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Direct syntheses using a fluorinated surfactant of silicas containing organofluorinated groups

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Direct syntheses of silicas containing organofluorinated groups have been achieved by co-condensation of tetraethylorthosilicate (TEOS) and a organofluorinated triethoxysilane, $R_F(CH_2)_2Si(OEt)_3$ [$R_F = CF_3(CF_2)_5$ or CF_3], in the presence of either the neutral fluorinated surfactant n-$CF_3(CF_2)_7(CH_2)_2NH_2$ or the cationic one, n-$CF_3(CF_2)_7(CH_2)_2NMe_3{}^+I^-$. Microporous silica with a wormhole structure containing the C_8 fluorinated chain was obtained in the presence of the nonionic surfactant. It was shown that the use of fluorinated surfactants allows the incorporation of an amount of (fluorinated) chains located in the channel pores that is superior to that obtained by using a hydrogenated surfactant. The cationic surfactant used under acidic conditions allowed the incorporation of only a low amount of the C_8 fluorinated chain, leading to a poorly structured material. In contrast, a mesoporous silica containing the $CF_3(CH_2)_2$ group and showing a hexagonal arrangement was obtained under the same experimental conditions.

Introduction

Functionalisation of the internal surface of mesoporous silica has attracted the attention of many researchers because of potential applications in different fields such as catalysis, adsorption, chromatography, photonics and nanotechnology. A large variety of functional groups have been introduced by grafting an organotrialkoxysilane, $RSi(OR')_3$, thanks to the reactive surface silanols.[1–4] An alternative one-step approach has been developed for the functionalisation of the internal surface of silica. It consists of the co-hydrolysis and polycondensation of tetraethylorthosilicate (TEOS) and an organotrialkoxysilane $RSi(OR')_3$ in the presence of a structure-directing agent.[5–13] This direct synthesis of mesoporous hybrid materials is particularly attractive in that it allows control of the organic loading and a more homogeneous distribution of organic groups at the surface.[14] This method supposes that the R group of the organotrialkoxysilane is hydrophobic enough to enter the core of the micelle and not too bulky in order to avoid bursting of the micelle. These are the main limits of this method.

Fluorinated chains are hydrophobic and to some extent lipophobic. They have the ability to dissolve large amounts of gases[15] and more recently, palladium nanoparticles have been stabilised by long polyfluorinated carbon chains.[16] Fluorinated materials are expected to be more hydrophobic and thermally resistant than their hydrocarbon counterparts, which make them attractive for surface treatments.[17] Hydrophobic mesostructured silicas are expected to be especially suitable materials for energy dissipation in mechanical dampers.[18] However, while a large variety of organic groups have been introduced at the internal surface of ordered mesoporous silica by either grafting or direct synthesis, the synthesis of ordered mesoporous fluoro-organically modified silicas has been scarcely explored. This is probably due to the lack of available fluorinated organotrialkoxysilanes.

Sanchez *et al.* have recently described the direct synthesis of ordered mesoporous silica containing fluorinated organic groups by using cetyltrimethylammonium bromide as a structure-directing agent.[19] Mesoporous fluorinated organosilicate films were also synthesised in the presence of cetyltrimethylammonium chloride.[20]

We decided to explore the preparation of ordered silica containing fluorinated chains in the presence of fluorinated surfactant as a template, which, to the best of our knowledge, has not been examined up to now. Indeed, fluorinated surfactants have many properties in common with their hydrocarbon analogues.[21] Thus, like hydrocarbon surfactants, they can self-assemble into various surfactant aggregates, depending on conditions such as water content, temperature, *etc.* However, they have also interesting particularities, which prompted us to use them. Indeed, they are more hydrophobic than their hydrocarbon homologues. Thus, the cmc of perfluorinated surfactants corresponds to that of a hydrocarbon surfactant with 1.5 to 1.7 times more carbon atoms.[22] Fluorinated chains are rigid; they prefer to form structures with less curvature than the hydrogenated ones.[22]

In this paper, we describe the direct synthesis of ordered mesoporous silicas containing fluorinated chains by co-hydrolysis and polycondensation of TEOS and fluorinated organotriethoxysilane $CF_3(CF_2)_5(CH_2)_2Si(OEt)_3$ or $CF_3(CH_2)_2Si(OEt)_3$ in the presence of either the neutral fluorinated surfactant n-$CF_3(CF_2)_7(CH_2)_2NH_2$ or the cationic one n-$CF_3(CF_2)_7(CH_2)_2NMe_3{}^+\ I^-$ (C_{10}-CTA_F). The physicochemical characteristics of materials were compared to those of corresponding materials prepared in the presence of analogous hydrogenated surfactants. The location of fluorocarbon groups was tentatively examined as a function of the nature of the surfactant.

