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Periodic Mesoporous Organosilicas with a Bifunctional Conjugated Organic Unit and Crystal-like Pore Walls

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The synthesis of a 2D hexagonal highly ordered periodic mesoporous 1,4-divinylbenzene-bridged organosilica (PMO) with crystal-like pore walls is reported. Both functionalities are realized by utilization of one single precursor (1,4-bis-((*E*)-2-(triethoxysilyl)vinyl)benzene (BTEVB) which was synthesized via Pd-catalyzed double Heck coupling of 1,4-dibromobenzene with vinyltriethoxysilane. Solid state ^{29}Si MAS NMR and FT-IR spectroscopy confirms that during the hydrothermal PMO synthesis and subsequent extraction procedure (i) no Si−C bond cleavage occurred and (ii) the organic bridge is preserved. The novel PMO material with a pore diameter of 2.6 nm, a molecular scale periodicity of 1.19 nm within the pore walls, and a specific surface area of $S_{\mathrm{BET}} = 730$ m^2/g offer various opportunities for further chemical modification within the mesopores as shown by bromination reactions.

Introduction

In 1999, a new type of inorganic−organic hybrid materials called periodic mesoporous organosilicas (PMOs) was discovered.[1−3] These materials contain organic groups such as aliphatic, aromatic, or heteroaromatic units covalently bonded and homogeneously distributed within the silica matrix. They are obtained by hydrolysis and condensation of bis-silylated organic precursors, $(\mathrm{R'O})_3\mathrm{Si{-}R{-}Si(OR')_3}$, in the presence of various kinds of surfactants, such as ionic tetraalkylammonium halides or nonionic triblock copolymers, depending on the desired pore size.[4,5] The synthesis of PMO materials with special morphologies such as thin films[6] or monodisperse spherical particles[7] was also reported in the literature. Very few PMOs with crystal-like pore walls have been synthesized so far by using ethylene-bridged precursors or aromatic precursors with phenylene or biphenylene units;[8−12] apart from the periodic arrangement of the mesopores, these materials exhibit a certain degree of structural order on the molecular length scale within the pore walls. Morell et al.[13] carried out in situ synchrotron SAXS studies on the formation process of biphenyl-bridged PMOs in basic media using OTAC as SDA. It could be shown that the formation of the mesophase and the periodicity within the walls occur simultaneously in a highly cooperative process during the hydrothermal treatment.

Very recently, Sayari and Wang[14] have reported on the synthesis of a new organosilica precursor (1,4-bis-((*E*)-2-(triethoxysilyl)vinyl)benzene [BTEVB]), which consists of an aromatic and an unsaturated component conjugated to each other, as well as the synthesis of the corresponding new PMO materials with 2D hexagonal mesostructures and crystal-like pore walls. They also studied the synthesis of this kind of hybrid material without utilizing structure-directing agents by the conventional sol−gel route. As expected, they obtained products without mesoscopic order, but interestingly the materials show periodicity on the molecular length scale.

Independent of the work by Sayari and Wang and nearly at the same time we have chosen the same precursor to prepare this kind of novel PMO material with a high degree of conjugation within the organic unit, extending over both aromatic and aliphatic components, however, with a slightly different aim. Our main objective was to synthesize a PMO material, which offers new opportunities for various kinds of modification by subsequent functionalization. The double bonds of the organic unit are suitable for addition reactions. This has already been shown for PMO materials by Asefa et al. They successfully carried out bromination experiments on ethylene bridging groups[15] as well as hydroboration reactions on terminal vinyl groups and subsequent quantita-

