Supporting information.

Thermally induced transition between open and closed spherical pores in ordered mesoporous silicas

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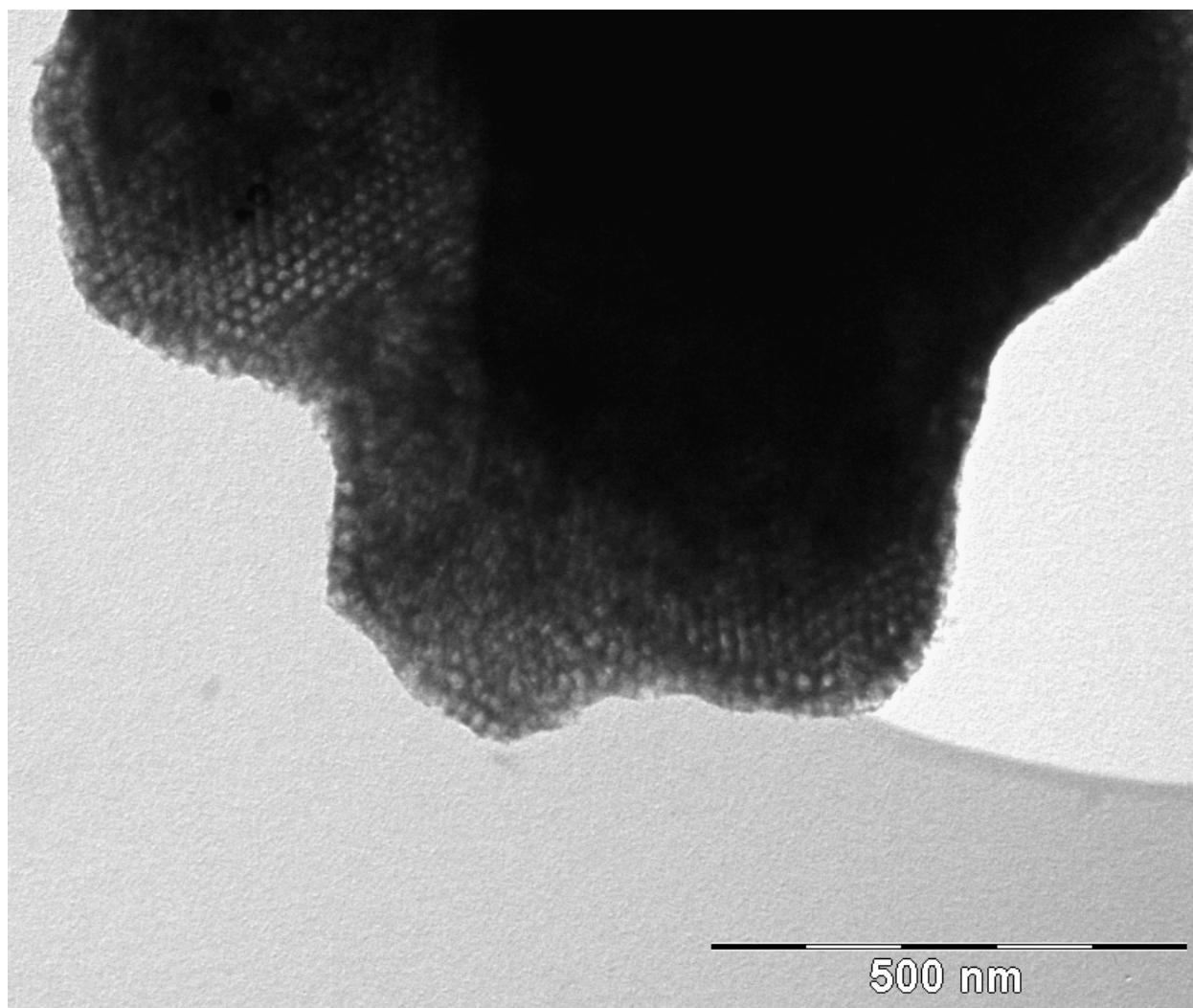
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Supporting Table S1. Structural properties of ordered mesoporous silicas and organosilicas.[a]
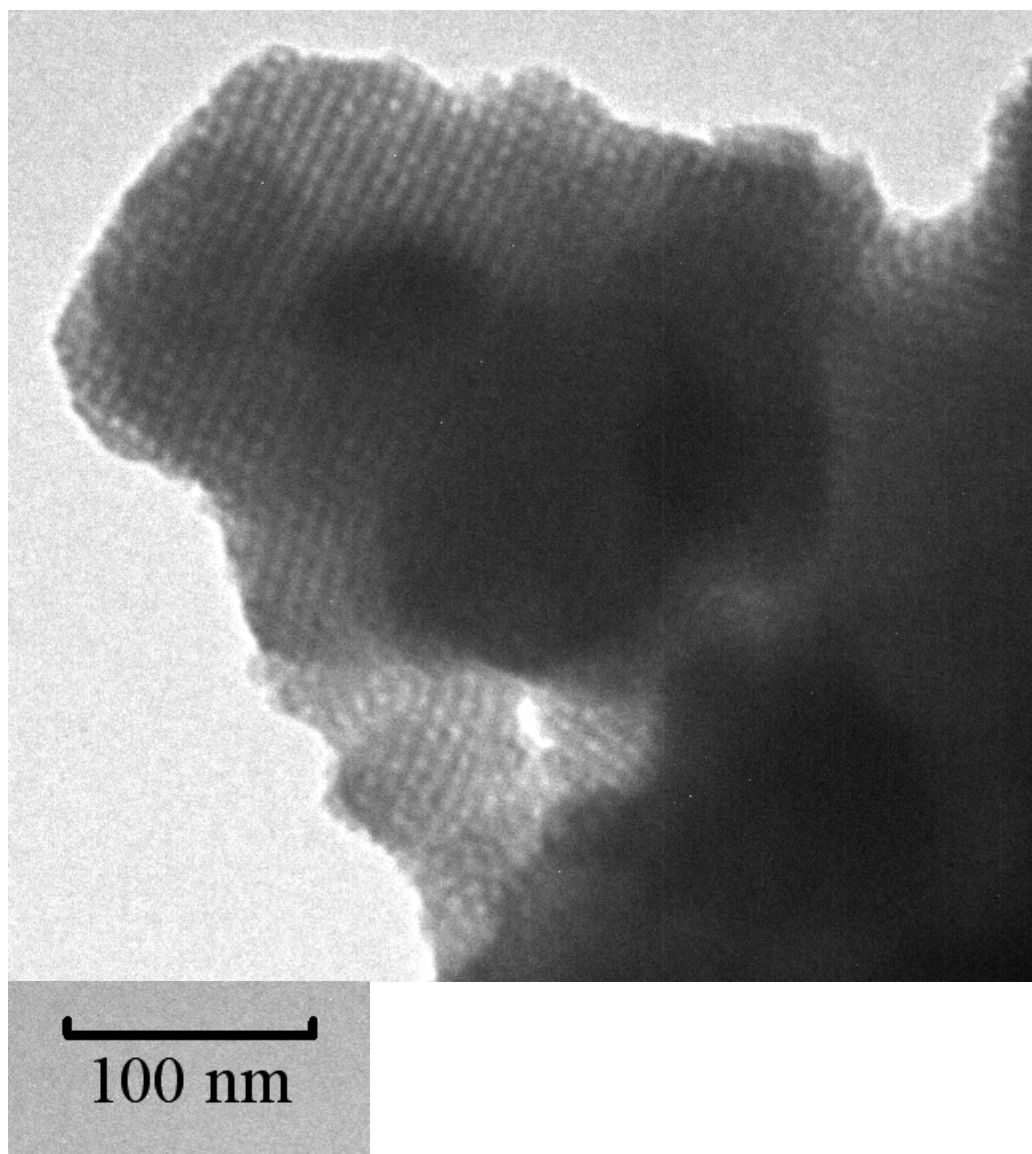
Sample	T (°C)	a (nm)	a/a_U	S_{BET} ($m^2\,g^{-1}$)	V_t ($cm^3\,g^{-1}$)	w (nm)
LP-FDU-12	450	32.7	0.86	400	0.39	15.0
LP-FDU-12	550	31.3	0.82	~30	0.04	14.7
LP-FDU-12	640	29.7	0.78	~0	~0.00	b
SBA-16	550	15.8	0.90	870	0.66	7.7
SBA-16	700	15.2	0.87	730	0.53	7.4
SBA-16	800	14.3	0.82	470	0.38	6.8
SBA-16	900	13.3	0.76	80	0.06	~6.0
SBA-16	950	12.8	0.73	~10	~0.00	b
Methylene PMO	300	41.1	c	930	0.49	13.0
Methylene PMO	500	c	c	430	0.25	11.5
Methylene PMO	600	32.7	0.80[d]	~0	~0.00	b

[a] T, calcination temperature; a, unit-cell parameter for calcined material calculated from (111) interplanar spacing for fcc structure (LP-FDU-12 and methylene PMO) or (110) interplanar spacing for bcc structure (SBA-16); a/a_U, degree of shrinkage upon calcination calculated as the the unit-cell parameter of calcined material, a, divided by the unit-cell parameter, a_u, of the uncalcined material; S_{BET}, BET specific surface area; V_t, total pore volume; w, pore diameter estimated using KJS method for cylindrical pores; this method was shown[16] to systematically underestimate the pore diameter by ~2 nm. [b] Not available because of very low adsorption capacity. [c] Not determined. [d] The unit-cell parameter at 300 °C was taken as a reference point for the evaluation of the degree of shrinkage at 600 °C.
