]</sup> Sylvana Scampini,<sup>[a]</sup> Catherine Bied,<sup>[a]</sup> Joël J. E. Moreau,<sup>[a]</sup> and Michel Wong Chi Man<sup>\*[a]</sup>

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The influence of the intrinsic self-assembling properties of rigid or semirigid aromatic units as the main substructures combined with the effect of the alkylene side chains as linkers on the nanostructure of bridged silsesquioxanes was studied. The symmetry of the organic units was found to control the dimensionality of the hybrid nanostructure. Bis(silyl-

#### Introduction

There has been a rapid growth in the number of reports on the synthesis and the use of bridged silsesquioxanes<sup>[1]</sup> over the past two decades. These hybrid materials are easily obtained by the sol-gel<sup>[2]</sup> hydrolysis/condensation of hydrolysable organosilanes and combine the properties of the organic unit with the silica matrix.<sup>[3]</sup> They can be obtained as powders, monoliths<sup>[4]</sup> or processed as films.<sup>[5]</sup> Thus, the organic functionalities can easily provide discrete properties to the resulting material according to the desired applications.<sup>[6]</sup> Subsequently, much effort is being devoted to the structuring of these hybrid materials since additional interesting properties might also be tuned by the organisation of the organic fragments in the hybrid silica framework.<sup>[7]</sup> Two main routes have been exploited to achieve the nanostructuring of these materials: (1) periodic mesoporous organosilicates (PMO) are obtained with uniform pores by using surfactants as external structuring agents,<sup>[8]</sup> and (2) another promising approach consists of exploiting the intrinsic associative interactions between the bridging organic fragments of the organosilane precursor to self-direct the structuring of the resulting hybrid.<sup>[9]</sup>

Fax: +33-4-67147212 E-mail: michel.wong-chi-man@enscm.fr

Homepage: http://am2n.icgm.fr

 [b] Institut de Physique et Chimie des Matériaux de Strasbourg, UMR CNRS-UdS 7504,

23, rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France

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ated) aromatic units lead to lamellar hybrids, whereas tris-(silylated) aromatic units tend to form hexagonal structures. The ordering of each type of structure depends directly on the conformation of the organic units, which determines the self-assembling of precursors through intermolecular interactions.

In this field, an important breakthrough was achieved by using organo-bridged silane precursors designed with additional self-assembling groups, which significantly improved the self-structuring of the bridged silsesquioxanes (Scheme 1).<sup>[10]</sup> Long alkylene chains as the main organic substructure can also influence the structuring of related silsesquioxanes.<sup>[11]</sup> These chains can form part of the main substructure as pendant chains<sup>[11a–11d,11g]</sup> and they can also be side chains.<sup>[11e,11f,11h]</sup> Similarly, synergetic effects can be obtained when long alkylene side chains (n = 10, 11) are combined with urea groups, which offers a rational route to achieve a variety of self-structured bridged silsesquioxanes (Scheme 1).<sup>[12]</sup>

In the case of the main structure that consists of long akylene groups (n > 8) and with a propylene side chain (n > 8)= 3) between the urea groups and the silicon atoms, we previously showed that the long-range ordering of the structure was favoured by cooperative hydrophobic and van der Waals interactions with intermolecular hydrogen bonds for alkylene chains that consist of at least eight carbon atoms.<sup>[13]</sup> The resulting self-assembly of the organic fragments hence creates the structuring of the bridged silsesquioxane. The self-structuring of the final bridged silsesquioxane has also been conducted by replacing the alkylene fragments by a phenylene unit as main substructure directly linked to bis(urea) groups. Although short, its rigidity allows a packing of the aromatic rings that strengthens the self-association of organic fragments additionally to the hydrogen-bonding interactions between urea groups.<sup>[14]</sup>

We report here the syntheses of a new family of molecular precursors (P1-6) that is based on arylene units with an adjustable combination of several types of weak interactions. The use of the arylene–alkylene–urea groups enables one to modulate the nanostructuring of the corresponding

 <sup>[</sup>a] Institut Charles Gerhardt, Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, Architectures Moléculaires et Matériaux Nanostructurés, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier Cedex 5, France



Scheme 1. Illustration of the organic units in bridged silsesquioxanes.



Scheme 2. Syntheses of precursors P1-6.

hybrid silicas (HS1-6). The organic unit was tuned according to their main substructure by following three approaches: (1) a rigid biphenylene and a semirigid methylenediphenylene unit in which  $\pi$ -stacking interactions and angular and steric constraints are considered; (2) both subunits were associated to propylene  $(C_3)$  or decylene  $(C_{10})$ side chains between the urea and the trialkoxysilyl groups; and (3) a rigid 1,3,5-tris(urea)-based phenylene unit was also investigated with propylene and undecylene side chains (Scheme 2). The purpose of this work was to study the role of the angular constraints of the biphenylene unit relative to the semiflexible methylenediphenylene unit; the associative role of long alkylene ( $C_{10}$  or  $C_{11}$ ) side chains relative to the shorter propylene side chain; and the role of multiple condensation sites on the substructure with three hydrolysable triethoxysilyl groups.

#### **Results and Discussions**

#### Synthesis of the Molecular Precursors P1–6 and the Corresponding Hybrid Bridged Silsesquioxanes HS1–6

Bis(silylated) molecular precursors **P1–4** were synthesised from commercially available diamines (benzidine and 4,4'-methylenedianiline) by treatment with 2 mol-equiv. of (3-isocyanopropyl)triethoxysilane or (10-isocyanodecyl)triethoxysilane (Scheme 2). Tris(silylated) precursors **P5** and **P6** were obtained by reaction of (1,3,5-triisocyano)benzene with (3-aminopropyl)triethoxysilane or (11-aminoundecyl)triethoxysilane, respectively.<sup>[15]</sup> These reactions were performed at room temperature in CH<sub>2</sub>Cl<sub>2</sub> under argon and led to bis- or tris(urea)-based precursors **P1–6** with yields of up to 75%.



Scheme 3. Syntheses of hybrid silicas HS1-6.

The corresponding hybrid silicas HS1–6 were obtained by an aqueous acid-catalysed hydrolysis/condensation of the corresponding precursors at 80 °C for 3.5 d (Scheme 3). The precursors with propylene (C<sub>3</sub>) side chains P1, P2 and P5 were first dissolved in THF, whereas those with decylene (C<sub>10</sub>) and undecylene (C<sub>11</sub>) side chains P3, P4 and P6 were dissolved in DMSO due to their lower solubility.

#### Characterisation of the Hybrid Materials

Elemental analyses performed on HS1, HS2, HS5 and HS6 give for every sample an Si/N molar ratio of 0.46, which is very close to that of their corresponding precursors P1, P2, P5 and P6 (0.5). These results indicate that the organic fragments were not affected by the hydrolysis/condensation reaction and are quantitatively present in the solid material. In addition, <sup>13</sup>C solid-state NMR spectroscopy exemplified by HS1-3 (Figure S1 in the Supporting Information) revealed a series of specific peaks at  $\delta \approx 160$  ppm (CO), at  $\delta = 137-119$  ppm (aromatic rings) and at  $\delta = 43-12$ 10 ppm (CH<sub>2</sub>) that correspond to the chemical shifts of the organic units. The last peak at  $\delta \approx 11$  ppm showed that C– Si covalent bonds were not cleaved during the reaction. <sup>29</sup>Si solid-state NMR spectra were recorded to study the formation and the condensation rate of the silica network. All spectra only exhibit T<sup>n</sup>-type signals in the  $\delta = -40$  to -80 ppm range, which also confirms that the organic unit remains interconnected to the silica network through covalent Si-C bonds (Table 1). Hybrids HS1-4 exhibit signals at  $\delta \approx -57$  ppm [T<sup>2</sup>] and  $\delta \approx -66$  ppm [T<sup>3</sup>], as exemplified by

HS1 in Figure S2a of the Supporting Information. These signals correspond to high condensation rates between 75 and 87%, thereby indicating that the organic moieties are linked to the others through an average of five Si-O-Si bonds. Nevertheless, HS3 and HS4 show an additional low T<sup>1</sup>-type signal at  $\delta \approx -48$  ppm (Figure S2b) that corresponds to a lower rate of condensation and might be related to the lower solubility of the corresponding precursors that contain C<sub>10</sub> linkers. According to hybrid silicas that contain threefold symmetry units, HS5 is featured by a dense silica network with the highest rate of condensation (90%). In contrast, HS6 exhibits the highest amount of T<sup>1</sup> signal (11%) and the lowest amount of  $T^3$  signals (22%), which corresponds to the lowest condensation rate (69%) observed among these hybrid materials. Again, this lower condensation rate might be attributed to the low solubility of **P6** with long  $C_{11}$  linkers that is closely similar to **P3** and P4.