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tive transformations into hydroxyl groups.[16] Another promising possibility could be the addition of chelating agents, for instance, those with dicarboxyl or diamino functionalities, which in turn can build complex compounds with transition metal ions. This would be a way to design new adsorbent materials based on PMOs, which could be used in order to remove toxic heavy metals within applications regarding wastewater treatment or as a substrate for selective immobilization of biomolecules (peptides and enzymes). This approach is, in our opinion, more straightforward and elegant than the use of precursors, which already contain such special coordination sites, since such precursors usually lack the necessary structural prerequisites to give PMO materials with crystal-like pore walls. Note hitherto only rigid and planar, e.g., ethylene-bridged or aromatic, precursors (this means those with a sp^2 hybridization of the carbon atoms) have lead to PMOs with molecular order within the pore walls. Analogous considerations apply to other subsequent functionalizations, such as introducing acid groups for use in catalytical applications. The precursor chosen has, in contrast to previous ones, the distinction of being aromatic and rigid, i.e., giving crystal-like pore walls, and simultaneously has the potential to overcome the narrow limitations of “chemically dead” organic bridges. Furthermore, even after successful application of the mentioned addition reactions, not only the structural integrity but also the rigid/aromatic character of the bridging groups remain, which is advantageous in terms of thermal stability of these kinds of materials.

With postsynthetic chemical modification of the double bonds the physical properties will be modified as well. In PMO materials with crystalline pore walls this could give rise to appealing features. It might be conceivable that by introducing polar groups in a cis addition reaction to the double bonds a nonzero net dipole moment is generated, which could be interesting in the field of developing nonlinear optical (NLO) devices.

Finally, the bifunctional conjugated divinylbenzene organic bridging unit may be regarded as a promising starting point for further, subsequent extension of the conjugation, beginning with the pure aromatic benzene-bridged organic unit, reaching now the conjugation level of divinylbenzene, The following candidate would be consequently the bis(1,3-butadienyl)benzene bridge. It is likely that the main UV absorption band will be shifted to lower wavelengths, perhaps reaching the visible region, resulting in a *colored* PMO material. For now we report here in the first instance on the synthesis of a 2D hexagonal highly ordered periodic mesoporous 1,4-divinylbenzene-bridged PMO material.

Experimental Section

Synthesis of the Precursor. All synthesis steps were carried out in vacuo dried glass vessels using purified and dry solvents under an argon atmosphere. The chemicals 1,4-dibromobenzene, vinyltriethoxysilane, and tetrakis(triphenylphosphine)palladium were purchased from Sigma-Aldrich, Fluka, and ABCR and were used without further purification.

The organosilane precursor 1,4-bis-((*E*)-2-(triethoxysilyl)vinyl)-benzene (BTEVB) was synthesized via a palladium-catalyzed double Heck coupling of 1,4-dibromobenzene with vinyltriethoxysilane. In a typical synthesis 30.12 g (0.128 mol) of 1,4-dibromobenzene was dissolved in 220 mL of dimethylformamide in a 500 mL three-necked-flask. To this solution 55 mL (0.261 mol) of vinyltriethoxysilane, 70 mL (0.512 mol) of triethylamine, and 0.493 g (4.27×10^{-4} mol) of tetrakis(triphenylphosphine)-palladium were added. After the reaction mixture was stirred for 4 d at 110 °C under an argon atmosphere, the resulting solution was cooled to 0 °C to complete the precipitation of the formed salt ($HNEt_3Br$). After removal of the salt by filtration, the solvent was removed under reduced pressure. The obtained raw product was purified by kugelrohr distillation. For further purification of the precursor this distillation step was repeated twice: 41.7 g (0.092 mol, yield: 71%) of the organosilane precursor was obtained as a slightly yellow transparent liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27 (t, $J = 6.89$ Hz, 18 H), 3.89 (q, $J = 6.89$ Hz, 12 H), 6.19 (d, $J = 19.2$ Hz, 2 H), 7.20 (d, $J = 19.2$ Hz, 2 H), 7.46 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 58.5, 118.2, 126.9, 137.9, 148.3.