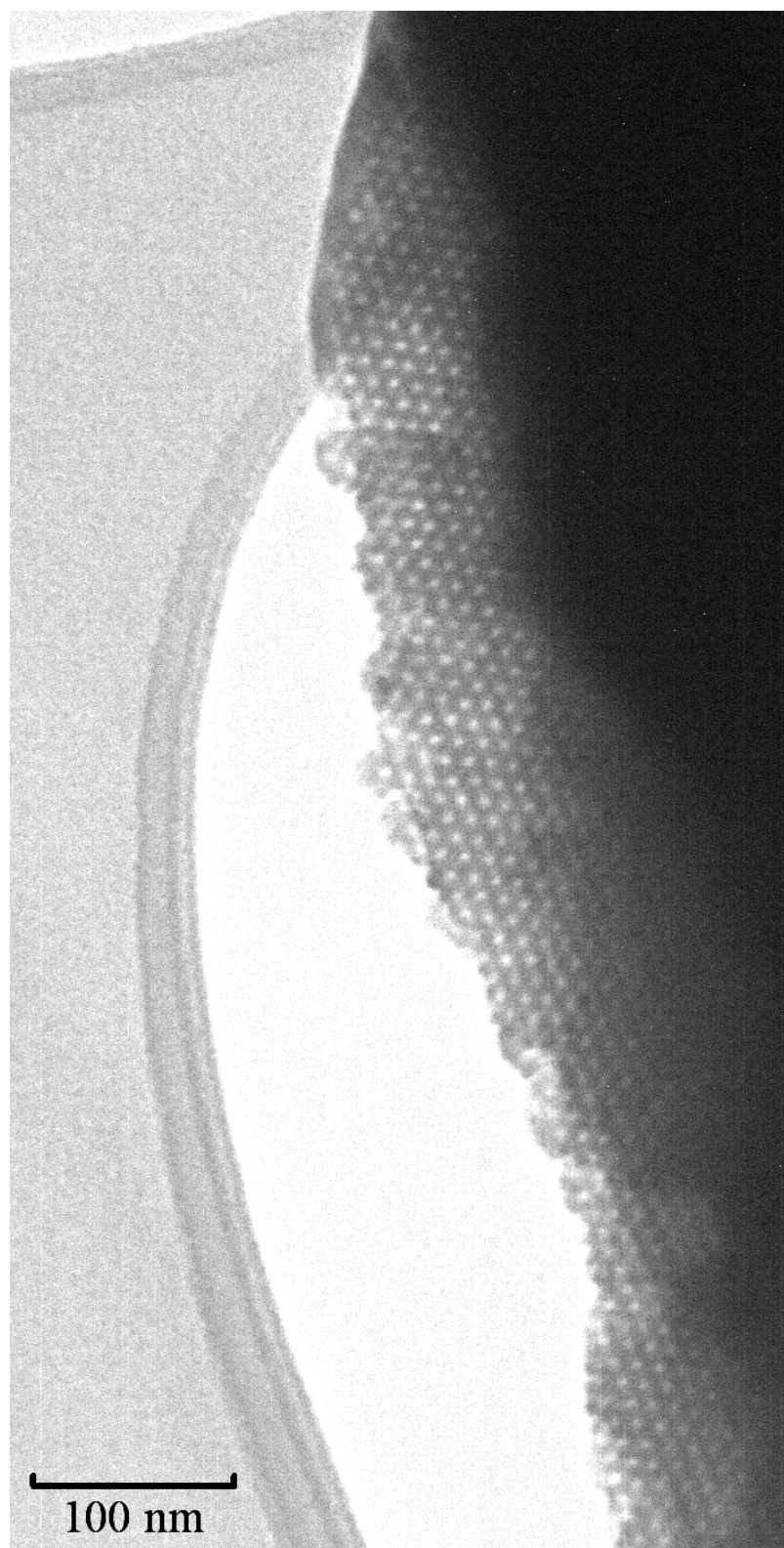
Calculation of the pore entrance length. The pore entrance length was estimated on the basis of the distance between the pore centers (evaluated on the basis of the unit-cell parameter and the structure type: a/sqrt(2) =23.1 nm for LP-FDU-12 with fcc structure and a*sqrt(3)/2 = 13.6 nm for SBA-16 with bcc structure) and the pore diameter. In the case of LP-FDU-12, we evaluated the pore diameter using a relation between the unit-cell parameter, mesopore volume, micropore volume and pore diameter, which was reported by Ravikovitch and Neimark, Langmuir 2002, 18, 1550 for fcc structure. The resulting pore diameter was 17.1 nm, which was about 2 nm larger than that assessed using the KJS method. 