

Synthesis and characterization of highly ordered bifunctional aromatic periodic mesoporous organosilicas with different pore sizes†

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The first syntheses of highly ordered bifunctional periodic mesoporous organosilicas (PMOs) containing different amounts of aromatic thiophene and benzene bridging groups are reported. Employing the triblock copolymer Pluronic P123 as well as the oligomeric Brij 76 surfactant under acidic conditions as supramolecular structure-directing agents, the syntheses of two series of bifunctional aromatic PMO materials with pore sizes in the range of 4.8–5.4 and 3.3 nm, respectively, have been realized. Independent of the molar ratios of the organosilanes in the initial reaction mixtures, highly ordered PMO materials with 2D hexagonal mesostructures have been obtained in all cases. After a one-off calibration based on ²⁹Si MAS NMR measurements, the quantification of the organic functional groups has been carried out for the first time, in case of PMO materials, using Raman spectroscopic methods.

Introduction

The discovery of long-range ordered mesoporous M41S silica and aluminosilicate phases by the Mobil Oil Company in 1992 was a major breakthrough in the efforts to extend the pore sizes of the well-known and long-established microporous zeolites.^{1,2} In the following years, the field of mesoporous materials was expanding by the application of these surfactant-templated methods to, for instance, non-silica metal oxides, metals and carbons.³ With regard to potential applications, such as in catalysis, adsorption, chromatography, and chemical sensing, considerable effort was spent on modifying the mesoporous silica frameworks of the M41S phases with organic functional groups. In general, this was realized by employing two pathways.^{4–7} The first is the grafting approach, where the organic functionalities are bound on the silica surface by a post-synthesis treatment and the second is the co-condensation method (so-called ‘one-pot’ synthesis) of tetraalkoxysilanes and terminal organotrialkoxysilanes in the presence of supramolecular structure-directing agents. While it was possible to modify the frameworks with a wide variety of organic groups, it should be noted that both pathways have their limitations and inherent drawbacks. The negative effects occurring when these synthesis approaches are employed include, for instance, pore blocking, limited loading, or inhomogeneous distributions of the organic functional groups. These problems were overcome successfully when the synthesis

of a new class of mesoporous organic–inorganic hybrid materials was developed in 1999 by three independently-working research groups.^{8–10} These new materials, called periodic mesoporous organosilicas (PMOs), could be synthesized *via* hydrolysis and condensation reactions of bridged organosilsesquioxane precursors [(R'O)₃Si–R–Si(OR')₃]—which have been known from sol–gel chemistry for quite some time—in the presence of supramolecular aggregates of long-chain surfactants serving as structure-directing agents.¹¹ In contrast to the organofunctionalized mesoporous silica, the organic units in PMOs are two-point attached within the silica matrix through covalent bonds and are thus completely homogeneously distributed, being a genuine part of the 3D framework structure. Furthermore, the PMO materials possess ordered pore arrangements accompanied by sharp pore size distributions as a result of employing structure-directing agents for the synthesis. By varying the organic spacer groups of the organosilica precursors, enormous possibilities are given to tune the chemical and physical properties of the PMOs in designated ways. Because of their ordered and uniform porosity, this kind of material is very interesting for applications such as catalysis, adsorption, chromatography or host–guest-chemistry. So far, the organic bridging groups of the organosilica precursors, which have been successfully converted into PMO materials, include for instance methylene,¹² ethane,^{8,10,13–15} ethylene,^{9,10} benzene,¹⁶ toluene,¹⁷ 2,5-dimethylbenzene,¹⁷ *p*-xylene¹⁸ or biphenyl¹⁹ units. Thiophene groups represent the only example of a heterocyclic organic functional group incorporated into a PMO material.^{16,20} Furthermore, PMOs carrying three point attached 1,3,5-benzene²¹ units or interconnected [Si(CH₂)₃]-rings have been synthesized.²² In addition, the syntheses of other classes of PMOs which were formed from single-source precursors containing siloxane–disilsesquioxane (DT² type) or siloxy–trisilsesquioxane (MT³ type) units and of the so called periodic mesoporous dendrisilicas (PMDs) containing SiC₄ building

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units have been reported.^{23,24} Very recently, Ozin *et al.* realized the synthesis of a new type of PMO materials with 4-phenylether- and 4-phenylsulfide organic bridging groups.²⁵ Instead of the common X-ray-amorphous pore walls, Inagaki *et al.* were the first to synthesize PMOs with crystal-like pore walls in case of 1,4- and 1,3- benzene- as well as biphenyl-bridged organosilicas in the presence of alkyltrimethylammonium halides as structure-directing agents under basic conditions.^{19,26,27} In addition, we could show by *in situ* synchrotron SAXS/XRD studies that the formation of periodicity both on the mesoscopic scale and within the pore walls occurs simultaneously as the result of a highly cooperative process.²⁸ Very recently, the synthesis of a new PMO material with crystal-like pore walls containing 1,4-divinylbenzene bridging groups was independently reported by Sayari *et al.* and Cornelius *et al.*, respectively.^{29,30}

In comparison to the common basic PMO syntheses using ionic alkylammonium surfactants, an alternative promising synthesis route to PMO materials under acidic conditions was established by employing nonionic oligomeric surfactants such as Brij 56 or Brij 76, respectively, as structure-directing agents.^{31–35} Thus it was also possible to obtain materials with a high degree of mesostructural order, large specific surface areas and narrow pore size distributions. As the pore diameters of the resulting materials in case of both aforementioned synthesis procedures are limited in the range of 2–5 nm, PMOs with larger pore sizes can be synthesized also under acidic conditions but using non-ionic triblock copolymers as structure-directing agents.^{15,20,31,36–38}

However, it was also possible to synthesize PMOs with morphologies other than powders, *e.g.* thin films^{39,40} and monodisperse spherical particles.^{41,42} Currently, a lot of effort is spent on the synthesis of bifunctional PMO materials containing two different organic groups within the pore wall framework. This was achieved by using co-condensation methods of bridged bis(trialkoxysilyl) organosilanes [(RO)₃Si–R'–Si(OR)₃] and terminal trialkoxysilyl organosilanes [(RO)₃Si–R"], resulting in materials which possess a combination of both organic bridging units and terminal organic functional groups protruding into the pore channels. Unfortunately, the degree of mesostructural order and the porosity of the resulting materials usually decreases with increasing amounts of terminal functional groups until finally a structural collapse occurs when the loading exceeded about 30 mol%.^{7,11}