Table 1. Integrated surfaces of  $T^n$  (n = 1, 2 or 3) signals observed in <sup>29</sup>Si solid-state NMR spectra and condensation rates of hybrid silicas.

Hybrid silica	Integrated surfaces [%] $T^1$ $T^2$ $T^3$			Condensation rate [%]		
HS1	_	53	47	92		
HS2	_	41	60	87		
HS3	3	67	30	75		
HS4	2	54	44	81		
HS5	0	30	70	90		
HS6	11	64	22	69		



Scanning electron microscopy (SEM) pictures of the bridged silsesquioxanes HS1-4 typically display two-dimensional morphologies (Figure 1). However, striking differences in the morphologies clearly demonstrate the influence of the main organic substructure. Hybrid HS1 exhibits interconnected and smaller plates (length: 1.5 µm; width: 0.5-3 µm) in contrast with the observable longer, larger and noninterconnected ones of HS2 (length: 5.0-50 µm; width:  $0.5-5 \,\mu\text{m}$ ), which have the highest aspect ratio (Figure 1a and b respectively). Such different morphologies are directly related to the main substructure of the arylene group. Indeed, biphenylene and methylenediphenylene groups influence the formation of the silica network, which results in different growth and morphologies. The growth of HS1 seems to proceed by the simultaneous growth of several plates from the same nuclei, whereas HS2 grows from specific and independent nuclei. In contrast, no significant dif-



Figure 1. SEM pictures of (a) **HS1**, (b) **HS2**, (c) **HS3**, (d) **HS4**, (e) **HS5** and (f) **HS6**.

ferences were observed between **HS3** and **HS4**, both of which have  $C_{10}$  side chains. Figure 1c and d show less defined plates that look larger and more flexible. Nevertheless, the increase of the hydrophobic and van der Waals interactions between  $C_{10}$  linkers favours the formation of the silica network in two dimensions.  $C_{10}$  linkers also predominate on the arylene main subunit since both morphologies of **HS3** and **HS4** are similar.<sup>[16]</sup> On the other hand, the trifunctional hybrid silicas exhibit completely different morphologies, and the threefold symmetry of the organic fragment does not favour anisotropic shapes. Indeed, **HS5** has a spheroidal and isotropic shape, whereas **HS6** exhibits a featureless morphology (Figure 1e and f).

The organic subunits also influence the nanostructure of hybrid silica as observed by X-ray diffraction (XRD). Hybrids HS1-4 exhibit sharp and intense Bragg peaks in the lower q region with regular spacing that are characteristic of lamellar structures (Figure 2). All patterns show at least the first three harmonics indexed as the (00l) reflections. The *d* spacing calculated for the (001) reflection is related to the period of the lamellar structure. Interestingly, these values increase with the length of the organic unit and are very close to the length calculated for the completely extended conformation of the molecular precursors by using the MM2 model of Chemdraw Pro 2004 (Table 2). In addition, a comparative study of the full width at half maximum (FWHM) of each (00l) reflection in all patterns revealed the long-range-ordered lamellar structure within these hybrids. More precisely, HS2 and HS4 with the methylenediphenylene unit display a longer-range order of the lamellar structure (369 and 285 Å, respectively) than HS1 and HS3 (273 and 153 Å) with the biphenylene unit on either the  $C_3$  or  $C_{10}$  linker. In contrast, in the case of  $C_{10}$  linkers, both hybrid silicas that contain biphenylene or methylenediphenylene units display a lower correlation length than  $C_3$  linkers. In these particular cases, a slight decrease of the long-range order of the lamellar structure is observed for those materials with C<sub>10</sub> linkers relative to those that bear  $C_3$  ones.

The lamellar structure of **HS3** and **HS4** was also analyzed by transmission electron microscopy (TEM). Figure 3 shows alternate stripes that correspond to the periodic repetition of the silica network and the organic units and con-



Figure 2. XRD patterns of (a) HS1 and HS2, and (b), (c) HS3 and HS4.

Hybrid silica	Length of the molecular precursors	$q_{(001)} \pm 0.2$ [Å <sup>-1</sup> ]	$d_{(001)} \pm 0.2$ [Å]	FWHM $\pm 0.002$ [Å <sup>-1</sup> ]	$\xi_{(001)} \pm 1$ [Å]
HS1	27.6	0.27	23.5	0.023	273
HS2	27.5	0.25	24.7	0.017	369
HS3	43.1	0.172	36.6	0.041	153
HS4	44.7	0.162	38.8	0.022	285

Table 2. Calculated length of the molecular precursors:  $q_{(001)}$  values,  $d_{(001)}$  distances, full width at half maximum (FWHM) and coherence lengths ( $\xi$ ) related to the (001) reflection.

firm the lamellar structure of both hybrid materials. These stripes could only be observed for organic units with  $C_{10}$  linkers. A periodicity of 38 and 40 Å was calculated from TEM micrographs for **HS3** and **HS4**, respectively, which is in full agreement with the  $d_{(100)}$  values (36.6 and 38.8 Å, respectively) calculated from XRD patterns (Table 2).



Figure 3. TEM images of (a) HS3 and (b) HS4.

In the case of the tris(silvlated) systems, the threefold symmetry of the organic unit of hybrid silicas HS5 and HS6 dramatically influences their structure (Figure 4). The pattern of the C<sub>3</sub>-linker-based HS5 shows very broad peaks, which clearly indicates its amorphous structure. In contrast, the presence of a  $C_{11}$  linker in **HS6** results in three peaks at low q values in the XRD pattern. Although these peaks are broad, they can be attributed to the (100), (110) and (200) reflections of a hexagonal structure (Figure S3 in the Supporting Information), as confirmed by the ratios between the corresponding q values (1:1.73:2, respectively). The hexagonal structure corresponds to a lattice parameter a of 38.9 Å as calculated from the formula  $d_{(100)} = a\sqrt{3/2}$ for a hexagonal lattice. This value is very close to the diameter (41.1 Å) of a threefold symmetry molecule in its extended conformation as calculated by a computational



Figure 4. XRD patterns of hybrid silica HS5 and HS6.

model. However, **HS6** displays a very local ordering of about 70 Å according to the FWHM value of the (100) peak. Whereas threefold-symmetry precursors result in a hexagonal structure, the structuring occurs with a lower-range order than for the bis(triethoxysilyl) precursors.

