From simple molecules to highly functionalised lamellar materials

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We describe here a new method permitting the one-step synthesis of ordered (lamellar phase) organosilicas highly functionalised with carboxylic acid or phosphonic acid groups. These materials were obtained by hydrolysis and polycondensation of monosilylated precursors cyanoalkyltrialkoxysilane (NC-(CH₂)_nSi(OR)₃) and diethylphosphonatoalkyltriethoxysilane ((EtO)₂(O)P-(CH₂)_nSi(OEt)₃) in acidic media without any structure-directing agent. The hydrolysis of -CN and -P(O)(OEt)₂ groups into -COOH and -P(O)(OH)₂ involves the *in situ* formation of dimers by strong hydrogen bonds, which is the crucial step to obtain a solid. The involvement of hydrophobic interactions between alkylene chains was also evidenced. All materials were characterised by X-ray diffraction measurements, elemental analyses and solid-state ¹³C and ²⁹Si NMR spectroscopies. The accessibility and adsorption capacity of these groups towards lanthanide ions were investigated.

Introduction

The study of functionalised organic-inorganic materials is an expanding field of investigation, which should give rise to advanced materials offering a wide range of possibilities in terms of chemical or physical properties.¹ Indeed, by changing the nature of the organic moieties, it is possible to obtain materials presenting a large variety of properties with promising applications in many areas such as catalysis, separation, environment optics, etc. Among the different routes which could give rise to such materials, the use of bridged organosilica precursors of general formula $[(R'O)_3Si]_m R \ (m \ge 2)$ is of special interest as they allow the formation of homogeneous hybrid organicinorganic materials. The control of the structure of hybrid materials during the sol-gel process is a great challenge with a view to obtaining such materials. Although classical sol-gel process usually results in the formation of amorphous materials,² self-assembly during the sol-gel process of organosilanes bearing hydrolysable groups offers an opportunity to create ordered hybrid materials. Recently, much effort has been directed towards the structural organisation of bridged silsesquioxanes at the nanometre length scale.3 However, up to now, only a few examples of bridged silsesquioxanes with long-range structure have been reported.4-6

Two years ago, we showed that it is possible to obtain long-range ordered hybrid materials by changing only the experimental conditions: while the hydrolytic polycondensation of α,ω -bis(trimethoxysilyl)alkylenes with long alkylene chains gives rise to amorphous solids in THF, in water there is the formation of long-range ordered (lamellar or hexagonal structure) materials thanks only to the hydrophobic interactions.⁷ It was shown that the length of the alkylene chains controls the structure. The great interest of these results prompted us to explore the formation of functional hybrid organic-inorganic materials from bridged organosilica precursors with long alkylene chains having a functionalised and chemically transformable core.

Thus, we have shown that hydrolysis and polycondensation of α, ω -bis(trimethoxysilyl)alkyldisulfide in water led to lamellar bridged organosilica containing disulfide cores.⁸ Subsequent reduction of disulfide cores gave rise to highly ordered organosilica with a high content of thiol groups.

We used also the reaction between CO_2 and monosilylated amines to get bridged organosilica precursors containing carbamate ammonium salts in the core.⁹ The hydrolytic polycondensation of these precursors by the sol–gel process gave rise to hybrid materials in which the ammonium carbamate salts were maintained. Subsequent loss of CO_2 upon heating generated materials with free amino groups in which the longrange order was also maintained.

As it is an exciting area of research in nanosciences and nanotechnology to control the organisation as well as the functionalisation of materials during the sol–gel process, we have extended our strategy to the preparation of lamellar materials containing -COOH or $-P(O)(OH)_2$ groups.

In this paper, we describe the formation of ordered and highly carboxylic and phosphonic acid-functionalised materials by hydrolysis and polycondensation of monosilylated precursors: cyanoalkyltrialkoxysilanes 1–3 (NC-(CH₂)_nSi(OR)₃ with n = 3 and R = Et for 1, n = 5 and R = ⁱPr for 2 and n = 11 and R = ⁱPr for 3) and diethylphosphonatoalkyltriethoxysilane 4–6 ((EtO)₂(O)P-(CH₂)_nSi(OEt)₃ with n = 3 for 4, n = 5 for 5 and n = 11 for 6) in acidic media. The hydrolysis of -CN and -P(O)(EtO)₂ groups into -COOH and -P(O)(OH)₂ respectively involves the *in situ* formation of dimers by strong hydrogen bonds, which is the crucial step to obtain a solid.

We demonstrated that van der Waals interactions in conjunction with hydrogen bonding interactions are required to increase the organisation degree. In these materials with high content of

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 $\mathrm{H}^{\scriptscriptstyle +}/\mathrm{g},$ we showed that the acids groups were accessible with a high salt uptake.