With regard to potential applications such as chromatography or adsorption, it will be desirable to synthesize other kinds of bifunctional PMOs composed of two bridging groups, which can be fine-tuned in terms of the content of both components without a loss of mesostructural order and porosity properties when varying the amounts of the organic units. Very recently, Burleigh *et al.* succeeded in the preparation of a new family of bifunctional or even multifunctional PMO materials containing different amounts of methylene, ethane, ethylene, benzene or ethylenediamine organic bridging groups *via* co-condensation of the corresponding bridged organosilanes in the presence of Brij 76 as a structure-directing agent.^{43,44}

Here we report the first syntheses of highly ordered bifunctional periodic mesoporous organosilicas containing

different amounts of thiophene and benzene bridging groups. By employing the triblock copolymer Pluronic P123 or the oligomeric Brij 76 surfactant as structure-directing agents, two series of bifunctional PMO materials with pore sizes in the range of 4.8–5.4 and 3.3 nm, respectively, have been prepared. We demonstrate that Raman spectroscopy after a one-off calibration based on ²⁹Si MAS NMR measurements can be used as a fast non-invasive tool for determining the relative compositions of the two types of bridging groups within the PMO pore walls. Due to a comparable chemical reactivity which reduces the problems of phase separations during the syntheses as well as the size of the organic spacer groups of the employed organosilica precursors [2,5-bis(triethoxysilyl)thiophene (BTET) and 1,4-bis(triethoxysilyl)benzene (BTEB)] the contents of both organic bridging groups in the obtained PMO materials can be varied over a wide range without any decrease of mesostructural order and porosity properties. Using different concentrations of the precursors for the syntheses the amount as well as the average distance of both benzene and thiophene units in the resulting materials can be tuned in designated ways which is illustrated in Fig. 1. Therefore, it is possible to tailor the surface properties of the PMOs possessing a combination of both the aromatic benzene as well as the heterocyclic thiophene functional groups incorporated within the pore walls, which makes these kinds of materials very interesting for applications such as chromatography or adsorption. Furthermore, with regard to the thiophene bridging groups the materials can serve as hosts for the immobilization of thiophilic compounds like, for example Au₅₅-clusters, whereas the loading as well as the average distance of the clusters can be controlled in designated ways by varying the amount of the coordinating thiophene functional groups.

Experimental

Syntheses

The two series of bifunctional PMO materials were synthesized using mixtures with different molar ratios of the organosilica precursors 2,5-bis(triethoxysilyl)thiophene (BTET) and 1,4-bis(triethoxysilyl)benzene (BTEB) in the presence of the triblock copolymer Pluronic P123 as well as the oligomeric Brij 76 surfactant as structure-directing agents under acidic conditions. While the organosilanes BTET and BTEB were synthesized in accordance with the literature,⁴⁵ the commercially available Pluronic P123 and Brij 76, respectively, were used without further purification.

Synthesis of bifunctional PMO materials in the presence of P123

All PMO materials were prepared using mixtures of the organosilica precursors BTET [(R'O)₃Si–C₄H₂S–Si(OR')₃] and BTEB [(R'O)₃Si–C₆H₄–Si(OR')₃] and following our recently reported synthesis protocol for the preparation of mesoporous thiophene-bridged organosilicas²⁰ while keeping the total numbers of moles of the organosilanes constant. The molar ratios of the two organosilica precursors in the reaction mixtures and the labels of the samples are listed in Table 1. In a typical synthesis, 0.512 g (0.088 mmol) of P123 were dissolved

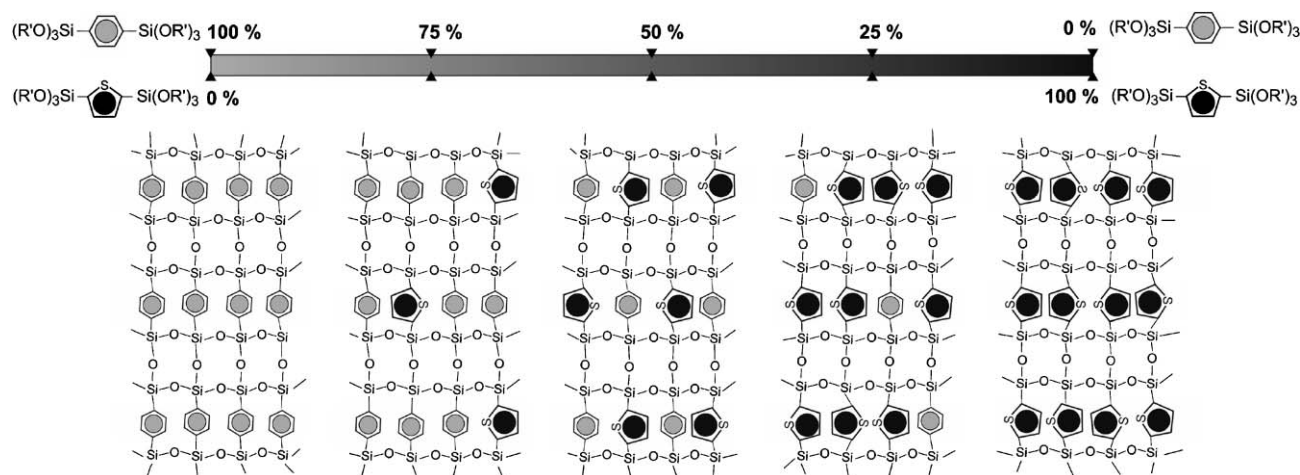


Fig. 1 Illustration of a bifunctional PMO material composed of thiophene and benzene bridging groups which can be fine-tuned in terms of the content of both components.

in a mixture of 19.2 g (1.067 mol) of distilled water and 0.166 g (1.5 mmol) of conc. HCl (32 wt%). After addition of the premixed organosilanes (1.3 mmol), the reaction mixture was kept for 20 h at 40 °C under vigorous stirring. After additional hydrothermal treatment for 24 h at 100 °C in a teflon-lined stainless steel autoclave, the obtained precipitate was filtered, washed three times with 50 ml of distilled water and dried in air overnight. Removal of the surfactant was accomplished by extraction with a mixture of ethanol–HCl (conc.) (100 : 3; v/v) using a Soxhlet apparatus for 48 h with subsequent drying of the product in air. The molar ratios of the components in the reaction mixture were as follows: organosilanes–P123–HCl–H₂O = 1 : 0.068 : 1.15 : 821.

