# Aromatic PMOs: tolyl, xylyl and dimethoxyphenyl groups integrated within the channel walls of hexagonal mesoporous silicas

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There exists a need to synthesize PMOs with bridging organic groups beyond the few that are accessible from commercially available bis(triethoxysilyl)organic precursors. To fulfill this need, three new periodic mesoporous arylsilicas, aromatic PMOs, having bridging aromatic organic groups as an integral part of the framework have been synthesized and structurally characterized. The surfactant-templated synthesis employed new precursors consisting of two triethoxysilyl groups connected via toluene, p-xylene or 1,4-dimethoxybenzene. Diffraction and microscopy together with ^{13}C CP-MAS NMR, ^{29}Si MAS NMR and FT-Raman/IR measurements proved that the aryl–silica bonds in the new precursors and aromatic PMOs are stable under hydrolytic polycondensation self-assembly and surfactant acid extraction conditions. These PMOs have an ordered hexagonal channel mesostructure, some degree of ordering of aromatic groups likely through π–π stacking in the channel walls, a large pore volume and surface area, and relatively thick arylsilica walls whose dimensions seem to scale with the spatial demands of the aryl group.

## Introduction

In 1999, a new class of materials, coined periodic mesoporous organosilicas, PMOs, was launched in solid-state chemistry.[1–4] The fabric of these materials was comprised of bridge-bonded organic groups integrated into silica as structural components that was cast around surfactant templates, to create a family of hybrid organic–inorganic materials having architectures based on a regular array of mesoscale channels or pores. Materials of this genre portend novel, tunable and synergistic properties deriving from molecular scale engineering and intermixing of inorganic and organic constituents. The synthetic strategy to PMOs comprised hydrolysis and polycondensation of tailor-made bis- or tris-(trialkoxysilylated) organic derivatives $((R'O)_3Si)_nR$, known as "bridged silsesquioxanes", in the presence of a structure directing surfactant micellar template. This type of synthesis ensures a homogeneous distribution of bridging organic groups inside the channel walls and permits populations of up to 100% organosilica sites. The new hybrids offer well-ordered mesoporous structures, finely tunable pore sizes, organic moieties that do not block pore space and high surface areas. It is expected that PMO nanocomposite materials will offer interesting electrical, optical,[5] mechanical,[6] separation and catalytic properties.

Thus far only a handful of stable PMO materials have been prepared. Precursors include bis-silylated ethene, methane, ethane, benzene and thiophene,[1–7] which show good stability under strongly acidic or basic synthesis conditions, form PMOs with crystalline mesoporosity and precise pore dimensions, and permit acid extraction or ion exchange of imbibed surfactant template. By contrast, bis-silylated ferrocene, acetylene and dithiophene precursors[4] showed substantial Si–C bond cleavage under the synthesis conditions employed, serving to decrease yields of the desired PMO and simultaneously create mixtures of periodic mesoporous silicas and organosilicas. The embedded organic groups in the channel wall of these hybrid periodic mesoporous organosilicas are accessible for further chemical manipulations and introduction of various functional groups via classical organic reactions. This has been described as chemistry of, rather than in, the channels. It provides an opportunity for manipulating the composition, the chemical and mechanical properties, and the hydrophobicity–hydrophilicity of the PMO. To rationally and systematically modify the properties of this class of nanocomposite materials, functionalizable and accessible organic groups need to be introduced into the channel walls of PMOs. Our research on PMOs continues to focus on this issue.

Of the few PMOs prepared to date, only the ethene derivative can be easily manipulated by common organic reactions. However, very little has been done in this respect and only one simple organic reaction was performed with the channel, namely electrophilic or radical addition of bromine. It was shown that such bromination[2,3] partially or completely eliminated the double bond, yielding the dibromo derivative, while maintaining the structural integrity and order of the mesoporous organosilica material intact. These results, although preliminary, proved that the organic functional groups incorporated in the channel walls of the PMO are accessible for chemistry. "Channel metamorphosis" of a PMO was also recently reported.[7] Temperatures around 400 °C caused a chemical transformation of the channel walls of a periodic mesoporous methylenesilica containing bridging methylene moieties to ones having terminally bonded methyl groups protruding in the mesopores. This thermally induced proton transfer from silanols to bridging methylene is a further nice example of "chemistry of the channels walls".