Experimental

General procedures

Tetraethylorthosilicate (TEOS) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich; perfluoroalkyl iodide and perfluoroalkyltriethoxysilanes were purchased from ABCR; all were used as supplied. The CP-MAS ^{29}Si solid-state

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NMR spectra were recorded on a Brucker FTAM 300 as well as CP-MAS ^{13}C solid-state NMR spectra, in the latter case by using the TOSS technique. The repetition times were 5 and 10 s with contact times of 5 and 2 ms, respectively. Chemical shifts (δ) were referenced to Me_4Si. Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2010 analyser. Fast atom bombardment (FAB) mass measurements [matrix *m*-nitrobenzyl alcohol (NBA)] were registered on a JEOL JMS-D3000 spectrometer. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS" (Vernaison, France). Powder X-ray diffraction patterns were measured on a Bruker D5000 diffractometer equipped with a rotating anode (Institut Européen des Membranes, Montpellier, France). Transmission electron microscopy (TEM) observations were carried out at 100 kV (JEOL 1200 EXII). Samples for TEM measurements were prepared using ultramicrotomy techniques and then deposited on copper grids. TOF-SIMS investigations were performed on a TRIFT I spectrometer (Charles Evans and Associates) at the CEMEF (Ecole Nationale Supérieure des Mines de Paris at Sophia Antipolis).

Synthesis of fluorinated surfactants

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylamine. 1-Iodoperfluoroalkyl-2-ethane was transformed into the corresponding azide according to the procedure described in the literature.[23] Azide was reduced into the corresponding amine in the following way: 17.35 g (35.47 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylazide were added dropwise to a suspension of $LiAlH_4$ (10.01 g, 263 mmol) in anhydrous THF (100 ml). After 6 h of stirring at room temperature, the reaction mixture was placed in an ice bath, then 10 ml of H_2O, 10 ml of 15% NaOH and 30 ml of H_2O were successively added while stirring. The suspension was then filtered and the salts were washed with 3 × 100 ml of CH_2Cl_2. After drying over $MgSO_4$, the solvent was removed. An orange oil was distilled under vacuum (69% yield). B.p. 55 °C at 5 mm Hg. ^1H NMR (200 MHz, $CDCl_3$, 293 K): δ 3.09 (t, 2H, $^3J_{HH}$ = 7.0 Hz, NCH_2), 2.27 (m, 2H, $^3J_{HF}$ = 19.1 Hz, $^3J_{HH}$ = 7.0 Hz, R_FCH_2), 1.28 (m, 2H, NH_2). IR (KBr, cm^{-1}): 3378 (ν_{NH}), 1140–1240 (ν_{CF}).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyltrimethylammonium iodide. Potassium carbonate (4.46 g, 32.26 mmol) was added to a stirred solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylamine (15 g, 32.25 mmol) in ethanol (150 ml), followed by addition of methyl iodide (28.46 g, 200 mmol). The reaction mixture was stirred 3 days at room temperature in a Schlenk tube. The white precipitate was filtered and washed with pentane. After drying under vacuum, 29.2 g of a white powder was obtained (94% yield). ^1H NMR (200 MHz, acetone-d_6, 2893 K): δ 4.21 (m, 2H, NCH_2), 3.65 (s, 9H, CH_3), 3.16 (m, 2H, R_FCH_2). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 59.10, 58.70, 49.85, 21.78, 21.02, 18.72, 8.55. $^{19}F\{^1H\}$ NMR (235 MHz, acetone-d_6): δ −80.8, −112.7, −121.6, −122.5, −125.9. FAB-MS (NBA): *m*/*z* 506 [M^+]. Anal. calcd. for $C_{13}H_{13}NF_{17}I \cdot 2KI$ (%): C, 16.17; H, 1.36; N, 1.45; F, 33.46; I, 39.44; K, 8.10; found (%): C, 15.69; H, 1.31; N, 1.37; F, 31.90; I, 40.78; K, 8.17.