Additional peaks are also observed at higher q values in the 1.3–1.8 Å<sup>-1</sup> region in all XRD patterns. For hybrids **HS1–4**, the particular peak at 4.4–4.6 Å (clearly seen as a sharp peak in the case of **HS1** and **HS2** in Figure 2a) can be related to the distance between two urea groups linked together by means of intermolecular hydrogen bonds as already reported.<sup>[14a,17]</sup> Splitting of this peak occurs for **HS3** and **HS4** (Figure 2c) and is very broad for **HS5** and **HS6** (Figure 4), which results in more difficult indexation. This disordering might be attributable to the *gauche* conformation of alkylene side chains.<sup>[12c]</sup>

Complementary insights into the composition of the organic subunit in hybrid silica can be drawn from Fourier transform infrared (FTIR) spectroscopy. All spectra were normalised on bands (1000–1150 cm<sup>-1</sup>) that correspond to the vSi–O–Si stretching mode due to the formation of the silica network. In addition, numerous characteristic vibration modes of the organic units (Figure 5 and Table 3) can be attributed in the following way: the vCH<sub>2</sub> bands correspond to the alkylene side chains, which are mostly intense for organic units with C<sub>10</sub> or C<sub>11</sub> linkers, and the specific amide A (vNH), amide I (vCO) and amide II ( $\delta$ NH) bands of the urea groups are also observed.

FTIR spectroscopy also resulted in very useful information about the nanostructure of hybrid silica and on the self-assembly of the organic units.

Firstly, the position of vCH<sub>2</sub> bands is indicative of the conformation of alkylene chains, which can be correlated to the ordering through hydrophobic and van der Waals interactions.<sup>[18]</sup> Hybrids **HS1** and **HS2** display broad vCH<sub>2</sub> asymmetric [vCH<sub>2(as)</sub>] and vCH<sub>2</sub> symmetric [vCH<sub>2(s)</sub>] bands at 2932 and 2868 cm<sup>-1</sup>. These bands are narrower and are shifted to lower wavelengths of 2925 and 2854 cm<sup>-1</sup> for **HS3** and **HS4**, respectively. This result shows that replacing C<sub>3</sub> by C<sub>10</sub> linkers increases the ordering of the alkylene chains in an all-*trans* conformation<sup>[19]</sup> on account of the higher hydrophobic nature and the van der Waals interactions of the long carbon chains. A similar behaviour was observed for hybrid silicas **HS5** and **HS6**, which contain threefold-symmetry organic units (Table 3).

Secondly, the vibration modes of amides A and I are very sensitive to the strength of intermolecular hydrogen bonds between urea groups. For HS1–4 and HS6, the positions of the vNH and vCO bands (around 3326 and 1638 cm<sup>-1</sup>,



Figure 5. FTIR spectra of hybrid silica of (a), (b) HS1-4 and (c) HS5-6.

Table 3. Vibration modes of alkylene and urea groups and the corresponding  $\Delta v$  values for HS1–6.

Hybrid silica	Vibration modes					$\Delta v$
-	$\nu CH_{2(as)}$	$\nu CH_{2(s)}$	$\nu \mathrm{NH}$	vCO	δNH	$(\nu CO-\delta NH)$
HS1	2932	2868	3324	1642	1557	85
					1597	45
HS2	2932	2868	3329	1635	1564	71
					1660	35
HS3	2925	2854	3324	1645	1555	90
					1593	52
HS4	2925	2854	3328	1636	1562	74
					1599	37
HS5	2937	2880	3403	1659	1557	102
HS6	2928	2853	3330	1645	1574	71

respectively) correspond to strong hydrogen-bonding interactions. In contrast, the shift to higher values (3403 and 1659 cm<sup>-1</sup>, respectively) for HS5 is characteristic of weaker hydrogen-bonding interactions. A careful observation of vCO bands shows that they are asymmetric and broad in HS1 and HS3 spectra (noted by arrows in Figure 5b). Such additional contributions correspond to weaker hydrogen bonds that are not observed for HS2 and HS4. This observation can be correlated to the difference between biphenylene and methylenediphenylene groups. The amide II bands are also depicted by two bands in the spectra of HS1-4 and correspond to two different vibrations modes at about 1590 and 1560 cm<sup>-1</sup> (more clearly seen for the methylenediphenylene hybrids). In contrast, the spectra of HS5 and HS6 exhibit only one broad  $\delta NH$  band, thus indicating the multidirectionality of the hydrogen bonds (Figure 5c).

Hydrogen bonds between urea groups can be quantified by the difference  $\Delta v$  between the vC=O and  $\delta$ NH vibration modes (Table 3); the smaller this value, the stronger the hydrogen-bond strength.<sup>[20]</sup> Hybrids HS2 and HS4 display two  $\Delta v$  values that are lower than those of HS1 and HS3 when comparing the hybrid silicas with the same aromatic unit. Hence the semirigid methylenediphenylene unit enables stronger hydrogen bonds between urea groups than the rigid biphenylene unit. It results in a better structuring for the hybrid silicas that contain methylenediphenylene units than those that contain biphenylene units, which is in good agreement with the better ordering observed by XRD. On the other hand, hybrid silicas that bear  $C_{10}$  side chains exhibit slightly higher  $\Delta v$  values than those with C<sub>3</sub> side chains. Although the hydrophobic and van der Waals interactions increase the ordering of methylene groups in alkylene chains, the higher flexibility of the organic units cannot counterbalance strains that result from the formation of the silica network. Therefore, the formation of hydrogen bonds between urea groups is disfavoured when long alkylene chains are combined with bifunctional arylene units and results in the lower ordering of hybrid silica. In contrast, the length of the linker influences the structure of threefoldsymmetry organic units much more dramatically. Strong interactions between C11 side chains favour a better structuring of HS6 than HS5 with shorter C3 side chains, which is amorphous (Table 3).

The results observed in this work clearly show that organosilane precursors with different organic units dramatically influence the nanostructure of the resulting bridged silsesquioxanes. Aromatic rings that consist of a different geometry and side chains with different lengths are very important parameters.

The bifunctional organic units **HS2** and **HS4**, which bear a semirigid methylenediphenylene unit, display longer-range ordering than **HS1** and **HS3** with a rigid biphenylene unit. This is directly related to stronger intermolecular hydrogen bonds between urea groups, which favour the self-assembling of organic units. The main difference between both organic units comes from the conformation of the aromatic rings. Molecular modelling performed with the MM2 model of Chemdraw Pro 2004 was applied to precursors **P1** 



Scheme 4. Molecular modelling of P1 and P2 carried out by using the MM2 model of Chemdraw Pro 2004.

and P2. Although this modelling was not applied to hybrid materials, which are very complex structures, this information collected from precursors might be helpful in understanding the formation mechanism. Different conformations of the aromatic rings were obtained (Scheme 4): The aromatic rings of the biphenylene unit exhibit a 30° tilting, whereas they are almost coplanar in the methylenediphenylene unit. The angular strain that exists in the biphenylene case is significantly suppressed by the presence of the methylene group between both aromatic groups in the latter case. The existence of coplanar aromatic rings, mainly due to the flexibility around the central methylene group, favours the assembling of organic units through  $\pi$  stacking.<sup>[14a]</sup> In addition, such a conformation of aromatic rings directly influences the formation of intermolecular hydrogen bonding between urea groups. Indeed, the conjugation of the  $\pi$  orbitals of the aromatic ring with the electronic doublet of the nitrogen atom closely results in the normal direction defined by the plane of aromatic and urea groups. Therefore, coplanar aromatic rings of interacting organic units favour well-aligned urea groups and strong intermolecular hydrogen bonds. Moreover, the combination of hydrogen bonds and  $\pi$ -stacking interactions favours the assembly of organosilane precursors in a specific direction, which results in the anisotropic growth of the silica network upon hydrolysis/ condensation and in long-range-ordered lamellar structures that consist of alternate layers of organic units and silica networks, as shown by TEM micrographs of HS3 and HS4 (Figure 3). Such an anisotropic structure is directly correlated to the common platelike morphology of HS1-4 hybrid silicas as obtained from other bifunctional organosilane precursors. Nevertheless, some morphological differences are directly correlated to the intrinsic self-assembly properties of organic units. The biphenylene unit in **HS1** leads to small and interconnected plates with a low aspect ratio of about 1, whereas the methylenediphenylene unit in **HS2** induces the growth of longer and independent plates with a higher aspect ratio of about 10. This difference is directly correlated to the variation of the aromatic unit. Longer plates correspond to a more anisotropic growth, which is ruled by stronger interactions between organic units.