In this work we report the synthesis of three new aromatic PMOs. The organic precursors used in the surfactant-templated synthesis are bis(triethoxysilyl) derivatives of toluene, p-xylene and p-dimethoxybenzene. These novel PMOs have active aryl organic bridging groups located inside the channel walls, which might facilitate simple organic chemical reactions to yield a flora of new functionalities. For instance, the methyl groups of toluene and xylene will enable easy access to active functional groups such as benzyl halides, benzyl alcohols, nitriles, amines, aldehydes and carboxylic acids. From the

embedded dimethoxybenzene it will be possible to generate hydroquinones, quinones and a wide range of derivatives with either donor or acceptor properties.

## Experimental section

### Synthesis of 2,5-bis(triethoxysilyl)toluene (1)

To a mixture of iodine-activated Mg turnings (1.95 g, 80 mmol) and chlorotriethoxysilane (8.75 g, 44 mmol)[8] in dry THF (100 mL), 2,5-dibromotoluene (5.00 g, 20 mmol) was added dropwise, under an atmosphere of nitrogen. The mixture was stirred for 24 h at room temperature, some Mg turnings and Mg salts were filtered off and the solvent evaporated *in vacuo*. The oily residue was washed with cold hexane (100 mL), some insoluble impurities were filtered off and the hexane evaporated. The crude product was distilled at $3 \times 10^{-5}$ mbar and the pure 2,5-bis(triethoxysilyl)toluene was collected between 120–136 °C. Yield 3.6 g, 44%.

$^1$H NMR ($\delta_H$ 300 MHz, CDCl$_3$, ppm); 1.25 (18H, t, $J = 6.9$ Hz), 2.51(3H, s), 3.87 (12H, q, $J = 6.9$ Hz), 7.45 (2H, overlapping s & d, $J = 6.8$ Hz), 7.71 (1H, d, $J = 6.8$ Hz); $^{13}$C NMR ($\delta_C$ 75.46 MHz, CDCl$_3$, ppm); 18.39, 18.43, 22.68, 58.76, 58.96, 131.12, 132.43, 133.34, 135.87, 136.01, 143.80.

### Synthesis of 2,5-bis(triethoxysilyl)-*p*-xylene (2)

This precursor was prepared in a similar procedure to (**1**) from activated Mg turnings (1.95 g, 80 mmol), chlorotriethoxysilane (8.75 g, 44 mmol) and 2,5-dibromo-*p*-xylene (5.28 g, 20 mmol) in dry THF (100 mL). The oily crude product was distilled at $3 \times 10^{-5}$ mbar and the fraction boiling between 127–130 °C was collected. Yield 3.44 g, 40%.

$^1$H NMR ($\delta_H$ 300 MHz, CDCl$_3$, ppm); 1.25 (18H, t, $J = 6.9$ Hz), 2.50 (6H, s), 3.89 (12H, q, $J = 6.9$ Hz), 7.68 (2H, s); $^{13}$C NMR ($\delta_H$ 75.46 MHz, CDCl$_3$, ppm); 18.40, 22.58, 58.84, 132.45, 135.67, 143.63.

### Synthesis of 2,5-bis(triethoxysilyl)-1,4-dimethoxybenzene (3)

To a mixture of iodine activated Mg turnings (1.95 g, 80 mmol) and chlorotriethoxysilane (8.75 g, 44 mmol) in dry THF (100 mL), 2,5-dibromo-1,4-dimethoxybenzene (5.92 g, 20 mmol) was added under nitrogen atmosphere. The mixture was stirred for 24 h at room temperature, salts and impurities filtered off and the solvent evaporated *in vacuo*. The residue was washed with cold dry diethyl ether (75 ml), filtered, and the solvent evaporated. The crude product was distilled under reduced pressure ($2 \times 10^{-5}$ mbar) and the fraction boiling between 135–140 °C was collected. Yield 2.9 g, 32%.