23.1 nm – 17.1 nm gives 6.0 nm as the estimate of the pore entrance length in LP-FDU-12. For the body-centered cubic structure of SBA-16, the relation between the pore diameter and other structural parameters was also established (see Matos, Kruk et al., Langmuir 2002, 18, 884 and the above work of Neimark and Ravikovitch), but the required estimate of the micropore volume is not sufficiently reliable for typical SBA-16 sample (see Ref. 20). Therefore, we used the KJS pore diameter (7.7 nm) incremented by 2 nm, as this is the extent of pore size underestimation when the KJS method is used for spherical pores (see Ref. 16). Consequently, the pore entrance length for SBA-16 was estimated as: 13.6 nm – (7.7 + 2) nm = 3.9 nm = ~4 nm.
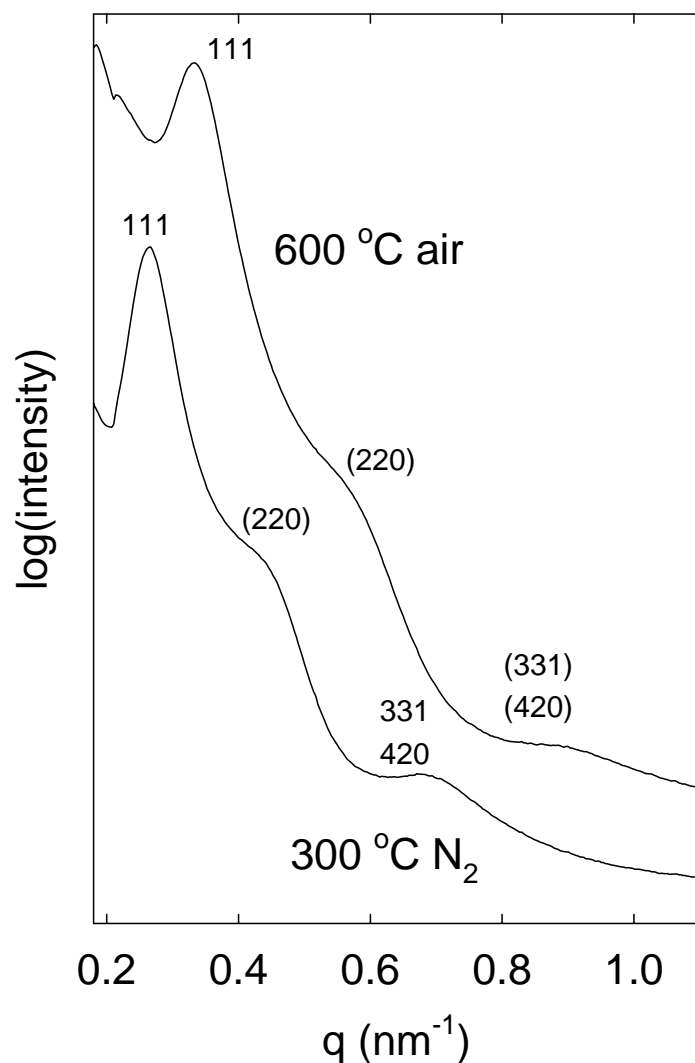
Supporting Figure S1. TEM image of LP-FDU-12 calcined at 640 °C. The image was acquired on TEM operated at 80 kV.
