Supporting Information

“Versatile Approach to Synthesis of 2-D Hexagonal Ultra-Large-Pore Periodic Mesoporous Organosilicas”

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Supporting Table S1. The interplanar spacing and other physicochemical properties of PMOs.

Bridging group, initial temperature, amount of precursor	d_{100} (nm)	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mic} (cm^3/g)	w_{BJH} (nm)
Methylene, 15°C, x=0.2	17.8	1197	1.28	0.26	12.0
Methylene, 15°C, x=0.3, H 100°C [a]	20.8	1230	1.61	0.28	22.2
Methylene, 15°C, x=0.3, H 130°C	22.7	1007	1.75	0.11	25.1
Methylene, 15°C, x=0.3, H 150°C	21.8	837	1.66	(-0.01)[f]	23.6
Methylene, 15°C, x=0.4	17.2	1204	1.10	0.35	12.6
Ethylene, 15°C, x=0.4, BTME	16.1	429	0.65	0.08	13.7
Ethylene, 15°C, x=0.4, BTEE	15.8	542	0.67	0.10	11.6
Ethylene, 12°C, x=0.4, BTEE	18.2	258	0.40	0.05	15.8
Ethylene, 11°C, x=0.4, BTEE	20.8	82	0.15	0.02	18.8
Ethylene, 15°C, x=0.7, BTME	16.8	534	0.56	0.16	13.8
Ethylene, 15°C, x=1.0, BTME [b]	16.7	690	0.51	0.25	13.4
Ethylene, 15°C, x=1.5, BTME	18.0	581	0.41	0.22	14.6
Ethenylene, 15°C, x=0.7	14.0	139	0.27	0.00	11.1
Phenylene, 17°C [c,d]	15.9	642	0.56	0.22	12.7
Phenylene, 16°C [b,d]	18.2	514	0.49	0.16	14.8
Phenylene, 15.5°C [c,d]	19.6	620	0.50	0.23	16.4
Phenylene, 15°C [b,d]	22.7[e]	553	0.52	0.19	21.1

Notation: d_{100}, (100) interplanar spacing for either calcined or extracted sample. $S_{BET,}$ BET specific surface area; $w_{BJH,}$ BJH pore diameter; $V_{t,}$ total pore volume, $V_{mic,}$ micropore volume, $V_{mes,}$ mesopore volume.

[a] Repeated synthesis. Data for other sample listed in Table 1.

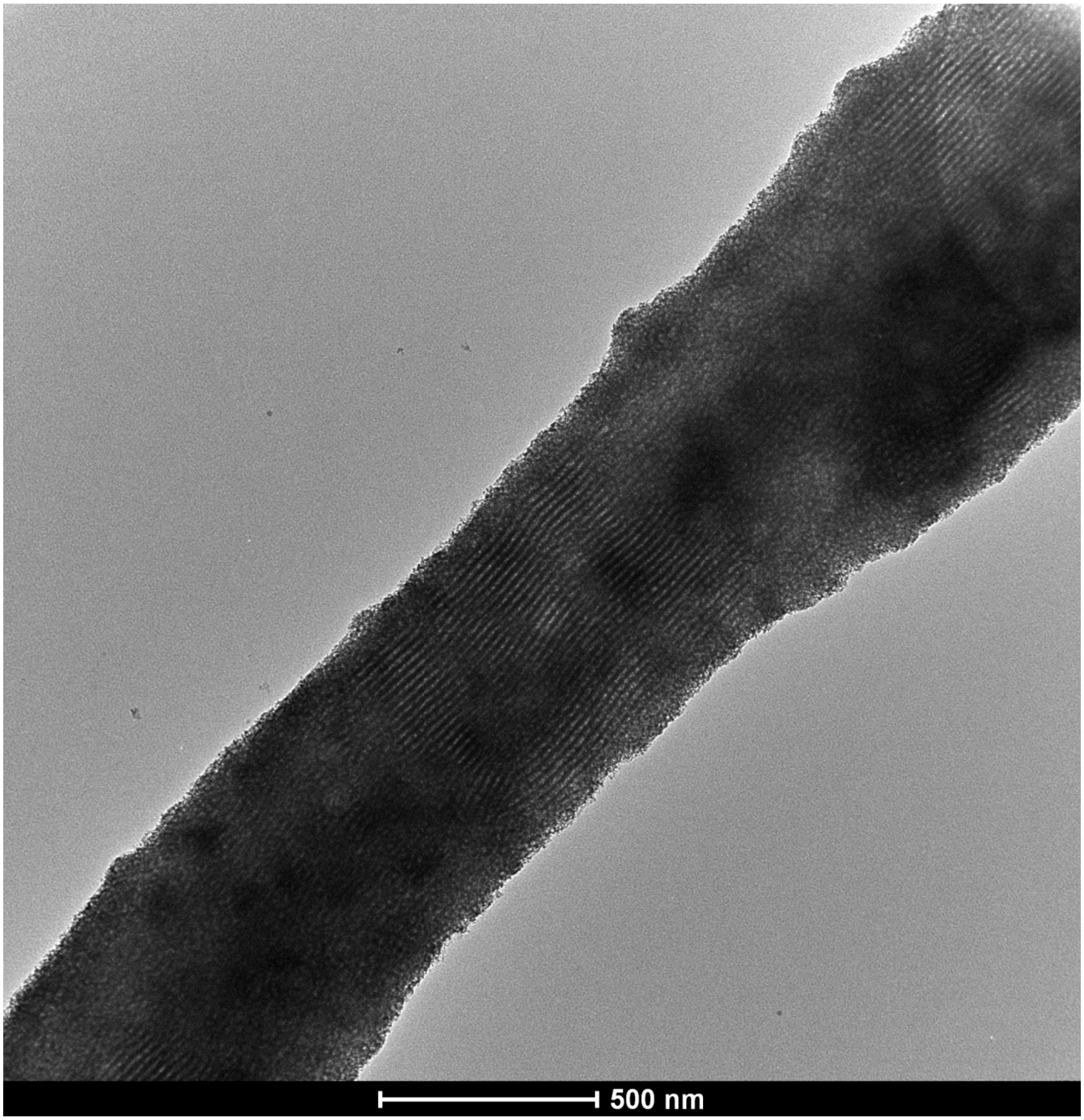
[b] Sample was calcined at 300 °C under nitrogen.