$^1$H NMR ($\delta_H$ 300 MHz, CDCl$_3$, ppm); 1.24 (18H, t, $J = 7.2$ Hz), 3.81(6H, s), 3.88 (12H, q, $J = 7.2$ Hz), 7.15 (2H, s); $^{13}$C NMR ($\delta_H$ 75.46 MHz, CDCl$_3$, ppm); 18.43, 55.60, 58.97, 118.65, 123.42, 158.50.

### Synthesis of toluene- and *p*-xylene-bridged mesoporous silicas

An acid-catalyzed surfactant-templating sol–gel technique[4] was employed to prepare these aromatic PMOs. Thus, 2,5-bis(triethoxysilyl)toluene (2 g, 4.78 mmol) or 2,5-bis(triethoxysilyl)-1,4-xylene (2 g, 4.65 mmol) were added to a mixture containing water (15 g, 0.83 mol), cetylpyridinium chloride (0.6 g, 1.76 mmol) and concentrated HCl (1.8 g of a 33 wt% solution in water, 16.5 mmol). After stirring the mixture moderately at room temperature for 30 min, a homogeneous solution was formed. The mixture was neutralized with portionwise addition of solid NaHCO$_3$, which caused the precipitation of a white microcrystalline solid, and to the slurry, catalytic amounts of NH$_4$F (0.1 mol%) were added. The suspension was aged for two days at 50 °C, the white powder filtered off, washed with copious amounts of water and then with acetone.

The material (1.0–1.4 g) was dried in air under ambient conditions.

### Synthesis of 1,4-dimethoxybenzene-bridged mesoporous silica

In the acid-catalyzed preparation of this aromatic PMO, 2,5-bis(triethoxysilyl)-1,4-dimethoxybenzene (2 g, 4.32 mmol) was added to a mixture of water (15 mL, 0.83 mol), cetylpyridinium chloride (0.4 g, 1.17 mmol) and concentrated HCl (3.6 g, 33 wt% in water, 31 mmol). The mixture was stirred for 30 min at room temperature then neutralized by addition of solid NaHCO$_3$. To the suspension, a catalytic amount of NH$_4$F was added and the slurry was aged for two days at 50 °C. The white powder (0.8 g) was filtered off, washed with large amounts of water then with acetone and dried at ambient temperature.

### Removal of the surfactant

To prepare the template-free aromatic PMO materials, a sample of **1–3** (0.5 g) was stirred in a mixture of methanol (100 mL) and 10 M HCl (6 g) for 24 h at ambient temperature. The solid was collected by suction filtration, washed with methanol (200 mL) then with acetone (100 mL). This extraction procedure was repeated in order to extract the surfactant completely. The twice-extracted material (0.20–0.25 g) was dried at 100 °C for 24 h.
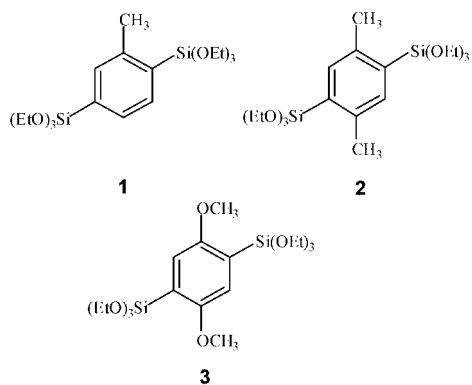
### Characterization

