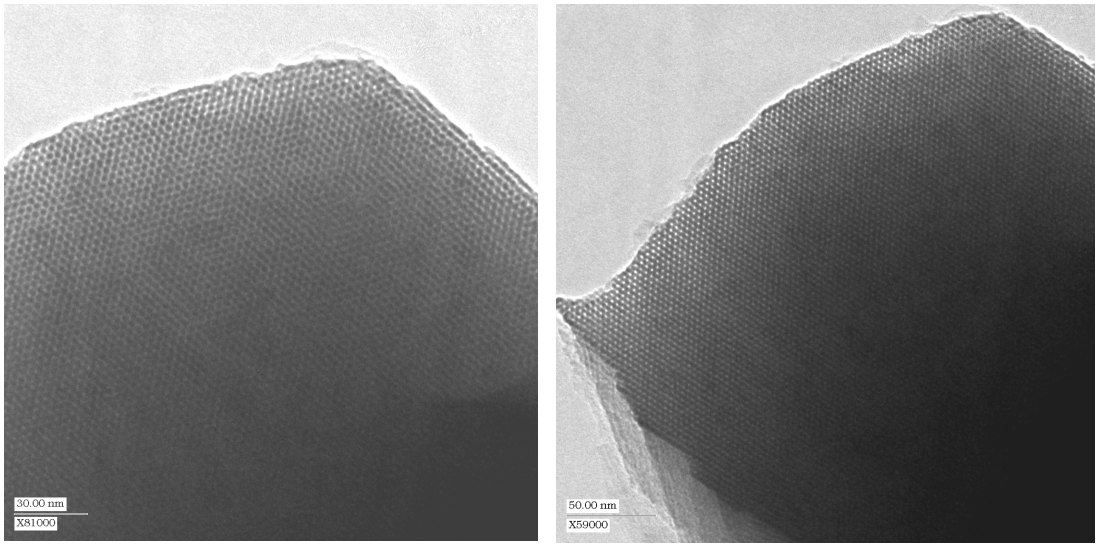
Fröba *et al.*: Supporting information

S1: Synthesis of 2,5-((*E*)-2-bis(triethoxysilyl)vinyl)aniline (BTEVA)

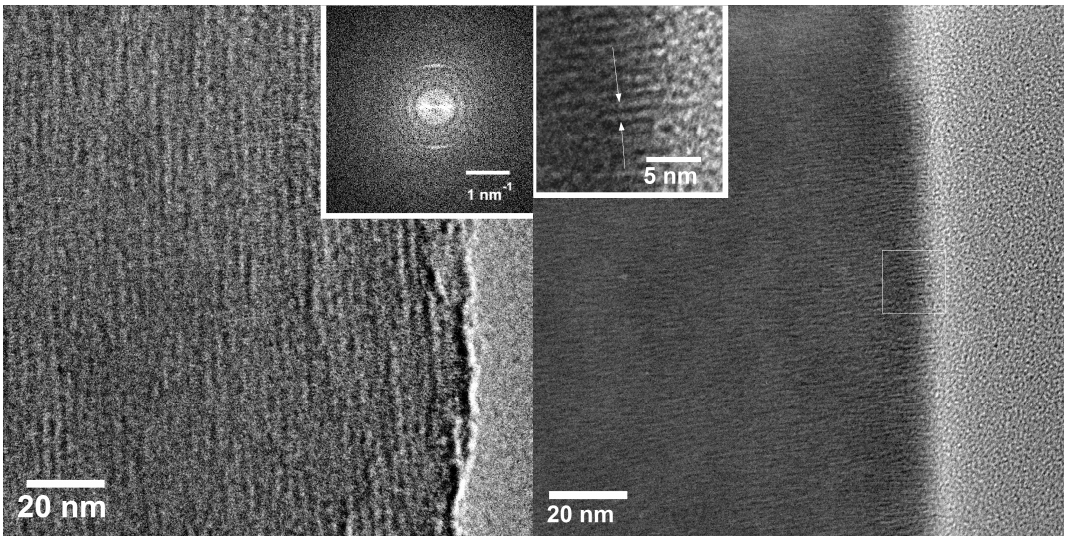
In a three-necked flask with a condenser 2,5-dibromoaniline (25 g; 0.1 mol), triethoxyvinylsilane (44 mL; 0.21 mol) and triethylamine (56 mL; 0.4 mol) were dissolved in 175 mL of dimethylformamide (DMF) under an atmosphere of nitrogen. After addition of tetrakis(triphenylphosphine)palladium (0.385 g; 0.33 mmol) the resulting solution was stirred for 4 days at 110 °C. The reaction mixture was cooled to 0 °C to ensure a complete precipitation of the formed ammonium salt. After filtration of the precipitates under an atmosphere of nitrogen DMF as well as excessive triethylamine were removed under reduced pressure. Then 150 mL of hexane were added and the mixture was stirred for 24 h at room temperature followed by filtration of the formed precipitates. After removal of hexane 27.4 g (0.06 mol) of BTEVA was obtained as a brown-yellow oil (yield: 58%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.15 Hz, 18 H); 3.90 (q, J = 7.15 Hz, 12 H), 4.14 (s, 2 H), 6.0-6.2 (m, 2 H), 6.7-7.4 (m, 5 H).