Side chains also directly influence the structure and the morphology of the hybrid silicas. Hybrids **HS3** and **HS4** display less defined platelike morphologies and lower-ordered lamellar structures than **HS1** and **HS2**, respectively. Interestingly, replacing the  $C_3$  linker with a  $C_{10}$  linker results in stronger hydrophobic and van der Waals interactions that are expected to increase the ordering.<sup>[12c]</sup> However, the flexibility of long alkylene chains has to be taken into account when considering the high strains that result from the formation of the silica network, which tend to disorganise the organic units.

The tris(silylated) organosilane precursors **P5** and **P6** result in a different control of the nanostructure of hybrid silicas **HS5** and **HS6**. The presence of a third triethoxysilyl group on the same aromatic unit directly connected by means of three urea groups increases strains<sup>[21]</sup> upon the formation of the silica network, which impacts the structuring of the organic units. Indeed, side chains have a dramatic influence on the structure of hybrid silica that contains threefold-symmetry organic units. Whereas **HS5** with C<sub>3</sub> linkers consists of amorphous spheres, **HS6** that bears C<sub>11</sub> linkers features a medium-range-ordered hexagonal struc-



Scheme 5. Schematic and ideal representation of the hexagonal packing of the organic units of HS6 self-assembled into columns and interconnected to the silica network (not represented for clarity).



ture. The threefold symmetry results in a planar geometry of organic units as we reported previously<sup>[15]</sup> on the selfassembling of P5 in a columnar structure directed by hydrogen bonding between urea groups and  $\pi$  stacking between coplanar aromatic rings. Such a self-assembly process results in a hexagonal structure distinguished by a cell parameter a, which is correlated to the diameter of a planar molecule (Scheme 5). With a third urea group, organic units cannot self-assemble along the stacking axis in the case of  $C_3$ linkers, which are too short and cannot counterbalance strains induced by the formation of the Si-O-Si linkages. Despite its flexibility, the C<sub>11</sub> linker favours a better organisation when combined with the threefold-symmetry arylene groups. It might result from the presence of three urea groups that provide further hydrogen bonds rather than in the case of the bis(functional) units. Therefore, it preferentially directs the formation of the silica network along the stacking direction of P6. Moreover, the nanostructure of HS6 is also favoured by a lower condensation rate of the silica network than in the case of HS5, although both hybrid silicas have been synthesised under similar experimental conditions.

#### Conclusion

We have presented six new organosilane precursors bearing organic units with different abilities to self-organise and to address the nanostructure of hybrid silica. Whereas weak intermolecular interactions are known to control the self-assembly of organic units that are interconnected to the silica network, the formation of the silica network results in strains that tend to disfavour the organisation of the organic units. Therefore, organic units with strong intrinsic self-assembly properties lead to the highest ordering of hybrid bridged silsesquioxanes. The organisation of the organic unit is mainly controlled by the conformation of the aromatic rings, the intermolecular hydrogen bonding between urea groups, the length of the alkylene linker and the number of triethoxysilyl groups linked to the organic unit. Bifunctional precursors led to the formation of long-rangeordered lamellar structures, which are favoured by a semirigid main unit that contains coplanar aromatic rings and short alkylene chains. In contrast, a trifunctional organic unit with a threefold symmetry favours the formation of a hexagonal structure when long alkylene linkers are used.

#### **Experimental Section**

**Chemicals:** 4,4'-Diaminobiphenyl, 4,4'-methylenedianiline, (3-isocyanopropyl)triethoxysilane and (3-aminopropyl)triethoxysilane were purchased from Aldrich. (10-Isocyanodecyl)triethoxysilane,<sup>[16,22]</sup> (11-aminoundecyl)triethoxysilane,<sup>[23]</sup> 1,3,5-triisocyanobenzene<sup>[21]</sup> and 1,3,5-tris{[3-(triethoxysilyl)propyl]ureido}benzene<sup>[15]</sup> (**P5**) were synthesised as reported previously. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from CaH<sub>2</sub> and pentane from LiAlH<sub>4</sub>. The molecular precursors were synthesised in Schlenk tubes under nitrogen. Distilled water, tetrahydrofuran (THF), dichloromethane and dimethyl sulfoxide (DMSO) were used without any further purification for the synthesis of the hybrid silsesquioxanes and were stored under nitrogen at 4  $^{\circ}$ C.

Techniques: Melting-point determinations were performed with an Electrothermal IA9000 Series apparatus. Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon-Vernaison (France). Mass spectra were measured with a JEOL JMS-DX 300 mass spectrometer. FTIR spectra were recorded from KBr pellets using a Perkin-Elmer 1000 instrument.  $^1\text{H},\,^{13}\text{C}$  and  $^{29}\text{Si}$  liquid-phase NMR spectra were recorded with a Bruker AC-200 or AC-250, with deuterated chloroform and DMSO as solvents. Chemical shifts,  $\delta$ , were indexed in ppm with respect to tetramethylsilane. 13C and 29Si cross-polarisation magicangle spinning (CP-MAS) solid-state NMR spectra were recorded with a Bruker FT AM 400 instrument. Condensation rates of the silica network were calculated by integrating the peak area of each  $T^n$  signal. Specific surface areas were measured by nitrogen adsorption/desorption and by Brunauer-Emmett-Teller (BET) analysis with a Micrometics Gemini 2375 apparatus. SEM images were obtained with a JEOL 6300F microscope. TEM studies were performed with a JEOL 1200EX II. X-ray diffraction measurements and data treatment were performed at the Laboratoire Charles Coulomb in Montpellier (France). The X-ray diffraction experiments were carried out on solid powders in glass capillaries (1 mm diameter) in a transmission configuration. A copper rotating anode X-ray source (4 kW) with a multilayer focusing "Osmic" monochromator that produced high flux (10<sup>8</sup> photons s<sup>-1</sup>) and pinhole collimation was employed. An "imaging plate" 2D detector was used, and the data obtained were radially averaged to yield the diffracted intensity as a function of the wave vector q. The diffracted intensity was corrected for exposition time, transmission and the background scattering that arises from an empty capillary.

