

Periodic mesoporous organosilicas derived from amphiphilic bulky polymethylsiloxane

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Electronic Supplementary Information

ESI 1 Experimental Part

Materials and reagents

Tetraethoxysilane (TEOS), octadecyltrimethylammonium bromide (ODTAB) and Pluronic P123 [Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide): M = 5800 g], absolute ethanol, hydrochloric acid (37 %) were obtained from Sigma Aldrich, sodium hydroxide was obtained from Carlo Erba and sodium chloride from Panreac.

PMSi was synthesized according to the protocol described in ref 6 (A. El Kadib, A. Finiels, N. Marcotte, D. Brunel, *Chem. Comm.*, 2013, **49**, 5168-5170).

Synthesis of PMSi-SiO₂-base

In a typical synthesis, the OTDAB surfactant (1.185 g, 310⁻³ mol) was dissolved in an aqueous solution of sodium hydroxide (0.5 g in 33.7 g H₂O) and stirred for 5 h at room temperature in a polypropylene Nalgene flask. Then, the **PMSi** precursor (2.71 g, 0.36 10⁻³ mole, M = 7412) was added dropwise. The molar composition of the gel was : 1SiO₂/0.21CTABr/ 0.89 NaOH/ 133 H₂O. The mixture was vigorously stirred at room temperature for 14 h and under static conditions at 95 °C for 24 additional hours. After filtration, the solid was washed with ethanol and dried in air (Yield: 1.7 g). Removal of the surfactant was accomplished by extraction with a mixture of ethanol and concentrated 37 wt % HCl (100 : 2 ; v :v) for 24 h using a Soxhlet apparatus with subsequent filtration of the product and drying at 55 °C in air. Yield :1.3 g.

Synthesis of PMSi-SiO₂-acid

Pluronic P123(1.2 g, 0.21 mmol, M= 5800 g) and sodium chloride (3.5 g) were dissolved in a solution of 5 cm³ of concentrated 37 wt % HCl in 34 cm³ H₂O and stirred for 4 h at room temperature. Then, the **PMSi** (3 g, 0.4 mmol) was added dropwise. The molar composition of the gel was : 1SiO₂/0.018 P123/ 5.44 NaCl/ 5.48 HCl/187 H₂O. The mixture stirred at 40 °C for 24 h, followed by ageing the suspension in a teflonned autoclave reactor at 80 °C for another 24 h under static conditions. After filtration, the solid was washed with ethanol (Yield : 1.48 g). Removal of the surfactant was accomplished by extraction with a mixture of ethanol and concentrated 37 wt % HCl (100 : 2 ; v :v) for 24 h using a Soxhlet apparatus with subsequent filtration of the product and drying at 80

°C in air. Yield : 1.18 g. The solid obtained is a mixture of a crystalline white powder and large and transparent spheres (1-2 mm of diameter) which have been separated by hand with a tweezer (55 mg).

