

Highly Ordered Functional Organosilicas by Template-Directed Hydrolysis-Polycondensation of Chiral Camphorsulfonamide Precursors

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Keywords: Mesoporous materials / Organic-inorganic hybrid composites / Sol-gel processes / Supported catalysts / Template synthesis

Trialkoxysilylated camphorsulfonamides have been used for the synthesis of functional organosilicas in a template-directed hydrolysis-polycondensation with tetraethylorthosilicate (TEOS). The sol-gel transformation leading to the formation of highly ordered materials indicates that trialkoxysilylated camphorsulfonamides allow the synthesis of func-

tional organosilicas with high structural regularity. This behaviour arises from the affinity of the chiral precursors towards the lyotropic phase of the ionic surfactants in the aqueous hydrolysis-polycondensation mixture.

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Introduction

Since the discovery of the template-directed synthesis of nanostructured silica by Kresge et al. in 1992,^[1] these materials have attracted considerable interest due to the unique properties related to their specific morphology, namely high specific surface, high pore volume and narrow pore-size distribution on a mesoscopic scale. These features make these materials the candidates of choice for numerous applications, for example in the fields of catalysis, separation and sensing.

The incorporation of functional organic groups into nanostructured silica can be achieved either in two steps by post-grafting of silylated precursor molecules onto the surface of nanostructured silica or in one step by a template-directed one-pot hydrolysis-polycondensation of a silica precursor with a functional organosilane.^[2,3] The two methodologies lead to organosilicas with different morphological features: although materials obtained by the post-grafting method are structurally better defined and hydrothermally more stable than samples obtained by the direct one-step method, they often suffer from inhomogeneous distribution of the functional groups on the support surface. Contrary to this, the one-step condensation procedure affords materials with a homogeneous distribution of the functional organic groups over the whole surface.^[4] However, in most cases only low functionalisation degrees can be achieved following the one-step method. Low-structured materials are obtained when high molar fractions of functional organosilane or bulky silylated precursors are

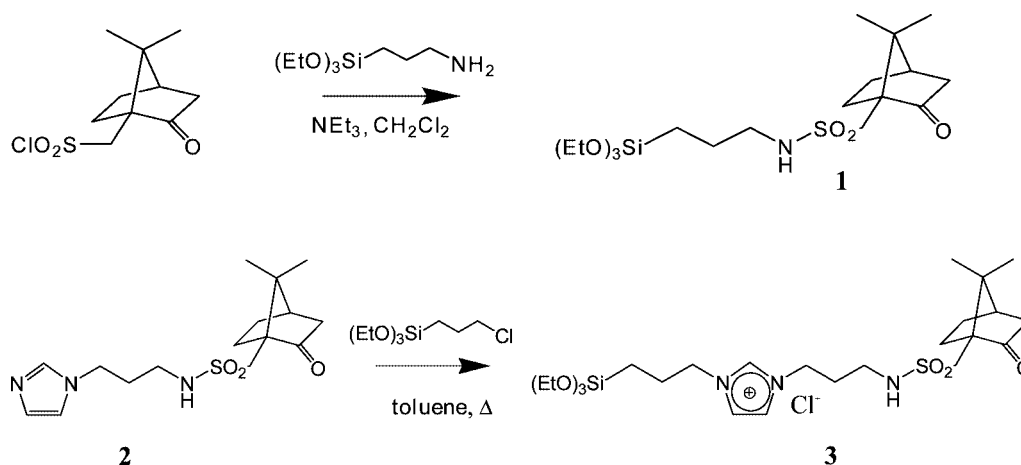
used.^[5,6] The upper limit of preservation of structural ordering is often reached with 20 mol-% of added organosilane.^[6] For this reason, the elaboration of methods that allow the incorporation of bulky functional groups within a highly structured mesoporous organosilica material is highly desirable.