Synthesis of the Periodic Mesoporous Organosilica Material. In a typical synthesis for these kinds of hybrid materials 0.86 g (2.3×10^{-3} mol) of the structure-directing agent OTAC was dissolved under vigorous stirring in a solution of 0.8 g (0.02 mol) of NaOH in 20 mL of distilled water. Afterwards, 0.75 mL (1.7×10^{-3} mol) of BTEVB was added in order to adjust the molar ratio of the reaction mixture to 1:1.4:11.9:660 BTEVB:OTAC:NaOH:H_2O. The suspension was stirred at room temperature for 24 h followed by a hydrothermal treatment in a closed PTFE autoclave at 95 °C for 12 h. After filtration, the as-synthesized composite material was obtained as a white powder, which was washed with 200 mL of distilled water three times. The surfactant was removed by Soxhlet extraction with ethanol/HCl (concentrated) (100:3; v:v) for 8 h.

Characterization. Powder X-ray diffraction patterns were recorded at room temperature with a Bruker AXS D8 Advance diffractometer using filtered Cu Kα radiation (40 kV, 40 mA; counting time: 2 s; steps: 0.01° (2θ)).

Transmission electron micrographs were obtained with a Philips CM30-ST microscope operating at 300 kV.

N_2 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.

^{29}Si MAS NMR spectra were recorded without cross-polarization to obtain data of the relative number of different silicon sites in the material. The spectra were acquired using a Bruker MSL-400 spectrometer. The samples were spun at 3.5 kHz. Further experimental parameters were as follows: single-pulse experiment, $\pi/2$ pulse width of 6 μs, recycle delay of 300 s, and 1500 scans.

Infrared spectra were acquired using a Bruker IFS 25 FT-IR spectrometer. The precursor sample was measured as a film and the PMO material sample with the KBr method. The spectral resolution was 2 cm^{-1}.

Results and Discussion

X-ray Powder Diffraction Analysis and Transmission Electron Microscopy. Figure 1 shows the XRD pattern of an extracted PMO sample. The low-angle region exhibits one sharp, intense reflection at $2\theta = 1.87°$ as well as two weakly resolved reflections in the region between 3.2° and 3.7°, indicating a 2D hexagonal mesostructure with a d_{10} spacing of 4.72 nm. In addition, four equidistant peaks at

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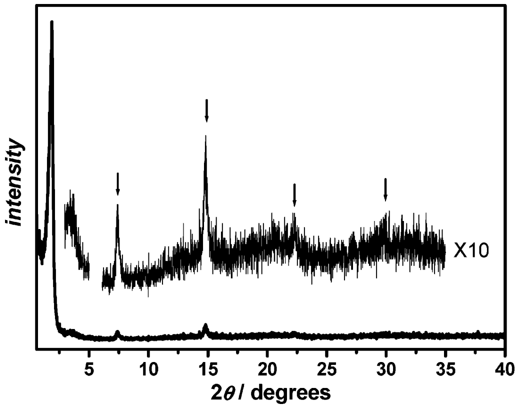

Figure 1. Powder X-ray diffractogram of a sample mesoporous 1,4-divinylbenzene-bridged PMO material revealing a 2D hexagonal mesostructure as well as crystal-like pore walls, indicated by the reflections marked by arrows.

