Shape-Controlled Bridged Silsesquioxanes: Hollow Tubes and Spheres

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Dedicated to Professor Dr. Walter Siebert on the occasion of his 65th birthday

Abstract: A new approach for the morphological control of bridged silsesquioxanes has been achieved by the hydrolysis of silylated organic molecules bearing urea groups. The urea groups are responsible for the auto-association of the molecules through intermolecular hydrogen-bonding interactions. The self-assembly leads to supramolecular architectures that have the ability to direct the organization of hybrid silicas under controlled hydrolysis. The hydrolysis of the chiral diureido derivatives of *trans*-(1,2)-diaminocyclohexane **1** under basic conditions has been examined. The solid-state NMR spectra (^{29}Si and ^{13}C) showed the hybrid nature of these materials with wholly preserved Si–C covalent bonds throughout the silicate network. Hybrid silicas with hollow tubular morphologies were obtained by the hydrolysis of the enantiomerically pure compounds, (*R*,*R*)-**1** or (*S*,*S*)-**1**, whereas the corresponding racemic mixture, rac-**1**, led to a hybrid with ball-like structures. The tubular shape is likely to result from a combination of two phenomena: the auto-association abilities and a self-templating structuration of the hybrid materials by the organic crystalline precursor. Electronic microscopy techniques (SEM and TEM) gave evidence for the self-templating pathway. The formation of the ball-like structures occurs through a usual nucleation growth phenomenon owing to a higher solubility of the corresponding crystals in the same medium.

Keywords: bridged silsesquioxanes · hybrid silica · nanostructures · self-assembly · sol-gel

Introduction

The increasing demand for new techniques to afford miniaturized devices has stimulated materials chemists to direct their research interest towards the design of nanostructured materials with tailored chemical and physical properties. Hybrid organic–inorganic materials produced by the sol-gel process[1–3] are developing into a considerable field of interest for the materials community and offer the opportunity to achieve such nanostructured materials. Bridged silsesquioxanes were introduced more than a decade ago[4, 5] and represent attractive hybrid materials with a wide variety of tunable properties, because of the organic fragment covalently linked to the silicate framework.[4–11] The solid-state properties and morphology depend not only on the organic component, but also on the synthetic conditions of the hydrolysis–condensation process (solvent, temperature, catalyst, etc.). Growing attention is being paid to shape-controlled materials with the aim of creating new composites with structuration at different scales.

Organogels consist of a self-assembly of organic molecules[12] and have been used as templating agents to transcribe their supramolecular architectures to produce inorganic silicas.[13–16] Helical fibers were successfully obtained by the hydrolysis of tetraethoxysilane (TEOS) in the presence of such templates.[13a–d, 14] Interestingly, a chirality transcription from a chiral supramolecular template to silicas was achieved leading to right- and left-handed tubular helices. Hollow tubular[13e,f] and vesicular silicates[17] have also been produced by the sol-gel hydrolysis of TEOS with organogels. This method has been applied to other inorganic materials. The synthesis of a helical morphology with cadmium sulfide (CdS)[15] and also with several transiton metal oxides (Ti, Ta, V)[16] have recently been reported. In all these cases, the materials are purely inorganic.

The development of surfactant-templated inorganic mesostructured materials[18–20] has led to considerable focus on the formation of highly organized, mesoporous hybrid silicas.[21–25] A bioinspired organic–inorganic hybrid silsesquioxane developed as bilayers of vesicular nanoparticles, with the use of monosilylated lipid vesicles, by means of this approach.[25]

In the recent years, periodic, mesoporous, bridged silsesquioxanes have been obtained by a similar templated route.[26–32] Interestingly highly ordered, hybrid mesoporous

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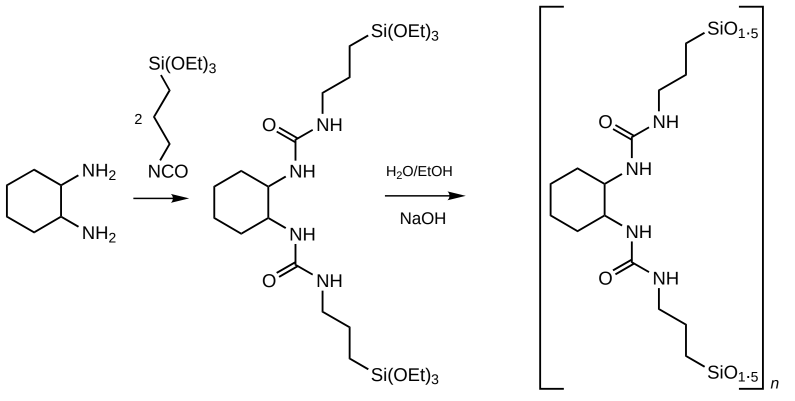
silicates with well-defined external morphologies have been achieved by this method.[33]