Synthesis of bifunctional PMO materials in the presence of Brij 76

The synthesis of PMO materials in the presence of Brij 76 was carried out using mixtures of the organosilica precursors BTET and BTEB and following in principle an earlier reported synthesis protocol for the preparation of mesoporous benzene-bridged organosilicas³⁵ while keeping the total numbers of moles of the organosilanes constant. The molar ratios of the two organosilanes in the reaction mixtures and the labels of the corresponding samples are listed in Table 1. The Brij 76 surfactant (0.8 g, 1.1 mmol) was dissolved in a mixture of 20 g (39 mmol) of 2 M HCl and 4 g (222 mmol) of distilled water at

50 °C. After addition of the premixed precursors (4.1 mmol), the reaction mixture was kept for 20 h at 50 °C and additionally for 24 h at 90 °C under static conditions in an autoclave. After washing and drying the obtained products, the surfactant removal was carried out by solvent extraction for 24 h as described above. The molar ratios of the components in the reaction mixture were as follows: organosilanes–Brij 76–HCl–H₂O = 1 : 0.27 : 9.5 : 54.

Characterization

Powder X-ray diffraction (P-XRD) patterns were recorded at room temperature with a Bruker AXS D8 Advance diffractometer using filtered Cu K α radiation.

Transmission electron micrographs were obtained with a Philips C 30 microscope operating at 300 kV.

N₂-Physisorption data were recorded with a Quantachrome Autosorb 6 at 77 K. The BET surface areas were calculated from $p/p_0 = 0.03$ –0.3 in the adsorption branch while the BJH pore size distributions were calculated from the desorption branch.

²⁹Si MAS NMR spectra were recorded with direct excitation and gated proton decoupling to obtain a measure of the relative number of different silicon sites in the material. The spectra were acquired with a 7 mm MAS system at a resonance frequency of 79.4 MHz using a Bruker MSL-400 spectrometer. The samples were spun at 3.5 kHz. Further experimental parameters were a $\pi/2$ pulse width of 6 μ s, a recycle delay of 300 s, and 1500 scans. The decomposition and simulation of the MAS NMR spectra were performed using Bruker software WINNMR and WINFIT.

Raman spectra were acquired using a Raman microscope system (Jobin–Yvon). The green line 514.5 nm of an Ar ion laser was used for excitation and a single grating monochromator with a CCD multi-channel detector system was used for acquiring the Raman spectra. The Rayleigh-scattered laser light was rejected using a holographic notch-filter. The excitation power on the sample was less than 20 mW and the spectral resolution of the detection system about 1 cm^{−1}.

Table 1 Labels of the bifunctional PMO materials and molar ratios of the corresponding organosilica precursors in the initial reaction mixtures (P = P123-templated; B = Brij 76-templated)

Sample		Molar ratios of organosilanes	
		BTET	BTEB
P(0 : 1)	B(0 : 1)	0	1
P(1 : 5)	B(1 : 5)	1	5
P(1 : 3)	B(1 : 3)	1	3
P(1 : 1)	B(1 : 1)	1	1
P(3 : 1)	B(3 : 1)	3	1
P(5 : 1)	B(5 : 1)	5	1
P(1 : 0)	P(1 : 0)	1	0

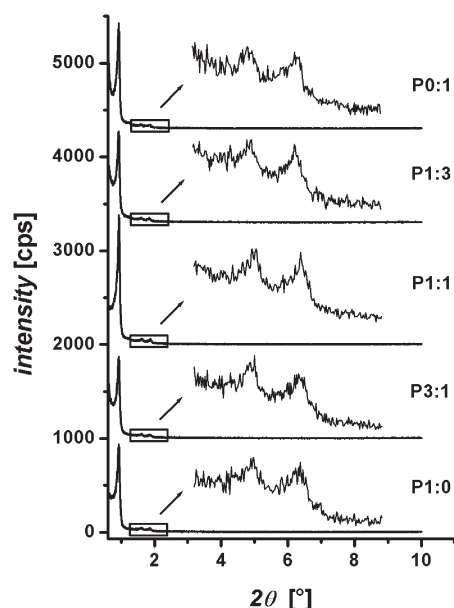


Fig. 2 P-XRD patterns of the bifunctional periodic mesoporous organosilicas synthesized with P123 as structure-directing agent.

Results and discussion

Powder X-ray diffraction

All P-XRD patterns of the solvent-extracted P123-templated PMOs [P(0 : 1) to P(1 : 0)] exhibit three sharp reflections in the low-angle region ($2\theta < 3^\circ$) indicating a high degree of mesostructural order independent of the molar ratios of the organosilica precursors in the reaction mixtures (Fig. 2). The patterns can be indexed as (100), (110) and (200) reflections according to a two-dimensional hexagonal symmetry (p6mm) of the materials. The interplanar d spacings corresponding to the (100) reflections are slightly shifting in the range of 9.5 to 9.7 nm and the lattice parameters ($a = 2d_{(100)}/\sqrt{3}$) from 11.0 to 11.2 nm (Table 2).

The P-XRD patterns of all extracted products [B(0 : 1) to B(1 : 0)] using Brij 76 as structure-directing agent also reveal three reflections (100, 110, 200) in the low angle region ($2\theta < 4^\circ$) indicating highly ordered mesoporous materials with 2D hexagonal (p6mm) mesostructures (Fig. 3). The smaller d spacings of the PMO materials corresponding to the (100) reflections compared to those of the P123-templated products indicate the existence of smaller mesopores as it was expected using this kind of surfactant. The d values are slightly

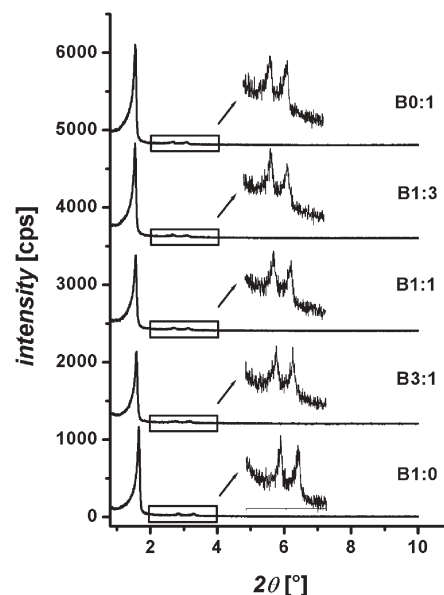


Fig. 3 P-XRD patterns of the bifunctional periodic mesoporous organosilicas synthesized with Brij 76 as structure-directing agent.

increasing from 5.2 to 5.7 nm and the lattice parameters from 6.2 to 6.5 nm with increasing amount of benzene units in the PMO materials (Table 3). Similar to the P123-derived products, no dependence on the molar ratios of the organosilanes in the initial reaction mixtures with regard to the degree of mesostructural order can be observed. In addition, in both cases of the series of bifunctional PMOs, no X-ray reflections in the higher-angle region—indicating a crystal-like pore wall structure—could be observed in the corresponding XRD patterns of the samples.