[c] Sample was extracted with ethanol and calcined at 250 °C under air.

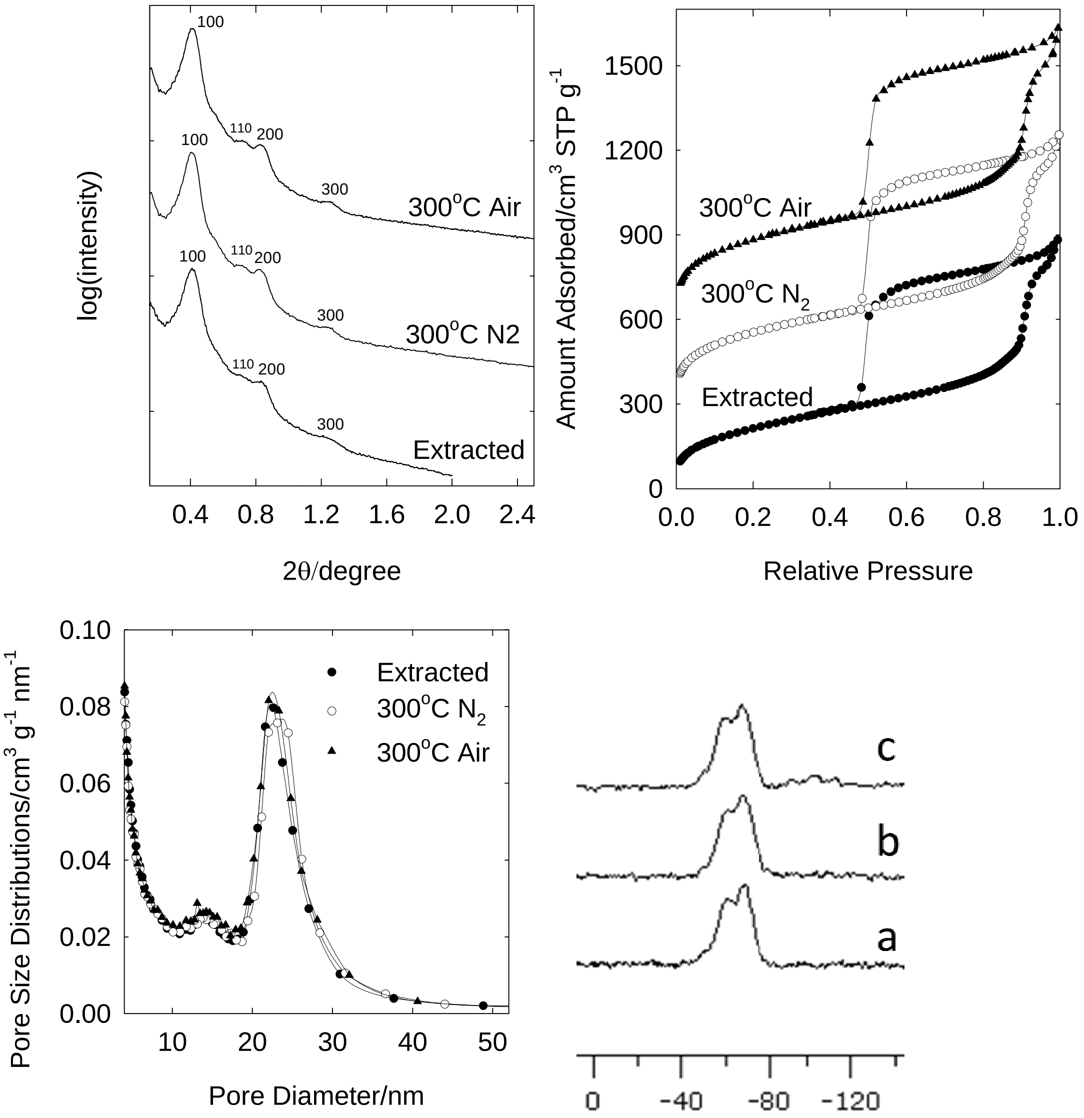
[d] Synthesized using 0.6 mL TIPB per 0.6 g of P123.

[e] Calculated assuming that the first peak is (100) reflection of 2-D hexagonal structure, which is consistent with TEM observation.

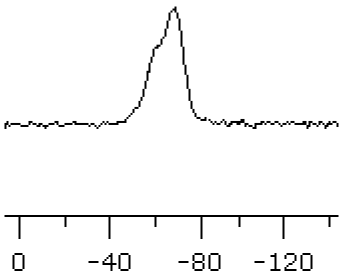
[f] Indicates that the micropore volume is negligible.