Recently, we developed a new approach based on hydrogen bonding of bis-urea groups to morphologically-controlled bridged silsesquioxanes.[34–35] The use of appropriate silylated organic molecules capable of forming supramolecular architectures led, after hydrolytic condensation, to lamellar solids with architectures at different scales.[34] Interestingly, a chiral silylated diureidocyclohexyl derivative (Scheme 1) led to helical hybrids with controlled handedness according to the configuration of the organic substructure.[35] Whereas in acidic aqueous medium right- or left-handed helical fibers formed from the hydrolysis of the pure enantiomers (*R*,*R*)-**1** or (*S*,*S*)-**1**, respectively, the hydrolysis of the racemic mixture of precursors rac-**1** in the same medium led to a featureless granular solid. This chirality transcription from the enantiopure precursors to the hybrid material was found to be dependent on the hydrolysis–condensation conditions. The morphologies of these hybrids do not only arise from the intrinsic properties of the organic fragment, but also depend on the reaction medium and the temperature at which the reaction is performed. These results prompted us to explore the role of the reaction conditions for the hydrolysis of these hybrid precursors. We examined the hydrolysis of these compounds in the presence of a base (NaOH) in a solvent mixture (ethanol and water). From these studies, we report, in this paper, the synthesis of tubular and spherical hybrid silicas by the hydrolysis of **1** (Scheme 1) according to a new mechanism involving both templating and self-association properties.



(*R*,*R*)-**1**, (*S*,*S*)-**1**, or rac-**1**

(*R*,*R*)-**1HS**, (*S*,*S*)-**1HS**, or rac-**1HS**

Scheme 1. Synthesis of the molecular precursors and hybrid silicas.

Results and Discussion

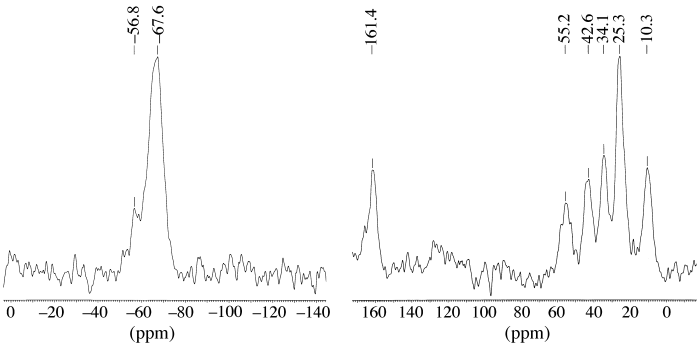
Synthesis of the molecular precursors: The molecular precursors **1** were synthesized in CH_2Cl_2 by the reaction of 3-isocyanatopropyltriethoxysilane with the pure enantiomers, *trans*-(1*R*,2*R*)- and *trans*-(1*S*,2*S*)-diaminocyclohexane, and also with the corresponding racemic compound leading respectively to (*R*,*R*)-**1**, (*S*,*S*)-**1** and rac-**1** (Scheme 1) in high yield (84–93%).