Synthesis of fluorine-containing silicas

Preparation of the fluorine-containing silica 1 in the presence of the neutral surfactant *n*-$C_8F_{17}C_2H_4NH_2$. The samples were synthesised from a mixture having the following molar compositions: 0.25 $R_F(CH_2)_2NH_2$: 22.7 H_2O : 8.6 EtOH : 0.04 NaF : (1 − *x*) TEOS : *x* $C_6F_{13}C_2H_4Si(OEt)_3$. In a typical preparation, 1.16 g (2.5 mmol) of *n*-$C_8F_{17}C_2H_4NH_2$ was dissolved in 4.1 ml of H_2O and 5.1 ml of absolute ethanol at 30 °C. The solution rapidly became transparent. The appropriate amounts of TEOS (1.97 g, 9.5 mmol), 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (0.26 g, 0.5 mmol) and NaF (17 mg, 0.39 mmol) were added. The solution became cloudy and a white precipitate appeared after 5 min. The mixture was stirred vigorously for 24 h at 30 °C. The precipitate was washed 3 times with H_2O, ethanol and acetone. The surfactant was removed by Soxhlet extraction over ethanol heated at reflux for 24 h. The resulting material was washed again with acetone and dried under vacuum at 120 °C for 12 h to give 0.59 g (98%) of a white powder. ^{29}Si CP-MAS NMR (60 MHz): δ −57 (T^2), −66 (T^3), −100 (Q^3), −109 (Q^4).

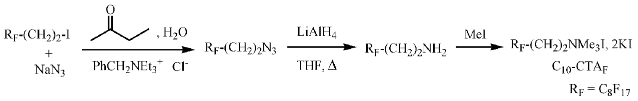
Preparation of the fluorine-containing silicas 3 and 7a–e in the presence of the cationic surfactant *n*-$C_8F_{17}C_2H_4NMe_3{}^+I^- \cdot 2KI$ (C_{10}-CTA_F). The samples were synthesised under acidic conditions from a mixture of the following molar compositions: 0.12 $R_F(CH_2)_2NMe_3{}^+I^-$: 112 H_2O : 9.5 EtOH : 9.2 HCl : 0.04 NaF : (1 − *x*) TEOS : *x* $C_6F_{13}C_2H_4Si(OEt)_3$ or $CF_3C_2H_4Si(OEt)_3$. In a typical preparation, 1.1 g (5.3 mmol) of TEOS and 0.1 g (0.34 mmol) of 3,3,3-trifluoropropyltrimethoxysilane were prehydrolyzed in an aqueous solution at pH = 1.2 under gentle stirring. After 1 h, this solution was added with vigorous stirring to a solution containing 0.661 g (0.68 mmol) of *n*-$C_8F_{17}C_2H_4NMe_3{}^+I^- \cdot 2KI$, 8.17 g (450 mmol) of H_2O, 1.43 g (31.2 mmol) of ethanol and 4.3 ml of 37% HCl (51.6 mmol) at 30 °C. NaF (10.1 mg, 0.24 mmol) was then immediately added and the mixture was vigorously stirred for 3 days. The precipitate was filtered and washed 3 times with ethanol and acetone. The surfactant was removed by Soxhlet extraction over ethanol heated at reflux for 24 h. The resulting material was washed again with H_2O, acetone and dried under vacuum at 120 °C for 12 h to give 0.38 g (93%) of a white powder. ^{29}Si CP-MAS NMR (60 MHz): δ −57 (T^2), −66 (T^3), −100 (Q^3), −109 (Q^4).

Preparation of silica 4 in the presence of the cationic surfactant *n*-$C_8F_{17}C_2H_4NMe_3{}^+I^- \cdot 2KI$ (C_{10}-CTA_F). Silica **4** was prepared according to the same procedure as **3** and **7a–e**, starting from TEOS as the only silica source. The complete removal of surfactant by Soxhlet extraction over ethanol at reflux for 24 h was checked by solid-state ^{13}C NMR spectroscopy of the silica.

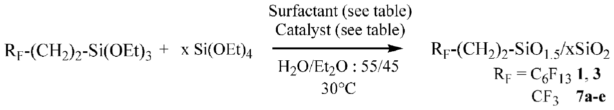
Results and discussion

Ordered microporous silicas containing $CF_3(CF_2)_5(CH_2)_2$ groups, prepared in the presence of *n*-$CF_3(CF_2)_7(CH_2)_2NH_2$ as template

The neutral surfactant $CF_3(CF_2)_7(CH_2)_2NH_2$ was prepared as depicted in Scheme 1 from the commercial iodide derivative. Co-hydrolysis and polycondensation of $CF_3(CF_2)_5(CH_2)_2Si(OEt)_3$ and 19 equiv. of TEOS was first carried out in the presence of the neutral fluorinated surfactant according to the experimental conditions previously described for the direct synthesis of hybrid materials in the presence of *n*-hexadecylamine as surfactant (Scheme 2).[24] This gave rise to an amorphous hybrid material. In order to facilitate mesostructure formation, we added fluoride ions,[25] which catalyse



Scheme 1 Synthesis of *n*-$CF_3(CF_2)_7(CH_2)_2NH_2$ and *n*-$CF_3(CF_2)_7(CH_2)_2NMe_3I \cdot 2KI$ (C_{10}-CTA_F).