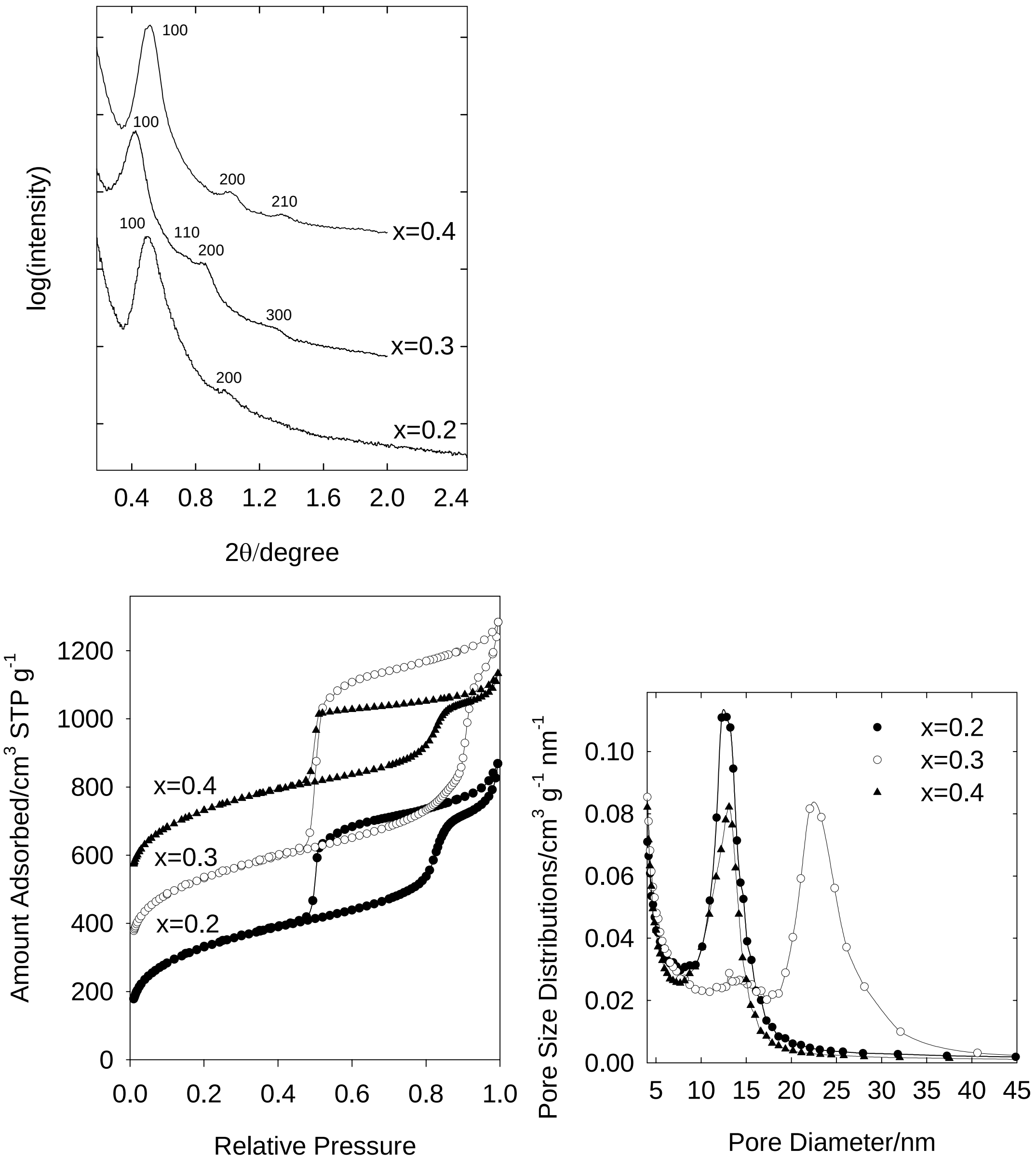
Supporting Figure S1. TEM image of calcined methylene-bridged PMO synthesized using a hydrothermal treatment at 150 °C for two days.



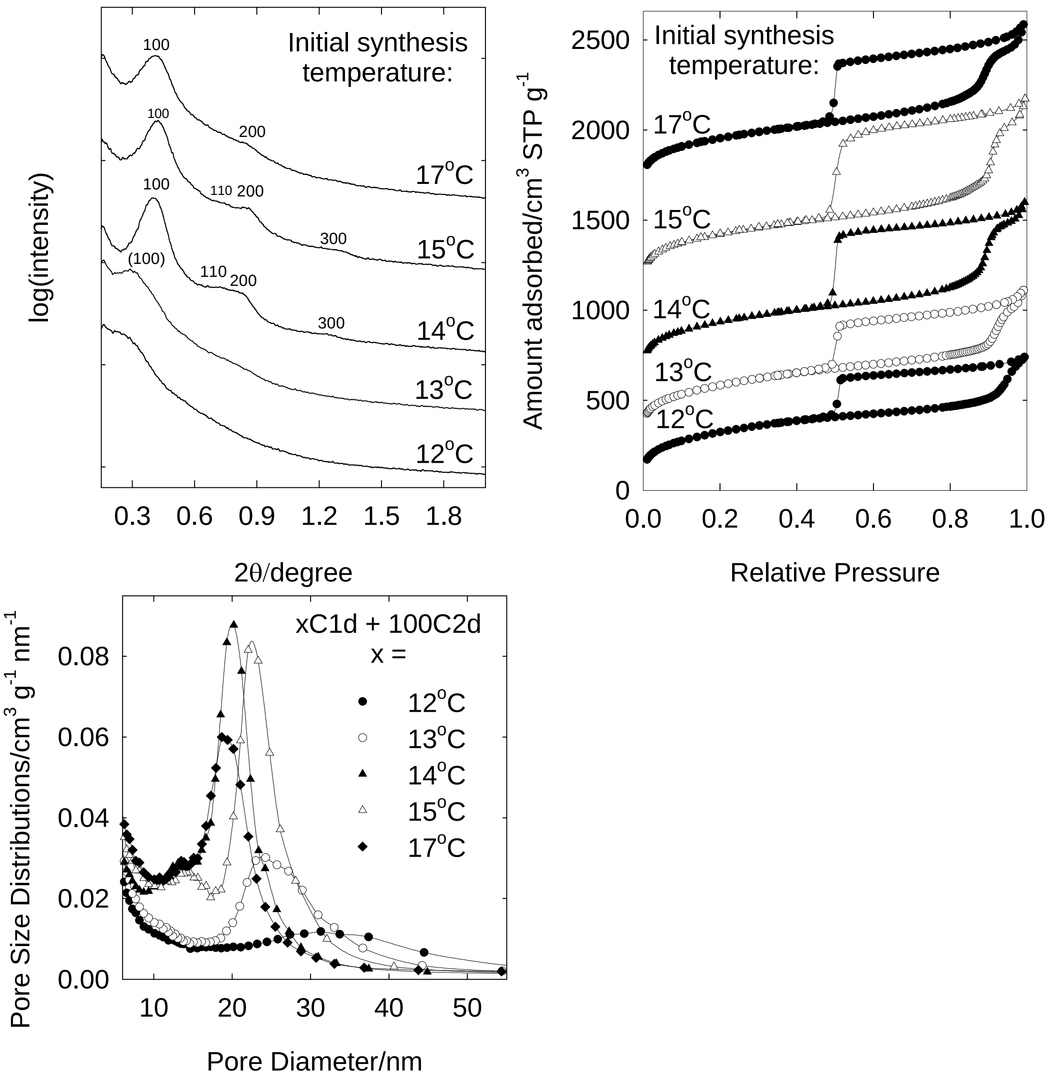
Supporting Figure S2. SAXS patterns (top left), nitrogen adsorption isotherms (top right), pore size distributions (bottom left) for methylene-bridged PMOs. Isotherms for samples calcined at 300 °C under N_2 and under air were offset vertically by 250 and 550 cm^3 STP g^{-1} for clarity. ^{29}Si CP MAS NMR (bottom right) for methylene-bridged PMOs a) as synthesized, b) calcined at 300 ^{o}C under nitrogen, c) calcined at 300 °C under air (scale in ppm).