Compounds (*R*,*R*)-**1** and (*S*,*S*)-**1** gelate common organic solvents (cyclohexane, toluene, and THF) at very low concentration (1–5 $mg\,mL^{-1}$), whereas a greater amount is needed for rac-**1** ($\sim$40 $mg\,mL^{-1}$) to form the organogel.[34, 36] This phenomenon typically occurs because of the auto-association of the molecules through hydrogen bonding of the urea groups in these solvents. Higher intermolecular associations in the case of (*R*,*R*)-**1** and (*S*,*S*)-**1** relative to rac-**1** are evidenced by the FTIR spectra of the compounds in chloroform. Characteristic vibrations are observed at 1574 (δ_{NH}), 1631 (ν_{CO}) 3313 cm^{-1} (ν_{NH}) for (*R*,*R*)-**1**, whereas the corresponding absorptions are at 1570 (δ_{NH}), 1638 (ν_{CO}) and 3348 cm^{-1} (ν_{NH}) for rac-**1**. The frequency difference between the amide I (ν_{CO}) and amide II (δ_{NH}) bands of (*R*,*R*)-**1** ($\Delta\nu$ = 57 cm^{-1}) is smaller than that of rac-**1** ($\Delta\nu = 68$ cm^{-1}). Moreover, the NH stretch band (δ_{NH}) is located at a lower frequency value for (*R*,*R*)-**1** than that of rac-**1**. These observations are in accord for a better aggregation of (*R*,*R*)-**1** through hydrogen bonding than rac-**1**.[37, 38a] The easier gel formation in the case of the pure enantiomers is attributable to the presence of much favored intermolecular hydrogen bonding, as already observed in similar derivatives between the urea groups.[38] The resulting supramolecular architectures usually develop as fibers or ribbons and have the ability to form an entangled network in solvents to end up with an organogel.

Synthesis of the tubular hybrid silica: The hydrolysis of (*R*,*R*)-**1** or (*S*,*S*)-**1** was performed in a 2:5 volume ratio of ethanolic/aqueous medium to give the corresponding hybrid silicas (*R*,*R*)-**1HS** and (*S*,*S*)-**1HS**, respectively (Scheme 1). The precursor was first completely dissolved in dry ethanol, and when water was added a white precipitate appeared. An aqueous solution of NaOH (3 M) was then immediately added to attain pH 12, and the mixture was heated at 80 °C for 6 days. It should be noted that the precipitate was not completely soluble in the reaction mixture, but after 1 hour the formation of a significant volume fraction of solid was observed. After filtration, the white solid was washed successively with water, ethanol, and acetone, and then dried at 110 °C for 6 h.

Hybrid silicas (*R*,*R*)-**1HS** and (*S*,*S*)-**1HS** display identical characteristics. The elementary analyses confirm the presence of the organic moieties in the silica network (N/Si = 2).

Solid-state NMR spectra show that these materials consist of an organic–inorganic network and are represented for (*R*,*R*)-**1HS** in Figure 1. The ^{29}Si NMR spectrum (Figure 1a) exhibits a low intensity signal at -56.8 ppm and a predom-



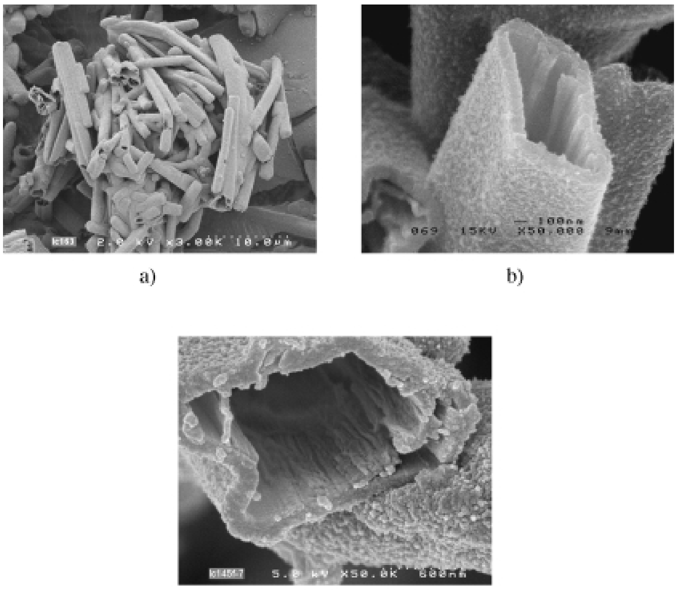
a) b)

Figure 1. Solid-state NMR of (*R*,*R*)-**1HS**: a) ^{29}Si and b) ^{13}C.

inant one at −67.6 ppm, assigned to *Si*C(OH)(OSi)$_2$ (T^2) and *Si*C(OSi)$_3$ (T^3) units, respectively; no SiO$_4$ unit (Q type) is observed. The ^{13}C CP-MAS spectrum (Figure 1b) exhibits a peak at 161 ppm (C=O) and several sp^3 carbon atoms (55.2, 42.8, 34.1, 25.3 and 10.3 ppm) characteristic of the organic fragment.