Scheme 2 Synthesis of materials **1**, **3** and **7a–e**.

the hydrolysis polycondensation process (see Experimental) to afford material **1**.

The X-ray pattern of the material prepared in the presence of NaF is displayed in Fig. 1. It reveals the formation of a wormhole structure, with a *d* spacing of 39 Å for a $R_F(CH_2)_2Si(OEt)_3$: TEOS ratio of 1 : 19. However, the material prepared under the same conditions but with a $R_F(CH_2)_2Si(OEt)_3$: TEOS ratio of 1 : 9 no longer has a wormhole structure. This strongly suggests that the fluorinated chains enter the core of the micelle and that the micelle bursts when the loading is too high. Indeed, this is similar to what is observed for the direct synthesis of hybrid materials using hydrocarbon surfactants for which a superior limit to the amount of organic moieties incorporated is always observed.[11]

The hybrid material containing the organofluorinated group $CF_3(CF_2)_5(CH_2)_2$ was also prepared in the presence of *n*-hexadecylamine in order to compare the contribution of this surfactant to that of the fluorinated one. It was prepared according to the procedure previously described,[24] that is to say without NaF, and is called **2**. It presents a powder X-ray pattern (Fig. 1) that is characteristic of a wormhole structure, as for **1**, but **2** appears to be slightly more ordered.

The physicochemical characteristics of both materials prepared from a molar ratio $R_F(CH_2)_2Si(OEt)_3$: TEOS of 1 : 19 are given in Table 1.

The N_2 adsorption-desorption isotherms of **1** and **2** are reported in Fig. 2. They are characteristic for microporous materials (type I isotherm) with high specific surface areas.

It is interesting to note that the content of organofluorinated groups, which was inferred from the results of elemental analysis (Si and F), was very close to the theoretical value in both cases. Thus, the direct synthesis method allows a control of the loading in organofluorinated groups, whether the surfactant is fluorinated or not.

The solid-state ^{29}Si MAS NMR spectra of both materials are similar and displayed signals at −58 and −66 ppm, assigned to substructures T^2 and T^3, respectively, in addition to Q substructures. This clearly indicates that the linkage of the organofluorinated groups to the silica matrix is effective.

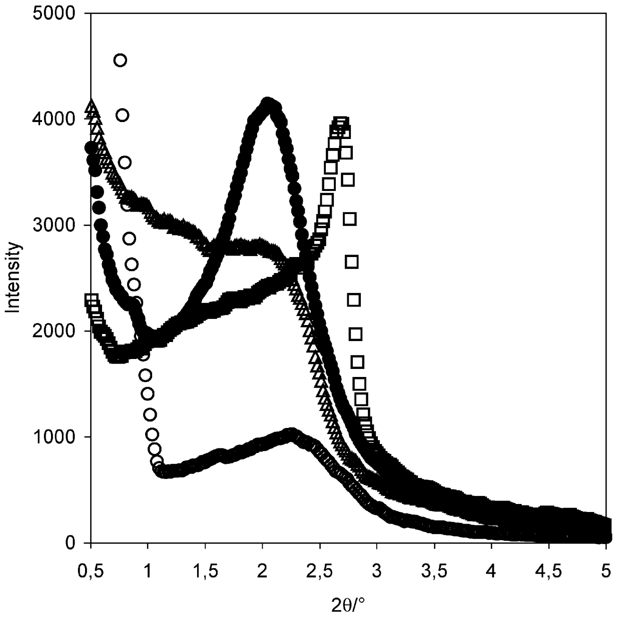


Fig. 1 X-Ray diffraction patterns for the hybrid silicas **1** (●), **2** (○), **3** (Δ) and **7a** (□).

