Generic way for functionalised well-ordered cubic mesoporous silica *via* direct synthesis approach†

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Applications of functionalised mesoporous silica are dependent upon the location, the quantity and the accessibility of the functional groups attached in the inner pores, particularly in the case of cubic ordered porous structure. Facilitating such material synthesis could be of great interest. Herein, we present a controlled and generic route to functionalised and well-ordered cubic mesoporous silica by direct synthesis and an efficient method for complete template removal without structure collapse nor loss of organic content, leading to better functional accessibility and thus material capability. Materials were obtained by co-condensation of tetraethylorthosilicate (TEOS) and an organotriethoxysilane Σ-$(CH_2)_3$-$Si(OR')_3$ (with R' = Me or Et and Σ = CN, SH, $CH_3COCHCOCH_3$ (acac) and $PO(OEt)_2$) in the presence of F127 as structure-directing agent in acidic media. All materials were characterised by XRD, TEM, TGA, ^{13}C and ^{29}Si NMR spectroscopies, nitrogen gas adsorption–desorption measurements as well as elemental analyses. Functional accessibility and adsorption capacity of such materials were proved by complexation of lanthanide ions thanks to acac groups.

Introduction

Since their discovery, ordered mesoporous silicas have reached considerable attention. In particular, many investigations have focused on their functionalisation to render them suitable for applications such as catalysis, separation, chemical sensors *etc.*[1] Two main approaches have been used to anchor organic groups onto the inner pore surface of mesoporous silicas: grafting method (post-synthesis) and co-condensation method (direct synthesis). Post-synthesis grafting of an organotrialkoxysilane $RSi(OR')_3$ onto the pore surface of the mesoporous silica was the first method established for functionalisation.[2] This method is generic and allows the incorporation of many R groups including bulky ones. However, neither the loading control nor the distribution of the functional groups, which depend on several parameters such as the number of the residual silanol (SiOH) groups at the surface as well as their accessibility are possible.[3] The other strategy called "direct synthesis", consists in the copolymerisation of tetraethylorthosilicate (TEOS) and an organotrialkoxysilane $RSi(OR')_3$ in the presence of a structure-directing agent.[4] This one-step method, more challenging and also more attractive than the grafting one is often preferred. Indeed, this method allows regular R groups distribution inside the channel pores as well as a loading control within the limits of the content supported by the micelle.[5] However, it has also its own limitations. The organic R group has to be sufficiently lipophilic to enter the core micelle and not too bulky (to avoid bursting). If the functional group is rather hydrophilic, the functionalisation could occur partially within the framework. This has been observed by Linden *et al.* for aminopropyl-functionalised mesoporous SBA-15. Analysis of this material prepared by direct synthesis under acidic conditions revealed that most of the amino groups were embedded in the framework of the silica and not located on the pore surface.[6] A possible way to incorporate amino groups into the channel pores of mesostructured silica by direct synthesis under acidic conditions consists in their protection with -*tert*-butyloxycarbonyl group (Boc).[7] Protected amino groups cannot be protonated and thus remain in the core micelle, leading to a channel pore location after deprotection. This problem of the pendant organic location was also mentioned by Yang *et al.* when they prepared sulfonic acid ($-SO_3H$) functionalised periodic mesoporous silicas by direct synthesis, the $-SO_3H$ moieties being generated *in situ* by oxidation of the propylthiol.[8] In comparison, when the sulfonic acid groups were prepared in two steps,[5c,d,9] first by direct synthesis of propylthiol-functionalised mesoporous silica, followed by oxidation of the SH groups, all the SH groups were located in the channel pores.[5c,d] These examples show that the preparation of pore-functionalised ordered mesoporous silicas by direct synthesis is not a routine task and remains a challenge.