Nitrogen physisorption measurements

The nitrogen physisorption measurements on the P123-templated PMOs [P(0 : 1) to P(1 : 0)] reveal in all cases type IV isotherms with H1 hysteresis which are typical of mesoporous materials employing this kind of surfactant (Fig. 4). The specific surface areas of the products decrease from 800 to 440 m² g^{−1}, whereas the pore diameters increase from 4.8 to 5.4 nm with increasing amount of thiophene units in the materials. The framework wall thicknesses obtained by subtracting the pore sizes from the lattice parameters are increasing from 5.7 to 6.3 nm with decreasing content of thiophene groups in the pore wall frameworks (Table 2).

Table 2 Powder X-ray diffraction and nitrogen physisorption data of the bifunctional PMO materials synthesized with P123 as structure-directing agent

Sample	d_{100}/nm	a/nm	Pore size/nm	BET surface area/m ² g ^{−1}	Wall thickness/nm
P(0 : 1)	9.6	11.1	4.8	800	6.3
P(1 : 5)	9.7	11.2	5.2	780	6.0
P(1 : 3)	9.6	11.1	5.1	760	6.1
P(1 : 1)	9.5	11.0	5.1	640	5.9
P(3 : 1)	9.6	11.1	5.1	450	6.0
P(5 : 1)	9.6	11.1	5.4	490	5.7
P(1 : 0)	9.6	11.1	5.4	440	5.7

Table 3 Powder X-ray diffraction and nitrogen physisorption data of the bifunctional PMO materials synthesized with Brij 76 as structure-directing agent

Sample	d_{100}/nm	a/nm	Pore size/nm	BET surface area/m ² g ^{−1}	Wall thickness/nm
B(0 : 1)	5.7	6.5	3.3	1110	3.2
B(1 : 5)	5.7	6.5	3.3	1130	3.2
B(1 : 3)	5.7	6.5	3.3	1110	3.2
B(1 : 1)	5.7	6.5	3.3	1120	3.2
B(3 : 1)	5.6	6.4	3.3	1070	3.1
B(5 : 1)	5.6	6.4	3.3	1070	3.1
B(1 : 0)	5.2	6.2	3.3	1020	2.9

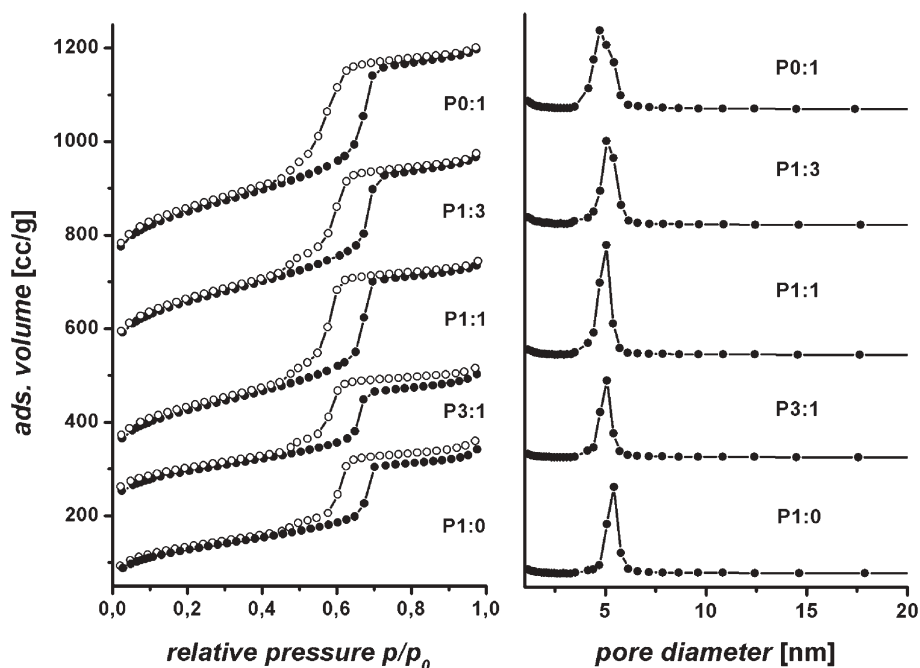


Fig. 4 Nitrogen adsorption-desorption isotherms and pore size distributions of the bifunctional periodic mesoporous organosilicas synthesized with P123 as structure-directing agent.

The isotherms of the Brij 76-templated PMOs [B(0 : 1) to B(1 : 0)] also are of type IV in all cases indicating the existence of mesoporous materials (Fig. 5). The specific surface areas vary between 1020 and 1110 m² g⁻¹, whereas the calculated pore diameters are approximately 3.3 nm for all products. The calculated wall thicknesses are decreasing from 3.2 to 2.9 nm with increasing loading of thiophene groups in the pore walls (Table 3). In contrast to those of the P123-derived

PMOs, the isotherms do not exhibit distinct hysteresis loops, which is characteristic of mesoporous materials with smaller pore sizes.⁴⁶

TEM

Consistent with the results of the XRD and the physisorption measurements, respectively, the analyses of the transmission

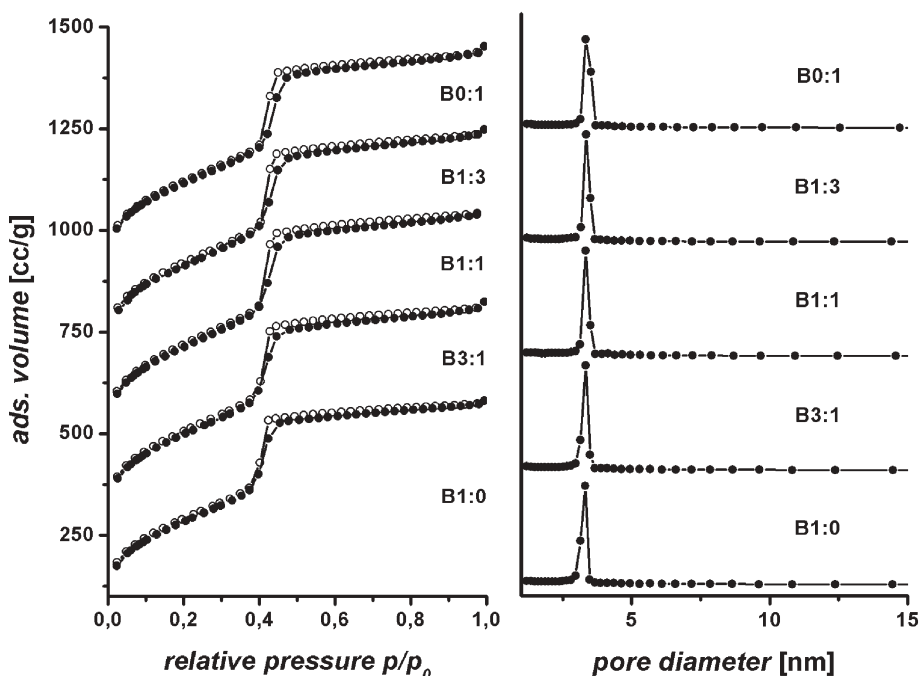


Fig. 5 Nitrogen adsorption-desorption isotherms and pore size distributions of the bifunctional periodic mesoporous organosilicas synthesized with Brij 76 as structure-directing agent.