Experimental

General procedures

3-Cyanopropyltriethoxysilane, 3-chloropropyltriethoxysilane, NaH, p-toluene sulfonyl chloride and NaCN were purchased from Aldrich and used as supplied. 3-Cvanopropyltrichlorosilane, 4-bromobutene, 5-bromopentene, 11-bromoundecene, benzylbromide, triethoxysilane (HSi(OEt)₃) and potassium pentadionate were purchased from Alfa Aesar. Karstedt's catalyst was from ABCR. Diethyl malonate and triethylphosphite were from Acros. 2-(4-Butenyl)propane-1,3-diol ditosylate was prepared according to the procedure previously described¹⁰ for 2-(3-propenyl)propane-1,3-diol ditosylate. Cyanopentyltriisopropoxysilane and cyanoundecyltriisopropoxysilane were prepared according to the procedure previously described.¹¹ The CP-MAS ²⁹Si and ¹³C solid-state NMR spectra were recorded on a BRUKER FTAM 300, in the latter case by using the TOSS technique. The repetition time was 5 (for ¹³C) and 10 s (for ²⁹Si) with contact times of 3 (for ¹³C) and 5 (for ²⁹Si) ms. The duration of the ¹H pulse was 4.2 (for ¹³C) and 4.5 (for ²⁹Si) µs and the MAS rate was 10 (for ¹³C) and 5 (for ²⁹Si) kHz. Chemical shifts (δ , ppm) were referenced to Me₄Si (13C and 29Si). Powder X-ray diffraction experiments were carried out on a high resolution Bonse-Hart camera with two germanium channel cuts for very small q values. The wavelength used was 1.542 Å (CuKa radiation). Elemental analyses of Si, C, N, P, K and Eu were performed by the Service Central d'Analyse (CNRS, Vernaison, France).

Syntheses

Synthesis of 2 and 3. 2 and 3 were prepared according to the procedure previously described.¹¹

Synthesis of 4. Triethoxysilylpropyldiethylphosphonate 4 was prepared by Arbuzov reaction between 3-iodopropyltriethoxysilane¹² and triethylphosphite. 3-Iodopropyltriethoxysilane (16.6 g, 50 mmol) was added to P(OEt)₃ (20.0 g, 120 mmol). The mixture was heated at reflux for 24 h under Ar, then the excess of P(OEt)₃ was removed under vacuum. The crude product was purified by distillation (120 °C at 5×10^{-2} mbar) to give 4 as a colourless liquid (12.0 g, 35 mmol, 70% yield). ¹H NMR (δ , 200 MHz, CDCl₃): 0.63 (2 H, m), 1.25 (9 H, t, ³*J*_{H,H} = 7.0 Hz), 1.34 (6 H, t, ³*J*_{H,H} = 7.0 Hz), 1.81 (4 H, m), 3.80 (6 H, q, ³*J*_{H,H} = 7.0 Hz), 4.12 (4 H, q, ³*J*_{H,H} = 7.0 Hz). ¹³C NMR (δ , 50 MHz, CDCl₃): 10.3, 16.3, 16.9, 27.0, 29.4, 61.4 and 65.2. ³¹P NMR (δ , 100 MHz, CDCl₃): 32.7. ²⁹Si NMR (δ , 40 MHz, CDCl₃): -43.0.

Synthesis of 5. A mixture of 5-bromopentene (10.0 g, 66.5 mmol) and triethoxysilane (22.0 g, 133.0 mmol) in the presence of Karstedt's catalyst (10 mol%) was heated at 80 °C for 24 h giving rise to 5-bromopentyltriethoxysilane in high yield (80%) after distillation (90 °C at 8×10^{-2} mbar). The Arbuzov reaction was carried out by mixing 12.8 g of triethylphosphite (77.0 mmol) and 5-bromopentyltriethoxysilane (10.0 g, 31.0 mmol). The resulting solution was stirred for 24 h at reflux. The residual P(OEt)₃ was evaporated under vacuum. The crude

product was purified by distillation (100 °C at 2×10^{-2} mbar) to give **5** as a colourless liquid (9.4 g, 25.4 mmol, 82% yield). ¹H NMR (δ , 200 MHz, CDCl₃): 0.61 (2 H, m), 1.26 (9 H, t, ³J_{H,H} = 7.0 Hz), 1.30 (2 H, m), 1.32 (6 H, t, ³J_{H,H} = 7.0 Hz), 1.34 (2 H, m), 1.66 (2 H, m), 1.82 (2 H, t, ³J_{H,H} = 6.4 Hz), 3.81 (6 H, q, ³J_{H,H} = 7.0 Hz), 4.10 (4 H, q, ³J_{H,H} = 7.0 Hz). ¹³C NMR (δ , 50 MHz, CDCl₃): 12.3, 16.7, 16.9, 23.0, 31.2, 61.7 and 65.0. ³¹P NMR (δ , 100 MHz, CDCl₃): 33.5. ²⁹Si NMR (δ , 40 MHz, CDCl₃): -43.1.