Our current interest in the preparation of ordered organosilicas led us to explore the synthesis of nanostructured silica hybrids containing ionic species.^[7] As an example, we achieved the immobilisation of bis-alkylated imidazolium species on a silica support by a template-directed hydrolysis-polycondensation procedure. Supported ionic liquid phases have attracted large interest in the last few years^[8] as these materials that consist of an ionic layer that covers the whole surface of a solid support are promising systems for applications in catalysis,^[9–12] separation^[13] and chromatography.^[14] We were interested in exploring whether functional precursor molecules bearing ionic substructures would allow us to enhance the structural regularity of the obtained functional materials in template directed sol-gel processes. We report here a new nanostructured organosilica containing ionic and non-ionic (+)-camphorsulfonamide substructures as these moieties have been shown to be efficient auxiliaries in asymmetric catalysis.^[15,16]

Results and Discussion

We first focused on the synthesis of functional organosilanes bearing camphor substructures. The synthesis of the trialkoxysilylated camphorsulfonamide precursors **1** and **3** is shown in Scheme 1. The precursor **1** was obtained by the reaction of (+)-camphorsulfonyl chloride with 3-aminopropyltriethoxysilane (Scheme 1, top). Compound **3**, which bears an ionic imidazolium substructure, was synthesised by

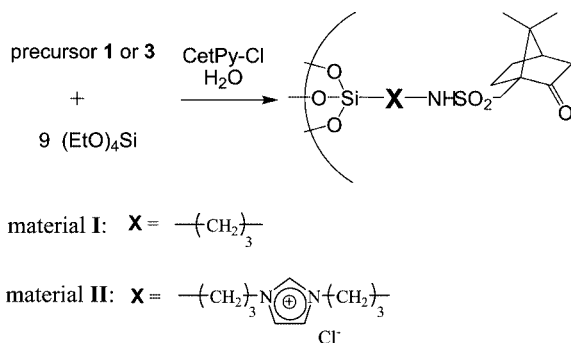
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Scheme 1. Synthesis of the trialkoxysilylated camphorsulfonamides **1** (top) and **3** (bottom).

grafting 3-chloropropyltriethoxysilane to the camphorsulfonamide **2**^[15] (Scheme 1, bottom). All reactions were quantitative, and the products could be used without further purification.

The synthesis of the organosilicas incorporating chiral camphorsulfonamide entities was then realised by a hydrolysis-polycondensation involving the chiral precursor **1** or **3** and tetraethoxysilane (TEOS; Scheme 2). All materials were prepared from alkaline mixtures containing TEOS, the trialkoxysilylated precursor **1** or **3**, water, ammonia and the surfactant hexadecylpyridinium chloride in the molar composition 0.9:0.1:114:8:0.12. We chose a pyridinium salt as template rather than an ammonium halide as the interaction between the imidazolium precursor **3** and pyridinium salts may be more favourable than that between imidazolium salts and surfactants based on ammonium substructures such as CTAB.^[17] The resulting reaction mixture was heated to 80 °C for 48 h. The surfactant was then removed by washing in a Soxhlet apparatus and the materials were finally dried at 110 °C for 24 h.



Scheme 2. Immobilisation of camphorsulfonamide species on the surface of mesoporous nanostructured silica.

Elemental analysis of the materials **I** and **II** indicated nearly complete incorporation of the organic precursors **1** and **3** into the organosilica materials during the sol-gel procedure. The incorporation of the organic entities within the silica network was also qualitatively monitored by FT-IR and ²⁹Si/¹³C-CP MAS NMR spectroscopy. The ²⁹Si CP-

MAS NMR spectrum of material **I** is shown as an example in Figure 1. As reported for other functionalised mesoporous silica materials,^[6] the spectrum shows the T³ peak at $\delta = -65.8$ ppm arising from the RSiO₃ substructures and the Q³ and Q⁴ peaks ($\delta = 101.4$ and 109.6 ppm) which can be ascribed to SiO₄ substructures with different condensation degrees.

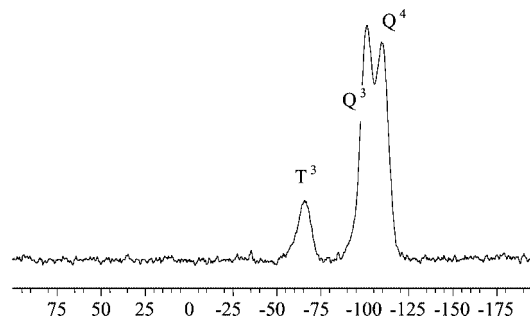


Figure 1. ²⁹Si CP MAS NMR spectrum of material **I**.