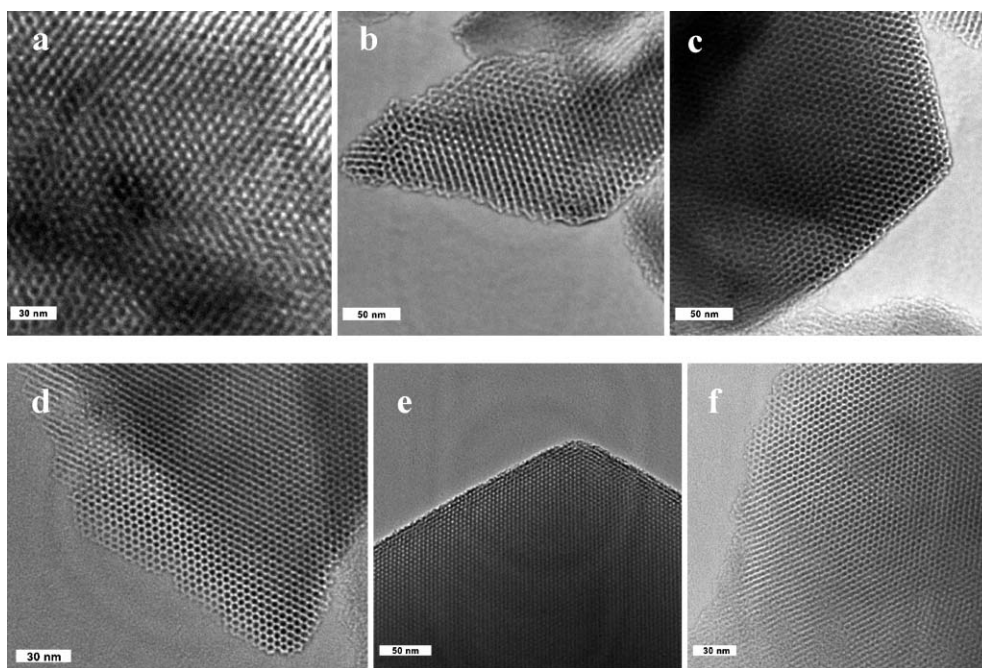


Fig. 6 Representative TEM images of the bifunctional periodic mesoporous organosilicas synthesized with P123 [a: P(1 : 0), b: P(1 : 1), c: P(0 : 1)] and Brij 76 [d: B(1 : 0), e: B(1 : 1), f: B(0 : 1)] as structure-directing agents (view parallel to the pore axes).

electron microscope (TEM) images of both series of PMO materials also confirm the 2D hexagonal arrangements of well-defined mesopores with a high degree of mesostructural order as well as the calculated pore sizes [Fig. 6a–f shows examples of the TEM images of (a) P(1 : 0), (b) P(1 : 1), (c) P(0 : 1), (d) B(1 : 0), (e) B(1 : 1) and (f) B(0 : 1)].

²⁹Si MAS NMR spectroscopic measurements

The ²⁹Si MAS NMR spectra of the extracted P123-templated bifunctional PMO materials [P(0 : 1) to P(1 : 0)] are shown in Fig. 7. The spectrum of the thiophene-bridged PMO (P(1 : 0)) exhibits three *T*ⁿ signals which can be assigned to the following Si species covalently bonded to the carbon atoms: *T*¹ [C–Si(OSi)(OH)₂, δ –65.6], *T*² [C–Si(OSi)₂(OH), δ –74.6], and *T*³ [C–Si(OSi)₃, δ –83.6]. The corresponding *T*ⁿ signals of the benzene-bridged material [P(0 : 1)] show chemical shifts at δ –61.1 (*T*¹), δ –70.2 (*T*²) and δ –78.7 (*T*³), respectively, while the spectra of the bifunctional PMOs [P(1 : 5) to P(5 : 1)] exhibit the superpositions of six *T*ⁿ signal species according to the presence of Si species bonded to both aromatic units in the pore wall structure of the materials. The absence of any *Q*ⁿ signals [Si(OSi)_n(OH)_{4–n}, *n* = 2–4] between –98 and –111 in all spectra [P(0 : 1) to P(1 : 0)] confirms that no Si–C bond cleavage has occurred during the syntheses and solvent extractions.

To determine the different contents of the aromatic groups in the bifunctional PMO materials, the relative intensities of the different *T*ⁿ signals have been determined by simulation and separation of each spectrum. For example the spectra of P(1 : 5) and P(5 : 1) with the different simulated and separated *T*ⁿ signals are shown in Fig. S1 in the ESI. The integrated peak areas on a percentage basis for each separated signal as well as the ratios of the sum of the peak areas of the corresponding

separated signals according to the benzene and to the thiophene species, respectively, are listed in Table 4. The calculated ratios of the peak areas can be correlated to different contents of the aromatic units in the materials. Moreover they are in good agreement with the molar ratios of the corresponding organosilica precursors in the initial reaction mixtures.

The spectrum of the extracted Brij 76-templated thiophene-bridged PMO [B(1 : 0)] (Fig. 8) exhibits besides three *T*^{1–3}

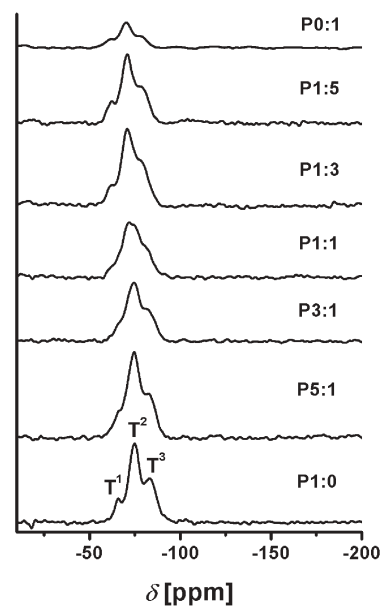
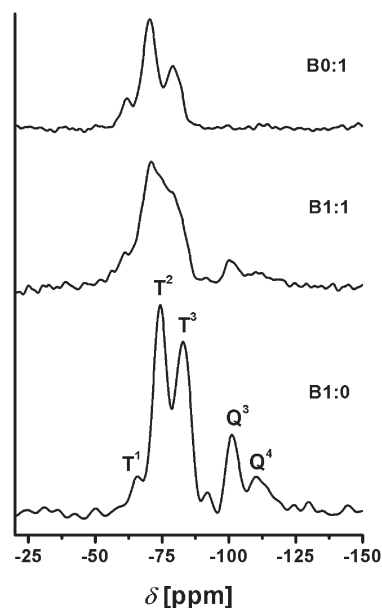


Fig. 7 ²⁹Si MAS NMR spectra of the bifunctional periodic mesoporous organosilicas synthesized with P123 as structure-directing agent.