Up to date, a large variety of functionalised mesoporous 2-D hexagonal silicas have been obtained by direct synthesis process.[10] In contrast, the number of long-range order cage-like cubic mesoporous silicas functionalised with pendant organic groups currently reported is notably inferior whatever the non ionic[11] or ionic nature of the surfactant.[12] This is

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probably due to stricter experimental conditions than those giving rise to the corresponding functionalised 2-D hexagonal mesoporous silicas. In addition, removing the template from functionalised cage-like mesostructures when triblock copolymers are used as structure-directing agent is still an issue.[11b,d] Yet, this family of ordered mesoporous materials is fascinating. Indeed, they exhibit a 3-D network of nearly spherical mesopores interconnected through small windows forming a multidirectional system, which should facilitate mass transfer and restrict pore blockage. A recent study has shown that the tridimensional cage structure of SBA-16 allows a much more rapid diffusion of heptane, cumene and mesitylene than the straight cylindrical pore shape of SBA-15.[13] These features render these materials particularly attractive for many chemical or physical applications such as catalysis, separation of molecules, gas sensing or 3-D ordered nanoparticles growth.

Therefore, our interest was to find an easy, generic and highly reproducible method to prepare functionalised cage-like cubic mesoporous silicas *via* direct synthesis approach. Herein, we report a way to synthesise 3-D cubic mesoporous silicas (body-centered $Im\bar{3}m$, SBA-16 type), functionalised with different pendant organic groups [-$(CH_2)_3$-Σ with Σ = CN, SH, $CH_3COCHCOCH_3$ (acac) and $PO(OEt)_2$]. The influence of various contents in organic groups on the formation of the cubic mesostructure is studied. It is worth noting that all these functional groups were previously introduced into the channel pores of 2-D hexagonal mesoporous silicas by direct synthesis [CN,[5d,14] SH,[5c,d,9] $CH_3COCHCOCH_3$[5c,d] (acac) and $PO(OEt)_2$[15]] as they could give rise to a range of applications. Carboxylic acid groups resulting from the hydrolysis of cyano groups can be used to complex a variety of salts including lanthanides. They can also serve as anchor sites for biomolecules. Thiol-functionalised mesoporous silicas are particularly suitable materials for heavy-metal ion-trapping agents,[16] stabilisation of gold nanoparticles[17] as well as precursor of sulfonic-acid functionality for solid acid catalysis.[18] Acac groups were proved to be efficient for lanthanide complexation[5c,d] and diethyl phosphonate groups were used to control the growth of indium[19] and ruthenium nanoparticles.[20] Finally, an efficient and simple method for complete template elimination without structure collapse nor loss of organic content is shown, enhancing organic groups accessibility and may therefore be effective for improving functionalised 3-D cubic mesoporous silica applications.

Experimental

Chemicals

Pluronic F127 triblock copolymer ($PEO_{106}PPO_{70}PEO_{106}$ with PEO = poly-(ethylene oxide), PPO = poly-(propylene oxide) and M_{av} = 12 600) was purchased from Aldrich, $Eu(acac)_3$ salts and 3-mercaptopropyltrimethoxysilane (MPTMS) **1** from Alfa Aesar, 3-cyanopropyltriethoxysilane **2** from ABCR. All of them were used as supplied.

3-Diethylphosphonatopropyltriethoxysilane **3**[20] and 3-(3-(triethoxysilyl)propyl)-2,5-pentanedione **4**[21] were prepared according to previously described procedures.

Synthesis of functionalised SBA-16 type materials

All materials were prepared under the exact same conditions. Surfactant-free samples were named **M-Σ^x**,**M** for Materials, **Σ** referring to the nature of the functional groups and **x** to the molar percentage of organic groups in the initial mixture.