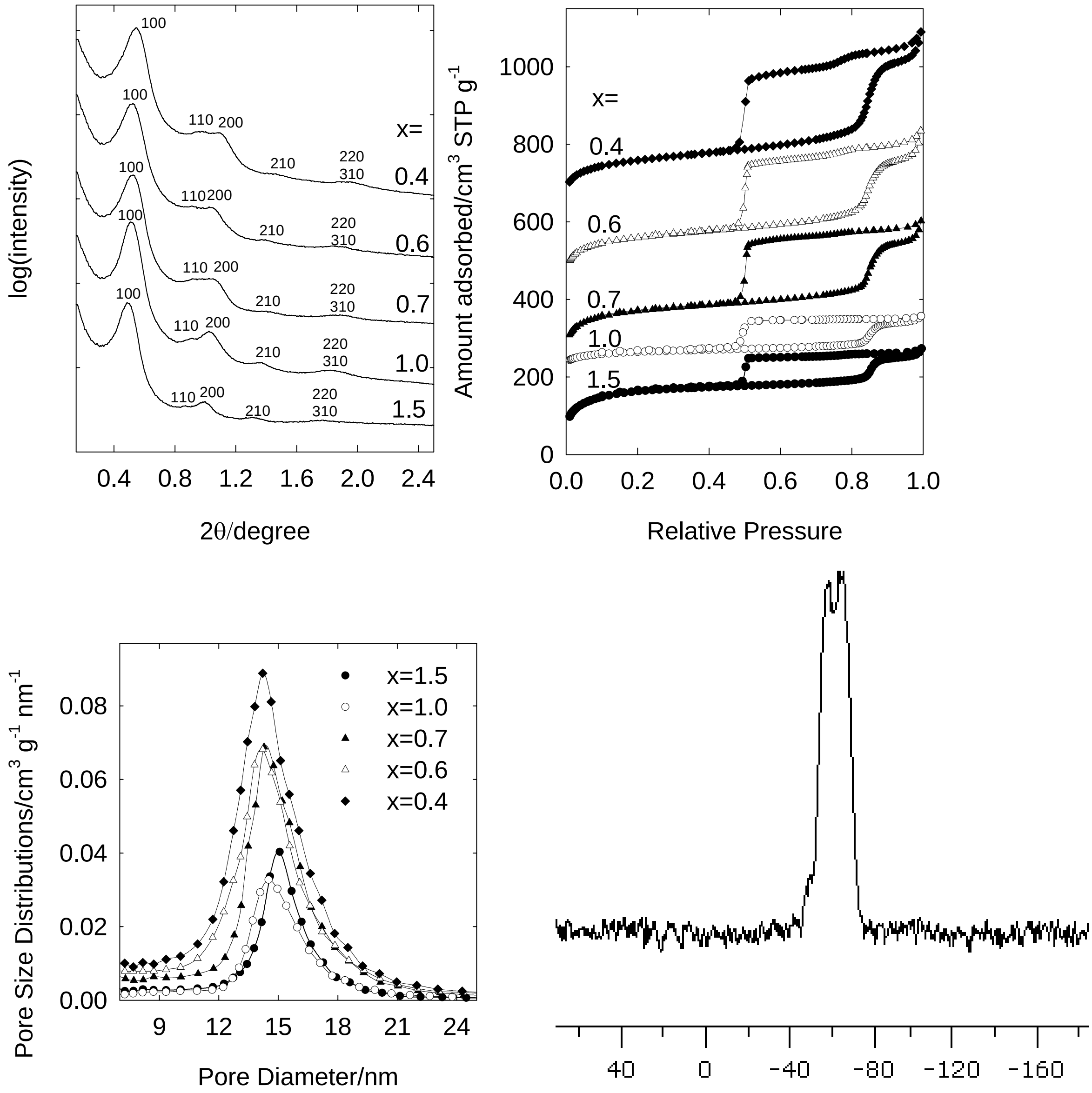
Supporting Figure S3. ^{29}Si CP MAS NMR for a methylene-bridged PMO hydrothermally treated at 150 °C for two days (scale in ppm).