The existence of hydrogen bonding between the urea groups in these materials is evidenced by FTIR studies with vibrations at $\nu_{NH} = 3341$, $\nu_{CO} = 1634$, and $\delta_{NH} = 1574$ cm^{-1}. These values are similar to those of the helical silsesquioxanes.[35] Powder X-ray diffraction measurements showed these hybrids to be completely amorphous.

Scanning electronic microscopy (SEM) images of (*R*,*R*)-**1HS** or (*S*,*S*)-**1HS** reveal similar tubular structures (Figure 2a). Under higher magnification these tubes appear hollow and rectangular channels are often observed (Figure 2b and c). The sizes range from 0.5 – 2 µm for the external width and the length is up to 15 µm. The diameter of the channel is 0.3 – 1.6 µm and the shells are 0.1 – 0.6 µm thick. Interestingly, the inner part of the tubes consists of a lining up of fiberlike structures with a rough outer surface. No chiral morphology could be perceived from these analyses.



a) b) c)

Figure 2. SEM images of tubular hybrid silicas (*R*,*R*)-**1HS** or (*S*,*S*)-**1HS**: a) magnification × 3000; b) and c) magnification × 50000.

The transmission electronic microscopy (TEM) images of (*R*,*R*)-**1HS** are shown in Figure 3 and confirms the hollow tubular structures. Here again, long fiberlike structures 15 – 25 nm wide can be distinguished. It seems likely that these solids consist of a longitudinal juxtaposition of these fibers.

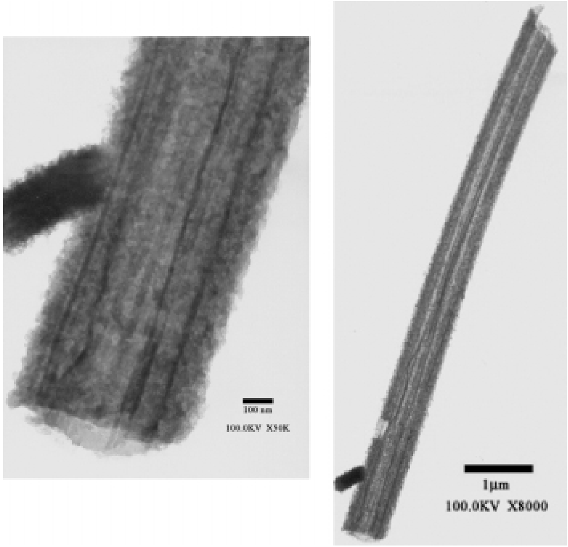


Figure 3. TEM images of tubular hybrid silicas (*R*,*R*)-**1HS** or (*S*,*S*)-**1HS**.

For a better understanding of the formation of the tubes, we analyzed the precipitate that formed at the initial stage in the EtOH/H$_2$O mixture before the addition of NaOH. It was recovered by filtration and was identified as microcrystals of the nonhydrolyzed precursor by NMR spectroscopy. At this stage no hydrolysis had occurred. SEM images of this precipitate show rectangular rodlike crystals (Figure 4) that are 2 – 12 µm long and 0.3 – 1.5 µm wide; they show an interesting size and shape similarities with the observed hollow structures in the final hybrid solid after hydrolysis.

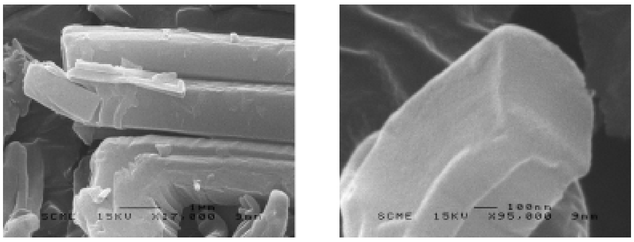


Figure 4. SEM images of microcrystals of (*R*,*R*)-**1**.