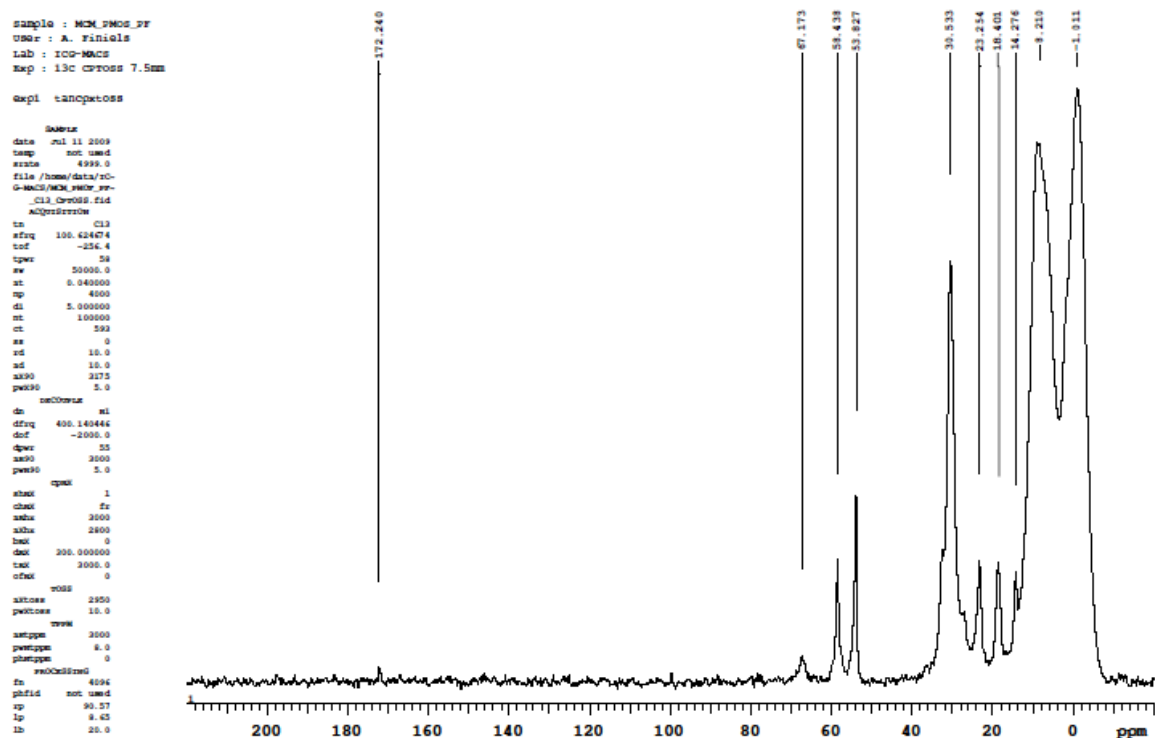
Synthesis of PMOS-MCM-*bis*

A detailed description of the reaction procedure is as follows, 2.53 g of CTABr ($7 \cdot 10^{-3}$ mol, M= 364) and 100 g of H₂O were stirred in a Nalgen bottle, and 6.2 ml of ethylamine (70 % in water) were added drop by drop. The mixture was stirred at room temperature during 1 hour. Then, 9.33 g of TEOS (0.045 mol, M= 208) were added to the solution under strong stirring for 15 min. Then, 2.18 g of PF ($8.06 \cdot 10^{-3}$ mol de PF/29) were added and the mixture was stirred strongly at room temperature for 4 h, and then aged in autoclave at 100 °C for 48 h under static conditions. The solid was filtered off, washed with ethanol (Yield: 5 g). Removal of the surfactant was accomplished by extraction with a mixture of ethanol and concentrated 37 wt % HCl (100:2; v:v) for 24 h using a Soxhlet apparatus with subsequent filtration of the product and drying at 80 °C in air (Yield: 2.5 g). The molar composition of the gel was : 1 Si/0.13 CTAB/1.46 EA/106 H₂O with the Si(PF)/TEOS ratio : 0.19