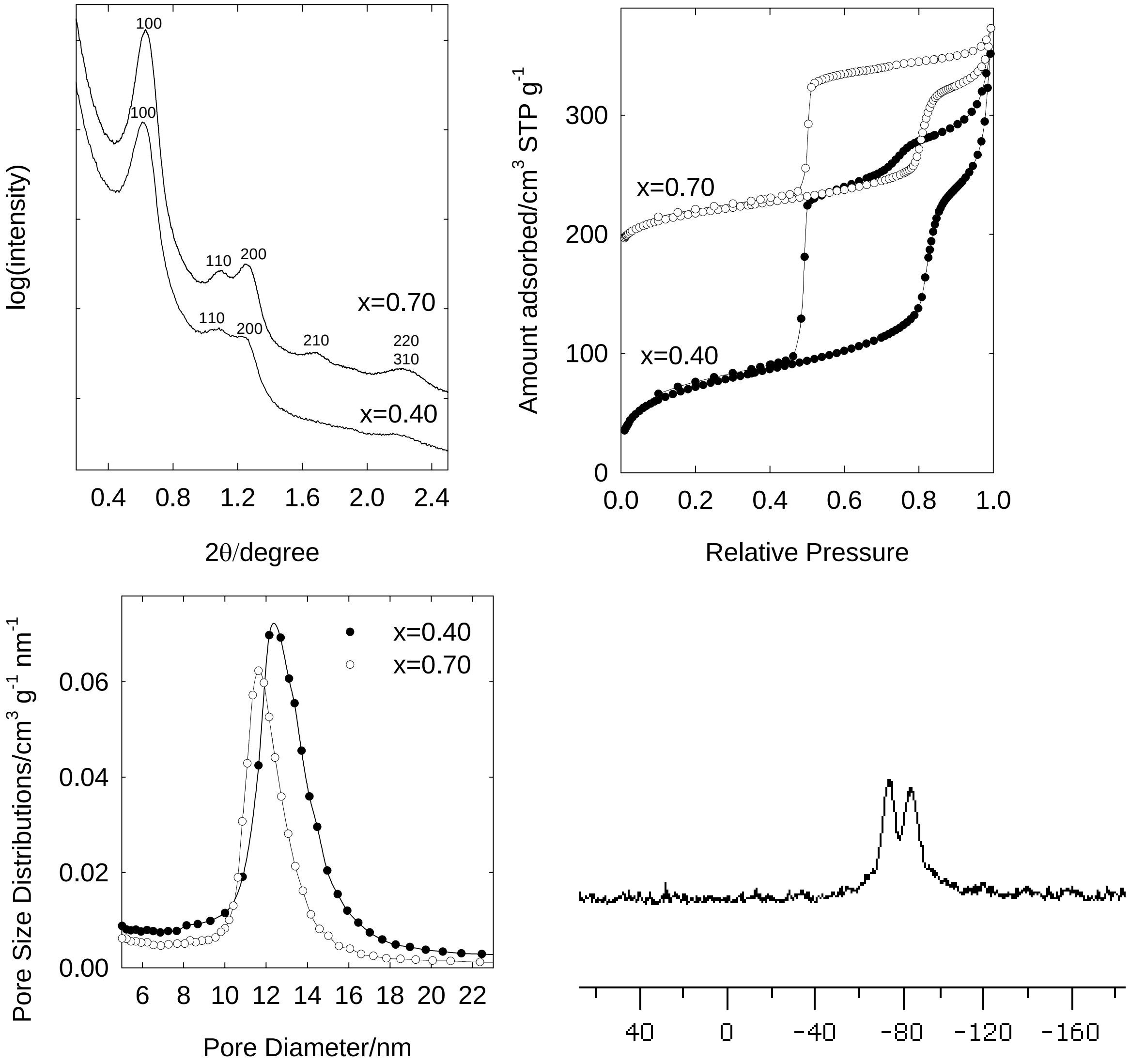
Supporting Figure S4. (top) SAXS patterns, (bottom left) nitrogen adsorption isotherms and (bottom right) pore size distributions of calcined methylene-bridged PMO synthesized with different amount of precursor in the presence of cyclohexane as a micelle expander. The isotherms are offset vertically by 200, and 400 cm^3 STP g^{-1} for x=0.3, and x=0.4 respectively.