The preparation of the **M-SH^{10}** material is given as an example. In a typical synthesis, 2.00 g (0.16 mmol) of Pluronic F127, 7.19 g (123 mmol) of NaCl, 60 mL of permuted water and 20 mL of a 2M HCl solution were placed in a teflon bottle, which was then closed hermetically. After stirring vigorously for about 1.5 h, a clear solution was obtained. The bottle was then placed in a thermostated oil-bath at 40 °C. After stirring for 1 h, 7.55 g (36.3 mmol) of TEOS were first added to this mixture rather rapidly with a syringe followed immediately by 0.79 g (4.0 mmol) of MPTMS. The molar composition of the resulting mixture was the following MPTMS/TEOS/F127/NaCl/H_2O/HCl was 1/9/0.04/30/820/10. The mixture was further stirred vigorously at 40 °C for 20 h. After this time, a white "cloud" was observed. The closed bottle was then placed in an oven for 2 h at 110 °C. After decantation, the white precipitate was filtered off, washed 3 times with 30 mL of ethanol, then acetone. The powder was crushed in a mortar and dried under vacuum at 100 °C for 5 h. Surfactant was completely removed by extracting about 4 g of the as-synthesised material with a mixture of 30 mL of pyridine, 30 mL of permuted H_2O and 5 mL of a 2M HCl solution at 70 °C overnight. The pH has to be adjusted at 6–7 by addition of 2M HCl to avoid basic conditions, which could damage the silica. After washing three times with ethanol then acetone, followed by a pulverising step, the solid was dried at 100 °C under vacuum for 6 h giving rise to **M-SH^{10}** as white powder in about 85% yield.

M-SH^3. TEOS (8.10 g, 39.0 mmol); **1** (0.26 g, 1.3 mmol). White powder. ^{13}C CP-MAS NMR (δ, ppm, 75 MHz): 10, 23, 27. ^{29}Si CP-MAS NMR (δ, ppm, 60 MHz): −58 (T^2), −66 (T^3), −91 (Q^2), −102 (Q^3), −112 (Q^4). Anal. calcd. Si/S 30. Found 29.6. S_{BET} 955 $m^2\ g^{-1}$. *Dp* 4.5 nm. Vp 0.26 $cm^3\ g^{-1}$.

M-SH^5. TEOS (7.97 g, 38.3 mmol); **1** (0.40 g, 2.0 mmol). White powder. Anal. calcd. Si/S 20. Found 19.0. S_{BET} 970 $m^2\ g^{-1}$. *Dp* 4.7 nm. Vp 0.31 $cm^3\ g^{-1}$.

M-CN^3. TEOS (8.10 g, 39.0 mmol); **2** (0.31 g, 1.3 mmol). White powder. ^{13}C CP-MAS NMR (δ, ppm, 75 MHz): 11, 19, 120. ^{29}Si CP-MAS NMR (δ, ppm, 60 MHz): −66 (T^3), −91 (Q^2), −101 (Q^3), −109 (Q^3). Anal. calcd. Si/N 30. Found 24.1. S_{BET} 820 $m^2\ g^{-1}$. *Dp* 5.6 nm. Vp 0.29 $cm^3\ g^{-1}$.

M-CN^5. TEOS (7.97 g, 38.3 mmol); **2** (0.46 g, 2.0 mmol). White powder. Anal. calcd. Si/N 20. Found 23.6. S_{BET} 930 $m^2\ g^{-1}$. *Dp* 5.6 nm. Vp 0.34 $cm^3\ g^{-1}$.

M-CN^{10}. TEOS (7.55 g, 36.3 mmol); **2** (0.93 g, 4.0 mmol). White powder. Anal. calcd. Si/N 10. Found 10.7. S_{BET} 755 $m^2\ g^{-1}$. *Dp* 4.7 nm. Vp 0.26 $cm^3\ g^{-1}$.

M-PO(OEt)$_2^3$. TEOS (8.10 g, 39.0 mmol); **3** (0.46 g, 1.3 mmol. White powder. ^{13}C CP-MAS NMR (δ, ppm, 75 MHz): 15, 27, 62. ^{29}Si CP-MAS NMR (δ, ppm, 60 MHz): −65 (T^3), −92 (Q^2), −100 (Q^3), −108 (Q^4).

^{31}P CP-MAS NMR (δ, ppm, 120 MHz): 34. Anal. calcd. Si/P 30. Found 31.0. S_{BET} 715 m^2 g^{-1}. *Dp* 5.3 nm. Vp 0.29 cm^3 g^{-1}.

M-PO(OEt)$_2$^{5}. TEOS (7.97 g, 38.3 mmol); **3** (0.69 g, 2.0 mmol). White powder. Anal. calcd. Si/P 20. Found 19.8. S_{BET} 735 m^2 g^{-1}. *Dp* 4.7 nm. Vp 0.26 cm^3 g^{-1}.