Table 4 ^{29}Si MAS NMR data of the bifunctional PMO materials synthesized with P123 as structure-directing agent

Sample	T^n (thiophene) [%]			T^n (benzene) [%]			Ratio $\Sigma T^n_{\text{thiophene}} : T^n_{\text{benzene}}$
	T^1	T^2	T^3	T^1	T^2	T^3	
P(0 : 1)	—	—	—	13	67	20	
P(1 : 5)	2	11	5	9	54	19	1 : 4.6
P(1 : 3)	4	18	7	7	48	16	1 : 2.4
P(1 : 1)	3	32	16	5	32	12	1 : 1
P(3 : 1)	4	44	26	1	18	7	2.8 : 1
P(5 : 1)	7	50	26	1	12	4	4.9 : 1
P(1 : 0)	7	61	32	—	—	—	

**Fig. 8** ^{29}Si MAS NMR spectra of the bifunctional periodic mesoporous organosilicas synthesized with Brij 76 as structure-directing agent.

signals [$\delta -65.1$ (T^1), $\delta -74.2$ (T^2), $\delta -82.9$ (T^3)] two Q^n signals, which can be assigned to the following silica species surrounded by four oxygen atoms: Q^3 [$\text{Si}(\text{OSi})_3(\text{OH})$, $\delta -101.1$] and Q^4 [$\text{Si}(\text{OSi})_4$, $\delta -111.0$]. The integrated peak areas of the Q^n signals indicate that about 22% of the Si–C bonds have been cleaved during the synthesis (Table 5). The reason for the higher degree of Si–C bond cleavage compared to the corresponding P123-templated PMO (P(1 : 0)) is the higher acid concentration used in the synthesis. However, this was necessary to achieve a comparable degree of mesostructural order, as the mesostructural order was found to be lower at higher pH values. In contrast, the spectrum of the extracted Brij 76-templated benzene-bridged PMO [B(0 : 1)], which was synthesized using the same conditions as for its

thiophene-bridged counterpart [B(1 : 0)], shows only the three T^n signals [$(\delta -61.6$ (T^1), $\delta -70.3$ (T^2), $\delta -79.4$ (T^3))] and no Q^n signals indicating that no Si–C bonds have been cleaved. In case of the extracted bifunctional PMO B(1 : 1), the calculated ratios of the integrated peak areas of the separated signals (including the Q^n signals) are in good agreement with the molar ratios of the corresponding organosilica precursors in the initial reaction mixtures as in the case of the P123-templated materials. Furthermore, as the sum of the peak areas of the thiophene-related T^n signals and that of the Q^n signals equals that of the benzene-related T^n signals, it can be concluded that the presence of the Q^3 and Q^4 signals with a contribution of about 11% arises due to Si–C bond cleavage for the precursor BTET only, and not for the precursor BTEB (Table 5). These results indicate that the Si–C bonds of the precursor BTEB are, contrarily to the precursor BTET, resistant against hydrolysis at this lower pH value used in the synthesis. The partially occurring hydrolysis of the Si–C bonds in case of BTET is due to the higher reactivity of the thiophene unit with respect to an electrophilic substitution compared to that of the benzene bridge.

Raman spectroscopic measurements

Laser Raman spectroscopy was performed on the two series of bifunctional PMOs. Fig. 9 depicts exemplarily a survey of Raman spectra of the two benzene-bridged PMOs [P(0 : 1) and B(0 : 1)] of different pore size in comparison with the corresponding precursor BTEB [$(\text{R}'\text{O})_3\text{Si}-\text{C}_6\text{H}_4-\text{Si}(\text{OR}')_3$] as well as the pure benzene being the bridging functional group. The precursor as well as the PMO products show a significantly larger number of Raman features than the simple benzene molecule. In the lower-frequency region the precursor as well as the PMOs exhibit considerably more features than the aromatic molecule alone. This is partly due to the reduction of symmetry of the C_6 ring environment. An unsubstituted benzene molecule has D_{6h} symmetry while the PMO as well as the precursor are essentially *para*-substituted benzene with D_{2h} symmetry. Fig. 10 schematically shows how the symmetry classes of the vibrational modes of the benzene ring develop upon *para*-substitution. Indeed, BTEB as well as the benzene-bridged PMOs both yield Raman spectra, which are indicative for *para*-benzene with a strong feature at approx. 1600 cm^{-1} , no strong signals between 990 and 1055 cm^{-1} but with medium to strong features in the 620 to 660 cm^{-1} range.⁴⁷ However, the large increase of the number of Raman active modes for BTEB and the PMOs compared to benzene cannot be explained by symmetry considerations (Fig. 10) alone. Therefore, some of the additional peaks arise from internal vibrations of the substituents and their coupling to the ring modes.

Table 5 ^{29}Si MAS NMR data of the bifunctional PMO synthesized with Brij 76 as structure-directing agent

Sample	T^n (thiophene) [%]			Q^n (thiophene) [%]		T^n (benzene) [%]			Ratio $\Sigma T^n, Q^n_{\text{thiophene}} : T^n_{\text{benzene}}$
	T^1	T^2	T^3	Q^3	Q^4	T^1	T^2	T^3	
B(0 : 1)	—	—	—	—	—	8	61	31	
B(1 : 1)	2	26	11	6	5	5	30	15	1 : 1
B(1 : 0)	3	41	34	14	8	—	—	—	

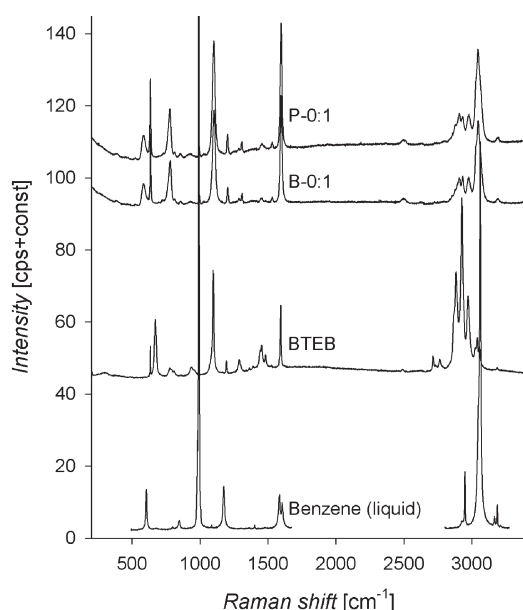


Fig. 9 Raman spectra of pure benzene, BTEB and two benzene-bridged PMOs synthesized with P123 and Brij 76, respectively.