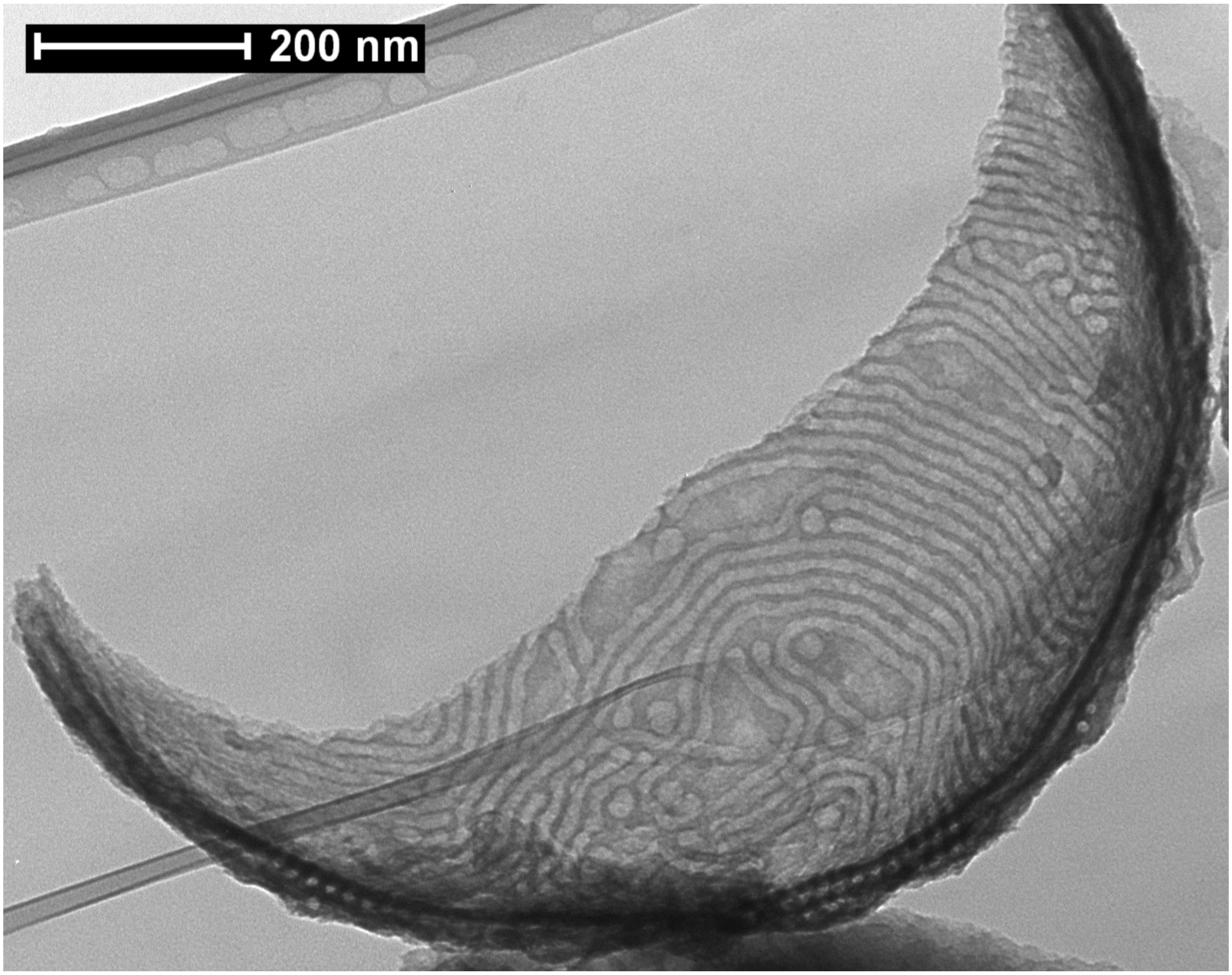
Supporting Figure S5. (top left) SAXS patterns, (top right) nitrogen adsorption isotherms and (bottom left) pore size distributions for calcined methylene-bridged PMOs synthesized at different initial temperature using cyclohexane as micelle expander. The isotherms were offset vertically by 260, 600, 1090 and 1640 cm^3 STP g^{-1} for samples synthesized at initial synthesis temperature of 13, 14, 15 and 17 ^{o}C respectively.



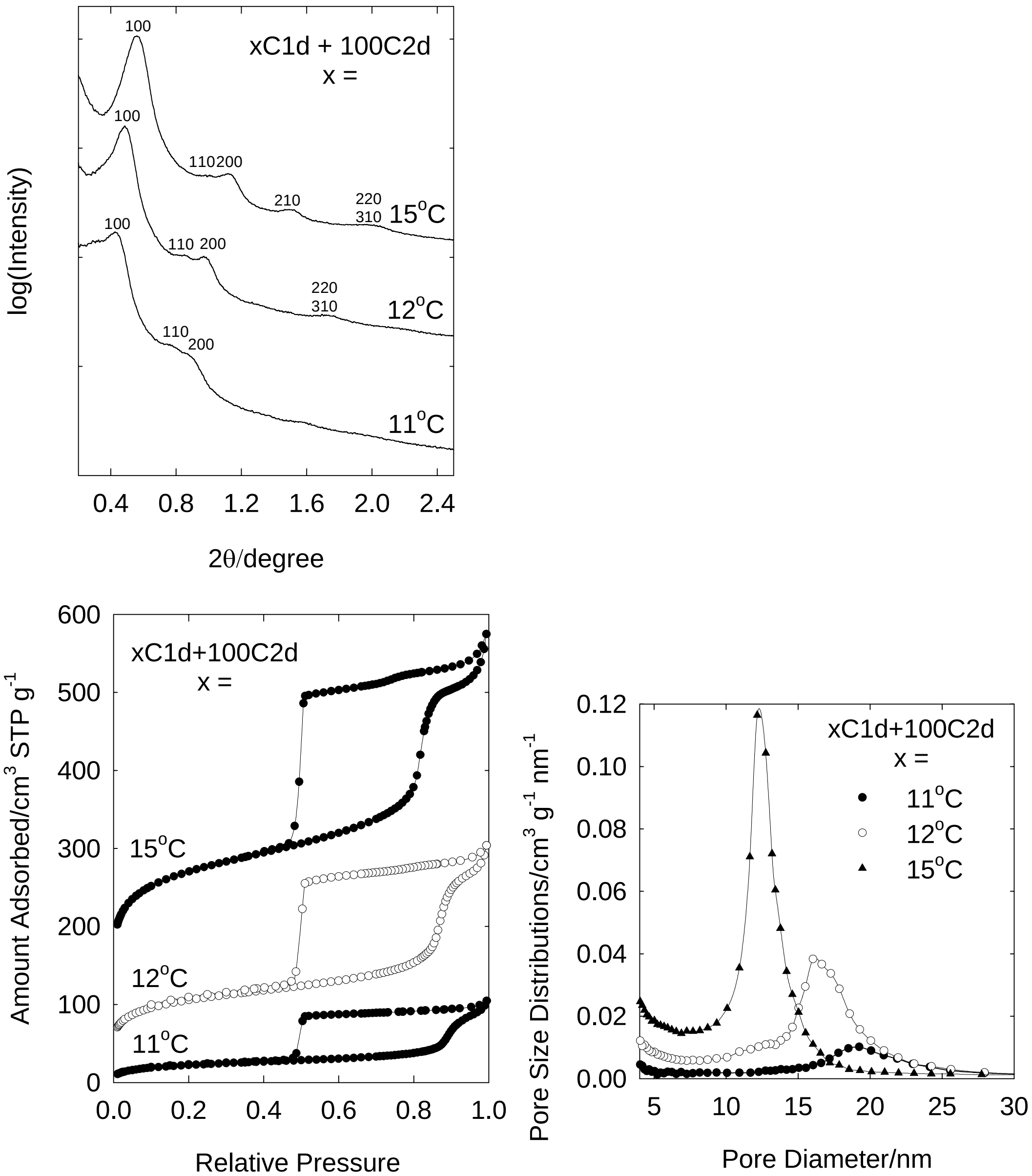
Supporting Figure S6. (top left) SAXS patterns, (top right) nitrogen adsorption isotherms and (bottom left) pore size distributions of extracted ethylene-bridged PMOs with different amounts of precursors using cyclohexane as a micelle expander at initial temperature of 15 °C. Isotherms were offset vertically by 220, 220, 420, and 640 cm^3 STP g^{-1} for samples synthesized with x= 1.0, 0.7, 0.6, and 0.4 respectively. (bottom right) ^{29}Si CP MAS NMR for extracted ethylene-bridged PMOs.