The morphological properties of materials **I** and **II** were investigated by XRD, TEM and nitrogen adsorption/desorption experiments. The XRD patterns of **I** and **II** are nearly identical and contain the (100), (110) and (200) peaks characteristic of hexagonal silica mesophases (Table 1). We have already obtained a material with a hexagonal architecture, although less regularly structured, using an ionic silylated dodecylimidazolium precursor.^[7] The X-ray diffractograms of **I** and **II** are shown in Figure 2.

Table 1. XRD spacings of materials **I** and **II**.

	<i>d</i> Spacings [nm]		
	100	110	200
Material I	4.00;	2.31	2.00
Material II	4.00	2.30	1.99

The morphology of the materials was also studied by TEM. The TEM micrographs of **I** and **II** show a highly structured regular hexagonal array of two-dimensionally

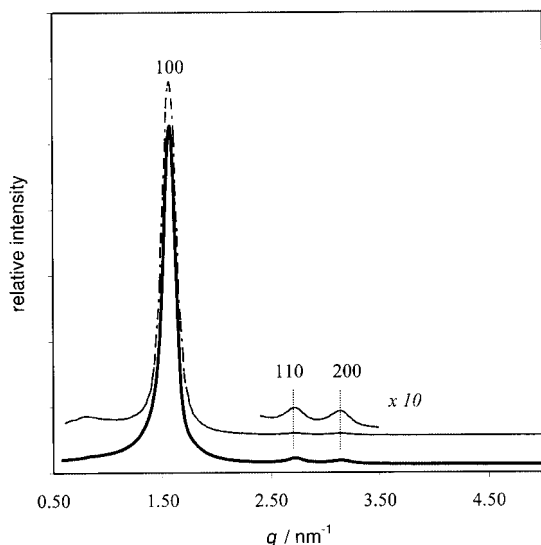


Figure 2. XRD patterns of the organosilica materials **I** (solid line) and **II** (dashed line).

aligned channels (Figure 3). In both cases, the distance between two pore centres was determined to be 4.0 nm, which corresponds to the (100) reflection in the XRD patterns.

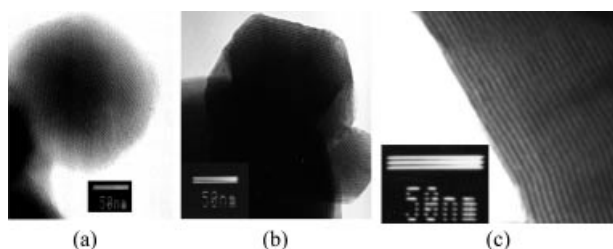


Figure 3. TEM micrographs of the functionalised organosilicas **I** (a) and **II** (b) along the (100) direction. (c) View along the (110) direction.

Thus, the TEM and XRD experiments give concordant results concerning the morphologies of materials **I** and **II**, which both appear as highly regularly structured solids with hexagonal symmetry. It has to be pointed out that the ionic substructure of precursor **3** does not have a significant effect on the structuration of the functionalised organosilica. The high structuration can rather be explained by the cosurfactant behaviour of the hydrolysed silylated precursors **1** and **3** in the basic aqueous media during the template-directed sol-gel procedure.

In a second experiment we studied the reduction of the carbonyl groups of the immobilised camphorsulfonamide

entities in the porous material **II**. This reaction was performed with a suspension of sodium borohydride in methanol under reaction conditions identical to those reported for the reduction in homogeneous media.^[15] This led to the formation of silica-supported borneol (material **III**). The reaction was monitored by FT-IR spectroscopy (disappearance of the absorption of the carbonyl group at $\tilde{\nu} = 1738 \text{ cm}^{-1}$). The ratio of the immobilized diastereoisomers could not be determined, but both borneol (*endo*) and isoborneol (*exo*) are probably formed. In solution, a 60:40 ratio has been reported (Scheme 3).^[15]