Synthesis of 6. 6 was prepared according to the procedure used for **5** and was obtained in 80% yield after distillation (135 °C at 2 $\times 10^{-2}$ mbar). ¹H NMR (δ , 200 MHz, CDCl₃): 0.60 (2 H, m), 1.22– 1.40 (16 H, m), 1.26 (9 H, t, ³J_{H,H} = 7.9 Hz), 1.34 (6 H, t, ³J_{H,H} = 7.0 Hz), 1.66 (2 H, m), 2.40 (2 H, m), 3.80 (6 H, q, ³J_{H,H} = 7.9 Hz), 4.10 (4 H, q, ³J_{H,H} = 7.0 Hz). ¹³C NMR (δ , 50 MHz, CDCl₃): 12.3, 16.7, 22.7–33.6, 61.8 and 65.1. ³¹P NMR (δ , 100 MHz, CDCl₃): 33.7. ²⁹Si NMR (δ , 40 MHz, CDCl₃): -43.6.

Synthesis of 7. A mixture of 2-(4-butenyl)propane-1,3-diol ditosylate¹⁰ (8.0 g, 18.0 mmol) and triethoxysilane (6.0 g, 36.0 mmol) in the presence of Karstedt's catalyst (10 mol%) was heated at 80 °C for 24 h giving rise to 2-(4-triethoxysilylbutyl)propane-1,3-diol ditosylate. Subsequent isopropanolysis was achieved to give 2-(4-trisopropoxysilylbutyl)propane-1,3diol ditosylate (8.2 g, 12.6 mmol, 70%) after distillation (110 °C at 2×10^{-2} mbar). The dinitrile was prepared by mixing 8.0 g (12.4 mmol) of ditosylate, NaCN (2.6 g, 53.0 mmol) and DMSO (60 mL). The resulting solution was stirred at reflux for 24 h. The reaction mixture was cooled to room temperature and was taken up in water (50 mL) and Et₂O (80 mL). After extraction with Et₂O (2 \times 100 mL), the organic layer was dried under MgSO₄ and evaporated under vacuum. The crude product was purified by distillation (110 °C at 4×10^{-2} mbar) to give 4.1 g (11.6 mmol, 92%) of 2-(4-trisopropoxysilylbutyl)glutaronitrile 7. ¹H NMR (δ, 200 MHz, CDCl₃): 0.60 (2 H, m), 1.27 (18 H, d, ${}^{3}J_{H,H} = 6.9$ Hz), 1.40–1.80 (6 H, m), 2.16 (1 H, m), 2.57 (4 H, d, ${}^{3}J_{H,H} = 8.0$ Hz), 4.21 (3 H, sept, ${}^{3}J_{H,H} = 6.9$ Hz). ${}^{13}C$ NMR (δ, 50 MHz, CDCl₃): 11.3, 13.8, 22.5, 25.7, 27.9, 29.0, 32.6, 56.5 and 117.0. ²⁹Si NMR (δ, 40 MHz, CDCl₃): -44.0.

Synthesis of 8. To a suspension of K_2CO_3 (15.0 g, 108.6 mmol), undecylenic acid (10.0 g, 54.3 mmol) in DMF (200 mL), 7 mL (54.3 mmol) of benzylbromide were added at room temperature. The resulting mixture was heated at 80 °C for 36 h. After cooling to room temperature, the mixture was taken up in water (200 mL) and Et₂O (100 mL). After extraction with Et₂O (2 \times 100 mL), the organic layer was dried under MgSO₄ and evaporated under vacuum. 13.0 g (87%) of ester were obtained as a colourless liquid. Subsequent hydrosilylation was achieved as described above. 17.5 g (89%) of 8 were obtained after distillation (180 °C at 4 \times 10⁻² mbar). ¹H NMR (δ , 200 MHz, CDCl₃): 0.66 (2 H, m), 1.21-1.30 (14 H, m), 1.22 (9 H, t, ${}^{3}J_{H,H} = 7.9$ Hz), 1.63 (2 H, m), 2.30 (2 H, t, ${}^{3}J_{H,H} = 7.6$ Hz), 3.80 (6 H, q, ${}^{3}J_{H,H} = 7.9$ Hz), 5.40 (2 H, s), 7.38 (5 H, s). ${}^{13}C$ NMR (δ, 50 MHz, CDCl₃): 10.7, 18.7, 23.0-32.0, 34.7, 58.7, 59.5, 128.8, 174.0. ²⁹Si NMR (δ, 40 MHz, CDCl₃): -44.1.

Synthesis of 9. To a solution of silylated ester 8 (4.0 g, 9.1 mmol) in AcOEt (60 mL), 700 mg of Pd/C were added at

room temperature. The resulting mixture was stirred at room temperature under hydrogen atmosphere for 12 h. After filtration, the organic layer was evaporated under vacuum. 3.20 g (92%) of **9** were obtained as colourless liquid. **9** was used immediately as obtained without further purification. ¹H NMR (δ , 200 MHz, CDCl₃): 0.60 (2 H, m), 1.20–1.33 (14 H, m), 1.25 (9 H, t, ³J_{H,H} = 7.9 Hz), 1.61 (2 H, m), 2.33 (2 H, t, ³J_{H,H} = 7.6 Hz), 3.82 (6 H, q, ³J_{H,H} = 7.9 Hz).