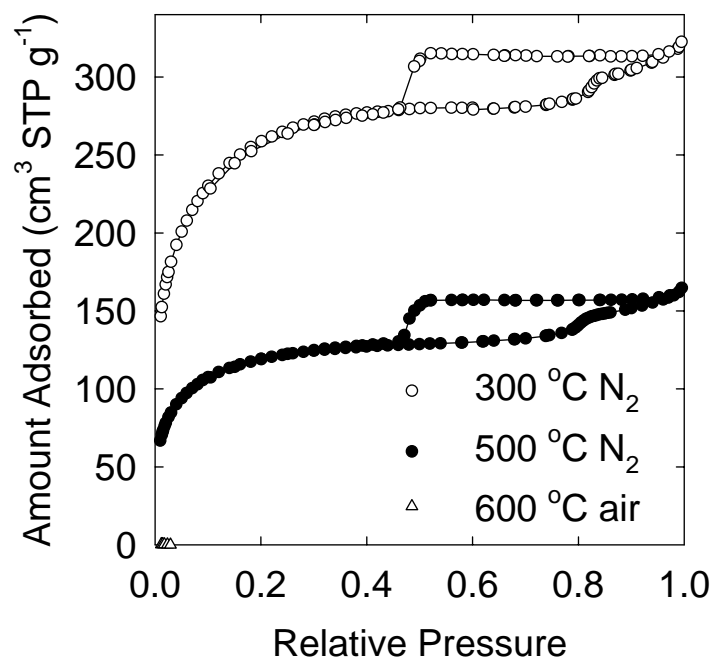
Supporting Figure S2. TEM image of SBA-16 silica calcined at 950 °C. The image can be assigned as [100] projection of body-centered cubic structure. The image was acquired on Philips CM 100 TEM operated at 80 kV.

Supporting Figure S3. TEM image of SBA-16 silica calcined at 950 °C. The image can be assigned as [111] projection of body-centered cubic structure. The image was acquired on Philips CM 100 TEM operated at 80 kV.

Supporting Figure S4. SAXS patterns for large-pore methylene periodic mesoporous organosilica (PMO) synthesized using bis(triethoxysilyl)methane, $(C_2H_5O)_3Si-CH_2-Si(OC_2H_5)_3$ as a precursor. The sample was calcined at 300 °C under nitrogen and under these conditions the $Si-CH_2-Si$ moiety of the precursor is expected to be fully preserved in the structure of the material (see Asefa et al., Angew. Chem. Int. Ed. 2000, 39, 1808). The sample was also calcined at 600 °C under air and under these conditions the $Si-CH_2-Si$ moiety is expected to be converted to siloxanes (Si-O-Si linkages) or to $Si-CH_3$ (see Asefa et al., Angew. Chem. Int. Ed. 2000, 39, 1808). The SAXS patterns resemble the SAXS patterns of some of ethane PMOs reported by Zhou et al., Chem. Mater. 2007, 19, 1870 and thus likely to correspond to the face-centered structure. The peaks and shoulders were indexed on the basis of this assumption. The interplanar spacing corresponding to the first SAXS peak was 23.7 nm and 18.9 nm, for the sample calcined at 300 and 600 °C, respectively, and thus the degree of shrinkage was ~20%.