Supporting Figure S7. (top left) SAXS patterns of extracted ethenylene-bridged PMOs with different amount of precursor using cyclohexane as a micelle expander. (top right) nitrogen adsorption isotherms and (bottom left) pore size distributions of extracted ethenylene-bridged PMOs with different amount of precursor using cyclohexane as a micelle expander. The isotherms are offset vertically by 180 cm^3 STP g^{-1} for x=0.70. (bottom right) ^{29}Si CP MAS NMR for extracted ethenylene-bridged PMOs.

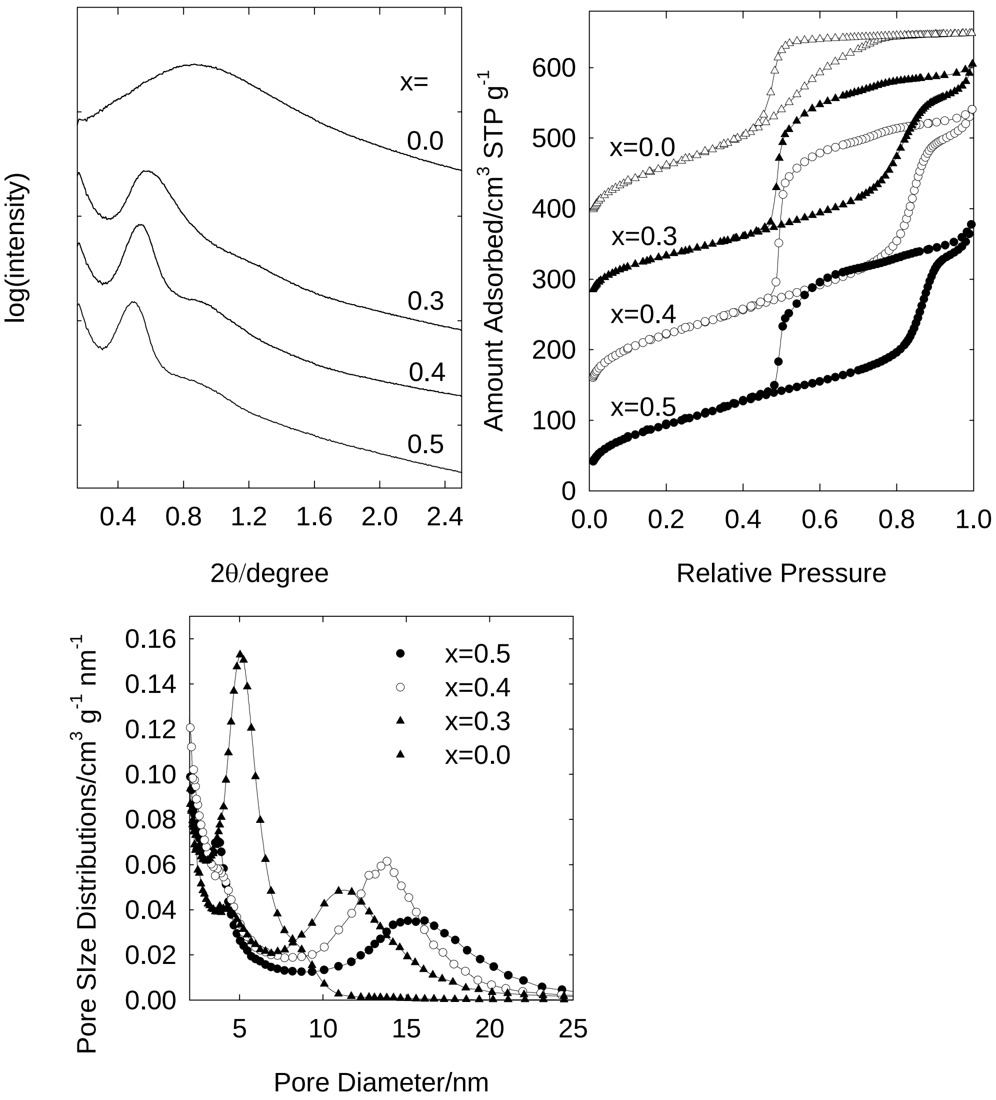


Supporting Figure S8. TEM image of as-synthesized ethylene-bridged PMO synthesized at initial temperature of 10.5 °C.