Preparation of materials

M1. To 3.00 g (13.0 mmol) of cyanopropyltriethoxysilane 1, 65 mL of sulfuric acid solution (9 M) were added at 30 °C. The mixture was stirred at 30 °C for 30–45 min. Ethanol was removed under vacuum from the resulting clear solution in order to avoid subsequent esterification. The resulting solution was placed into a Teflon bottle and kept at 150 °C for 6 h without stirring. The corresponding solid M1 was recovered by filtration and washed successively with water (500 mL), acetone (20 mL) and ether (20 mL). After drying at 120 °C under vacuum for 12 h, 1.78 g (98%) of M1 were obtained as a white powder. ¹³C NMR (δ , 75 MHz, CP-MAS): 12.0, 20.8, 42.3, 61.1 and 180.6. ²⁹Si NMR (δ , 60 MHz, CP-MAS): -68.8 (T³). Anal. Calc.: C/Si molar ratio = 4. Found: C/Si = 4.29.

M2. Starting from **2** (2.00 g, 6.50 mmol) and 40 mL of sulfuric acid (9 M). 0.98 g (90%) of **M2** was obtained as a white powder. ¹³C NMR (δ , 75 MHz, CP-MAS): 14.4, 17.9, 22.5, 24.7, 32.4 and 179.9. ²⁹Si NMR (δ , 60 MHz, CP-MAS): -68.0 (T³). Anal. Calc.: C/Si molar ratio = 6. Found: C/Si = 6.10.

M3. Starting from **3** (2.00 g, 5.19 mmol) and 32 mL of sulfuric acid (9 M). 1.14 g (87%) of **M3** were obtained as a white powder. ¹³C NMR (δ , 75 MHz, CP-MAS): 14.3, 25.3, 30.5, 34.4 and 179.5. ²⁹Si NMR (δ , 60 MHz, CP-MAS): -65.4 (T³). Anal. Calc.: C/Si molar ratio = 12. Found: C/Si = 12.25.

M5. To 1.00 g (2.50 mmol) of **5**, 10 mL of HCl solution (12 N) were added at 30 °C. The mixture was stirred at 30 °C for 30–45 min. The resulting solution was placed into a Teflon bottle and kept at 100 °C for 12 h without stirring. The corresponding solid **M5** was recovered by filtration and washed successively with water (200 mL), acetone (20 mL) and ether (20 mL). After drying at 50 °C under vacuum for 12 h, 0.40 g (80%) of **M5** was obtained as a white powder. ¹³C NMR (δ , 75 MHz, CP-MAS): 14.2, 23.4, 26.4, 28.1 and 34.6. ³¹P NMR (δ , 120 MHz, CP-MAS): 32.1. ²⁹Si NMR (δ , 60 MHz, CP-MAS): -68.5 (T³). Anal. Calc.: C/Si molar ratio = 5. Found: C/Si = 5.10.

M6. Starting from **6** (3.00 g, 6.60 mmol) and 10 mL of HCl solution (12 N), 1.80 g (95%) of **M6** were obtained as a white powder. ¹³C NMR (δ , 75 MHz, CP-MAS): 13.4, 25.4, 29.4, 29.7–29.9, 32.3 and 36.5. ³¹P NMR (δ , 120 MHz, CP-MAS): 32.4. ²⁹Si NMR (δ , 60 MHz, CP-MAS): -67.3 (T³). Anal. Calc.: C/Si molar ratio = 11. Found: C/Si = 9.79.

M7. Starting from 7 (1.00 g, 2.80 mmol) and 30 mL of sulfuric acid (9 M), 0.50 g (75 %) of **M7** was obtained as a white powder. ¹³C NMR (δ , 75 MHz, CP-MAS): 11.6, 22.5, 30.0, 32.5, 38.8 and

M9. To 1.00 g (2.65 mmol) of **9** freshly prepared, 10 mL of HCl solution (pH at 1.5) were added at 30 °C. After a few minutes, a white solid appears. This solid was recovered by filtration and washed successively with water (100 mL), acetone (20 mL) and ether (20 mL). After drying at 120 °C under vacuum for 12 h, 0.50 g (83%) of **M9** were obtained as a white powder. ¹³C NMR (δ , 75 MHz, CP-MAS): 24.7, 29.6–33.8 and 179.8. ²⁹Si NMR (δ , 60 MHz, CP-MAS): -67.0 (T³). Anal. Calc.: C/Si molar ratio = 11. Found: C/Si = 11.20.