PXRD patterns were obtained on a Siemens D5000 diffractometer using Ni-filtered high power Cu-K$\alpha$ radiation $\lambda = 1.54178$ Å operating at 50 kV/35 mA. Transmission electron microscopy images were recorded on microtomed thin sections with a Philips 430 microscope operating at an accelerating voltage of 100 kV. Nitrogen adsorption isotherms were recorded at 77 K using a Quantachrome Autosorb-1 system. $^{13}$C (100.6 MHz) and $^{29}$Si NMR (79.5 MHz) solid-state NMR spectra were recorded on a Bruker DSX400 spectrometer. Experimental conditions: $^{13}$C CP-MAS NMR (6.0 kHz spin rate; 2.5 ms contact time; 3 s recycle delay; 1000 scans), $^{29}$Si MAS NMR (3.0 kHz spin rate; 100 s recycle delay; 1700 scans). TGA data were obtained at a heating rate of 5 °C min$^{-1}$ under a flow of N$_2$ on a Perkin-Elmer TGA7 instrument. FT-Raman microscope spectra were obtained on a S. A. LabRam Raman microscope by manually placing the probe tip near the desired point of the sample on a glass slide.

## Results and discussion

The new hybrid aromatic PMOs were synthesized from aryl compounds substituted with two triethoxysilyl groups.[9] Thus, 2,5-dibromotoluene, 2,5-dibromo-*p*-xylene and 2,5-dibromo-1,4-dimethoxybenzene reacted in a Grignard type reaction with chlorotriethoxysilane (prepared by partial alcoholysis of silicon tetrachloride[8]) in the presence of dry and iodine-activated Mg turnings. The pure precursors (Scheme 1), 2,5-bis(triethoxysilyl)toluene (**1**), 2,5-bis(triethoxysilyl)-1,4-xylene (**2**) and 2,5-bis(triethoxysilyl)-1,4-dimethoxybenzene (**3**) were obtained in average yields after distillation *in vacuo* and were characterized by $^1$H and $^{13}$C NMR spectroscopy. To prepare hexagonal mesoporous arylsilicas we used a cetylpyridinium-templated synthesis procedure similar to one proven successful for other PMOs.[4] Surfactant was removed from the aromatic PMOs by extraction with methanol–hydrochloric acid solution.

### Structure and composition

The structure and order of the as-synthesized and surfactant extracted aromatic PMOs were investigated by powder X-ray diffraction (PXRD) and transmission electron microscopy

**Scheme 1** Chemical structures of the aromatic-bridged silsesquioxanes 1–3.



**Fig. 2** TEM images of hexagonal mesoporous *p*-xylylsilica: A, perpendicular to the channel axis; B, parallel to the channel axis.

(TEM). FT-Raman/IR, ^{13}C cross polarization magic angle spinning (CP-MAS) NMR and ^{29}Si MAS NMR were recorded in order to study the structure and the stability of Si–C bonds in precursors and PMO products towards hydrolytic polycondensation and surfactant removal processes. The thermal properties of the new aromatic PMOs were also studied by thermogravimetric analysis (TGA) under nitrogen. Surfactant-free materials were characterized by gas adsorption to determine porosity and by comparison with PXRD and TEM data, an estimate of aryl group dependence of channel wall thickness, could be obtained.