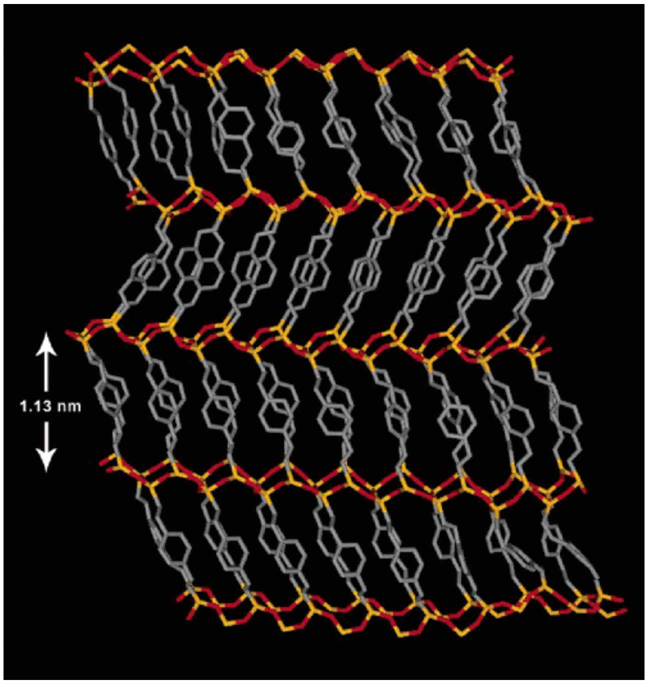

Figure 2. Model of a section of the pore wall of the 1,4-divinylbenzene-bridged PMO material (result of COMPASS force field calculations); visualization of the arrangement of the organic functionalities within the pore walls; calculated periodic distance 1.13 nm.

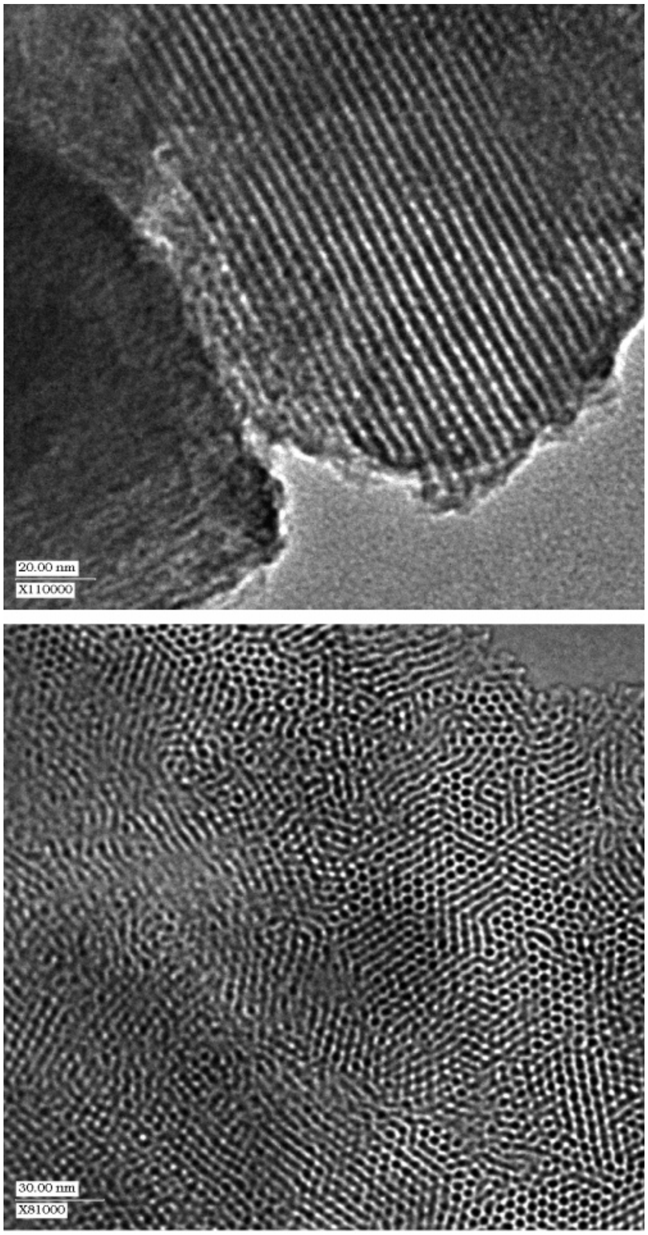

Figure 3. Representative TEM images of a sample mesoporous 1,4-divinylbenzene-bridged PMO material (top: view perpendicular to the channel axis; bottom: view along channel axis) showing locally well-ordered 2D hexagonal mesostructure.