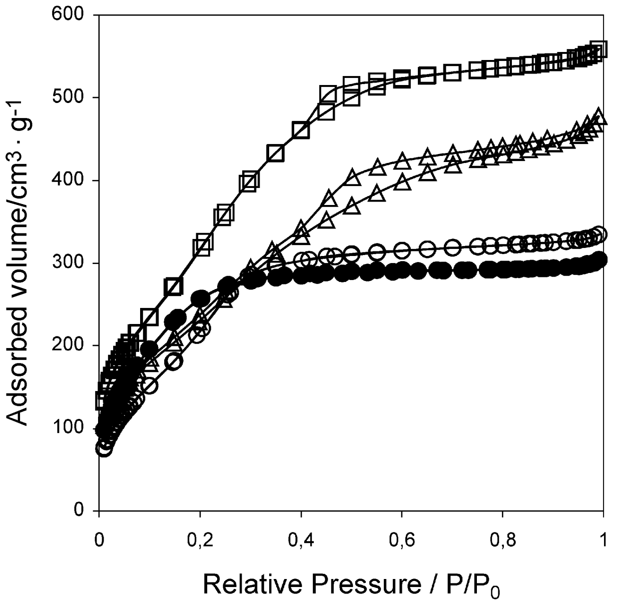


Fig. 2 Nitrogen adsorption-desorption isotherms for the hybrid silicas **1** (●), **2** (○), **3** (Δ) and **7a** (□).

In order to confirm the location of the organoperfluorinated groups inside the channel pores of the materials prepared in the presence of the fluorinated surfactant, time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis was performed on materials **1** and **2**. This analytical method probes the uppermost layers of the surface (*ca.* 1 nm) and is widely used for the analysis of polymer surfaces.[26–29] Fig. 3 exhibits the ratio of the main ions characteristic of the fluorinated chains and the matrix, originating from **1** and **2**. It is worth stressing that the comparison of these ratios is significant as the content in fluorinated chains is almost the same in both materials (Table 1).

The results reveal the presence of fluorine in both materials. This indicates that in both cases, a part of the fluorinated chains are anchored at the external surface of the material or in the upper layer (1 nm) and not at the internal surface of the channel pores. However, the relative intensities of the ratios $CF_3^+ : Si^+$, $CF_3^+ : SiOH^+$ and $F^- : O^-$ are significantly higher for **2** than for **1**. This suggests that the use of a fluorinated

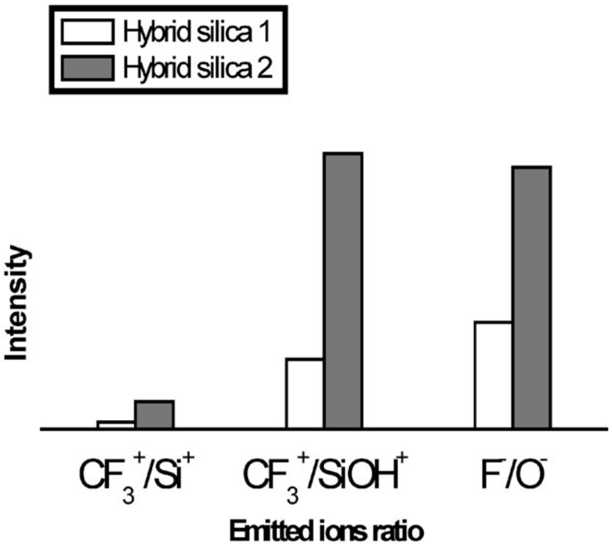


Fig. 3 TOF-SIMS analysis for materials **1** and **2**.

Table 1 Physicochemical characteristics of materials **1**–**9**

Material	Surfactant	R_F	Catalyst	S_{BET} /m^2 g^{-1}	V_p /cm^3 g^{-1}	D_p[a]/Å	a^0 /Å	Molar ratio[b] $R_F(CH_2)_2SiO_{1.5}:SiO_2$
1	n-$C_8F_{17}(CH_2)_2NH_2$	—	NaF	839	0.47	21 (W)	39	1 : 19 (1 : 19)
2	n-$C_{16}H_{33}NH_2$	—	—	869	0.52	26 (W)	43	1 : 19 (1 : 19)
3	C_{10}-CTA_F	$CF_3(CF_2)_5$	NaF/HCl	869	0.74	< 30 (W)	42	1 : 32 (1 : 19)
4	—	—	—	693	0.72	36 (W/H)	42	—[c]
5	CTAB	—	HCl	290	0.18	< 20 (W)	43	1 : 24 (1 : 19)
6	—	—	NaOH	752	0.46	< 20 (W)	—	1 : 19 (1 : 19)
7a	—	—	—	1217	0.86	< 30 (H)	37	1 : 43 (1 : 19)
7b	—	—	—	910	0.66	< 30 (H)	38	1 : 19 (1 : 15)
7c	C_{10}-CTA_F	—	NaF/HCl	898	0.70	< 30 (H)	37	1 : 18 (1 : 12)
7d	—	CF_3	—	982	0.60	< 50 (L)	—	1 : 11 (1 : 9)
7e	—	—	—	857	0.55	< 20 (A)	—	1 : 6 (1 : 4)
8	CTAB	—	HCl	500	0.31	< 20 (w)	—	1 : 31 (1 : 19)
9	—	—	NaOH	883	0.48	< 20 (H)	38	1 : 20 (1 : 19)