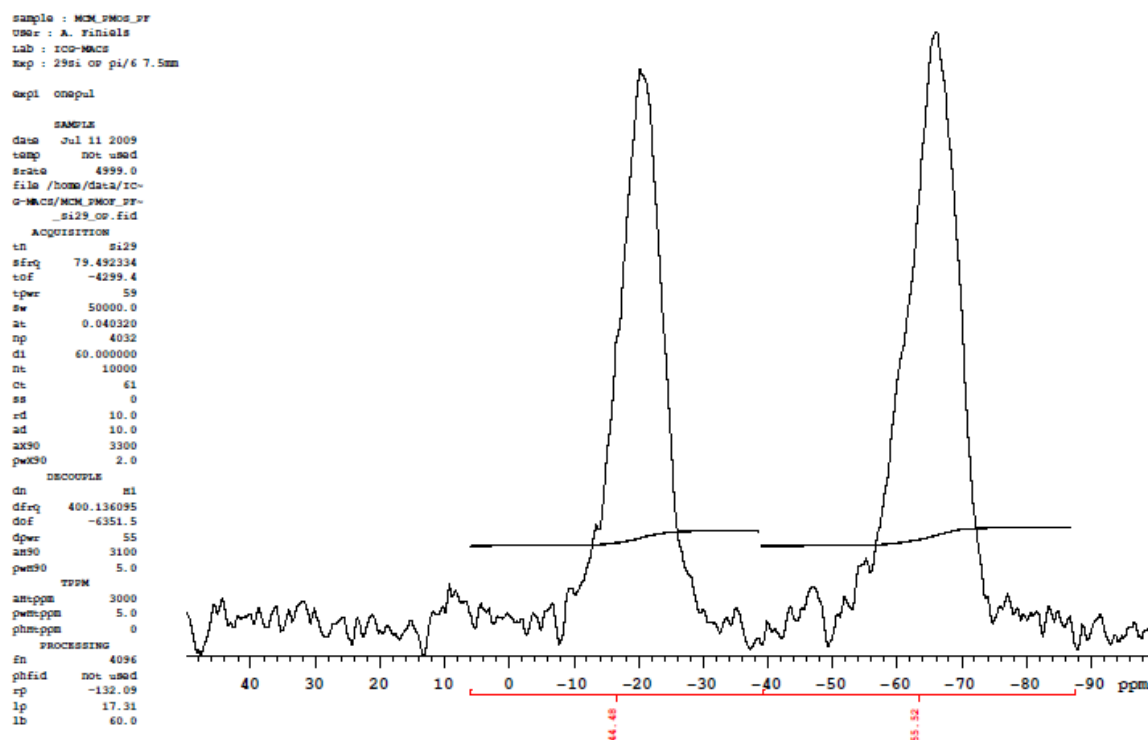
Synthesis of PMOS-SBA-*bis*

2.7 g P123 ($4.65 \cdot 10^{-4}$ mol, M= 5800) were stirred in 69 cm³ H₂O in an Erlenmeyer with 15.34 g (13 cm³) HCl at 37 % and 7.85 g (0.13 mol) NaCl at 40 °C during 3 h 30 until total dissolution. Then 5.70 g TEOS (0.027 mole) were added drop by drop under stirring and after 30 min, 1 g ($3.9 \cdot 10^{-3}$ mol) PF was added drop by drop and stirred at 40 °C during 22 h. The mixture is put in a teflonned autoclave reactor at 80 °C for another 24 h under static conditions. After filtration, the solid was washed with ethanol (Yield: 3.35 g). Removal of the surfactant was accomplished by extraction with a mixture of ethanol and concentrated 37 wt % HCl (100:2 ;v :v) for 24 h using a Soxhlet apparatus with subsequent filtration of the product and drying at 80 °C in air (Yield: 2.75 g). The molar composition of the gel was : 1 Si/0.015 P123/5 HCl/4.3 NaCl/141 H₂O with the Si(PF)/TEOS ratio : 0.14.

a) ^{13}C CP MAS spectrum of **PMSi-MCM-41**



b) ^{29}Si OP MAS NMR spectrum of **PMSi-MCM-41**



ESI 3

Estimation of a minimum Si/C ratio by NMR

After analysis and deconvolution of the ^{29}Si NMR single pulse spectra of **PMSi-MCM-41-*bis*** and **PMSi-SBA-15-*bis***, we have estimated the relative proportions of D^1 , D^2 , T^2 , T^3 , Q^2 , Q^3 and Q^4 sites. From these, it was possible to calculate the molar proportions of D , T and Q units in each sample. Considering that all the SiOR pending groups are SiOEt groups (maximum C content), it was then possible to determine minimum values for the molar ratio Si/C.