M-PO(OEt)$_2$^{10}. TEOS (7.55 g, 36.3 mmol); **3** (1.38 g, 4.0 mmol). White powder. Anal. calcd. Si/P 10. Found 9.9. S_{BET} 525 m^2 g^{-1}. *Dp* 3.7 nm. Vp 0.17 cm^3 g^{-1}.

M-acac^3. TEOS (8.10 g, 39.0 mmol); **4** (0.41 g, 1.3 mmol. White powder. ^{13}C CP-MAS NMR (δ, 75 MHz): 11, 20, 29, 67, 111, 191, 208. ^{29}Si CP-MAS NMR (δ, 60 MHz): −58 (T^2), −65 (T^3), −91 (Q^2), −101 (Q^3), −110 (Q^4). S_{BET} 910 m^2 g^{-1}. *Dp* 5.0 nm. Vp 0.32 cm^3 g^{-1}.

M-acac^5. TEOS (7.97 g, 38.3 mmol); **4** (0.61 g, 2.0 mmol). White powder. S_{BET} 550 m^2 g^{-1}. *Dp* 4.8 nm. Vp 0.24 cm^3 g^{-1}.

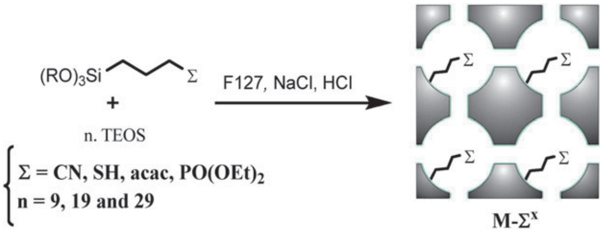
M-acac^{10}. TEOS (7.55 g, 36.3 mmol); **4** (1.22 g, 4.0 mmol). White powder. S_{BET} 645 m^2 g^{-1}. *Dp* 3.9 nm. Vp 0.19 cm^3 g^{-1}.

Characterisations

The solid-state CP-MAS ^{29}Si NMR spectra were recorded on a BRUKER FTAM 300 as well as solid state CP-MAS ^{13}C NMR spectra, in the latter case by using the TOSS technique. The repetition time was 5 (for ^{13}C) and 10 s (for ^{29}Si) with contact times of 3 (for ^{13}C) and 5 (for ^{29}Si) milliseconds. The duration of the ^{1}H pulse was 4.2 (for ^{13}C) and 4.5 (for ^{29}Si) microseconds and the MAS rate was 10 (for ^{13}C) and 5 (for ^{29}Si) kHz. Chemical shifts (δ, ppm) were referenced to Me_4Si (^{13}C and ^{29}Si). Q^n and T^n notations are given for $(SiO)_nSi(OH)_{(4-n)}$ and $R(SiO)_nSi(OH)_{(3-n)}$ environments, respectively. The nitrogen adsorption isotherms were measured at liquid temperature (77 K) using a Micromeritics Tristar 3000 analyser. Before the measurements, the samples were out gassed under vacuum for 12 h at 100 °C. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method (using 74 points and starting from 0.01 as value for the relative pressure) and the pore size distributions were determined by the DBdB method applied to the adsorption branch. It is worth noting that this method is considered to slightly undervalue the pore size for the pores inferior to 6 nm.[11*b*] 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 (Cu-Kα radiation). Transmission Electron Microscopy (TEM) observations were carried out at 100 kV on a JEOL 1200 EXII microscope. Samples for TEM measurements were prepared using ultramicrotomy techniques and then deposited on copper grids. Thermogravimetric profiles were recorded between 25 °C and 700 °C with a slope of 5 °C min^{-1} under air on a Netzsch STA 409 PC apparatus. Elemental analyses of Si, N, S, and P were performed by the Service Central d'Analyse (CNRS, Vernaison, France).