[a] Calculated from $4V_p/S_{BET}$ (W = wormhole, H = hexagonal, L = lamellar, A = amorphous). [b] Calculated from elemental and/or thermogravimetric analysis [the $R_F(CH_2)_2Si(OEt)_3$: TEOS ratio of the mother solution is given in parentheses]. [c] Silica synthesis from TEOS.

surfactant allowed the incorporation of fluorinated chains inside the channel pores of the resulting material to an extent superior to that obtained by using the hydrocarbon surfactant n-$C_{16}H_{33}NH_2$. Thus, the TOF-SIMS analysis confirmed the interest of using the fluorinated surfactant in place of the hydrocarbon one to locate fluorinated moieties inside the channel pores of porous materials.

Mesoporous hybrid materials containing $CF_3(CF_2)_5(CH_2)_2$ groups and prepared in the presence of $CF_3(CF_2)_7(CH_2)_2NMe_3{}^+I^-$ as template

Very little is known about fluorinated cationic surfactants. This is probably due to the difficulty in preparing them with high purity and also to their instability.[30] As we wanted to compare the behaviour of a fluorinated cationic surfactant to that of a hydrogenated one, we prepared $CF_3(CF_2)_7(CH_2)_2NMe_3{}^+I^-$ (C_{10}-CTA_F), from the corresponding neutral surfactant n-$CF_3(CF_2)_7(CH_2)_2NH_2$ (see Experimental and Scheme 1); this fluorinated surfactant is analogous to cetyltrimethylammonium bromide (CTAB). The reaction was quantitative. However, the yield as well as the microanalysis of C_{10}-CTA_F revealed that salts (KI) formed during the synthesis were not separated from the surfactant.

Hybrid material **3** containing organofluorinated chains $CF_3(CF_2)_5(CH_2)_2$ was prepared in the presence of C_{10}-CTA_F under acidic conditions (Scheme 2), the surfactant being unstable under basic conditions. The N_2 adsorption-desorption isotherm (Fig. 2), which is of type IV, is representative of a mesoporous material with small mesopores (< 30 Å) and presenting a high specific surface area (869 m^2 g^{-1}).

The solid-state ^{29}Si CP-MAS NMR spectrum of this material displayed signals at −58 and −66 ppm assigned to substructures T^2 and T^3, respectively, in addition to Q substructures. This demonstrates that the linkage of the organofluorinated groups to the silica matrix was effective. However, the results of elemental analyses of the material indicate that the loading in organofluorinated groups was notably inferior to the theoretical value. Indeed, the molar ratio $R_F(CH_2)_2SiO_{1.5}:SiO_2$ was found to be 1 : 32 instead of 1 : 19, the expected value.

The XRD pattern of material **3** revealed a poorly ordered worm-like structure (Fig. 1 and Table 1) while pure silica **4**, prepared according to the same procedure, presented a mixture of worm-like and hexagonal structures with a mean pore diameter of 36 Å (Table 1). This strongly suggests that the organofluorinated chains enter the core of the micelle and disrupt it at this concentration, probably because the chain is too long [$CF_3(CF_2)_5(CH_2)_2$] in comparison to that of the surfactant [$CF_3(CF_2)_7(CH_2)_2$].

It is worth noting that the presence of KI likely has an impact on the structure of the resulting material.[31] However, in our case, this effect could not be determined.

Mesoporous hybrid materials containing $CF_3(CF_2)_5(CH_2)_2$ groups and prepared in the presence of CTAB as template