Powder X-ray diffraction patterns for the three new aromatic PMOs, as-synthesized and solvent extracted, are shown in Fig. 1. The presence of diagnostic (100), (110) and (200) peaks in the diffraction pattern depicts well-ordered hexagonal symmetry aromatic PMOs. As-synthesized tolylsilica PMO displays a sharp low-angle peak at a $d_{100}$ spacing = 36.6 Å, Fig. 1A. After removal of the surfactant from the channels, the intensity of the low angle peak increased about three times. This is consistent with the creation of an aromatic PMO with a higher electron density contrast between channel walls and air spaces.[10] After 24 h at 100 °C, the diffraction intensity showed
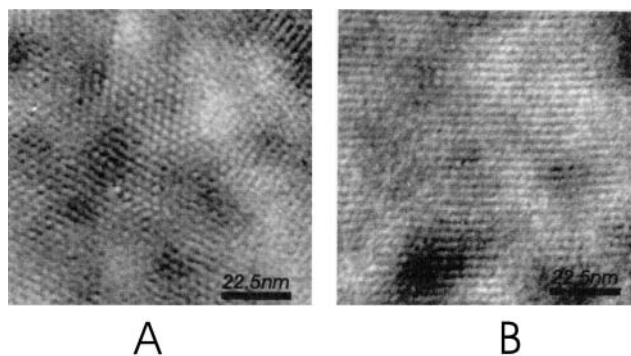
a further increase of about eight times. PXRD patterns for surfactant extracted tolylsilica PMO showed less well resolved (110) and (200) reflections. As TEM images of surfactant free material display a hexagonal mesostructure, the observed loss of resolution and intensity of (110) and (200) reflections probably originates from some loss of long range order.

PXRD patterns for as-synthesized *p*-xylylsilica PMO also showed a diagnostic low-angle peak at $d_{100}$ spacing = 40.6 Å, Fig. 1B. After template extraction and water removal this peak shifted to $d_{100}$ = 39.3 Å and its relative intensity increased about 6.5 times. TEM images like those in Fig. 2, confirm the hexagonal symmetry mesostructure of this material. Both the tolyl and xylyl PMOs also displayed broad diffraction halos around $d$ = 10 Å, which may indicate the presence of some arylsilica ordering in the channel walls arising from π–π stacking of bridging aromatic groups in the precursor $(EtO)_3Si–R–Si(OEt)_3$ or in early stage organosilicate polymerization species located in the micro-phase separated region of the surfactant assembly. In other words, the surfactant-templated synthesis of aromatic PMOs is envisioned as a kind of "double self-assembly" involving simultaneous pre-organization and co-assembly of both surfactant micellar and
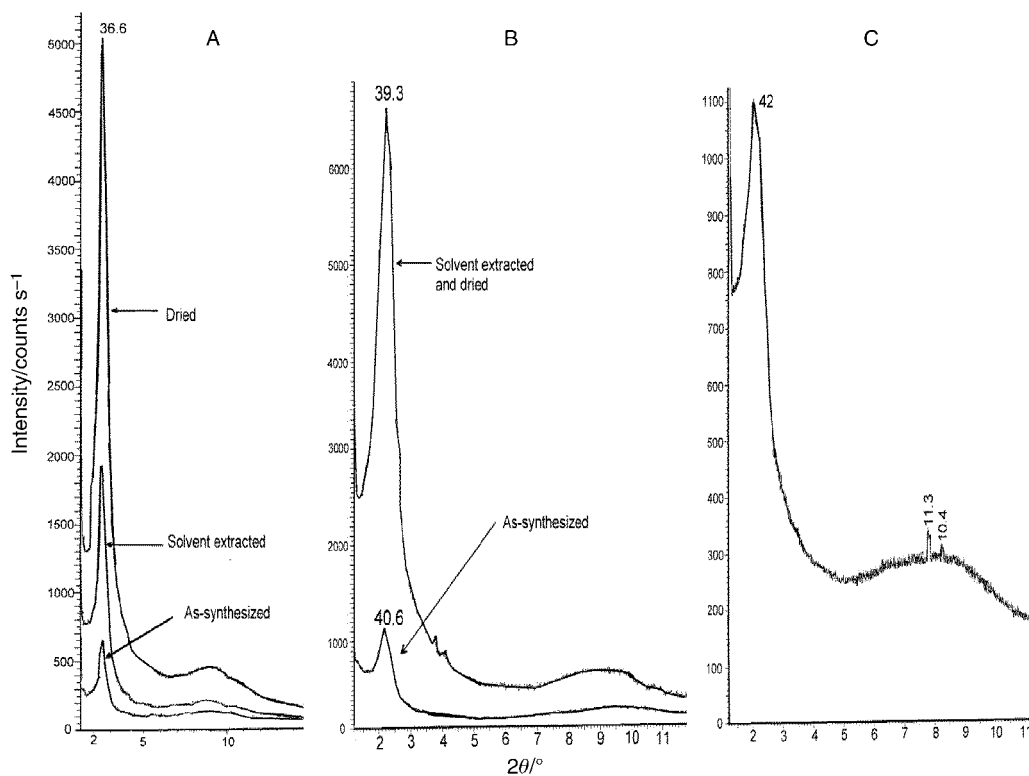