Results and discussion

All materials were prepared under the exact same conditions *via* direct synthetic approach by hydrolysis and polycondensation of TEOS and an organotriethoxysilane $\Sigma(CH_2)_3Si(OR)_3$ with Σ = CN, SH, $CH_3COCHCOCH_3$ (acac), $PO(OEt)_2$ and R = Me or Et, in the presence of F127 as structure-directing agent (Scheme 1). It is worth noting that the synthesis was inspired from that described by Jaroniec *et al.*[22]



Scheme 1 Synthesis of materials **M-Σ^x** (R = Me, Et; x = 10, 5 and 3%).

Different methods have been explored to obtain surfactant-free materials (the first attempts gave rise to non-porous materials):

(i) centrifugation of the as-synthesised materials at 20 000 rpm for 15 min in THF followed by ultrasonic treatment in an ultrasonic water bath for 10 min at 20 °C. This procedure was repeated three times. No surfactant extraction was observed.

(ii) heating the as-synthesised materials at 140 °C under air for two days in a tubular oven. Despite some F127 decomposition at this temperature, the pores remained blocked.

(iii) soxhlet extraction with ethanol containing 2% of 36 wt% HCl heated at reflux for 24 h. This extraction method was abandoned as no reproducibility was found.

(iv) soxhlet extraction with THF containing 5% of 36 wt% HCl at reflux for 48 h. Though this procedure worked in some cases, leading to 3-D cubic mesoporous silica with S_{BET} in the range of 600 m^2 g^{-1}, it was found not reproducible and therefore discarded.

(v) heating process at 140 °C under air, followed by soxhlet extraction with THF containing 5% of 36 wt% HCl. This combination of both steps previously presented separately allowed porous materials achievement in many cases with S_{BET} in the range of 400–500 m^2 g^{-1}. Nevertheless, this method was also abandoned, again for repeatability issue.

(vi) finally, the surfactant was completely removed by extracting about 4 g of the as-synthesised material with an aqueous solution of pyridine/HCl (pH = 6–7) at 70 °C overnight (see experimental). After washing three times with ethanol then acetone, followed by a pulverising step, the solid was dried at 100 °C under vacuum for 6 h giving rise to **M-Σ^x** as a white powder in about 85% yield. This method was found to be highly reproducible and is so far the only one allowing complete template removal.

Powder X-ray diffraction (XRD) investigation combined with Transmission Electron Microscopy (TEM) analyses permit to determine the mesoporous materials symmetry characterisations.

According to the XRD patterns, all the surfactant-free **M-Σ^x** materials exhibit three well-resolved diffraction peaks which can be indexed as (110), (200) and (211) reflections, corresponding to a 3-D cubic structure ($Im\bar{3}m$ space group).

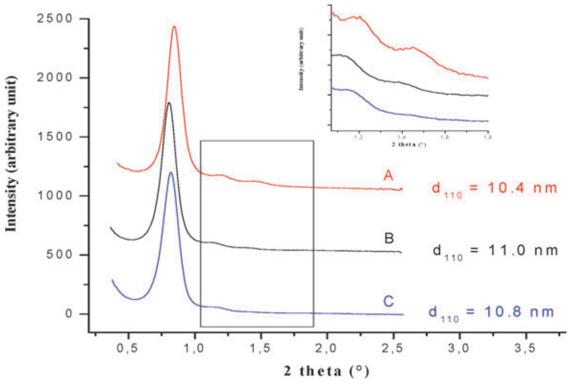


Fig. 1 Powder XRD patterns of extracted **M-PO(OEt)$_2$^{x}**. (A) x = 10, (B) x = 5 and (C) x = 3.

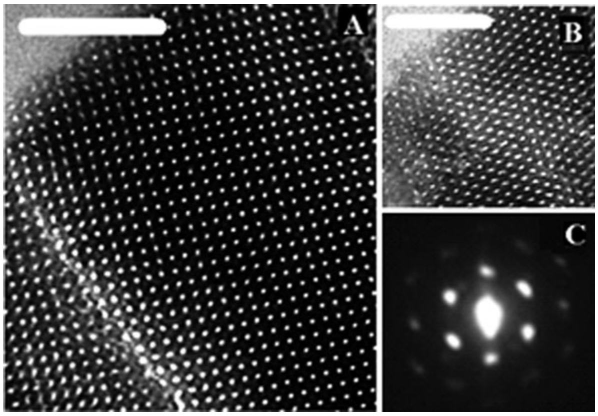


Fig. 2 TEM images of **M-SH^3** along: (A) [100] direction, (B) [111] direction. The length of white bar represents 100 nm. (C) Electron diffraction pattern from region B.