It is conceivable that the incipient crystallization is responsible for the hollow tubular morphologies of (*R*,*R*)-**1HS** or (*S*,*S*)-**1HS**. A possible mechanism might involve, at the early stages, the hydrolysis – condensation at the surface of the crystalline precursor (*R*,*R*)-**1** as soon as NaOH is added. Ethanol, which is a better solvent than water for (*R*,*R*)-**1**, is gradually released and facilitates the in-situ solubilization of the crystals in solution. The dissolved compound, which forms self-assembled fibrous structures,[35, 36] tends to condense at the external surface, causing a thickening of the walls of the materials. On this basis we presume that the hollow tubular structure results from a self-templating process of the hybrid materials by the organic crystalline precursor itself. Recently, organic crystals were used as external templates for the formation of hollow tubular silica. It formed by sol–gel deposition of silica on the outer surface of organic crystals that were subsequently removed.[39–40]

To further corroborate our assumption for the existence of the self-templating mechanism, we again performed the hydrolysis reaction and stopped it simply by filtration after one hour. The resulting sample was washed with water and dried. By carefully examining the resulting solid through TEM techniques, we were able to obtain pictures in which clear partial hydrolysis of the enantiopure compound has occurred (Figure 5).

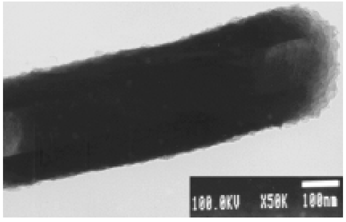


Figure 5. TEM image of tubular sample after 1 h hydrolysis of (*R*,*R*)-**1**.

A rigid rodlike stucture can be seen that is not completely transparent contrarily to the fully hydrolyzed relating hybrid solid (Figure 3). In this picture, it looks likely that the solubilization of the precursor occurs at both ends after an initial hydrolysis at the external surface of the crystal. The transparent parts of the solid correspond to areas in which the organic crystalline template has completely dissolved. The inner dark part could represent nondissolved (*R*,*R*)-**1** and the outer one can be assigned to the condensed hybrid silica. These results give additional support for the crystal self-templating process for the formation of the hollow tubes in the case of the pure enantiomers.

Synthesis of the spherical hybrid silica: For comparison we also performed the hydrolysis of the racemic mixture of precursors rac-**1** in exactly the same reaction conditions leading to rac-**1HS**.

The compound rac-**1** formed crystals that look similar in shape to those obtained from (*R*,*R*)-**1** or (*S*,*S*)-**1**, as observed by SEM images (not shown here) after the addition of water to the ethanolic solution in which rac-**1** was completely dissolved. After the addition of the aqueous solution of NaOH, the mixture was heated to 80 °C. In contrast to the pure enantiomers, a complete dissolution of the microcrystals occurred followed by the formation of a colloidal solution after 5 min; this then turned into a white precipitate with time. This observation suggests that the initial hydrolysis–condensation in the case of rac-**1** proceeds through a conventional liquid-state reaction and, hence, precludes any possibility for organic crystalline self-templating of the precursor to occur as for the pure enantiomers. The particulates only formed and grew according to the usual nucleation growth pathway.

The solid-state NMR spectra of the corresponding material, rac-**1HS**, were identical to those of the enantiopure materials with similar elementary analysis results (N/Si = 2). The hybrid obtained from rac-**1** exhibits weaker hydrogen-bonding interactions than the related hybrids arising from the pure enantiomers as observed by FTIR for the vibrations of the urea groups (3352, 1640, and 1573 cm^{-1}). This is shown by a greater $\Delta\nu$ value between the ν_{CO} and the δ_{NH} and also by the higher ν_{NH} value[37, 38a] relative to the values observed for the tubular materials.

An SEM image exclusively shows spheres with a 0.3–2 μm diameter (Figure 6). These spheres are completely dense: only dark balls are observed from TEM analysis.

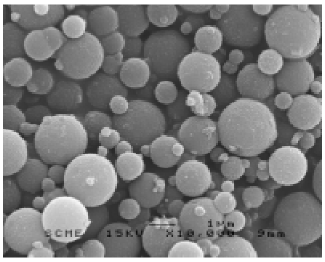


Figure 6. SEM image of spherical hybrid silica rac-**1HS**.