In order to have more information concerning the location of organofluorinated groups in the material prepared in the presence of C_{10}-CTA_F, the co-hydrolysis and polycondensation of TEOS and $CF_3(CF_2)_5(CH_2)_2Si(OEt)_3$ was also performed in the presence of CTAB under acidic and basic conditions to afford, respectively, materials **5** and **6**. The relevant physicochemical characteristics of these materials are reported in Table 1. They are slightly different from those of material **3** prepared in the presence of fluorinated surfactant: their N_2 adsorption-desorption isotherms are of type I, characteristic of microporous materials. It is worth noting that hybrid materials containing hydrogenated organic groups and prepared in the presence of CTAB were also microporous, whatever the experimental conditions (acidic[32] or basic[33]). Their X-ray diffraction patterns display only a rather broad peak, which indicates worm-like ordering, material **6** being nevertheless more ordered. Such a poor degree of order was also observed for hybrid materials prepared in the presence of CTAB under acidic conditions after extraction of the surfactant.[32] In contrast, hybrid materials prepared in the presence of CTAB under basic conditions are more ordered with a hexagonal arrangement.[8] This suggests that the organofluorinated groups interact with the core of the micelles and partially disrupt them, probably because of the rigidity of the perfluorinated part. Finally, whatever the experimental conditions (acidic or basic) the content in fluorinated organic groups (Table 1), which was inferred from the results of elemental analyses, was found to be notably superior to that of **3** prepared in the presence of C_{10}-CTA_F.

The different amounts of perfluoro groups for materials **3** and **5** render a comparative study by SIMS uninformative and thus they were not further investigated.

Hybrid materials containing $CF_3(CH_2)_2$ groups prepared in the presence of $CF_3(CF_2)_7(CH_2)_2NMe_3{}^+I^-$

As the incorporation of the long chains $CF_3(CF_2)_5(CH_2)_2$ did not give rise to well-ordered hybrid materials in the presence of the cationic surfactant C_{10}-CTA_F, we have also investigated the incorporation of the short fluorinated chain $CF_3(CH_2)_2$

by direct synthesis in the presence of the same surfactant. Materials **7a–e** were prepared using different amounts of the organofluorinated precursor (Scheme 2) and their relevant physicochemical characteristics are reported in Table 1.

The results of elemental analyses of these materials revealed that the incorporation of organofluorinated chains was in all cases inferior to the theoretical value, even for the most dilute material **7a**. Confirmation of the incorporation of the organofluorinated chains was given by the presence of a signal at −67 ppm (substructure T^3) in solid-state ^{29}Si MAS NMR spectroscopy.

Type IV N_2 adsorption-desorption isotherms, characteristic for mesoporous materials, were obtained for the hybrid materials **7a–c**. The N_2 adsorption-desorption isotherm for material **7a** is given in Fig. 2. These materials present large specific surfaces and pore volumes with small mesopores (<30 Å). It is worth noting that when the concentration in $CF_3(CH_2)_2$ groups increases, there is a decrease of the specific surface area and pore volume. That suggests that the location of the organic groups is within the pore channels. Finally, the powder X-ray patterns for these materials display a rather narrow diffraction peak corresponding to the d_{100} spacing. The X-ray pattern of material **7a** is depicted in Fig. 1. A TEM image of material **7a** showing parallel channels and providing evidence for a 2D hexagonal structure is presented in Fig. 4. The cell parameter *a* was estimated to be 31 Å from the TEM image, which is slightly inferior to the value determined from the XRD data.

To resume, hexagonal mesoscopic ordering was obtained for hybrid materials containing the short chain $CF_3(CH_2)_2$, while a poorly ordered material was obtained when the longest chain $CF_3(CF_2)_5(CH_2)_2$ was incorporated. This confirms that this latter chain is too long in comparison to that of the surfactant to obtain such an organisation.

When the concentration in $CF_3(CH_2)_2$ was increased, formation of a lamellar arrangement was observed for material **7d**, which collapsed after removal of the surfactant. Finally, for a ratio $R_F(CH_2)_2SiO_{1.5} : SiO_{1.5} = 1:4$ (**7e**), the material was amorphous. These results are in agreement with the location of the $CF_3(CH_2)_2$ chains in the core of the micelle: indeed, in that case, as the concentration in the chains increases, there is also progressively an increase in the hydrophobic volume and a decrease in the polar head surface, that is to say a progressive increase in the packing parameter g ($g = v/la_o$). For silica systems, it has been shown that an increase in the parameter g (*i.e.*, a decrease in the curvature of the micelle) leads to phase transitions.[34,35] This is what we observed with a transition from a hexagonal organisation for materials **7a–c** to a lamellar organisation for material **7d** as the concentration increases. Finally, when the concentration in chains is too high, the micelles should be disrupted, leading to an amorphous solid as observed for material **7e**.