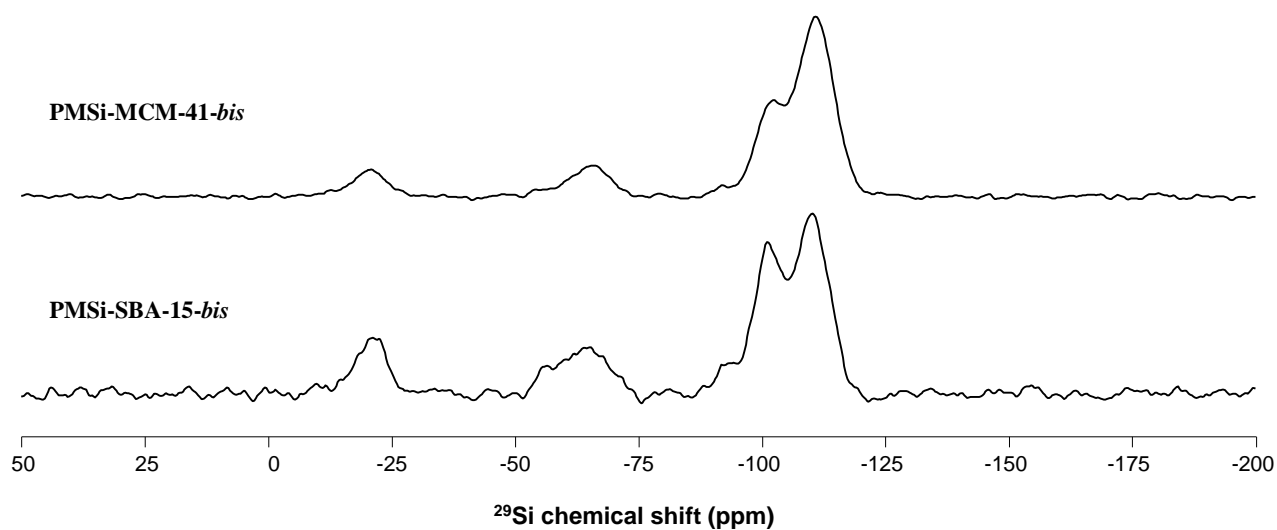
Table 1. Chemical compositions of the samples

materials	from NMR	From ATG			From Elementary Analysis		
	Si/C *	Si/C	Organic part ** mol.g ⁻¹ dry sample	SiO ₂ *** mol.g ⁻¹ dry sample	Si/C	Organic part mol.g ⁻¹ dry sample	SiO ₂ mol.g ⁻¹ dry sample
PMSi-MCM-41-<i>bis</i>	2.32	1.75	9.2 10 ⁻⁵	1.5 10 ⁻²	2.25	7.9 10 ⁻⁵	1.6 10 ⁻²
PMSi-SBA-15-<i>bis</i>	1.61	1.55	9.7 10 ⁻⁵	1.4 10 ⁻²	2.06	6.9 10 ⁻⁵	1.3 10 ⁻²

* Minimum values calculated from ^{29}Si OP NMR spectra (below) considering a maximum of SiOEt pending groups