**Fig. 1** Powder X-ray diffraction patterns of mesoporous aromatic silicas: A, tolyl; B, *p*-xylyl; C, dimethoxybenzene.

**Table 1** Nitrogen adsorption and unit cell data

| PMO | BET surface area/m$^2$ g$^{-1}$ | BJH pore volume/cm$^3$ g$^{-1}$ | Pore diameter/Å | $a_0(=2d/\sqrt{3})$/Å | Wall thickness/Å |
|---|---|---|---|---|---|
| Tolylsilica | 794 | 0.46 | 23 | 42 | 19 |
| p-Xylylsilica | 1108 | 0.62 | 23 | 45 | 22 |
| Dimethoxybenzenesilica | 568 | 0.32 | 23 | 48 | 25 |

precursor species resulting in a PMO with periodic mesoporosity and some degree of ordering of aromatic groups in the channel walls. In this context, extensive TEM imaging studies of large areas of product indicate that the aromatic PMO phase dominates over any accompanying amorphous arylsilica phase and that the observed ordering of aromatic groups most likely occurs mainly in the channel walls of the PMO and not within a co-existing amorphous phase.

The electron-rich dimethoxybenzene-silica PMO also showed the low angle peak located at $d_{100} = 42$ Å, Fig. 1C. However it was less pronounced even after surfactant removal and drying. Interestingly, the broad diffraction halo in the area of $d = 10$ Å was more intense compared to the other aromatic PMOs. It seems that this material is less ordered than the others and may include an amorphous arylsilica phase. Indeed TEM images show areas of ordered aromatic PMO as well as an amorphous material.

The spatial, steric and electronic demands of the integrated aryl groups are also reflected in the nitrogen adsorption isotherms which were measured for the surfactant-extracted aromatic PMOs. The Brunauer–Emmett–Teller (BET) surface

areas, the Barrett–Joyner–Halenda (BJH) adsorption pore volumes as well as the pore diameter $a_0$-value calculated from $a_0 = 2d/\sqrt{3}$ and channel wall thickness are summarized in Table 1.

Similarly to inorganic mesoporous materials such as MCM-41 and FSM-16, the new materials are highly porous. For example, the surface area, pore volume and pore diameter for p-xylenesilica PMO are 1108 m$^2$ g$^{-1}$, 0.62 cm$^3$ g$^{-1}$ and 23 Å, respectively. The distinct changes in the channel wall thickness, obtained from a combination of diffraction, microscopy and adsorption data, for the aromatic PMOs seem to reflect increasing spatial demands of the bridging aromatic group. This supports the proposition that the aryl groups are indeed integrated within the arylsilica channel walls of the PMO.