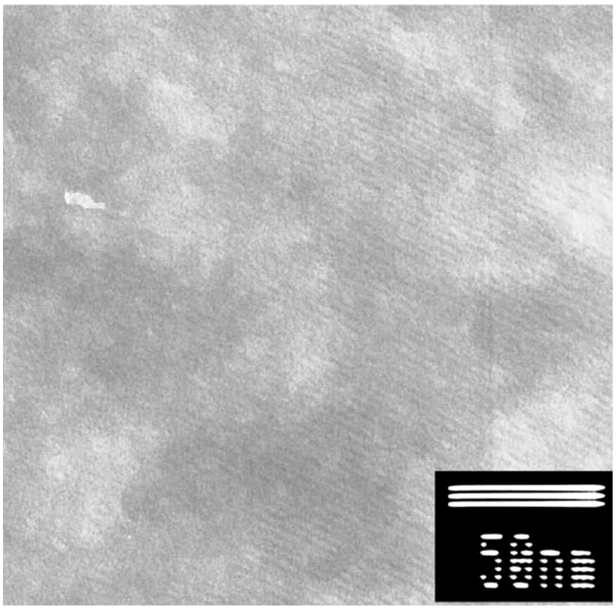


Fig. 4 TEM image of the hybrid material **7a**.

Hybrid materials containing $CF_3(CH_2)_2$ groups prepared in the presence of CTAB

Hybrid materials containing $CF_3(CH_2)_2$ groups have also been prepared in the presence of CTAB under acidic (material **8**) and basic (material **9**) conditions. In both cases, the ratio $R_F(CH_2)_2SiO_{1.5} : SiO_{1.5}$ was chosen to be 1 : 19. The physicochemical characteristics of these materials are reported in Table 1. Both materials, prepared in the presence of CTAB, exhibit type I N_2 adsorption-desorption isotherms, characteristic for microporous materials with a mean pore diameter inferior to 20 Å.

The XRD patterns of materials prepared under acidic conditions display a broad diffraction peak characteristic of a worm-like structure. As silica prepared under the same experimental conditions presents a hexagonal structure,[36] it appears that the addition of a fluorinated precursor $R_F(CH_2)_2Si(OEt)_3$ disrupts the micelle. In contrast, the synthesis of the corresponding material prepared under basic conditions gives rise to a material with hexagonal structure. These results are in agreement with those described in the literature: the structuration of hybrid materials in the presence of CTAB under basic conditions[8] is better than under acidic conditions.[32]

It is interesting to compare the materials incorporating the long organofluorinated chains $CF_3(CF_2)_5(CH_2)_2$ (**5**, **6**) to those incorporating the short organofluorinated chains $CF_3(CH_2)_2$ (**8**, **9**), both prepared in the presence of CTAB. Under basic conditions, material **6** incorporating the longest chain is less ordered than material **9** incorporating the short one (worm-like structure instead of hexagonal one). This result is in agreement with the location of the fluorinated chains in the core of the micelle, the longest one disrupting the micelle more than the short one. In contrast, under acidic conditions, the reverse is observed. The material incorporating the longest chain **5** is slightly more ordered than material **8**. This could suggest that, under acidic conditions, the organofluorinated chain is located at the surface of the particle and not in the channel pores of material **5**.

Conclusion

Organofluorinated silicas have been prepared in one step by co-condensation of tetraethylorthosilicate (TEOS) and a organofluorinated triethoxysilane, $R_F(CH_2)_2Si(OEt)_3$ [with $R_F = CF_3(CF_2)_5$ or CF_3] in the presence of either the neutral fluorinated surfactant n-$CF_3(CF_2)_7(CH_2)_2NH_2$ or the cationic one n-$CF_3(CF_2)_7(CH_2)_2NMe_3{}^+I^-$. It appears that the structuration of the resulting hybrid material depends on both the nature of R_F and the surfactant: the hybrid materials prepared in the presence of the neutral fluorinated surfactant are microporous with a large specific surface area (800 m^2 g^{-1}) and rather large pore volumes (0.5 cm^3 g^{-1}), and have a worm-like structure. They incorporate the expected content of fluorinated chains. Furthermore, it has been shown that the use of a fluorinated surfactant instead of a hydrogenated one allows the incorporation of an higher amount of organofluorinated moieties into the channel pores. The hybrid materials prepared in the presence of the cationic fluorinated surfactant are mesoporous with small pore diameters (inferior to 30 Å), high specific surface areas (from 800 to 1200 m^2 g^{-1}) and large pore volumes. The structuration strongly depends on the nature and amount of incorporated fluorinated moieties. The incorporation of the longest chain (C8) does not allow an ordered material to be obtained. In contrast, when the fluorinated chain is short [$CF_3(CH_2)_2$], it is possible to get a hybrid material with a hexagonal structure, the location of the organo-fluorinated groups being inside the channel pores.

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