Nitrogen adsorption/desorption experiments with materials **I–III** give information about the porosity and the pore volume of the samples. The isotherms of materials **I** and **II** reflect the formation of mesoporous silica hybrid materials with specific surface areas of 832 and 759 $\text{m}^2 \text{g}^{-1}$ and pore volumes of 0.52 and 0.49 mL g^{-1} , respectively. In both cases, the sorption curves show typical type-IV isotherms, thereby suggesting an ordered silica mesophase with pore diameters of 2.5 nm. The isotherm of material **II** shows a slight hysteresis loop due to capillary condensation of adsorbed nitrogen within the pores.^[18] In contrast, material **III** shows a strongly reduced specific surface (82 $\text{m}^2 \text{g}^{-1}$), even after washing with acidic ethanol in a Soxhlet apparatus for three days. The reduced porosity of material **III** is probably due to the inclusion of borate ions within the pores during the reduction reaction. However, TEM and XRD experiments with material **III** confirm that the regular hexagonal structure of the silica framework is not affected. The sorption isotherms of materials **I–III** are presented in Figure 4.

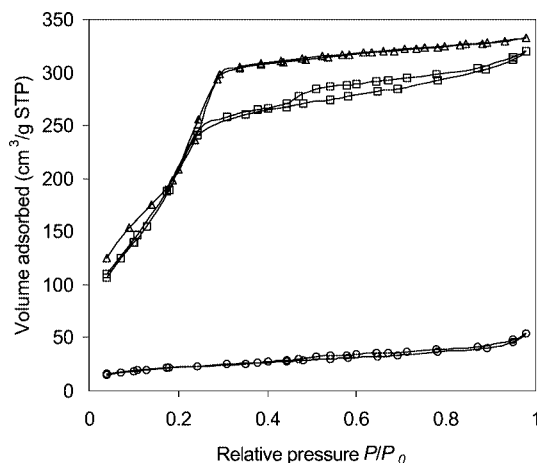
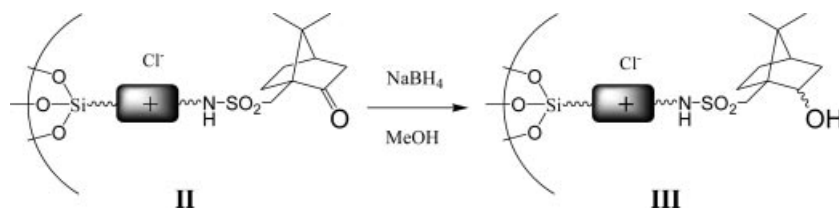
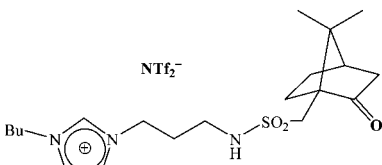
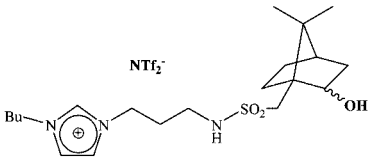


Figure 4. N_2 sorption curves of materials **I** (Δ), **II** (\square) and **III** (\circ).



Scheme 3. Reduction of the immobilized camphorsulfonamide entities.

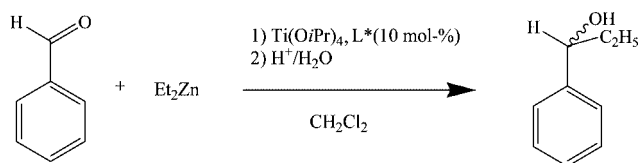
Table 2. Enantioselective addition of diethylzinc to benzaldehyde.^[a]

Entry	Used chiral auxiliary	Conversion ^[b]	ee ^[c]	Ref.
1	Material II	>99%	3%	this study
2		>99%	40%	[15]
3	Material III	>99%	30%	this study
4		>99%	50%	[15]
5	Material III , second cycle	95%	no selectivity detected	this study

[a] General reaction conditions: benzaldehyde:ligand:Ti(OiPr)₄:Et₂Zn = 1.0:0.1:1.1:1.2 (molar ratio), reaction time 18 h, reaction temperature 25 °C. [b] Determined by ¹H NMR spectroscopy. [c] Determined by HPLC using a Daicel Chiralcel OD column.

Heterogeneous Asymmetric Catalysis Using the Functional Organosilicas

The use of catalysts supported on mesoporous silica has been studied intensively.^[19,20] Our interest in organic-inorganic hybrid materials as heterogeneous auxiliaries in asymmetric catalysis^[21–23] led us to investigate materials **II** and **III**, which contain imidazolium substructures, as chiral auxiliaries in the asymmetric addition of diethylzinc to benzaldehyde. We also compared the catalytic properties of **II** and **III** with similar imidazolium salts bearing camphor or borneol substructures in homogeneous catalysis. The results of the utilisation of the various chiral auxiliaries in the addition of diethylzinc to benzaldehyde^[24,25] (Scheme 4) are shown in Table 2.