XRD patterns of **M-PO(OEt)$_2$^{x}** in Fig. 1 are given as examples. It is worth noting that the second and third diffraction peaks disappeared when the materials are treated at 110 °C during a prolonged time (24 h or more) instead of 2 h showing thus how strict should be the experimental conditions.

Further evidence for a highly ordered 3-D cage-like pore structure was provided by Transmission Electron Microscopy images and Electron Diffraction (ED) pattern (Fig. 2). TEM images of **M-Σ^x** viewed along several directions confirm an ordered $Im\bar{3}m$ mesostructure. Fig. 2A and B show images corresponding to projections along [100] and [111] reflection plans, respectively in the $Im\bar{3}m$ symmetry for the material **M-SH^3**, demonstrating large and highly ordered domains for this material.

Composition and physico-chemical data of **M-Σ^x** are given in Table 1. Elemental analyses were performed to estimate the organic group contents. The values obtained from elemental analysis are rather close to the expected values calculated on the basis of the composition of the initial mixture (Table 1).

The nitrogen adsorption–desorption isotherms of all materials **M-Σ^x** measured at 77 K are type IV, with a sharp H2-type hysteresis loop suggesting that the samples have ordered 3-D cage-like pore structure with high surface area (from 550 to 970 m^2 g^{-1}) and narrow pore size distribution (between 3.6 and 5.6 nm). Isotherms of **M-PO(OEt)$_2$^{x}** samples before and after full surfactant elimination are given as examples in Fig. 3. It appears that in each series, the materials with the highest organic loading present the lowest surface areas, except for **M-acac**. It is worth noting that similar results have already been observed for 2-D hexagonal functionalised mesoporous materials.[5]

As described above, we attempted different template extraction procedures and found that only the pyridine/HCl mixture at pH = 6–7 allows complete and reproducible

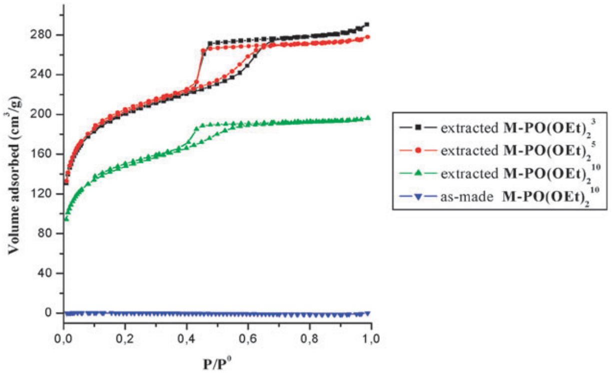


Fig. 3 Nitrogen adsorption–desorption isotherms at 77 K for as-made **M-PO(OEt)$_2$^{10}** and extracted **M-PO(OEt)$_2$^{x}** (x = 10, 5 and 3).