The value of  $d_{hkl}$  can be calculated from Bragg's law [Equation (1)] with  $2\theta$ , the diffraction angle and  $\lambda_{Cu} = 1.54$  Å:

$$2d_{hkl}\sin\theta = \lambda \tag{1}$$

The value of q is related to  $\theta$  by the relation according to Equation (2):

$$q = 4\pi \sin\theta / \lambda \tag{2}$$

From Equations (1) and (2), we can deduce Equation (3), in which  $q_{hkl}$  is the *q* value that corresponds to the associated Bragg peak position:

$$d_{\rm hkl} = 2\pi/q^{hkl} \tag{3}$$

#### Synthesis of the Molecular Precursors

**Precursor P1:** 4,4'-Diaminobiphenyl (920 mg, 5 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) in a Schlenk tube under nitrogen. (3-Isocyanopropyl)triethoxysilane (2.59 g, 10.5 mmol) was added dropwise with a syringe, and the reaction mixture was stirred overnight. The solvent was removed under vacuum. The solid obtained was washed with dry pentane to remove the excess amount of isocyanate and then dried under vacuum to give a white powder. Yield: 75% (2.5 g, 3.69 mmol). M.p. 220 °C. <sup>1</sup>H NMR (200 MHz, [D<sub>6</sub>]DMSO): δ = 0.56 (t, 4 H, CH<sub>2</sub>Si), 1.15 (t, 18 H, CH<sub>3</sub>), 1.48 (qt, 4 H, CH<sub>2</sub>), 3.07 (qd, 4 H, NCH<sub>2</sub>), 3.73 (qd, 12 H, OCH<sub>2</sub>), 6.17 (m, 2 H, N*H*), 7.44 (s, 8 H, *H*<sub>ar</sub>), 8.44 (m, 2 H, N*H*) ppm. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ = 7.2 (CH<sub>2</sub>Si), 18.1 (CH<sub>3</sub>), 23.3 (CH<sub>2</sub>), 41.7 (CH<sub>2</sub>N), 57.6 (CH<sub>2</sub>O), 117.8 and 126.0 (CH<sub>ar</sub>), 132.5 and 139.3 (*C*<sub>ar</sub>), 155.1 (CO) ppm. <sup>29</sup>Si NMR (50 MHz, CDCl<sub>3</sub>): δ = -45.2 ppm. IR (KBr):  $\tilde{v} = 563$ , 1592 (δ<sub>NH</sub>), 1638 (v<sub>CO</sub>), 3321 (v<sub>NH</sub>)

cm<sup>-1</sup>. MS (FAB): m/z (%) = 678 (60).  $C_{32}H_{54}N_4O_8Si_2$  (678.97): calcd. C 56.61, H 8.02, N 8.26; found C 56.78, H 8.05, N 7.92.

Precursor P2: 4,4'-Methylenedianiline (500 mg, (2.52 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) in a Schlenk tube under nitrogen. (3-Isocyanopropyl)triethoxysilane (1.38 g, 5.59 mmol) was added dropwise with a syringe, and the reaction mixture was stirred overnight. The solvent was removed under vacuum. The solid obtained was washed with dry pentane to remove the excess amount of isocyanate and then dried under vacuum to give a white powder. Yield: 88% (1.54 g, 2.22 mmol). M.p. 194 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 0.64$  (t, 4 H, CH<sub>2</sub>Si), 1.21 (t, 18 H, CH<sub>3</sub>), 1.68 (m, 4 H, CH<sub>2</sub>), 3.24 (qd, 4 H, CH<sub>2</sub>), 3.80 (qd, 12 H, OCH<sub>2</sub>) and (m, 2 H, CH<sub>2</sub>), 5.08 (t, 2 H, NH), 6.39 (s, 2 H, NH), 7.15 (dd, 8 H, H<sub>ar</sub>) ppm. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.8 (CH<sub>2</sub>Si), 18.3 (CH<sub>3</sub>), 23.6 and 42.8 (CH<sub>2</sub>), 58.4 (CH<sub>2</sub>O), 120.3 and 129.3 (CH<sub>ar</sub>), 135.6 and 137.0 (Car), 156.8 (CO) ppm. <sup>29</sup>Si NMR (50 MHz, [D<sub>6</sub>]-DMSO):  $\delta = -45.2$  ppm. IR (KBr):  $\tilde{v} = 1567, 1594 \ (\delta_{\rm NH}), 1644$  $(v_{CO})$ , 3325  $(v_{NH})$  cm<sup>-1</sup>. MS (FAB): m/z (%) = 647 (25) [M -EtO]<sup>+</sup>. C<sub>33</sub>H<sub>56</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>2</sub> (693.00): calcd. C 57.19, H 8.15, N 8.08; found C 57.22, H 8.12, N 8.32.

Precursor P3: 4,4'-Diaminobiphenyl (500 mg, 2.72 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) in a Schlenk tube under nitrogen. (10-Isocyanodecyl)triethoxysilane (2.44 mg, 7.07 mmol) was added dropwise with a syringe, and the reaction mixture was stirred overnight. The solvent was removed under vacuum. The solid obtained was washed with dry pentane to remove the excess amount of isocyanate and then dried under vacuum to give a white powder. Yield: 69% (1.63 g, 1.86 mmol). M.p. 233 °C. <sup>1</sup>H NMR (200 MHz,  $[D_6]DMSO$ :  $\delta = 0.54$  (t, 4 H,  $CH_2Si$ ), 1.14 (t, 18 H,  $CH_3$ ), 1.2 to 1.4 (m, 32 H, CH<sub>2</sub>), 3.07 (t, 4 H, CH<sub>2</sub>NH), 3.72 (qd, 12 H, OCH<sub>2</sub>), 6.10 (t, 2 H, NH), 7.45 (s, 4 H,  $H_{ar}$ ), 8.42 (t, 2 H, NH) ppm. <sup>13</sup>C NMR (50 MHz,  $[D_6]DMSO$ ):  $\delta = 10.4$  (CH<sub>2</sub>Si), 18.3 (CH<sub>3</sub>), 22.8 and 27.3 (CH2), 29.3 to 29.6 (5 CH2), 30.5 and 33.2 (CH2), 58.3 (CH<sub>2</sub>O), 118.2 and 126.3 (CH<sub>ar</sub>), 132.0 and 139.4 (C<sub>ar</sub>), 155.3 (CO) ppm. <sup>29</sup>Si NMR (50 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = -45.0 ppm. MS (FAB): m/z (%) = 875 (60). IR (KBr):  $\tilde{v}$  = 1555, 1585 ( $\delta_{\rm NH}$ ), 1637 ( $v_{\rm CO}$ ), 3330 (v<sub>NH</sub>) cm<sup>-1</sup>. C<sub>46</sub>H<sub>82</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>2</sub> (875.35): calcd. C 63.12, H 9.44, N 6.40; found C 63.38, H 9.30, N 6.62.

Precursor P4: 4,4'-Methylenedianiline (500 mg, 2.52 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) in a Schlenk tube under nitrogen. (10-Isocyanodecyl)triethoxysilane (1.93 g, 5.59 mmol) was added dropwise with a syringe, and the reaction mixture was stirred overnight. The solvent was removed under vacuum. The solid obtained was washed with dry pentane to remove the excess amount of isocyanate and then dried under vacuum to give a white powder. Yield: 85% (1.91 g, 2.15 mmol). M.p. 172 °C. <sup>1</sup>H NMR (200 MHz, [D<sub>6</sub>]-DMSO):  $\delta = 0.63$  (t, 4 H, CH<sub>2</sub>Si), 1.22 (t, 18 H, CH<sub>3</sub>), 1.25 to 1.4 (m, 28 H, CH<sub>2</sub>), 1.50 (m, 4 H, CH<sub>2</sub>), 3.21 (qd, 4 H, CH<sub>2</sub>), 3.70 (s, 2 H, CH<sub>2</sub>), 3.81 (qd, 12 H, OCH<sub>2</sub>), 5.68 (t, 2 H, NH), 7.02 (dd, 8 H, H<sub>ar</sub>), 7.08 (s, 2 H, NH) ppm. <sup>13</sup>C NMR (50 MHz, [D<sub>6</sub>]DMSO):  $\delta = 10.4$  (CH<sub>2</sub>Si), 18.3 (CH<sub>3</sub>), 22.8, 27.2, 29.3, 29.5, 29.6, 29.65, 29.7, 30.4, 33.2, 40.3 (CH<sub>2</sub>), 58.3 (CH<sub>2</sub>O), 120.0 and 129.2 (CH<sub>ar</sub>), 135.3 and 137.2 (Car), 157.2 (CO) ppm. <sup>29</sup>Si NMR (50 MHz, [D<sub>6</sub>]-DMSO):  $\delta = -45.0$  ppm. IR (KBr):  $\tilde{v} = 1568$ , 1593 ( $\delta_{NH}$ ), 1635  $(v_{CO})$ , 3319  $(v_{NH})$  cm<sup>-1</sup>. MS (FAB): m/z (%) = 844 (57) [M -EtO]<sup>+</sup>. C<sub>47</sub>H<sub>84</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>2</sub> (889.37): calcd. C 63.47, H 9.52, N 6.30; found C 63.62, H 9.45, N 6.71.