Results and discussion

1. Preparation and characterisation of COOH-functionalised materials M1–M3

Cyanoalkyltriisopropoxysilane 2 and 3 were synthesised as previously described.¹¹

Hydrolysis and polycondensation of 1-3 were achieved in the presence of a sulfuric acid solution (9 M) as described in detail in the Experimental section (Scheme 1). The materials obtained were recovered by filtration and denoted Mn [M for material and *n* to specify the starting precursor]. M1-M3 were obtained as white powders in high yield. Their compositions were inferred from the results of Si and C elemental analyses. The C/Si molar ratio was found to be 4.29 for M1, 6.10 for M2 and 12.25 for M3 while the theoretical values were 4, 6 and 12 respectively (Table 1). This confirms the high degree of polycondensation of materials and the conservation of the Si-C bonds. In addition, the absence of nitrogen revealed by elemental analysis indicates that the hydrolysis of cyano groups was complete. More informations about the incorporation and the conservation of organic groups in the final materials was given by solid-state NMR spectroscopies. The ²⁹Si CP-MAS NMR spectra of samples M1, M2 and M3 displayed only one signal at -68.8, -68.0, and -65.4 ppm respectively attributed to the T³ [C-Si(OSi)₃] substructure, indicating fully condensed materials (Fig. 1). The absence of resonance near -100 ppm corresponding to Q substructures denotes also that there is no cleavage of Si-C bonds during the sol-gel process and the hydrothermal treatment.

The CP-MAS ¹³C NMR spectra of **M1–M3** show clearly that the organosiloxanes units were incorporated. The ¹³C NMR spectrum of **M1** is given as an example (Fig. 2). It displayed three signals (12.00, 20.86 and 42.35 ppm) assigned to the propyl spacer and an additional one at 180.66 ppm attributed to carbonyl resonances of carboxylic acid groups. The absence of a peak at 120 ppm shows clearly that there is no residual nitrile (CN) group in the material obtained. The signal at 61.13 ppm revealed the formation of a small amount of ester by reaction

$(RO)_3Si \longrightarrow_n CN$	$\xrightarrow{H_2SO_4/H_2O}$	O _{1.5} Si ∕ ⟨∕ _n COOH
1: n = 1; R = Et	2) 150 °C	M1 : n = 1
2 : $n = 3$; $R = {}^{i}Pr$		M2: n = 3
3 : $n = 9$; $R = {}^{i}Pr$		M3: n = 9

Scheme 1 Preparation of materials M1–M3.

 Table 1
 Elemental analyses data for materials M1–M3 and their corresponding salts (theoretical values in parentheses)

Molar ratio	M1	M2	M3	M1K	M2K	M3K	M1Eu	M2Eu	M3Eu
C/Si ^a K/Si ^a	4.29 (4) 0	6.10 (6) 0	12.25 (12) 0	4.10 (4) 0.90 (1)	6.05 (6) 0.99 (1)	11.70 (12) 0.93 (1)	$\frac{-}{<5} \times 10^{-5}$	$\frac{-}{<5} \times 10^{-5}$	
Eu/Si	0	0	0	0	0	0	$0.34;^a 0.32^b$	$0.32;^a 0.33^b$	$0.51;^a 0.53^b$

^a Calculated from elemental analyses. ^b Determined from titration results.



Fig. 1 CP-MAS ²⁹Si NMR spectra of M1 and M1K.



Fig. 2 CP-MAS ¹³C NMR spectra of M1 and M1'.

between acid groups and some remaining EtOH. It is worth noting that the signal corresponding to ester groups disappeared when starting from trichlorosilyl instead of trialkoxysilyl groups. In fact, hydrolysis and polycondensation of cyanopropyltrichlorosilanes under the same conditions give rise to a material denoted **M1**'. The ¹³C NMR spectrum of **M1**' is shown in Fig. 2. This spectrum shows clearly the absence of the resonance at about 61 ppm attributed to the carbonyl of the ester group.

The nitrogen adsorption measurements of samples indicate that **M1–M3** are nonporous with a low surface area ($S_{\text{BET}} < 10 \text{ m}^2 \text{ g}^{-1}$).

Powder X-ray diffraction patterns of **M1–M3** are represented in Fig. 3. The XRD pattern of **M1** exhibited a well-defined (100) peak at q = 4.60 nm⁻¹ as well as a second broad and weak peak (200) at q = 8.40 nm⁻¹. These peaks are characteristic of a lamellar structure with 1.36 nm as interlayer distance ($d = 2\pi/q$). The peak at q = 15.70 nm⁻¹ corresponds to 0.40 nm.



Fig. 3 XRD patterns of M1, M2 and M3.

This distance can be attributed to alkylene chains packing within the layers. The X-ray powder diffraction pattern of **M2** is very similar with an interlayer distance of about 1.57 nm. Interestingly, a higher organisation was observed for **M3** (Fig. 3). In all cases, the first order distance is close to the length of the organic spacers. As an example, the first peak at q = 1.97 nm⁻¹ observed in the XRD pattern of **M3** corresponding to an interlayer distance of 3.19 nm is very close to the theoretical distance obtained by ChemDraw 3D calculation (3.20 nm).

The formation of solids **M1–M3** can be explained in the following way: first, there is hydrolysis of alkoxy groups into silanols at 30 °C. Then, the increasing of the temperature to 150 °C induces the hydrolysis of the cyano groups into carboxylic acid groups, which dimerise, by hydrogen bonding.¹³ Finally, self-assembly,⁷ thanks to hydrophobic interactions, of the bis-silylated units formed *in situ* allows the polycondensation, giving rise to the materials (Scheme 2).