S2: TEM images of the divinylaniline-bridged PMO material



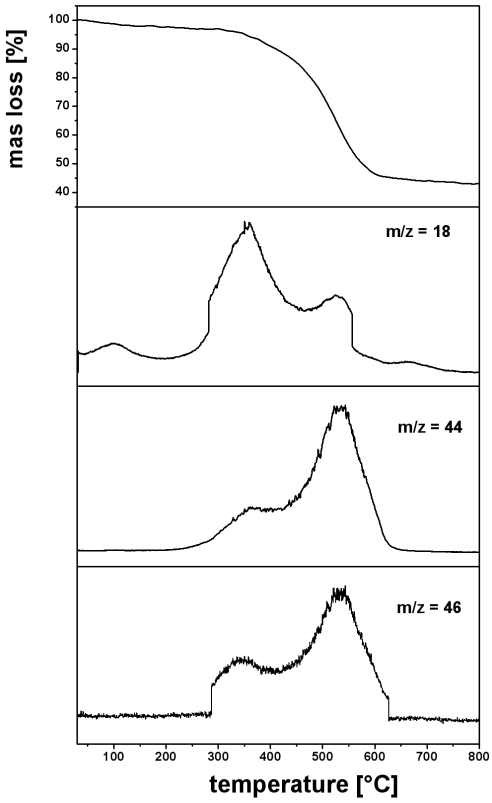
(a) **(b)**

In addition, the HR-TEM images (Figure S2c+d) exhibit a lot of lattice fringes also confirming the presence of crystal-like pore walls within the material. The distance between these fringes which indicate the molecular order of the organic units in the pore walls can be calculated to 1.14 nm and is therefore in a good agreement with the XRD measurements.



(c) **(d)**

S3: TG/MS data of the divinylaniline-bridged PMO material



S4: Characterization methods

Powder X-ray diffaction measurements: The powder X-ray diffraction (P-XRD) pattern was recorded at room temperature with a STOE Stadi P diffractometer using filtered CuKα radiation.

TEM analysis: The transmission electron micrograph was obtained with a Philips C 30 microscope operating at 300 kV.

Nitrogen physisorption measurements: Nitrogen physisorption data were recorded with a Quantachrome Quadrasorb-SIMP at 77 K. The BET surface area was calculated from $p/p_0 = 0.03\text{-}0.3$ in the adsorption branch and the BJH pore size distribution was calculated from the adsorption branch.

TG/MS measurements: TG/MS data were recorded with a STA 449 *F3 Jupiter*® from Netzsch and a QMS 403 C *Aëolos*® - quadrupol masspectrometer from Netzsch. The heating rate was 5 K/min.

^{29}Si MAS NMR measurements: The solid−state NMR spectra were run at 75.5 MHz for ^{13}C and 59.6 MHz for ^{29}Si, on a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with 4 mm double resonance MAS probe. The samples were spun at the magic angle at a spinning speed of 15 kHz, and ramped-amplitude cross-polarization (RAMP-CP) transfer of magnetization was applied. The 90° pulse for proton was 2.9 μs.