**Precursor P6:** 1,3,5-Triisocyanobenzene (240 mg, 1.23 mmol) was dissolved in  $CH_2Cl_2$  (40 mL) in a Schlenk tube under nitrogen. (11-Aminoundecyl)triethoxysilane (1.36 g, 4.07 mmol) was added dropwise with a syringe, and the reaction mixture was stirred overnight. The solvent was removed under vacuum. The solid obtained was

washed with dry pentane to remove the excess amount of isocyanate and then dried under vacuum to give a yellow powder. Yield: 72% (2.05 g, 1.7 mmol). M.p. 180 °C. <sup>1</sup>H NMR (200 MHz, [D<sub>6</sub>]-DMSO):  $\delta = 0.54$  (t, 6 H, CH<sub>2</sub>Si), 1.14 (t, 27 H, CH<sub>3</sub>), 1.25 (m, 54 H, CH<sub>2</sub>), 3.03 (qd, 6 H, NCH<sub>2</sub>), 3.73 (qd 18 H, OCH<sub>2</sub>), 5.94 (t, 3 H, NH), 7.09 (m, 3 H, H<sub>ar</sub>), 8.25 (s, 3 H, NH) ppm. <sup>13</sup>C NMR (50 MHz, [D<sub>6</sub>]DMSO):  $\delta = 9.8$  (CH<sub>2</sub>Si), 18.1 (CH<sub>3</sub>), 22.2, 26.2, 28.5, 28.7, 28.8, 28.9 (2 CH<sub>2</sub>), 29.7, 32.2, 41.2 (CH<sub>2</sub>N), 57.5 (CH<sub>2</sub>O), 99.9 (CH<sub>ar</sub>) and 140.8 (C<sub>ar</sub>), 155.0 (CO) ppm. <sup>29</sup>Si NMR (50 MHz, [D<sub>6</sub>]DMSO):  $\delta = -45.2$  ppm. IR (KBr):  $\tilde{v} = 1572 (\delta_{NH})$ , 1639 (v<sub>CO</sub>), 3313 (v<sub>NH</sub>) cm<sup>-1</sup>. MS (FAB): *m*/*z* (%) = 1155 (5) [M – EtO]<sup>+</sup>. C<sub>60</sub>H<sub>120</sub>N<sub>6</sub>O<sub>12</sub>Si<sub>3</sub> (1201.90): calcd. C 59.96, H 10.06, N 6.99; found C 59.32, H 10.19, N 7.53.

#### Syntheses of the Hybrid Bridged Silsesquioxanes

**Hybrid Silica HS1:** Precursor **P1** (142 mg, 0.21 mmol) was dissolved in THF (1.1 mL). Then distilled water (2.2 mL) was added while stirring. A white precipitate appeared. A 1 M HCl solution (36.8 μL) was added. The following molar ratio was used: **P1/**THF/ H<sub>2</sub>O/HCl, 1:65:600:0.2. After heating the reaction mixture at 80 °C, the precipitate completely dissolved in a few minutes. After 2 h, a precipitate appeared, and the mixture was aged under static conditions. After 3.5 d, the solvents were removed by filtration. The solid product was washed successively with water, ethanol and acetone and finally dried at 110 °C. A grey powder was obtained. <sup>13</sup>C NMR CP-MAS:  $\delta = 10.5$ , 24.2, 42.3, 119.4, 125.4, 130.0, 137.0, 158.4 ppm. <sup>29</sup>Si NMR CPMAS:  $\delta = -57.4$ , -66.0 ppm (T<sup>2</sup> and T<sup>3</sup> sites). N<sub>2</sub> BET surface area: 17.0 m<sup>2</sup>g<sup>-1</sup>. IR (KBr):  $\tilde{v} = 1557$ , 1597 ( $\delta_{\rm NH}$ ), 1642 (v<sub>CO</sub>) and 3324 (v<sub>NH</sub>) cm<sup>-1</sup>. Elemental analysis: found C 50.53, H 5.48, N 11.73, Si 12.70.

**Hybrid Silica HS2:** Precursor **P2** (145 mg, 0.21 mmol) was dissolved in THF (1.1 mL). Then distilled water (2.2 mL) was added while stirring. A white precipitate appeared. A 1 m HCl solution (36.8 μL) was added. The following molar ratio was used: **P2/**THF/H<sub>2</sub>O/HCl, 1:65:600:0.2. After heating the reaction mixture at 80 °C, the precipitate completely dissolved in a few minutes. After 2 h, a precipitate appeared, and the mixture was aged under static conditions. After 3.5 d, the solvents were removed by filtration. The solid product was washed successively with water, ethanol and acetone and finally dried at 110 °C. A white powder was obtained. <sup>13</sup>C NMR CPMAS:  $\delta$  = 11.9, 25.1, 36.8, 42.7, 123.4, 130.5, 132.3, 135.5, 157.9 ppm. <sup>29</sup>Si NMR CP-MAS:  $\delta$  = -57.5, -66 ppm (3 T<sup>2</sup> and T<sup>3</sup> sites). N<sub>2</sub> BET surface area: 38.2 m<sup>2</sup>g<sup>-1</sup>. IR (KBr):  $\tilde{v}$  = 1564, 1600 ( $\delta_{NH}$ ), 1635 ( $v_{CO}$ ) and 3329 ( $v_{NH}$ ) cm<sup>-1</sup>. Elemental analysis: found C 50.66, H 5.73, N 10.91, Si 11.80.

**Hybrid Silica HS3:** Precursor **P3** (148 mg, 0.17 mmol) was dissolved in DMSO (2.8 mL). Then distilled water (1.7 mL) was added while stirring. A white precipitate appeared. A 1 m HCl solution (31.3 μL) was added. The following molar ratio was used: **P3**/DMSO/H<sub>2</sub>O/HCl, 1:215:600:0.2. After heating the reaction mixture at 80 °C for 2 h, a precipitate appeared, and the mixture was aged under static conditions. After 3.5 d, the solvents were removed by filtration. The grey solid product was washed successively with water, ethanol and acetone and finally dried at 110 °C. A grey powder was obtained. <sup>13</sup>C NMR CP-MAS:  $\delta = 13.5$ , 31.3 (7 *C*), 41.0, 45.2, 119.0, 125.7, 129.9, 136.9, 157.6 ppm. <sup>29</sup>Si NMR CP-MAS:  $\delta = -45.4, -56.6, -66.7$  ppm (T<sup>1</sup>, T<sup>2</sup> and T<sup>3</sup> sites). N<sub>2</sub> BET surface area: 23.4 m<sup>2</sup>g<sup>-1</sup>. IR (KBr):  $\tilde{v} = 1555$ , 1593 ( $\delta_{NH}$ ), 1645 ( $v_{CO}$ ) and 3329 ( $v_{NH}$ ) cm<sup>-1</sup>.