Scheme 4. Addition of diethylzinc to benzaldehyde.

Materials **II** and **III** act as catalytic auxiliaries and lead to the formation of 1-phenylpropanol in quantitative yield (entries 1 and 3) after hydrolytic work-up with hydrochloric acid (1 N). Despite its low porosity, material **III** shows a higher enantioselectivity than material **II**. However, the selectivities of both materials are lower than those obtained with the related imidazolium salts in homogeneous solution, thus indicating a limited complexation of the catalytic Ti^{IV} species by the immobilised chiral camphorsulfonamide entities (entries 2 and 4). The reduced enantioselectivities obtained with silica-immobilised camphorsulfonamide ligands are probably due to the reaction being catalysed by Ti^{IV} species in a nonchiral environment, for example by Ti(OiPr)₄ in homogeneous solution or by Ti^{IV} species

grafted onto the silica surface via Si–O–Ti bonds. Furthermore, material **III** appears to be of low recyclability. The second utilisation still gave high conversion, but no enantioselectivity was observed. We conclude therefore that the acidic work-up after the first reaction cycle strongly modifies the surface of the material by condensing oxidic Ti and Zn species, thus inhibiting the accessibility of the immobilised chiral ligand.

Conclusion

We have shown the formation of highly ordered mesoporous silica with a hexagonal architecture containing chiral camphorsulfonamide substructures located in the pores. Both ionic and non-ionic precursors lead to the formation of highly structured materials with hexagonal symmetry. The high structuration of the materials can be explained by the high affinity of the silylated camphorsulfonamides towards the organised micellar phase of the surfactants in aqueous medium: the trialkoxysilylated camphorsulfonamides behave as co-surfactants and fit in the micellar arrangement of the hexadecylpyridinium chloride.^[26] The ionic imidazolium substructure of precursor **3** does not show a significant effect during the template-directed hydrolysis polycondensation: material **II** does not show a higher structural regularity than material **I**. The utilisation of these functional organosilicas as chiral auxiliaries in asymmetric catalysis indicated inferior catalytic properties of the materials compared to related task-specific imidazolium salts in terms of selectivity and recyclability. These results are probably due to incomplete complexation of the titanium-based complexes to the camphorsulfonamide sites; considerable amounts of titanium may be linked to the silica support by covalent Si–O–Ti bonds.

To the best of our knowledge, material **II** is the first example of a chiral ionic substructure grafted onto a nano-

structured silica support. We believe that these highly porous functionalised materials may find applications in molecular recognition, in particular as chiral stationary phases in liquid chromatography.

Experimental Section

General: All reactions were performed under nitrogen or argon using Schlenk-tube techniques when necessary. Elemental analyses were performed by the "Service Central de Microanalyse du CNRS" at Vernaison, France. Mass spectra were measured with a Jeol JMS-DX300 mass spectrometer. FT-IR spectra were recorded from KBr pellets or films with a Perkin-Elmer 1000 FT-IR spectrometer. ^1H , ^{13}C and ^{29}Si liquid NMR spectra were recorded with a Bruker AC-250 spectrometer. CDCl_3 and $[\text{D}_6]\text{DMSO}$ were used as NMR solvents. Chemical shifts are reported as δ values in ppm relative to TMS. ^{13}C and ^{29}Si CP MAS solid-state NMR spectra were recorded with a Bruker FT AM 400 FT-NMR spectrometer. Specific surface areas were determined by nitrogen adsorption/desorption experiments using a Micromeritics Gemini 2375 apparatus. TEM was performed with a Jeol 1200EX II electron microscope. X-ray diffraction measurements and data treatment were performed at the Groupe de Dynamique de Phases Condensées at the University of Montpellier 2. 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 giving high flux (10^8 photons per second) and a pinhole collimation was employed. An "image 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 exposure time, transmission and the background scattering arising from an empty capillary. The enantiomeric excess of 1-phenylpropanol was determined by chiral HPLC using a Waters 515 HPLC pump with a Waters 2487 UV detector and a Daicel Chiralcel OD column using a hexane/2-propanol mixture as eluent. All reagents were obtained from commercial sources and used without purification. In experiments requiring dry solvents, THF, toluene and diethyl ether were distilled from sodium/benzophenone, DMF was distilled from CaH_2 , dichloromethane was distilled from P_2O_5 and alcohols were distilled from Mg. *C*-(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-(3-imidazol-1-ylpropyl)-methanesulfonamide (**2**) was synthesised as described before.^[15]