The different shapes are probably related to the aggregation mode during the hydrolysis–condensation steps of the precursors. While (*R*,*R*)-**1** and (*S*,*S*)-**1**, which exhibit strong self-assembly properties,[35] tend to form fiberlike aggregates during acid-mediated hydrolysis, rac-**1**, with much weaker auto-association, grows up into a featureless solid.[36] Furthermore, the complete solubility of rac-**1** at the initial stage of the reaction is in full agreement with a nontemplating pathway for the formation of the spherical solids.

Conclusion

The tubular structures represent the first shape-controlled hybrid silicas obtained by a self-templating method. Only inorganic hollow tubes were previously obtained by the sol–gel hydrolysis of metallic alkoxides and by using an external cristalline molecule as template. Our approach combines the crystal nature and the auto-association abilities of the precursor to generate interesting structured materials. The auto-association properties of the main organic group play an important role for the shape of the final solid: the strongly associated enantiopure precursors afforded hollow tubes, whereas, under the same reaction conditions, only spheres formed from the racemic mixture with weaker hydrogen-bonding interactions. The complete solubilization of rac-**1** at the beginning of the reaction accounts for the nontemplating effect during the hydrolysis–condensation step. The hollow tubes represent a new class of hybrid materials with well-defined organic substructures regularly spread on the molecular scale over the whole silica network. The incorporation of chiral units in the walls of the tubular hybrid silica may lead to materials with interesting properties and which may find applications in various domains such as molecular recognition, chromatographic separation, or enantioselective catalysts.[6a,b,d] The development of this method for the preparation of other hybrid silicas with targeted functionalities should bring to the development of new hybrid materials with sought-after properties.

Experimental Section

General information and techniques: The syntheses of the molecular precursors were carried out under nitrogen atmosphere by using a vacuum line and schlenk techniques. *trans*-(1*R*,2*R*)- and *trans*-(1*S*,2*S*)-diaminocyclohexanes were resolved according to literature[41] from a commercial *cis*/*trans* mixture of (1,2)-diaminocyclohexane, which was purchased from Aldrich, as was 3-isocyanotopropyltriethoxysilane. Dichloromethane was distilled from P_2O_5 and ethanol from magnesium turnings. Melting points were determined on an electrothermal apparatus (IA9000 series) and are uncorrected. Optical rotations were measured using a Perkin–Elmer (Norwalk, CT) 214 polarimeter with solutions in a 1 dm cell in $CHCl_3$. IR data were obtained on a Perkin–Elmer 1000 FT-IR spectrophotometer. Elemental analyses were carried out by the "Service Central d'Analyse du CNRS" in Vernaison (France).

^1H, ^{13}C, and ^{29}Si NMR spectra in solution were recorded on Bruker AC-200 and AC-250 spectrometers at room temperature with deuterated chloroform as solvent and TMS as internal reference. ^1H, ^{13}C, and ^{29}Si solid-state NMR spectra were obtained from Bruker FT-AM 200 or FT-AM 400 spectrometers by using cross-polarization and magic-angle spinning techniques (CP-MAS) and TMS as reference for the chemical shifts. Mass spectra were measured on a JEOL MS-DX 300 mass spectrometer.

X-ray diffraction spectra were carried out on a Philips PW goniometer (anticathode Cu) and registered from $\theta = 1$ to 20°.

The TEM images were obtained with JEOL 200 CX and JEOL JEM 2010 microscopes. SEM images were realized on a JEOL 6300F apparatus.

General method for the preparation of (*R*,*R*)-1, (*S*,*S*)-1, and rac-1: These molecular precursors were prepared in a similar manner. In a typical synthesis *trans*-(1*R*,2*R*)-diaminocyclohexane (114 mg, 1 mmol) was dissolved in CH_2Cl_2 (30 mL) under a nitrogen atmosphere in a dried schlenk tube. 3-Isocyanotopropyltriethoxysilane (519 mg, 2.1 mmol) was slowly added by means of a syringe at room temperature, and the reacting mixture was stirred for 2 h. The solvent was evaporated and the white precipitate (*R*,*R*)-**1** was washed with pentane. The solution was filtered to remove the solvent and the excess of 3-isocyanatopropyltriethoxysilane. The remaining white solid was then dried in vacuo.