It is worth noting that under the same experimental conditions the hydrolysis of chloropropyltriethoxysilane does not allow the formation of a material due to the absence of formation of bis-silylated derivatives by dimerisation. This result demonstrates that the crucial step to get a solid starting from cyanoalkyltrialkoxysilanes is the *in situ* formation of dimers between the carboxylic acid units by hydrogen bonding.

In addition, the better self-assembly of **M3** in comparison to **M1** and **M2** shows the involvement of hydrophobic interactions between the long alkylene chains to get lamellar structure. This is in agreement with long-range order formed during the hydrolytic polycondensation of bridged organosilica with long alkylene chains [(MeO)₃Si-(CH₂)_n-Si(OMe)₃ with n = 12 and 18] in water, thanks to hydrophobic interactions.⁷ The self-assembly of long alkylene chains involves the polycondensation of silanols groups, which come into close proximity (Scheme 2).



Scheme 2 Formation of the materials *via* the hydrogen bond interactions between monomeric species.

2. Role of the hydrogen bonding interactions

In order to point out the role of the hydrogen bonding interactions for the formation and the organisation of the materials, we prepared precursors 7 and 9 and the corresponding materials. Firstly, compound 7 containing two nitrile groups was synthesised as depicted in Scheme 3. Hydrolysis and polycondensation of 7 was achieved in sulfuric acid solution (9 M) giving rise to material M7 in high yield (Scheme 3).

As for M1–M3, M7 was fully condensed as indicating by the presence of a single peak at -67.3 ppm in the ²⁹Si NMR spectrum. The ¹³C NMR spectrum of M7 displays five signals (see Experimental section) assigned to the C_{sp3} and an additional one at 177.9 ppm attributed to the C=O of the carboxylic acid groups. The powder X-ray diffraction pattern of M7 (Fig. 4) exhibits a well-defined (100) peak at q = 3.39 nm⁻¹ as well as a second and weaker peak (200) at q = 6.75 nm⁻¹. These peaks are characteristic of a lamellar structure with 1.85 nm as interlayer distance. This value is similar to the theoretical distance (1.76 nm) obtained by ChemDraw 3D calculation. Interestingly, both peaks of M7 are narrower than those of M2 indicating an higher organisation degree for M7 due to the number of carboxylic acid groups.



Scheme 3 Preparation of 7 and the corresponding material M7.



Fig. 4 XRD patterns of M7, M2 and M9. Patterns were vertically offset for clarity.



Scheme 4 Preparation of 9 and the material M9.

The second precursor **9** already contains the carboxylic acid group. It was synthesised as depicted in Scheme 4 from the commercially available undecylenic acid. First, the esterification of undecylenic acid was carried out in good yield by using benzylbromide. Then, hydrosilylation of the vinyl groups gave rise to compound **8**. Finally, hydrogenolysis of **8** at room temperature afforded **9** as a colourless liquid in satisfactory yield.

The hydrolysis of 9 in water (pH = 1.5) at room temperature afforded rapidly and quantitatively the corresponding material M9 (Scheme 4) whereas starting from precursors containing nitrile groups, a concentrated sulfuric acid solution and high temperature (150 °C) were required to form the solid. This result indicates clearly that the formation of bis-silylated units by dimerisation of the carboxylic acid groups is a crucial step for the polycondensation process. In addition, material M9 was well organised in lamellar phase (Fig. 4) due to the fast self assembly during the synthesis. Finally, it is important to note that no material was obtained by hydrolysis of 8 under the same experimental conditions. Indeed, under these experimental conditions, the hydrolysis of the ester groups dos not occur.

3. Preparation and characterisation of PO(OH)₂functionalised materials M5 and M6

As the phosphonate groups are also hydrolysed into phosphonic acid $-P(O)(OH)_2$ under strong acid conditions and are known to



form robust hydrogen bonds.¹⁴⁻¹⁶ We applied the same methodology starting from trialkoxysilylalkyl diethylphosphonate. Three precursors **4**, **5** and **6** containing different chain lengths were selected and prepared for that purpose. **4** was prepared by Arbuzov reaction between 3-iodopropyltriethoxysilane¹² and triethylphosphite. **5** and **6** were prepared by hydrosilylation of 5-bromopentene and 11-bromoundecene respectively followed by Arbuzov reaction (Scheme 5).