Supporting Figure S5. Nitrogen adsorption measurements at -196 °C for large-pore methylene periodic mesoporous organosilica (PMO) synthesized using bis(triethoxysilyl)methane, $(C_2H_5O)_3Si-CH_2-Si(OC_2H_5)_3$ as a precursor. The sample was calcined at 300 °C under nitrogen and under these conditions the $Si-CH_2-Si$ moiety of the precursor is expected to be fully preserved in the structure of the material (see Asefa et al., Angew. Chem. Int. Ed. 2000, 39, 1808). The sample was calcined at 500 °C under nitrogen and under these conditions the $Si-CH_2-$ Si moiety is expected to be converted to $Si-CH_3$ (see Asefa et al., Angew. Chem. Int. Ed. 2000, 39, 1808; Asefa, Kruk et al., J. Am. Chem. Soc. 2003, 125, 11662). The sample was also calcined at 600 °C under air and under these conditions the $Si-CH_2-Si$ moiety is expected to be converted to siloxanes (Si-O-Si linkages) or to $Si-CH_3$ (see Asefa et al., Angew. Chem. Int. Ed. 2000, 39, 1808).

PMO with methylene groups in the framework structure was selected for our study because of the facile thermal stability of the organic groups, giving the hope of the pore closure at temperatures below the onset of thermal degradation of the organic groups. Since the synthesis of copolymer-templated methylene PMO with cage-like pore structure has not been reported in the literature, we developed a synthesis for this material. The synthesis of was carried out using bis(triethoxysilyl)methane, $(C_2H_5O)_3Si-CH_2-Si(OC_2H_5)_3$, (BTEM) as a precursor under synthesis conditions generally similar to those reported by Zhou et al, Chem. Mater. 2007, 19, 1870 for PMOs with ethylene (-CH_2CH_2-) groups in the framework, but with different organosilica-precursor/copolymer ratio. Briefly, 0.50 g of Pluronic F127 block copolymer ($EO_{106}PO_{70}EO_{106}$) was dissolved in 45 mL of 2.0 M HCl in a polypropylene bottle under mechanical stirring at 15 °C in a refrigerated water bath. Subsequently, 0.70 mL trimethylbenzene and 2.5 g KCl were added. After two hours, 2.04 g of BTEM was added while mechanical stirring was continued and the temperature was maintained at 15 °C. After a day, the PP bottle was capped and the synthesis mixture was transferred to an oven and kept therein at 100 °C for one day. Then, the organosilica/copolymer composite was filtered out, dried and calcined in a tube furnace under

nitrogen or air under selected temperatures and/or extracted in Sohxlet apparatus (with ethanol) to remove the block copolymer template.

As can be seen in Supporting Figure S4, the SAXS pattern for PMO calcined at 300 °C under nitrogen (the conditions suitable for the preservation of the methylene linkages in the structure) featured a strong peak at q value of 0.265 nm^{-1} (corresponding to d-spacing of 23.7 nm), a shoulder, and another peak at q value of 0.67 nm^{-1}. The comparison with the SAXS data reported by Zhou et al, Chem. Mater. 2007, 19, 1870 suggests that these peaks are reflections of face-centered cubic structure. The peaks on the SAXS patterns shifted to higher q values as the calcination temperature was increased to 600 °C and the atmosphere was changed to air (which may result in a substantial degree of loss of organic groups). The interplanar spacing corresponding to the position of the main SAXS peak decreased by 20% as the calcination temperature was increased. As seen in Supporting Figure 5S, the material calcined at 300 °C adsorbed an appreciable amount of nitrogen and exhibited a sharp capillary condensation step at a relative pressure of 0.83, indicating the presence of accessible large mesopores of uniform size. The calcination at 500 °C led to a marked decrease in the uptake of nitrogen, while the capillary condensation step shifted to the relative pressure of 0.80, signifying the decrease in the pore diameter. The calcination at 600 °C resulted in a material that exhibited very low uptake on nitrogen, showing the lack of porosity accessible to nitrogen molecules at -196 °C. At the same time, the material still exhibited one strong peak and two shoulders on the SAXS pattern, indicating the preservation of the ordered nanoporous structure. Note that thee structural parameters for the considered samples are listed in Supporting Table S1. Similar results were obtained for another methylene PMO synthesized under different conditions and for ethylene PMO. Clearly, PMOs are susceptible to the pore closure. The ability to close the pores of PMOs below the onset of the decomposition of the organic groups has not been demonstrated yet, but is subject of our continuing studies.