**Hybrid Silica HS4:** Precursor **P4** (151 mg, 0.17 mmol) was dissolved in DMSO (2.8 mL). Then distilled water (1.7 mL) was added while stirring. A white precipitate appeared. A 1 m HCl solution

(31.3 µL) was added. The following molar ratio was used: **P4**/ DMSO/H<sub>2</sub>O/HCl, 1:215:600:0.2. After heating the reaction mixture at 80 °C for 2 h, a precipitate appeared, and the mixture was aged under static conditions. After 3.5 d, the solvents were removed by filtration. The solid product was washed successively with water, ethanol and acetone and finally dried at 110 °C. A grey powder was obtained. <sup>13</sup>C NMR CP-MAS:  $\delta = 13.5, 26.6, 31.6$  (8 *C*), 41.6, 124.0, 130.4, 132.5, 135.9, 157.8 ppm. <sup>29</sup>Si NMR CP-MAS: -48.4, -57.2, -67.5 ppm (T<sup>1</sup>, T<sup>2</sup> and T<sup>3</sup> sites). N<sub>2</sub> BET surface area: 25.6 m<sup>2</sup>g<sup>-1</sup>. IR (KBr):  $\tilde{v} = 1562, 1599$  ( $\delta_{\rm NH}$ ), 1636 (v<sub>CO</sub>) and 3328 (v<sub>NH</sub>) cm<sup>-1</sup>.

**Hybrid Silica HS5:** Precursor **P5** (125 mg, 0.14 mmol) was dissolved in THF (2.3 mL). Then distilled water (2.3 mL) was added while stirring. A white precipitate appeared. A 1 M HCl solution (43.3 μL) was added. The following molar ratio was used: **P5**/THF/H<sub>2</sub>O/HCl, 1:200:900:0.3. After heating the reaction mixture at 80 °C for 2 h, a precipitate appeared, and the mixture was aged under static conditions. After 3.5 d, the solvents were removed by filtration. The white solid product was washed successively with water, ethanol and acetone and finally dried at 110 °C. A white powder was obtained. <sup>13</sup>C NMR CP-MAS:  $\delta$  = 11.6, 24.9 and 42.7 (CH<sub>2</sub>), 105.3 and 140.6 (*C*<sub>ar</sub>), 157.1 (*C*=O) ppm. <sup>29</sup>Si NMR CPMAS: -57.3, -66.8 ppm (T<sup>2</sup> and T<sup>3</sup> sites). N<sub>2</sub> BET surface area: 0.0 m<sup>2</sup>g<sup>-1</sup>. IR (KBr):  $\tilde{v}$  = 1557 ( $\delta$ <sub>NH</sub>), 1659 (v<sub>CO</sub>) and 3403 (v<sub>NH</sub>) cm<sup>-1</sup>. Elemental analysis: found C 33.04, H 10.77, N 12.28, Si 12.54.

**Hybrid Silica HS6:** Precursor **P6** (125 mg, 0.1 mmol) was dissolved in DMSO (2.8 mL). Then distilled water (1.7 mL) was added while stirring. A white precipitate appeared. A 1 M HCl solution (30.8 μL) was added. The following molar ratio was used: **P6/** DMSO/H<sub>2</sub>O/HCl, 1:365:900:0.3. After heating the reaction mixture at 80 °C for 2 h, a precipitate appeared, and the mixture was aged under static conditions. After 3.5 d, the solvents were removed by filtration. The solid product was washed successively with water, ethanol and acetone and finally dried at 110 °C. A grey powder was obtained. <sup>13</sup>C NMR CP-MAS:  $\delta = 14.6$  (*C*H<sub>2</sub>), 18.5 (*C*H<sub>3</sub>), 30.9 (9 *C*H<sub>2</sub>), 40.6 (*C*H<sub>2</sub>), 58.3 (*C*H<sub>2</sub>O), 110.3 and 140.0 (*C*<sub>ar</sub>), 157.6 (*C*=O) ppm. <sup>29</sup>Si NMR CP-MAS: -45.7, -57.0, -65.6 ppm (T<sup>2</sup> and T<sup>3</sup> sites). N<sub>2</sub> BET surface area: 0.0 m<sup>2</sup>g<sup>-1</sup>. IR (KBr):  $\tilde{v} = 1574$ ( $\delta_{NH}$ ), 1645 (v<sub>CO</sub>) and 3330 (v<sub>NH</sub>) cm<sup>-1</sup>. Elemental analysis: found C 57.53, H 8.77, N 8.80, Si 9.41.

**Supporting Information** (see footnote on the first page of this article): <sup>29</sup>Si solid-state NMR spectra of hybrid silica **HS2** and **HS4** (Figure S1) and <sup>13</sup>C solid-state spectra NMR of hybrid silica **HS1– 3** (Figure S2).

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- a) R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. Wong Chi Man, *Chem. Mater.* **1992**, *4*, 1217–1224; b) K. J. Shea, D. A. Loy, O. W. Webster, *Chem. Mater.* **1989**, *1*, 572–574.
- [2] C. J. Brinker, G. W. Scherer, Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing, Academic Press, San Diego, 1990.
- [3] C. Sanchez, F. Ribot, New J. Chem. 1994, 18, 1007-1047.
- [4] O. J. Dautel, J. P. Lere-Porte, J. J. E. Moreau, M. Wong Chi Man, *Chem. Commun.* 2003, 2662–2663.