Hydrolysis and polycondensation of 4-6 were achieved in 12 M HCl solution at reflux (Scheme 6). Under these conditions, the phosphonate groups were quantitatively transformed into phosphonic acid groups.¹⁷ The obtained materials were recovered by filtration as white powders in high yield and named M5–M6. However, no material was obtained starting from the precursor 4. Final composition of M5 and M6 were inferred from the results of Si, C and P elemental analyses. The C/Si ratio was found to be 5.1 for M5 and 9.8 for M6 while the theoretical values were 5 and 11 respectively. In addition, the P/Si ratio for M5-M6 was about 1. These results confirm the high degree of polycondensation and the conservation of the Si-C bonds. The ²⁹Si CP-MAS NMR spectra of M5 and M6 displayed only one signal at -68.5 and -67.3 ppm, respectively, attributed to the T³ [C-Si(OSi)₃] substructures, indicating fully condensed materials. The absence of resonance near -100 ppm corresponding to Q substructures denotes also that there is no cleavage of Si-C bonds during the sol-gel process and the hydrothermal treatment. ¹³C CP-MAS NMR spectra of M5 and M6 revealed that the organic groups remained intact. The ¹³C NMR spectrum of M5 is given as an example (Fig. 5). It displayed signals at

	HCl 12N	
$(E(O)_{3}SI ~ (^{-}/_{n} P(O)(OE)_{2})$	100 °C	$-0_{1.551}$ (n_n $r(0)(01)_2$
4: n = 1 5: n = 3		No material : n = 1
6: n = 9		M5: n = 3 M6: n = 9

Scheme 6 Preparation of materials M5 and M6.



Fig. 5 CP-MAS ¹³C NMR and ³¹P NMR (inset) spectra of M5.



Fig. 6 XRD patterns of M5 and M6. Patterns are vertically offset for clarity.

14.2 ppm (resonance of Si-CH₂), 34.6 (resonance of P-CH₂) and the three additional signals (23.4, 26.4 and 28.1 ppm) attributed to the other carbon atoms in the pentylene spacer. A typical ³¹P CP-MAS NMR spectrum of these materials displayed a single signal at 32.1 ppm attributed to phosphonic acid groups (Fig. 5).

Powder X-ray diffraction patterns of M5 and M6 are represented in Fig. 6. They are different from those of M2 and M3. The XRD pattern of M6 exhibited a first peak with low intensity at q = 1.85 nm⁻¹ corresponding to 3.39 nm. This distance was attributed to the interlayer d_{100} spacing. It is close to the theoretical distance obtained by ChemDraw 3D calculation (3.51 nm). The XRD pattern of M6 displayed also a second intense and well defined peak (200) at q = 3.74 nm⁻¹ with d = 1.68nm as well as a broad peak at 7.75 nm⁻¹ with d = 0.81 nm attributed to the fourth order. These peaks are characteristic of a lamellar structure. The peak at $q = 14.28 \text{ nm}^{-1}$ corresponding to 0.44 nm was attributed to alkylene chains packing within the layers. For M5, a lamellar phase with a lower organisation degree was observed. The peak at q = 6.54 nm⁻¹ with d = 0.96 nm corresponds to the second order. It is close to the half of the theoretical interlayer distance obtained by ChemDraw 3D calculation (1.75 nm). The low intensity for the first order peak can be due to a contrast matching effect arising from the presence of phosphorus atoms. The difference between the experimental d-spacing and the theoretical values for an extended dimer structure can be explained by the hydrogen bonds formation as described in Scheme 7.18

The failure of the preparation of materials from $4((EtO)_2(O)P-(CH_2)_3Si(OEt)_3)$ while it succeeded from $1(NC-(CH_2)_3Si(OEt)_3)$ should be probably due to more complex hydrogen bonded structures formed with the tridentate -PO₃H₂ group¹⁸ in comparison to those formed with -COOH groups. This result indicates that the formation of dimers in conjunction with the van der Waals interactions are the key points in this methodology.

4. Study of the ion-exchange capacities of the carboxylic acid groups within M1–M3

The accessibility of the carboxylic acid groups in materials M1–M3 as well as their ion-exchange ability were investigated. For



Scheme 7

that purpose, the carboxylic acid groups were transformed into potassium carboxylate salts by treating M1-M3 with either a 'BuOK solution in 'BuOH at 25 °C or potassium acetylaceto-nate (K(acac)) in ethanol. In both cases, the reactions were achieved in the presence of 1 equivalent of reagent for 1 -COOH unit, giving rise to exactly the same materials named M1K-M3K (Scheme 8).

The exchange reactions were confirmed by elemental analyses. The K/Si molar ratio was found to be 0.90, 0.99 and 0.93 for **M1K**, **M2K** and **M3K** respectively (Table 1). These values are very close to the theoretical values (1), indicating that the overall -COOH groups were accessible. The ²⁹Si NMR spectra of these materials revealed the absence of signals in the Q region (region near -100 ppm) showing that the treatment did not affect the siloxane bonds. The ²⁹Si NMR spectrum of **M1K** is given as an example (Fig. 1). The XRD patterns of materials **M1K–M3K** show that the structures were maintained after chemical transformation. In addition, the interlayer distance increased to 1.97 nm for **M1K** (Fig. 7). This increase was explained by the intercalation of the potassium ions between the layers. In addition, the low intensity for the first order peak in comparison with the







Fig. 7 XRD patterns of M1 and M1K. Patterns were vertically offset for clarity.

second one, may be due to the higher electronic density of potassium ions.