Synthesis of the Trialkoxysilylated Precursors

1-(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-[3-(triethoxysilyl)propyl]methanesulfonamide (1**):** (+)-Camphor-10-sulfonyl chloride (1 g, 4 mmol), (3-aminopropyl)triethoxysilane (0.9 g, 4 mmol) and triethylamine (0.45 g, 4.5 mmol) were stirred in dichloromethane (10 mL) at room temperature for 6 h. After completion, dichloromethane was evaporated and the resulting residue was extracted with diethyl ether. After evaporation of the solvent, the product was obtained as a colourless oil. Yield: 1.66 g (95%). ^1H NMR (CDCl_3): δ = 0.68 (m, 2 H), 0.92, 1.04 (2 s, 6 H, $2 \times \text{CH}_3$), 1.23 (t, J = 7.1 Hz, 9 H), 1.4–1.5 (m, 1 H), 1.72 (m, 2 H), 1.85–2.45 (m, 6 H), 2.91 (d, J = 14.6 Hz, 1 H), 3.17 (m, 2 H), 3.41 (d, J = 14.6 Hz, 1 H), 3.83 (q, J = 7.1 Hz, 6 H), 5.42 (broad t, 1 H) ppm. ^{13}C NMR (CDCl_3): δ = 7.9, 18.6, 19.9, 20.2, 24.0, 26.7, 27.4, 43.1, 43.2, 46.4, 48.9, 49.6, 58.8, 59.4, 216.9 ppm. FT-IR (film): $\tilde{\nu}$ = 3288 cm^{-1} , 2973, 2888, 1746, 1330, 1147, 1079. HRMS [FAB⁺]: calcd. for $\text{C}_{19}\text{H}_{38}\text{NO}_6\text{SSi}$ [$\text{M} + \text{H}$]⁺ 436.2189; found 436.2193.

1-[3-(2-Hydroxy-7,7-dimethylbicyclo[2.2.1]hept-1-yl)methylsulfonylamino]propyl-3-(3-triethoxysilyl)propyl-1*H*-imidazol-1-ium Chloride (3**):** Under argon, 1 g (2.94 mmol) of **2** was dissolved in toluene (20 mL) and 3-chloropropyltriethoxysilane (0.71 g, 2.94 mmol) was added whilst stirring. The reaction mixture was heated to 80 °C during 48 h. After cooling to room temperature, the biphasic mixture was washed with diethyl ether (3 \times 30 mL). Finally, the ether-insoluble layer was dried under reduced pressure. The product was obtained as a highly viscous yellow liquid. Yield: 1.60 g (94%). ^1H NMR (CDCl_3): δ = 0.54 (m, 2 H), 0.84, 0.97 (2 s, 6 H, $2 \times \text{CH}_3$), 1.15 (t, 9 = H, J = 7.2 Hz), 1.38 (m, CH), 1.8–2.1 (m, 6 H, $3 \times \text{CH}_2$), 2.29 (m, 4 H, $2 \times \text{CH}_2$), 2.85 (d, J = 15 Hz, 1 H), 3.11 (m, 2 H, CH_2), 3.33 (d, J = 15 Hz, 1 H), 3.72 (q, J = 7.2 Hz, 6 H), 4.17 (t, J = 6.6 Hz, 2 H, NCH_2), 4.40 (t, J = 6.8 Hz, 2 H), 6.40 (t, J = 6.4 Hz, 1 H, NH), 7.68 (s, 2 H), 9.65 (s, 1 H) ppm. ^{13}C NMR (CDCl_3): δ = 7.6, 14.4, 18.7, 20.0, 20.3, 20.7, 24.5, 26.1, 27.4, 30.7, 34.5, 40.2, 43.2, 47.6, 48.3, 52.4, 59.0, 122.3, 123.4, 137.0, 216.5 ppm. HRMS [FAB⁺]: calcd. for $\text{C}_{25}\text{H}_{46}\text{N}_3\text{O}_6\text{SSi}$ [M]⁺ 544.2877; found 544.2859 (cation).