(*R*,*R*)-1: Yield: 548 mg, 91 %; m.p. 210 °C; $[\alpha]_D = +4.3$ ($c = 0.03$ in chloroform); IR (KBr pellet): $\tilde{\nu} = 1597$ (δ_{NH}), 1635 (ν_{CO}), and 3336 cm^{-1} (ν_{NH}); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.6$ (t, 4H; $SiCH_2$), 1.2 (t, 18H; CH_3), 1.5–2 (m, 12H; CH_2), 3–3.5 (m, 6H; NCH, NCH_2), 3.8 (t, 12H; OCH_2), 4.9 and 5.3 ppm (2m, 4H; 2NH); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 7.6$ (CH_2Si), 18.2 (CH_3), 23.6, 25 and 33.3 (3 CH_2), 43 (CH_2N), 54.6 (CHN), 58.3 (CH_2O), 159.2 ppm (CO); ^{29}Si NMR (250 MHz, $CDCl_3$): $\delta = -46$ ppm; MS (FAB): *m*/*z* (%): 609 (100) $[M^+ + H]$; elemental analysis calcd (%) for $C_{26}H_{56}O_8N_4Si_2$: C 51.28, H 9.27, N 9.20; found: C 51.01, H 9.13, N 9.33.

(*S*,*S*)-1: Yield: 560 mg, 93 %; m.p. 210 °C; $[\alpha]_D = -4.3$ ($c = 0.03$ in chloroform); IR and NMR spectra, and MS same as above.

rac-1: Yield: 511 mg, 84 %; m.p. 155 °C; IR (KBr pellet): $\tilde{\nu}$1572 (δ_{NH}), 1635 (ν_{CO}), 3342 cm^{-1} (ν_{NH}); NMR spectra and MS same as above.

General method for the preparation of the hybrid silicas (*R*,*R*)-1HS or (*S*,*S*)-1HS: In a typical synthesis, (*R*,*R*)-**1** or (*S*,*S*)-**1** (608 mg, 1 mmol) was completely dissolved in freshly distilled ethanol (3 mL) in a 25 mL round-bottomed flask. As soon as water (7.5 mL) was added a white precipitate appeared. The solution was then adjusted to pH = 12 by the addition of an aqueous solution of NaOH, and the flask containing the mixture was equipped with a reflux condenser and was dipped in an oil bath (80 °C). The mixture was left standing for 6 d at that temperature under static conditions. The molar ratio of the mixture was the following: (*R*,*R*)-**1** or (*S*,*S*)-**1**/H_2O/EtOH/NaOH = 1:423:52:0.1. No visible dissolution occurred during the whole reaction. The resulting white solid was filtered and washed successively with water, ethanol, and acetone. Careful drying at 110 °C of the gel for 6 h led to a white powder. (*R*,*R*)-**1HS**: IR (KBr): $\tilde{\nu} = 1574$ (δ_{NH}), 1634 (ν_{CO}), 3341 cm^{-1} (ν_{NH}); ^{13}C CPMAS NMR: $\delta = 10.3$, 25.3, 34.1, 42.8, 55.2, 161.0 ppm; ^{29}Si CPMAS NMR: $\delta = -56.8$, -67.6 ppm (T^2 and T^3 units); elemental analysis (%) calcd for completely condensed silsesquioxane $C_{14}H_{26}N_4O_5Si_2$: C 43.50, H 6.78, N 14.49, Si 14.53; found: C 41.58, H 6.83, N 13.48, Si 13.50.

Hybrid silica from rac-1: The same procedure as above was applied. In this case, the white precipitate formed after addition of water to the corresponding ethanolic solution rapidly dissolved into the solution when the mixture was dipped into the oil bath. A white precipitate reappeared after 15 min. The mixture was left standing at the same temperature under static conditions. The same workup was applied. IR (KBr pellet): $\tilde{\nu} = 1574$ (δ_{NH}), 1640 (ν_{CO}), 3352.2 cm^{-1} (ν_{NH}); ^{13}C CPMAS NMR: $\delta = 10.8$, 25.2, 34.7, 42.8, 54.2, 159.6 ppm; ^{29}Si CPMAS NMR: $\delta = -58.2$, -66.9 ppm (T^2 and T^3 units); elemental analysis (%) calcd for completely condensed silsesquioxane $C_{14}H_{26}N_4O_5Si_2$: C 43.50, H 6.78, N 14.49, Si 14.53; found: C 42.12, H 6.77, N 13.60, Si 14.15.

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