A detailed assignment of the PMO and precursor modes requires complex theoretical calculations exceeding the scope of this publication because the benzene modes may partly split, partly shift and partly even change their character from Raman-inactive to Raman-active or *vice versa*. The corresponding mode patterns usually involve atoms, which are either distributed over the entire molecule or which are localized on side groups which are loosely bonded to the rest of the molecule. In particular, vibrations of the Si–C bond alone (which forms the connection between the side group and the benzene ring), if they are eigenmodes of the precursor or the PMO products at all, will depend very strongly on the surroundings. Therefore, we refrain from an assignment of a Raman feature in the spectra to the Si–C vibration and we do not use this as an indication of the integrity of Si–C bonds in the PMOs because theoretical vibration simulations show that Raman spectroscopy does not seem to be the right tool for this purpose. Solid state NMR should be used instead as was

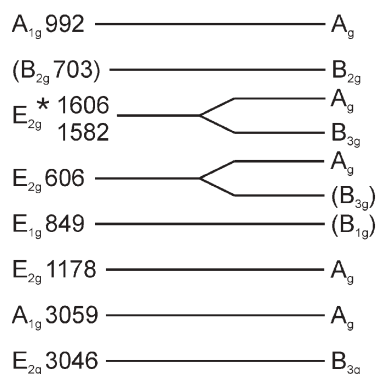


Fig. 10 Comparison of the vibrational modes in unsubstituted and *para*-substituted benzene. Modes set in brackets are Raman-inactive while the other modes are Raman-active. The known frequencies of the benzene in cm^{−1} modes are given. “*” indicates a Fermi resonance.

demonstrated above. However, we show in the following that Raman spectroscopy can be used to quantify the composition of these bifunctional PMOs.

We found for all PMOs under investigation that the spectra depend neither on the kind of structure-directing agent used nor on the pore size. Fig. 11 depicts examples of the series of spectra of the Brij 76-templated PMOs [B(0 : 1) to B(1 : 0)]. These spectra were recorded with the PMO samples pressed to the shape of small cylindrical pills (1 mm diameter) by a mechanical press. Such a procedure creates flat surfaces onto which the laser can easily be focused providing a sufficiently constant scattering geometry over the whole series. In a selected spectral range shown in the lower panel of the figure, two peaks were identified to be characteristic of thiophene- and benzene-bridged PMOs, respectively. The thiophene-related peak (“T”) is located at 1415 cm^{−1} while the one related to benzene (“B”) occurs at 1595 cm^{−1}. When BTET is successively replaced by BTEB in the synthesis, the 1415 cm^{−1} feature decreases while the 1595 cm^{−1} feature increases in

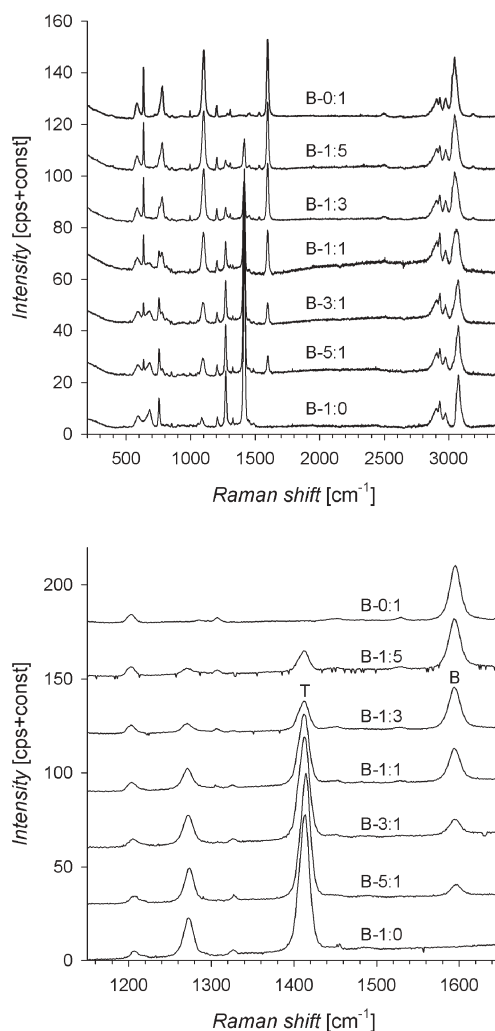


Fig. 11 Raman spectra of the series of the bifunctional PMOs synthesized with Brij 76 as the structure-directing agent. The total spectra are shown in the upper panel while a selected spectral range containing the two characteristic peaks (marked by “T” and “B”) is shown in the lower panel.

intensity. For both series of bifunctional PMOs (P(0 : 1) to P(1 : 0) and B(0 : 1) to B(1 : 0)) these two peaks were fitted with a Voigt-type line shape and the fitted curves were evaluated with respect to the peak areas. The dependence between the peak areas and the molar ratios of the respective precursors in the reaction mixture is shown in Fig. 12a–b for both bifunctional PMO series. For each of the precursors, a linear relationship between its molar ratio to the precursor mixture and the area of the corresponding Raman peak was found. This is true for both series of PMO materials. From this result it can be concluded that the contents of the aromatic units in the PMOs scale linearly with respect to the concentrations of the corresponding precursors in the reaction mixtures, because the intensity of a Raman peak is expected to scale linearly with the number of scattering centres responsible for the respective feature.