Synthesis of the Materials: Whilst stirring, the trialkoxysilylated precursor **1** or **3** was added to a solution of cetylpyridinium chloride in aqueous ammonia. The resulting mixture was vigorously stirred for 20 min at 30 °C. After this time, TEOS was added to the reaction mixture dropwise. The molar composition of the hydrolysis-polycondensation mixture was as follows: TEOS/**1**(**3**)/water/ammonia/hexadecylpyridinium chloride = 0.9:0.1:114:8:0.12. The resulting mixtures were heated to 80 °C for 48 h. The surfactant was removed by repeated washing with acidic ethanol and the materials were finally dried at 110 °C for 24 h.

Material I: ^{29}Si CP MAS NMR: δ = −65.8, −101.5, −109.6 ppm. ^{13}C CP MAS NMR: δ = 7.9, 18.1, 21.7–25.1, 42.6, 47.9, 58.7, 217.1 ppm. BET surface area: 832 m^2g^{-1} . FT-IR (KBr pellet): $\tilde{\nu}$ = 2969 cm^{-1} , 1640, 1224, 1067. Elemental analysis: C 15.83, H 2.87, N 1.56, S 2.73, Si 31.88.

Material II: ^{29}Si CP MAS NMR: δ = −66.3, −101.0, −110.0 ppm. ^{13}C CP MAS NMR: δ = 7.9, 21.9, 25.0, 42.9, 49.7, 58.3, 124.2, 133.7, 216.5 ppm. BET surface area: 759 m^2g^{-1} . FT-IR (KBr pellet): $\tilde{\nu}$ = 3452 cm^{-1} , 2973, 1738, 1636, 1225, 1146, 1071. Elemental analysis: C 18.23, H 3.20, N 3.26, S 2.50, Si 27.27.

Material III: The organosilica **II** (1.00 g) was suspended in methanol (10 mL) and cooled to 0 °C. Sodium borohydride (50 mg) was then added and the resulting mixture was stirred at this temperature for 2 h. The suspension was then filtered. The resulting residue was extracted in a Soxhlet apparatus with acidified ethanol for 72 h and finally dried at 110 °C for 24 h. Yield: 960 mg. ^{29}Si CP MAS NMR: δ = −66.1, −100.0, −109.1 ppm. ^{13}C CP MAS NMR: δ = 8.0, 19.0, 29.6, 45.5, 48.6, 49.8, 124.0, 134.0. BET surface area: 82 m^2g^{-1} . FT-IR (KBr pellet): $\tilde{\nu}$ = 3458 cm^{-1} , 2961, 1645, 1225, 1065. Elemental analysis: C 17.84, H 3.31, N 3.20, S 2.66, Si 26.73.

General Procedure for the Addition of Diethylzinc to Benzaldehyde:

The functional organosilica was placed in a Schlenk tube and dried under vacuum at 100 °C for 1 h. After cooling to room temperature, dichloromethane (10 mL) and $\text{Ti}(\text{iOPr})_4$ (313 mg, 1.1 mmol) were added to the solid. The resulting suspension was stirred at room temperature for 1 h. After this time, diethylzinc (1.2 mL of a 1 M solution in hexanes) was added and the mixture was stirred for another 15 min. Finally, after the addition of benzaldehyde (100 μL , 1 mmol), the suspension was stirred for 18 h at room temperature. The reaction mixture was then filtered and the residue was washed with dichloromethane. 1 mL of ethanol was added to the filtrate, which was completely hydrolysed by the addition of 15 mL of hydrochloric acid (1 N). Extraction of the solution with dichloromethane, drying and evaporation afforded the reaction products, which were analysed in order to determine the conversion

and the enantiomeric excess. The recovered organosilica was dried at 100 °C under reduced pressure.

Acknowledgments

The authors thank Dr. P. Dieudonné for XRD measurements and fruitful discussions. V. P. gratefully acknowledges the French “Ministère de la Recherche” for a postdoctoral fellowship.

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Received: March 31, 2006

Published Online: August 3, 2006