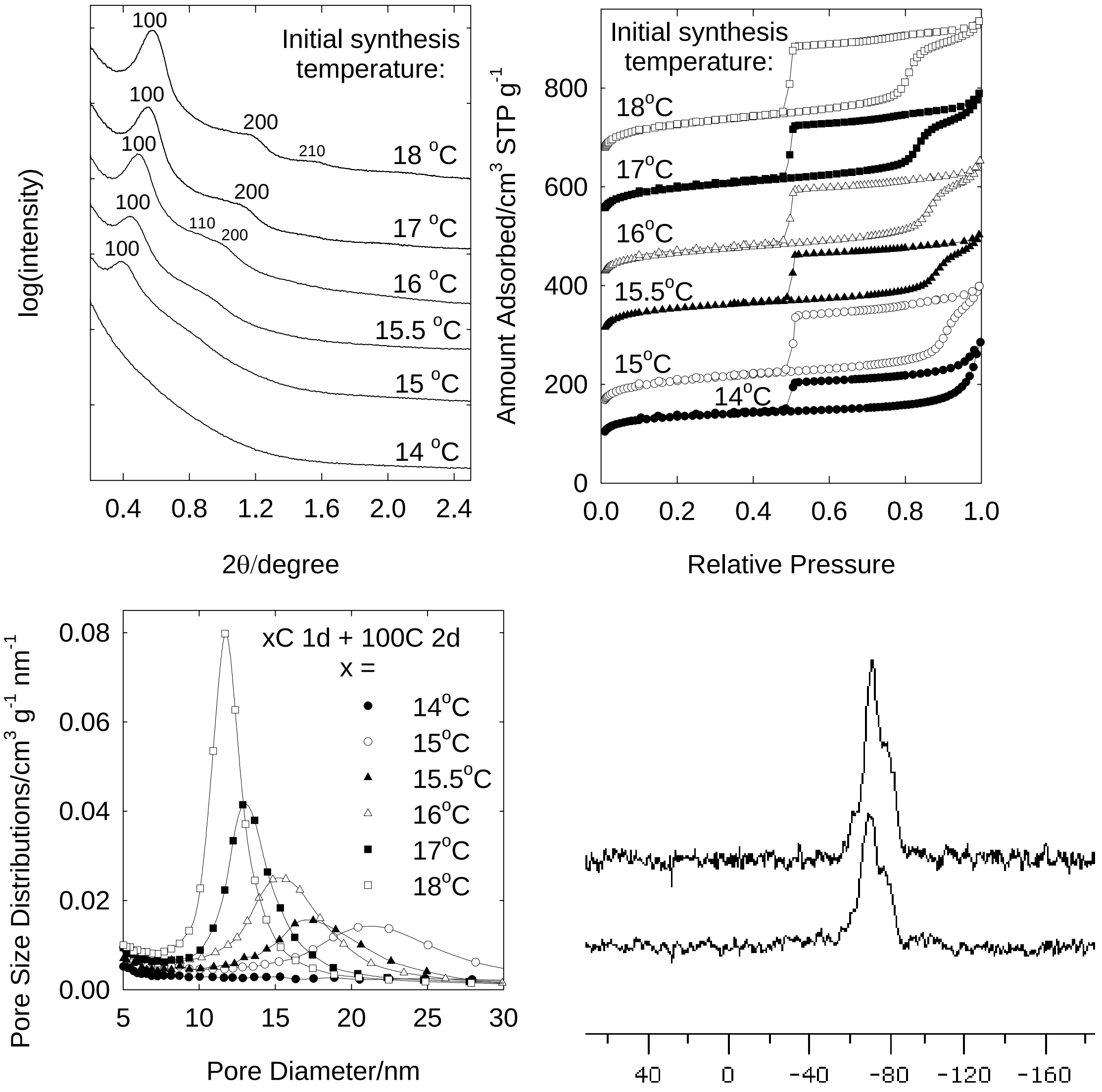


Supporting Figure S9. (top) SAXS patterns, (bottom left) nitrogen adsorption isotherms and (bottom right) pore size distributions for extracted ethylene-bridged PMOs synthesized at different initial synthesis temperature using bis(triethoxysilyl)ethane (BTEE) as precursor and cyclohexane as a micelle expander. The isotherms were offset vertically by 35, and 120 cm^3 STP g^{-1} for samples synthesized at initial synthesis temperature of 12, and 15 °C, respectively.

Supporting Figure S10. TEM image of extracted ethenylene-bridged PMO synthesized an initial temperature of 11.00 °C.



Supporting Figure S11. (top left) SAXS patterns, (top right) nitrogen adsorption isotherms and (bottom) PSDs of extracted PMOs synthesized using -$CH_2C(=CH_2)CH_2$-bridging group as precursor with different amount of precursor at an initial temperature 15 ^{o}C using cyclohexane as a micelle expander.



Supporting Figure S12. (top left) SAXS patterns of calcined phenylene-bridged PMOs synthesized at different initial temperature using 0.6 mL TIPB expander per 0.6 g P123. (top right) nitrogen adsorption isotherms and (bottom left) pore size distributions fort he corresponding samples. Isotherms for samples synthesized at initial synthesis temperature of 15, 15.5, 16, 17, and 18 °C are offset vertically by 50, 180, 320, 430, and 530 cm ^{3} STP g^{-1} respectively. Note that the sapme prepared at 18 °C was prepared under the same conditions as the sample denoted 18 °C (a) in Figure 8, but it was from a different batch. (bottom right) ^{29}Si CP MAS NMR for phenylene-bridged samples calcined at 300 °C under nitrogen (top spectrum) and calcined at 250 °C under air after extraction (bottom spectrum).