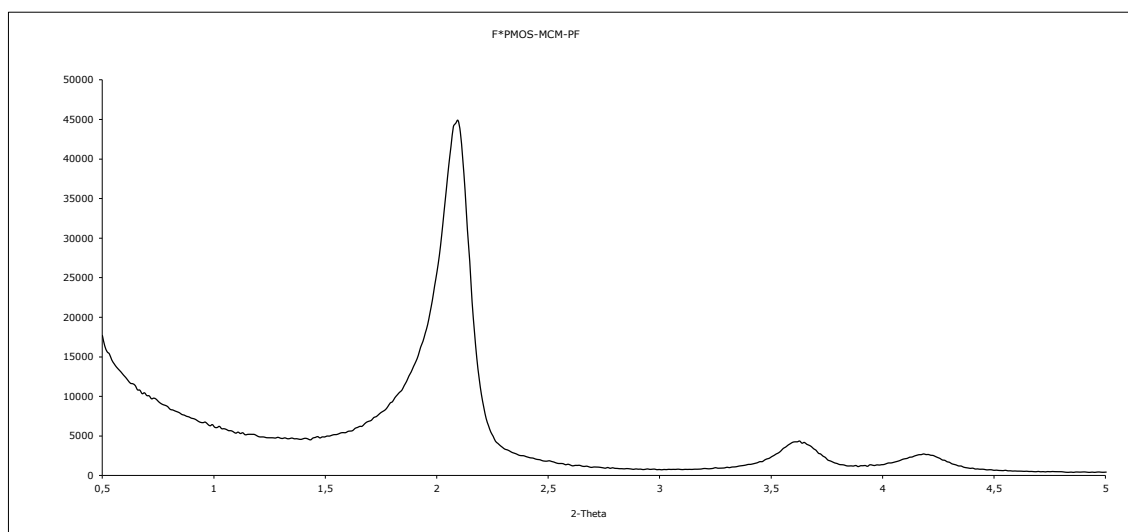
** determined from organic weight loss

*** determined from residual mineral weight at 700 °C

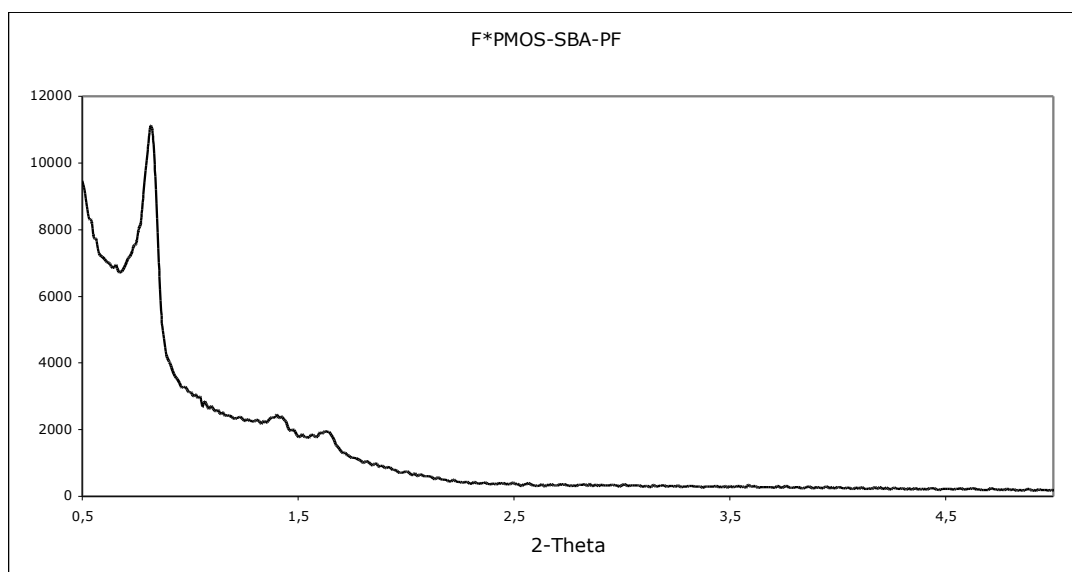


ESI 4 XRD

a) PMSi-MCM-41-*bis*



b) PMSi-SBA-15-*bis*



ESI 5

N₂ sorption analyses

Table 2: Textural properties of **PMSi-MCM-41-bis** and **PMSi-SBA-15-bis**

Material	d ₁₀₀ (Å)	a _o (Å)*	S _{BET} (m ² g ⁻¹)	C _{BET}	V _{mesop} (mL g ⁻¹)	Pore diameter D _p ** (Å)	Wall thickness*** (Å)
PMSi-MCM-41-bis	42	48.5	700	117	0.51	38	12.4
PMSi-SBA-15-bis	106.3	122.8	658****	187****	0.76	78	48.7

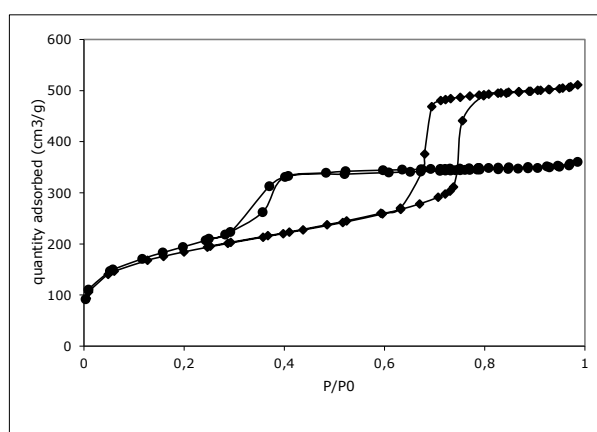
* a_o = lattice parameter from XRD data using the formula $a_o = 2 d_{100}/\sqrt{3}$

** determined by *BdB* treatment method.

*** Wall thickness = $a_o - 0.95 D_p$ regarding a pore hexagonal section having an equal surface ($S_p = 2\sqrt{3} \times r^2$ with r being the apothema of the hexagonal section) as the cylindrical pore section $S_p = \pi(D_p/2)^2$, then $2r = 0.95 D_p$ and thus the value of the wall thickness correspond to the unit cell value minus the 2r value.