$^{13}$C cross-polarization MAS NMR spectra of solvent extracted aromatic PMOs are shown in Fig. 3A. The spectra clearly show that aryl groups were incorporated intact into the channel wall. Moreover, Si–C bonds survived the hydrolytic polycondensation process and the acidic solvent extraction. In the spectra of the tolyl- and p-xylyl-silicas, characteristic aromatic carbons can be observed at 135 ppm and the methyl
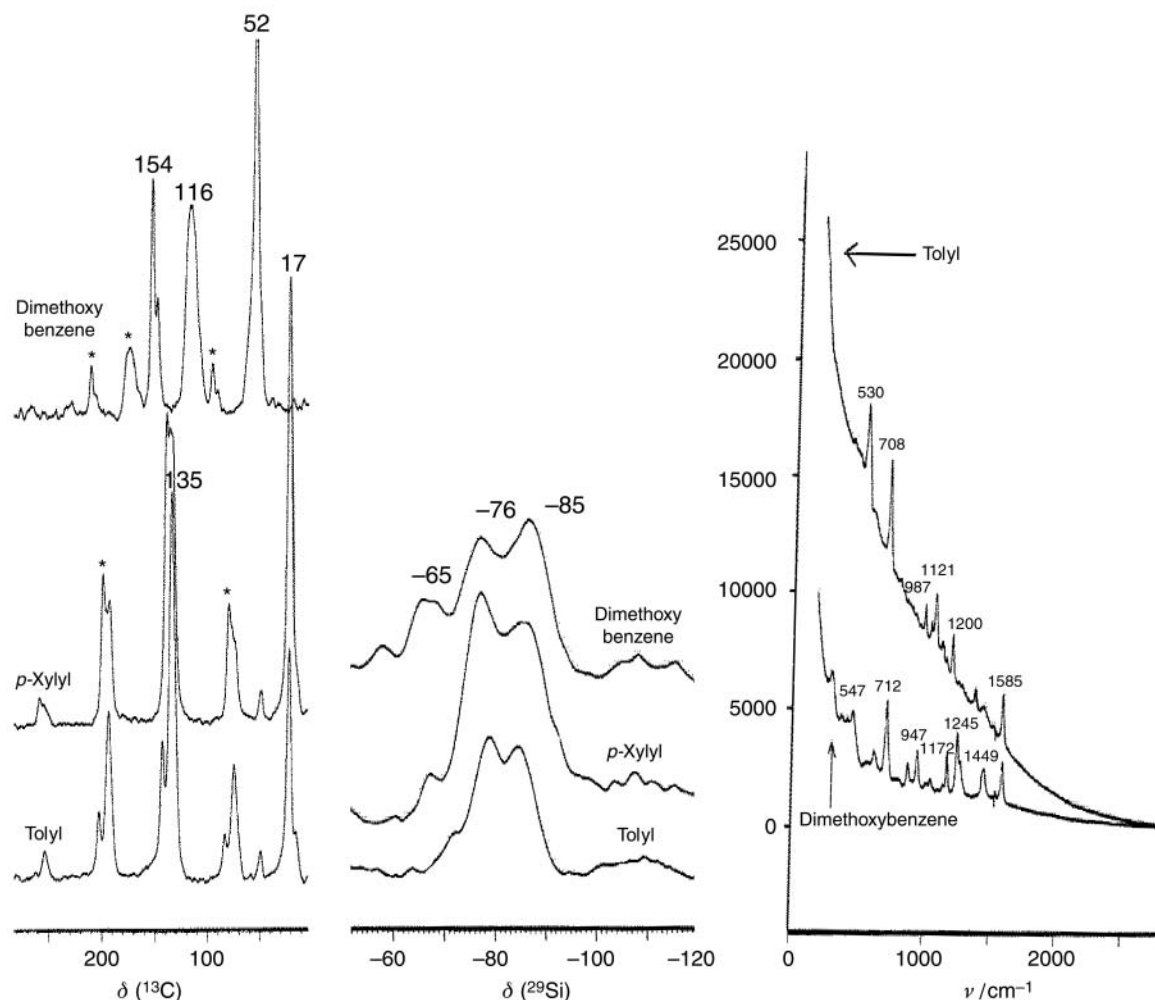


**Fig. 3** Spectral analysis of periodic mesoporous aromatic silicas: A, $^{13}$C CP-MAS NMR, asterisks signify peaks ascribed to spinning side bands; B, $^{29}$Si MAS NMR; C, FT-Raman spectra.

carbons at 17 ppm. In the spectrum of dimethoxybenzene PMO, the aromatic carbons attached to oxygen resonate at 154 ppm, the other aromatic carbons are observed at 116 ppm and the methoxy carbons at 52 ppm.