Even the finding of the ^{29}Si MAS NMR measurements that in case of the Brij 76-templated PMO series, a considerable amount of the Si–C bonds on the thiophene groups has been cleaved during synthesis while the ones at the benzene groups stay intact can be deduced from the Raman spectra. It is reflected in Fig. 12c (upper panel) by the finding that the

intensity ratio between the thiophene-related and the benzene-related peak is smaller for the Brij 76-templated (full circles) than for the P123-templated PMOs (full diamonds). Correspondingly, as depicted in the lower panel, the intensity ratio between the benzene-related and the thiophene-related peak is larger for the Brij 76-templated than for the P123-templated PMO materials. The data points for the Brij 76-templated PMOs can be corrected taking into account that about 20% of the thiophene units have been cleaved during synthesis while the benzene units are unaffected. If the correction is done, *i.e.* the corresponding [BTET]/[BTEB] ratio in the upper panel is reduced by the factor 0.8 and the corresponding [BTEB]/[BTET] ratio is stretched by a factor of $1.25 = (0.8)^{-1}$ in the lower panel, the open circles result. These corrected data points agree well with the ones (full diamonds) obtained for the P123-templated PMOs.

This demonstrates that after a one-off determination of the Raman intensities of the thiophene and benzene-related signals using calibration samples, which have been quantitatively characterized by ^{29}Si MAS NMR, it is possible to use Raman spectroscopic measurements as a fast and non-invasive characterization tool for determining the amounts of the

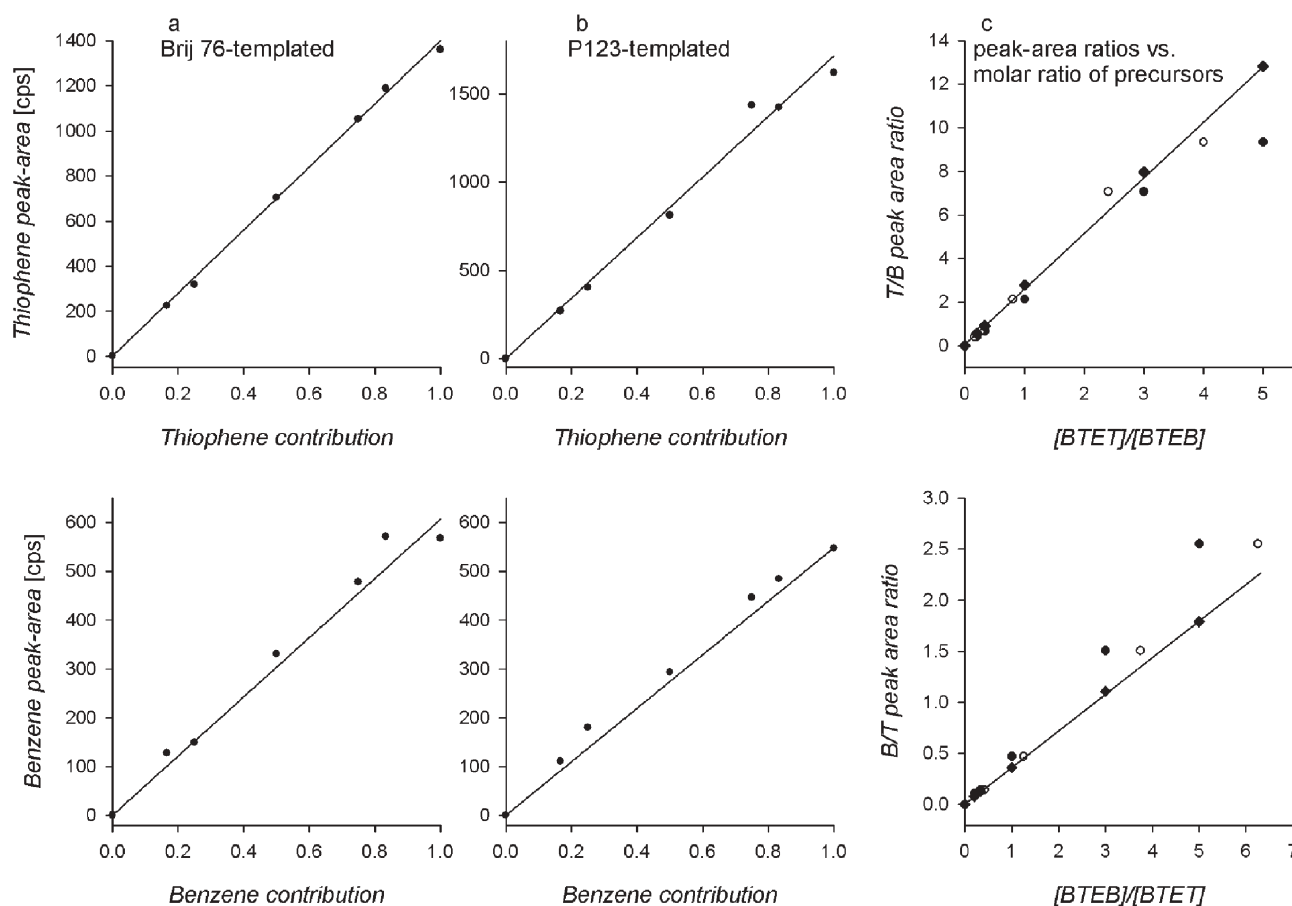


Fig. 12 (a–b): Relation between the area of the bridge-specific Raman peak in the PMO spectrum and the molar ratios of the corresponding precursors in the reaction mixtures for the thiophene-related (1415 cm⁻¹) peak (upper panels) and the benzene-related (1595 cm⁻¹) peak (lower panels). The results are shown for both series (a = Brij 76-templated; b = P123-templated) and linear fits to the data forced to cross the origins of the graphs are shown as black lines. (c) Dependence of the Raman peak area ratios on the corresponding molar ratios of the precursors. Full diamonds and full circles correspond to PMOs synthesized with P123 and Brij 76 as structure-directing agents, respectively. Open circles depict the data for the Brij 76-templated series with corrected molar ratios regarding the fact that during their synthesis about 20% of the thiophene units are lost.

different aromatic bridging molecules within the pore walls of any PMO samples of this type.

Conclusions

Highly-ordered bifunctional aromatic periodic mesoporous organosilicas containing different amounts of thiophene and benzene bridging groups have been synthesized for the first time by employing the triblock copolymer P123 as well as the oligomeric Brij 76 surfactant as structure-directing agents under acidic conditions. Two series of bifunctional aromatic PMO materials with pore sizes in the range of 4.8–5.4 and 3.3 nm, respectively, have been obtained whereas no decrease of mesostructural order and porosity properties by varying both contents of the organic bridging groups over a wide range in the obtained materials have been observed. We demonstrated that Raman spectroscopy after a one-off calibration based on ^{29}Si MAS NMR measurements can be used as a fast non-invasive tool for determining the relative compositions of the two types of bridging groups within the PMO pore walls. However, as it is possible to tune the surface properties of the bifunctional PMOs by varying the amount as well as the average distance of both organic functional groups these kinds of materials are very interesting to serve as adsorbents or hosts for the immobilization of thiophilic compounds like Au_{55} -clusters.

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