Table 1 Composition and physico-chemical characteristics of **M-Σ^x**

M-Σ^x	Molar Si/Σ^a	S_{BET}/m^2 g^{-1}	Vp/cm^3 g^{-1}	Dp^b/nm	d_{110}/nm	a_0/nm	Wall thickness/nm
M-CN^{10}	10.7 (10)	755	0.26	4.7	10.8	15.3	10.6
M-CN^5	23.6 (20)	930	0.34	5.6	11.3	16.0	10.4
M-CN^3	24.1 (30)	820	0.29	5.6	10.8	15.3	9.7
M-SH^{10}	10.2 (10)	650	0.29	3.6	9.7	13.7	10.1
M-SH^5	19.0 (20)	970	0.31	4.7	10.3	14.6	9.9
M-SH^3	29.6 (30)	955	0.26	4.5	10.0	14.1	9.6
M-acac^{10}	—	645	0.19	3.9	10.0	14.1	10.2
M-acac^5	—	550	0.24	4.8	10.4	14.7	9.9
M-acac^3	—	910	0.32	5.0	11.2	15.8	10.8
M-PO(OEt)$_2$^{10}	9.9 (10)	525	0.17	3.7	10.4	14.7	11.0
M-PO(OEt)$_2$^{5}	19.8 (20)	735	0.26	4.7	11.0	15.6	10.9
M-PO(OEt)$_2$^{3}	31.0 (30)	715	0.29	5.3	10.8	15.3	10.0

[a] Calculated from the elemental analysis of Si, N, S and P atoms (theoretical values). [b] Calculated from the adsorption branch by using the DBdB method.

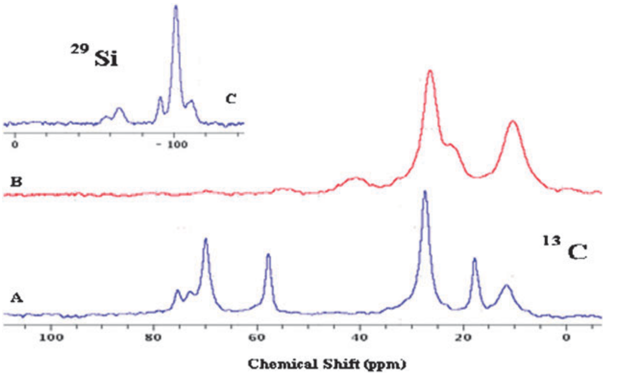


Fig. 4 ^{13}C and ^{29}Si CP-MAS NMR spectra of material **M-SH^{10}**. (A) as-made material, (B) and (C) extracted material.

extraction without structure collapse nor loss of the organic content. ^{13}C CP-MAS NMR was used to demonstrate the efficiency of the non-ionic template extraction procedure, a particular challenge for functionalised 3-D cage-like mesoporous silica[11,23] as well as to control the organic incorporation within the materials.

Fig. 4 shows the ^{13}C CP-MAS NMR spectra of **M-SH^{10}** before (A) and after template extraction (B). The comparison of both spectra shows clearly the disappearance of signals due to F127 indicating almost complete removal of the block copolymer surfactant: peaks at 18 ppm and from 70 to 76 ppm attributed, respectively to methyl groups of PO segments and –CH_2O– groups in F127 have disappeared after the extraction procedure. It is also worth noting that the signal at 58 ppm in Fig. 4(A) is not visible in Fig. 4(B). This signal could be assigned to residual –$SiOCH_2CH_3$ groups subsequently hydrolysed during surfactant extraction. Finally, resonances at 10, 23 and 27 ppm (Fig. 4B) refer, respectively to the carbons in α, β and γ of the silicon atom, settling the incorporation of –$(CH_2)_3SH$ groups in the material.

Organic group incorporation within the silica was also proved by ^{29}Si NMR spectroscopy. Indeed, materials spectra displayed large signals corresponding to T^2 [$RSi(OSi)_2OH$] and T^3 [$RSi(OSi)_3$] substructures, denoting thus the presence of organosilanes, the signal attributed to T^3 prevailing. The ^{29}Si CP-MAS NMR spectrum of **M-SH^{10}** is given as an example in Fig. 4C. It exhibits resonances at −58 and −66 ppm attributed to T^2 and T^3 substructures, respectively in addition to three signals at −91, −102 and −112 ppm assigned to Q^2 [$Si(OSi)_2(OH)_2$], Q^3 [$Si(OSi)_3(OH)$] and Q^4 [$Si(OSi)_4$] substructures, respectively from the silica.

Further ^{13}C and ^{29}Si NMR spectra of **M-Σ^{x}** are provided in supplementary information to complete these observations (see ESI 1 to ESI 6).