The $^{29}$Si MAS NMR of the aromatic PMOs displayed mostly T3 signals corresponding to aryl–Si(OSi)$_3$ sites and T2 signal corresponding to aryl–Si(OSi)$_2$OH sites, at approximately −85 and −76 ppm, respectively,[11] Fig. 3B. In the spectrum of dimethoxybenzene PMO, a relatively larger amount of T1 aryl–Si(OSi)(OH)$_2$ sites at −65 ppm is present,[12] which indicates a lower degree of dimethoxybenzenesilica polymerization. In all the cases, only minor Q3 (−105 ppm) and Q4 (−114 ppm) sites were observed,[13,14] which, again, confirms the stability of the aryl–Si bonds during surfactant assembly and extraction processes.

FT-Raman/IR spectroscopy of the new materials provided further data confirming the structure and the stability of the organic moieties during the assembly process. Thus, Raman bands typical of aryl groups at 1585 cm$^{-1}$, Fig. 3C, silicon–phenyl bonds at 1121 cm$^{-1}$ and 708 cm$^{-1}$ and Si–O–Si bonds between 947 and 987 cm$^{-1}$ could be observed. In the FT-IR, the aromatic C–H stretching modes around 2900 cm$^{-1}$ have been observed. The dimethoxybenzene derivative showed also aromatic ether absorption at 1245 cm$^{-1}$.

### Thermal properties

As shown in the TGA traces of the surfactant-extracted tolylsilica derivative, Fig. 4, all three aromatic PMOs displayed good thermal stability and survived heating until 340–360 °C. The first transition around 100 °C with loss of about 6–17% weight corresponds to water elimination. The second transition starting at 340–360 °C with loss of about 37–44% weight indicates cleavage of the aryl moieties of the PMOs and fits roughly the percentage of aryl groups integrated into the channel walls of the materials.

## Conclusions

Three new aromatic PMOs having bridge-bonded aryl groups as an integral part of the channel walls have been synthesized. Preparations conducted in the presence of a surfactant template and employing new precursors consisting of two triethoxysilyl groups connected *via* toluene, *p*-xylene or 1,4-dimethoxybenzene, generated new aromatic PMOs. Both NMR and FT-Ramam/IR measurements proved arene–silica bonds are quite stable under hydrolytic polycondensation and surfactant acidic extraction conditions. The aromatic PMOs have well-ordered hexagonal mesostructures, some degree of ordering of aromatic groups likely through π–π stacking in the channel walls, substantial pore volumes and surface areas and channel wall thickness that appear to reflect spatial demands of incorporated aryl groups, with tolylsilica < *p*-xylylsilica < 1,4-dimethoxybenzenesilica. Preliminary results suggest accessibility of incorporated methyl and methoxy groups to further chemical functionalization, such as oxidation, radical-halogenation and demethylation and this "chemistry of the
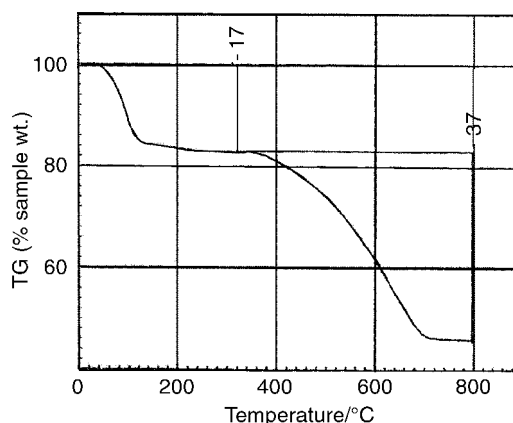


**Fig. 4** Thermogravimetric analysis of surfactant extracted mesoporous tolylsilica.

channels" and its influence on the properties of aromatic PMOs are under further investigation in our group.

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