- [5] a) I. Karatchevtseva, D. J. Cassidy, M. Wong Chi Man, D. R. G. Mitchell, J. V. Hanna, C. Carcel, C. Bied, J. J. E. Moreau, J. R. Bartlett, *Adv. Funct. Mater.* 2007, *17*, 3926–3932; b) J. Graffion, A. M. Cojocariu, X. Cattoen, R. A. S. Ferreira, V. R. Fernandes, P. S. Andre, L. D. Carlos, M. Wong Chi Man, J. R. Bartlett, *J. Mater. Chem.* 2012, *22*, 13279–13285.
- [6] a) A. Zamboulis, N. Moitra, J. J. E. Moreau, X. Cattoën, M. Wong Chi Man, J. Mater. Chem. 2010, 20, 9322–9338; b) A. Monge-Marcet, R. Pleixats, X. Cattoën, M. Wong Chi Man, Catal. Sci. Technol. 2011, 1, 1544–1563; c) X. Elias, R. Pleixats, M. Wong Chi Man, J. J. E. Moreau, Adv. Synth. Catal. 2006, 348, 751–762; d) S. S. Nobre, X. Cattoën, R. A. S. Ferreira, M. Wong Chi Man, L. D. Carlos, Phys. Status Solidi RRL 2010, 4, 55–57; e) J. Graffion, X. Cattoën, V. Freitas, R. A. S. Ferreira, M. Wong Chi Man, L. D. Carlos, J. Mater. Chem. 2012, 22, 6711–6715; f) L. Fertier, C. Théron, C. Carcel, P. Trens, M. Wong Chi Man, Chem. Mater. 2011, 23, 2100–2106.
- [7] a) X. Sallenave, O. J. Dautel, G. Wantz, P. Valvin, J. P. Lère-Porte, J. J. E. Moreau, *Adv. Funct. Mater.* 2009, *19*, 404–410;
  b) E. Besson, A. Mehdi, A. Van der Lee, H. Chollet, C. Réyé, R. Guilard, R. J. P. Corriu, *Chem. Eur. J.* 2010, *16*, 10226–10233; c) N. Mizoshita, T. Tani, S. Inagaki, *Chem. Soc. Rev.* 2011, *40*, 789–800; d) N. Mizoshita, T. Tani, H. Shinokubo, S. Inagaki, *Angew. Chem. Int. Ed.* 2012, *51*, 1156–1160.
- [8] a) S. Fujita, S. Inagaki, *Chem. Mater.* 2008, 20, 891–908; b) T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* 1999, 402, 867–871; c) B. J. Melde, B. T. Holland, C. F. Blanford, A. Stein, *Chem. Mater.* 1999, 11, 3302–3308; d) A. Sayari, S. Hamoudi, Y. Yang, I. L. Moudrakovski, J. R. Ripmeester, *Chem. Mater.* 2000, 12, 3857–3863; e) S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* 2002, 416, 304–307.
- [9] a) B. Boury, R. J. P. Corriu, V. Le Strat, P. Delord, M. Nobili, Angew. Chem. 1999, 111, 3366; Angew. Chem. Int. Ed. 1999, 38, 3172–3175; b) B. Boury, R. J. P. Corriu, Chem. Commun. 2002, 795–802; c) G. Cerveau, C. Chorro, R. Corriu, C. Lepeytre, J. P. Lere-Porte, J. J. E. Moreau, P. Thépot, M. Wong Chi Man in Hybrid Organic-Inorganic Composites (Eds.: J. E. Mark, C. Y. C. Lee, P. A. Bianconi), ACS Symposium Series 585, American Chemical Society, Washington, DC, 1995, pp. 210–225.
- [10] 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, J. L. Bantignies, P. Dieudonné, J. L. Sauvajol, J. Am. Chem. Soc. 2001, 123, 7957–7958; c) J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, P. Dieudonné, J. L. Bantignies, J. L. Sauvajol, Chem. Eur. J. 2005, 11, 1527–1537; d) T. Kishida, N. Fujita, K. Sada, S. Shinkai, J. Am. Chem. Soc. 2005, 127, 7298–7299; e) K. J. C. van Bommel, A. Friggeri, S. Shinkai, Angew. Chem. 2003, 115, 1010; Angew. Chem. Int. Ed. 2003, 42, 980–999; f) C. Y. Bao, R. Lu, M. Jin, P. C. Xue, C. H. Tan, T. H. Xu, G. F. Liu, Y. Y. Zhao, J. Nanosci. Nanotechnol. 2006, 6, 2560–2565; g) X. Zhou, S. Yang, C. Yu, Z. Li, X. Yan, Y. Cao, D. Zhao, Chem. Eur. J. 2006, 12, 8484–8490; h) R. Hu, Q. Zhu, W. Chen, H. Liu, B. Yao, J. Zhan, J. Hao, C. C. Han, Polymer 2012, 53, 267–271.
- [11] a) A. Shimojima, K. Kuroda, Angew. Chem. 2003, 115, 4191; Angew. Chem. Int. Ed. 2003, 42, 4057–4060; b) A. Shimojima, Z. Liu, T. Ohsuna, O. Terasaki, K. Kuroda, J. Am. Chem. Soc. 2005, 127, 14108–14116; c) L. D. Carlos, V. de Zea Bermudez, V. S. Amaral, S. C. Nunes, N. J. O. Silva, R. A. S. Ferreira, J. Rocha, C. V. Santilli, D. Ostrovskii, Adv. Mater. 2007, 19, 341– 348; d) M. Fernandes, R. A. S. Ferreira, X. Cattoën, L. D. Carlos, M. Wong Chi Man, V. De Zea Bermudez, J. Sol-Gel Sci. Technol. 2012, DOI: 10.1007/s10971-012-2739-1; e) H. Muramatsu, R. Corriu, B. Boury, J. Am. Chem. Soc. 2003, 125, 854– 855; f) J. Alauzun, A. Mehdi, C. Réyé, R. J. P. Corriu, J. Mater. Chem. 2005, 15, 841–843; g) E. Ruiz-Hitzky, S. Letaïef, V. Prévot, Adv. Mater. 2002, 14, 439–443; h) D. Lin, L. Hu, H. You, R. J. J. Williams, Eur. Polym. J. 2011, 47, 1526–1533.

- [12] a) J. J. E. Moreau, B. P. Pichon, C. Bied, M. Wong Chi Man, J. Mater. Chem. 2005, 15, 3929–3936; b) G. Arrachart, A. Bendjerriou, C. Carcel, J. J. E. Moreau, M. Wong Chi Man, New J. Chem. 2010, 34, 1436–1440; c) M. Fernandes, S. S. Nobre, Q. Xu, C. Carcel, J. N. Cachia, X. Cattoen, J. M. Sousa, R. A. S. Ferreira, L. D. Carlos, C. V. Santilli, M. Wong Chi Man, V. de Zea Bermudez, J. Phys. Chem. B 2011, 115, 10877–10891.
- [13] J. J. E. Moreau, L. Vellutini, P. Dieudonné, M. Wong Chi Man, J. L. Bantignies, J. L. Sauvajol, C. Bied, J. Mater. Chem. 2005, 15, 4943–4948.
- [14] a) J. J. E. Moreau, B. P. Pichon, M. Wong Chi Man, C. Bied, H. Pritzkow, J. L. Bantignies, P. Dieudonné, J. L. Sauvajol, Angew. Chem. 2004, 116, 205; Angew. Chem. Int. Ed. 2004, 43, 203–206; b) P. Dieudonné, M. Wong Chi Man, B. P. Pichon, L. Vellutini, J. L. Bantignies, C. Blanc, G. Creff, S. Finet, J. L. Sauvajol, C. Bied, J. J. E. Moreau, Small 2009, 5, 503–510.
- [15] B. P. Pichon, M. Wong Chi Man, P. Dieudonné, J. L. Bantignies, C. Bied, J. L. Sauvajol, J. J. E. Moreau, *Adv. Funct. Mater.* 2007, *17*, 2349–2355.
- [16] Q. H. Xu, J. J. E. Moreau, M. Wong Chi Man, J. Sol-Gel Sci. Technol. 2004, 32, 111–115.
- [17] a) S. S. Nobre, C. D. S. Brites, R. A. S. Ferreira, V. de Zea Bermudez, C. Carcel, J. J. E. Moreau, J. Rocha, M.

Wong Chi Man, L. D. Carlos, *J. Mater. Chem.* **2008**, *18*, 4172–4182; b) S. S. Nobre, X. Cattoen, R. A. S. Ferreira, C. Carcel, V. de Zea Bermudez, M. Wong Chi Man, L. D. Carlos, *Chem. Mater.* **2010**, *22*, 3599–3609; c) M. Fernandes, X. Cattoën, V. de Zea Bermudez, M. Wong Chi Man, *CrystEngComm* **2011**, 1410–1415.

- [18] J. L. Bantignies, L. Vellutini, D. Maurin, P. Hermet, P. Dieudonné, M. Wong Chi Man, J. R. Bartlett, C. Bied, J. L. Sauvajol, J. J. E. Moreau, J. Phys. Chem. B 2006, 110, 15797–15802.
- [19] a) R. A. Vaia, R. K. Teukolsky, E. P. Giannelis, *Chem. Mater.* **1994**, *6*, 1017–1022; b) R. G. Snyder, H. L. Strauss, C. A. Elliger, *J. Phys. Chem.* **1982**, *86*, 5145–5150.
- [20] J. Jadzyn, M. Stockhausen, B. Zywucki, J. Phys. Chem. 1987, 91, 754–757.
- [21] J. J. van Gorp, J. A. J. M. Vekemans, E. W. Meijer, J. Am. Chem. Soc. 2002, 124, 14759–14769.
- [22] P. Joly, N. Ardes-Guisot, S. Kar, M. Granier, J. O. Durand, O. Melnyk, *Eur. J. Org. Chem.* 2005, 2473–2480.
- [23] B. P. Pichon, M. Wong Chi Man, C. Bied, J. J. E. Moreau, J. Organomet. Chem. 2006, 691, 1126–1130.

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