**** The highest surface area and C_{BET} values determined by nitrogen sorption isotherm of SBA-15- type materials cannot be considered having physical signification due to the potential presence of supermicroporosity as precisely determined on parent pure silica material obtained through various synthesis temperatures using both argon sorption measurements and geometrical calculation considering a honeycomb structure of hexagonal mesopores separated by continuous pure silica wall. (A.Galarneau, H. Cambon, F. di Renzo, R. Ryoo, M. Choi and F. Fajula, *New J. Chem.*, 2003, 27, 73-79.)

Nitrogen sorption isotherm profile of **PMSi-MCM-41-bis** and **PMSi-SBA-15-bis**



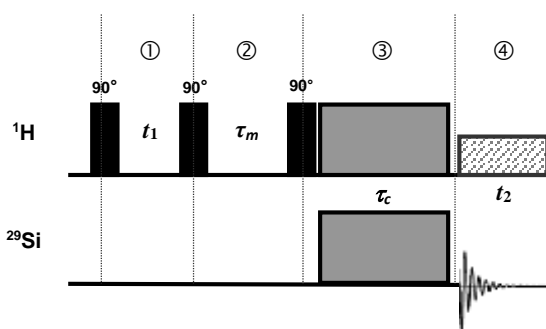
ESI 6

Solid-state NMR experimental conditions

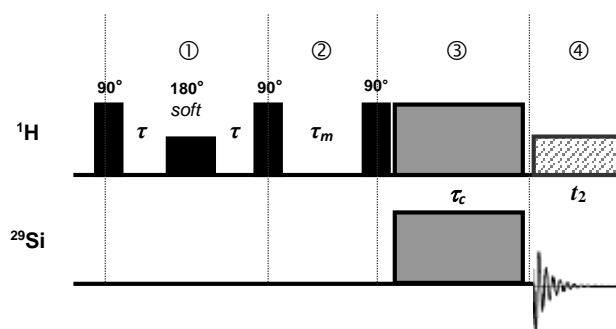
The $^{29}\text{Si}\{^1\text{H}\}$ experiments were undertaken on a Varian 400 spectrometer using 3.2 mm zirconia MAS rotors spun at 15 kHz. ^1H and ^{29}Si nutation frequencies were about 50 kHz, except for the 90° ^1H pulses (2.5 μs , 100 kHz). The contact time τ_m was fixed to 15 ms, and the recycling delay to 2 s.

The 2D ^{29}Si - ^1H NMR HETCOR spectra have been recorded using the well-known WISE pulse sequence scheme consisting in four blocks (Scheme 1): ① ^1H evolution during incremented t_1 , ② ^1H spin diffusion during a mixing time τ_m , ③ $^1\text{H} \rightarrow ^{29}\text{Si}$ cross polarisation during a contact time τ_c , and ④ ^{29}Si evolution during t_2 (acquisition with ^1H decoupling).^{1,2} The number of scans per slice was between 100 and 132.

$^{29}\text{Si}\{^1\text{H}\}$ NMR CP-MAS spectra with preliminary ^1H signal selection were recorded using a modified cross-polarisation pulse sequence consisting in four blocks (Scheme 2): ① ^1H frequency selection using a spin echo with a soft 180° pulse, ② ^1H spin diffusion during a mixing time τ_m , and ③ $^1\text{H} \rightarrow ^{29}\text{Si}$ cross polarisation during a contact time τ_c , and ④ ^{29}Si evolution during t_2 (acquisition with ^1H decoupling). The ^1H 180° soft pulse was 1.28 ms long (400 Hz nutation). The number of scans per slice was 2048.



Scheme 1



Scheme 2

References:

1. K. Schmidt-Rohr, J. Clauss, H. W. Spiess, *Macromolecules*, 1992, **25**, 3273–3277.
2. T. Janicke, C. C. Landry, S. C. Christiansen, D. Kumar, G. D. Stucky, B. F. Chmelka, *J. Am. Chem. Soc.* 1998, **120**, 6940-6951.

ESI 7

$^{29}\text{Si}\{^1\text{H}\}$ NMR CP-MAS with preliminary ^1H signal selection at ~ 5 ppm