$2\theta = 7.42°$ ($d = 1.19$ nm), 14.78° (0.60 nm), 22.17° (0.40 nm), and 29.82° (0.30 nm) are clearly visible at wider angles; these reflections are attributable to a crystal-like arrangement of the organic units within the pore walls with a periodicity of 1.19 nm. This value is in reasonable agreement with molecular modeling studies (see Figure 2), which yield a periodic distance of 1.13 nm. The model, which represents a section of the pore wall of one pore, was constructed as a bilayer and the respective constituents were at first connected manually. Terminal silicon atoms were saturated with hydroxyl groups. Finally, a geometry optimization (energy minimization) procedure with the COMPASS[17] force field was conducted. Apart from powder XRD, in situ small-angle X-ray scattering (SAXS) studies were also carried out, clearly demonstrating that the ordering process on both the mesoscopic and molecular level occur simultaneously.[18] In accordance with the XRD results, transmission electron microscopy (Figure 3) shows a locally well-ordered 2D hexagonal mesostructure.

N_2 Physisorption. Nitrogen physisorption (Figure 4) reveals a type-IV isotherm, typical of uniform, cylindrical mesopores, with a capillary condensation step around $p/p_0 = 0.3$; the mean pore diameter and total pore volume, as determined from the desorption branch by the BJH method, are 2.6 nm and 0.6×10^{-6} m^3/g, respectively. The specific BET surface area is 730 m^2/g. The mean pore diameter is slightly smaller compared with the samples of the corresponding PMO material synthesized by Sayari and Wang (3.0 nm)[14] and the pore diameter distribution is somewhat

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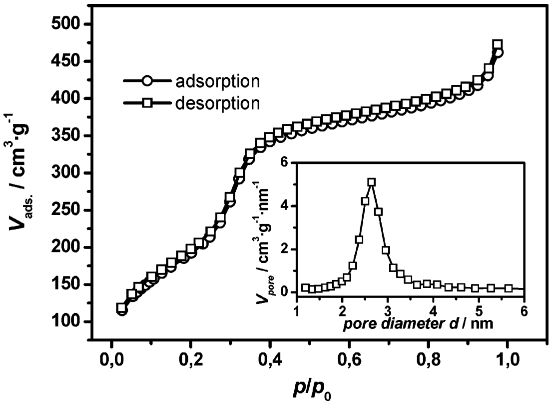

Figure 4. Nitrogen physisorption isotherms (○, adsorption; □, desorption) and BJH pore diameter distribution (inset, from the desorption branch) of 1,4-divinylbenzene-bridged PMO material, $S_{BET} = 730$ m^2/g (measured on a Quantachrome Autosorb 6 at 77 K).

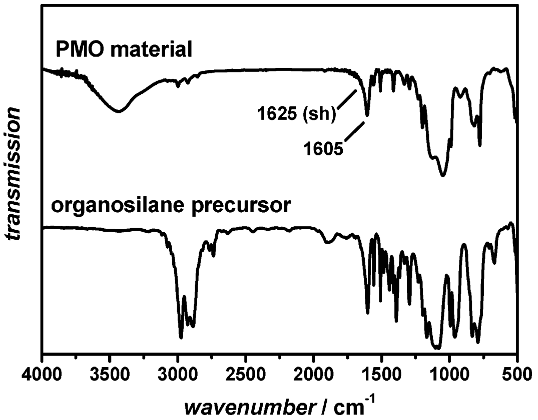

Figure 5. Infrared spectra of the BTEVB precursor and the corresponding 1,4-divinylbenzene-bridged PMO material. The band at 1625 cm^{-1} (sh) clearly proves the integrity of the C=C double bond after the synthesis (measured on Bruker IFS 25).

sharper and strictly monomodal; the specific surface areas are comparable. Based on the determined pore diameter and the calculated lattice parameter from XRD measurements, the pore wall thickness is about 2.85 nm.