In addition, the ^{31}P CP-MAS NMR spectrum of **M-PO(OEt)$_2$^{10}** (see ESI †) displays only one resonance at 34 ppm characteristic of phosphonate groups demonstrating the group preservation after all synthesis steps.

Thermogravimetric analysis of different samples conducted from 25 °C to 700 °C under air also confirmed the organosilane incorporation as well as the complete surfactant extraction. Fig. 5 reports the TGA curves for **M-acac^5** before (curve A) and after (curve B) surfactant extraction.

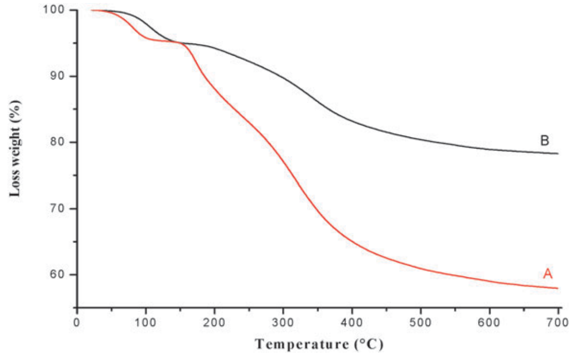
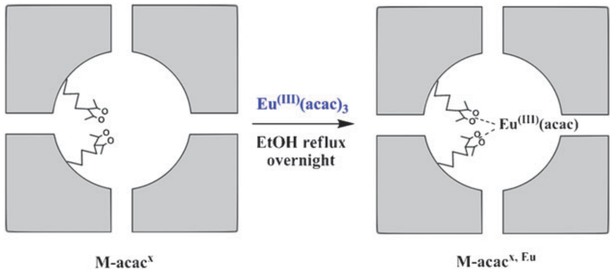


Fig. 5 Thermogravimetric analysis of material **M-acac^5**. (A) Before extraction and (B) after extraction.



Scheme 2 Complexation of **M-acac^x** by $Eu(acac)_3$ salts leading to **M-acac^{x,Eu}** materials (x = 5 and 10%).

A difference of weight loss of 19% at 400 °C was observed between A and B corresponding to the F127 mass ratio initially introduced. Besides, a 12% weight loss between 145 and 400 °C (curve B) is observable, attributed to the decomposition of the organic while the expected theoretical value was 10.6% assuming a fully condensed material.

Finally, in order to demonstrate the organic group accessibility within the silica pores, we used as a probe the complexation of Eu^{III} by acetylacetonate (acac) groups.[5d]

The materials **M-acac^{10}** and **M-acac^5** were treated with an excess of $Eu(acac)_3$ (2 equiv. of Eu^{III} *per* acac moieties incorporated within the material) in ethanol heated under reflux for 12 h. The resulting solids, named **M-acac^{10,Eu}** and **M-acac^{5,Eu}** were abundantly washed with hot ethanol to eliminate all non-complexed salts (Scheme 2). After filtration, excess of $Eu(acac)_3$ salts was titrated by complexometry measurements. The uptake of Eu^{III} ions was inferred from the titration measurements. It was found very similar for **M-acac^{10,Eu}** and **M-acac^{5,Eu}** [97 and 100% of the expected value, respectively] assuming that the Eu^{III} uptake requires two acac moieties located in the channel pores. Thus, in these materials, all the acac units are accessible and used for the complexation reaction.

Conclusions

A generic route to functionalised, surfactant-free and well-ordered mesoporous silicas with cubic symmetry ($Im\bar{3}m$ space group) was successfully obtained *via* the direct synthesis approach. As reported, many types of organic groups (CN, SH, $CH_3COCHCOCH_3$ (acac) and $PO(OEt)_2$) with different contents (3, 5 and 10%) have been introduced with success. Furthermore, an efficient method for complete template removal without any alteration of the organic moieties nor structure collapse was described. Finally, the accessibility and adsorption capacity of acetylacetonate groups towards lanthanide ions were also demonstrated. All combined results make these functionalised surfactant-free 3-D cubic mesoporous silicas as significant candidates in many various chemical or physical applications such as catalysis, separation of molecules, gas sensing or 3-D ordered metallic nanoparticles growth.

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