Finally, the chelating ability of **M1K–M3K** towards europium salts was tested. The solids were treated with an ethanolic solution of EuCl₃ at room temperature, arbitrarily for 12 h. The resulting solids were copiously washed with ethanol to eliminate any non-complexed salts and named **M1Eu**, **M2Eu** and **M3Eu** respectively (Scheme 8). The titration by EDTA of the whole filtrate containing the non-complexed salt was done and revealed the incorporation of one Eu^{III} per three carboxylate units for **M1K** and **M2K** on average. Interestingly, the Eu^{III} uptake within **M3K** was found to be 1 Eu^{III} per two carboxylate units. Elemental analyses (Table 1) of Si and Eu in **M1Eu–M3Eu** confirmed the europium content obtained by titration. Furthermore, it is worth noting that the potassium content in **M1Eu–M3Eu** was found to be very low (<50 ppm) showing that all the carboxylate groups were operative.

The Eu^{III} uptake within **M3K** requiring only two carboxylate units instead of three within **M1K** and **M2K** was explained as the consequence of a more regular packing arrangement of the carboxylate groups. It is worth noting that there is no Eu^{III} uptake directly from **M1–M3**.

Conclusions

We have described a new approach to obtain ordered and highly functionalised silicas containing carboxylic and phosphonic acid groups starting from monosilylated precursors. This method is based on the *in situ* formation of acid dimers followed by the polycondensation of silanol groups. We have shown that long-range order was promoted by the force and the number of acid groups and also by the van der Waals interactions between the long alkylene chains. Furthermore, these materials were proved to be able to chelate very high contents of lanthanide ions. The longer the alkylene chains, the better the structural order, which makes easier the Eu^{III} uptake. This renders these materials good candidates for ion separation including actinides.

Finally, these materials with high content of H^+/g could be also good candidates for high proton conductivity,^{19,20} which is particularly useful in the fuel cells area.

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References

- 1 C. Sanchez, B. Julian, P. Belleville and M. Popall, J. Mater. Chem., 2005, 15, 3559.
- 2 C. J. Brinker and G. W. Sherer, *Sol-Gel Science*, Academic Press, San Diego, CA, 1990.
- 3 B. Boury and R. J. P. Corriu, *Chem. Commun.*, 2002, 795; B. Boury and R. J. P. Corriu, *Chem. Rec.*, 2003, **3**, 120.
- 4 N. Liu, K. Yu, B. Smarsly, D. R. Dunphy, Y. B. Jiang and C. J. Brinker, J. Am. Chem. Soc., 2002, **124**, 14540.
- 5 Y. Fujimoto, A. Shimojima and K. Kuroda, *Chem. Mater.*, 2003, **15**, 4768; A. Shimojima and K. Kuroda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4057.
- 6 J. J. E. Moreau, B. Pichon, C. Bied and M. Wong Chi Man, J. Mater. Chem., 2005, 15, 3929.
- 7 J. Alauzun, A. Mehdi, C. Reyé and R. J. P. Corriu, J. Mater. Chem., 2005, 15, 841.

- 8 J. Alauzun, A. Mehdi, C. Reyé and R. J. P. Corriu, *Chem. Commun.*, 2006, 347.
- 9 J. Alauzun, A. Mehdi, C. Reyé and R. J. P. Corriu, J. Am. Chem. Soc., 2005, **127**, 11205; J. Alauzun, E. Besson, A. Mehdi, C. Reyé and R. J. P. Corriu, Chem. Mater., 2008, **20**, 503.
- 10 E. Samu, P. Huszthy, L. Somogyi and M. Hollosi, *Tetrahedron:* Asymmetry, 1999, 10, 2775.
- 11 R. Mouawia, A. Mehdi, C. Reyé and R. J. P. Corriu, J. Mater. Chem., 2007, 17, 616.
- 12 V. Matsura, Y. Guari, J. Larionova, C. Guerin, A. Caneschi, C. Sangregorio, E. Lancelle-Beltran, A. Mehdi and R. J. P. Corriu, J. Mater. Chem., 2004, 14, 3026.
- 13 P. H. Wine, R. J. Astalos and R. L. Mauldin, J. Phys. Chem., 1985, 89, 2620.
- 14 A. Clearfield, Metal phosphonate chemistry, Wiley, New York, 1998.
- 15 T. E. Mallouk and J. A. Gavin, Acc. Chem. Res., 1998, 31, 219.
- 16 K. Latham, A. M. Coyle, C. J. Rix, A. Fowless and J. M. White, *Polyhedron*, 2007, 26, 222.
- 17 R. J. P. Corriu, L. Datas, Y. Guari, A. Mehdi, C. Reyé and C. Thieuleux, *Chem. Commun.*, 2001, 763.
- 18 S. Pawsey, M. McCormick, S. De Paul, R. Graf, Y. S. Lee, L. Reven and H. W. Spiess, J. Am. Chem. Soc., 2003, 125, 4147.
- 19 G. Alberti and M. Casciola, Solid State Ionics, 1997, 97, 177.
- 20 Y. Jin, S. Qiao, J. C. Diniz da Costa, B. J. Wood, B. P. Ladewig and G. Q. Lu, *Adv. Funct. Mater.*, 2007, **17**, 3304.