IR Spectroscopy. IR spectroscopy (Figure 5) confirms that the organic bridge is preserved during the hydrothermal PMO synthesis and subsequent extraction procedure. To analyze the state of the C=C double bond within the extracted PMO material, its IR spectrum was compared to that of the BTEVB precursor. The bands are assigned as follows: ν(Si−OH) (including those which are involved in H-bonded bridged species) at 3650−3200 cm^{-1}, $\nu(C{=}C)_{\text{vinylic}}$ at 1625 cm^{-1} (sh), $\nu(C{=}C)_{\text{aromatic}}$ at 1605 cm^{-1}, and ν(Si−O) at 1078 cm^{-1}. The appearance of the shoulder at about $\nu = 1625$ wavenumbers indicates not only the conjugation of the olefinic and the aromatic parts but also the integrity of the organic bridge within the silica matrix. To ensure the correct assignment of the bands, DFT frequency calculations of the respective precursor were performed with the help of the *Gaussian 03* software package[19] at the B3LYP/6-31G(d,p) level of theory. The results ($\nu(C{=}C)_{\text{vinylic}} = 1624$ cm^{-1}, $\nu(C{=}C)_{\text{aromatic}} = 1604$ cm^{-1}) are in excellent agreement with the experimental data.

Accessibility and Reactivity of the Double Bonds. To demonstrate the accessibility of the vinylic double bonds in the PMO material bromination experiments were conducted. For this purpose, a certain amount of the solid material was added to an aqueous bromine solution. This solution was stirred at room temperature for 24 h in a sealed flask, which resulted in a complete decolorization, thereby confirming the accessibility of the vinylic double bonds. Further investigations of the resulted material are underway and additional experiments with various other addition reagents (as outlined in the Introduction) will be carried out soon.

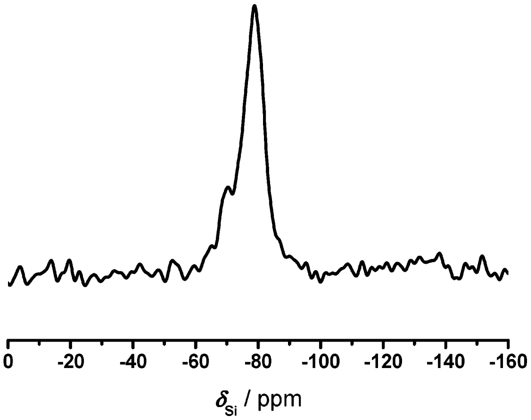

Figure 6. ^{29}Si MAS NMR spectrum of 1,4-divinylbenzene-bridged PMO material showing a T^2 signal at −69.69 ppm and T^3 signal at −78.78 ppm. No Q signal due to SiO$_4$ species are detected, indicating that no Si−C bond cleavage has occurred during the synthesis or extraction procedure.

^{29}Si MAS NMR. The ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum (Figure 6) shows two signals at −69.69 and −78.78 ppm. The first peak is attributed to T^2 [RSi(OSi)$_2$(OH)], a partially condensed silica species, and the other to T^3 [RSi(OSi)$_3$], a completely condensed silica species. The integration of the signals lead to a T^2:T^3 signal ratio of 1:5. No Q^n signals corresponding to silicon atoms connected entirely to OSi and/or OH units were detected, which indicates that all silicon atoms are covalently bonded within the PMO framework and no Si−C bond cleavage has occurred during the hydrothermal treatment or the extraction procedure.

Conclusions

In summary, we have introduced the synthesis of a new organosilica precursor and its utilization for the preparation of 2D hexagonally ordered PMO materials. The products exhibit crystal-like periodicity within the pore walls. The

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specific nature of the organic unit, i.e., the presence of two organic functionalities, vinyl and aromatic, offers new opportunities for further chemical modification within the mesopores; both functional groups are realized by one single precursor. So far, existing PMO materials contained organic groups which were considerably less reactive, such as purely aromatic units. Thus, functionalization was restricted and required harsh reaction conditions. It is reasonable to assume that our products will be suitable for electrophilic addition at the vinylic C═C double bond, for example, hydroboration or epoxidation reactions. Such types of modification will offer new possibilities to tailor more complex and specific chemical properties within the pore systems. The mild reaction conditions will ensure that the high degree of structural order will not be affected by these functionalizations.

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