Supporting Information

Three dimensional nanoscale analysis reveals aperiodic mesopores in covalent organic framework and conjugated microporous polymer

Craig T. Stoppiello, Helena Isla, Marta Martínez-Abadía, Michael W. Fay, Christopher D. J. Parmenter, Martin J. Roe, Belén Lerma-Berlanga, Carlos Martí-Gastaldo, Aurelio Mateo-Alonso, and Andrei N. Khlobystov.

Contents

1. Synthesis of materials

Reagents for synthesis were purchased from Fluorochem and Acros. COF-5 was synthesised as previously described by Cote et al.(*22*) Solid-State ^{1}H and ^{13}C/CP MAS NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer at a MAS rate of 12 kHz and a CP contact time of 2 ms. ATR-FTIR spectra were recorded on a Bruker ALPHA ATR-IR spectrometer, elemental analysis was carried out in a Euro EA Elemental Analyzer from EuroVector. The X-ray powder diffraction patterns were collected by using a PHILIPS X'PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta-theta configuration, secondary monochromator with Cu-K_α radiation (λ = 1.5418 Å) and a PIXcel solid state detector (active length in 2θ 3.347°). Thermogravimetric analysis was performed in a TGA Q500 from TA Instruments under nitrogen with a heating rate of 10°C/min, and air was introduced at 800°C. All spectra and graphical data can be found in the SI file.

Synthesis of Aza-CMP

In a vial with PTFE/silicone septa and aluminium crimp-cap were placed 170 mg (0.6 mmol) of 1,2,4,5-benzenetetraamine chlorohydrate and 125 mg (0.4 mmol) of hexaketocyclohexane octahydrate, then 14 mL of distilled water was added and the vial was crimped. The vial was subjected to vacuum/N_2 cycles through the septum 3 times and the vial was sonicated (5 min). Finally the vial was placed into the oven for 6 days at 135°C.

The vial was opened at room temperature and the mixture was filtered off through a PTFE filter (0.45 μm pore size). The black solid was suspended and filtered again with an aqueous solution of 0.2 M hydrochloric acid, distilled water, methanol and tetrahydrofuran. Then the PTFE filter was folded with filter paper and introduced into a soxhlet cartridge for soxhlet extraction with distilled water (48 hr), methanol (48 hr), tetrahydrofuran (48 hr) and dichloromethane (48 hr). The cartridge was then sonicated in the presence of methanol (20 min), tetrahydrofuran (20 min), dichloromethane (20 min) and diethyl ether (20 min), taken from the filter and dried under vacuum at 150° C for 48 hr. Finally a quantitative amount (107 mg) of a black powder was obtained.

^{1}H CP/MAS NMR ∂ 7.15 ppm; ^{13}C CP/MAS NMR ∂ 139.32, 128.63, 110.06 ppm ; FTIR (wavelength, cm^{-1}) 3186 broad, 1690, 1578, 1460, 1390, 1223, 1050, 857; XRD broad band at 2θ= 27° (corresponds to a distance of 3.3 Å).

2. COF-5 Characterization

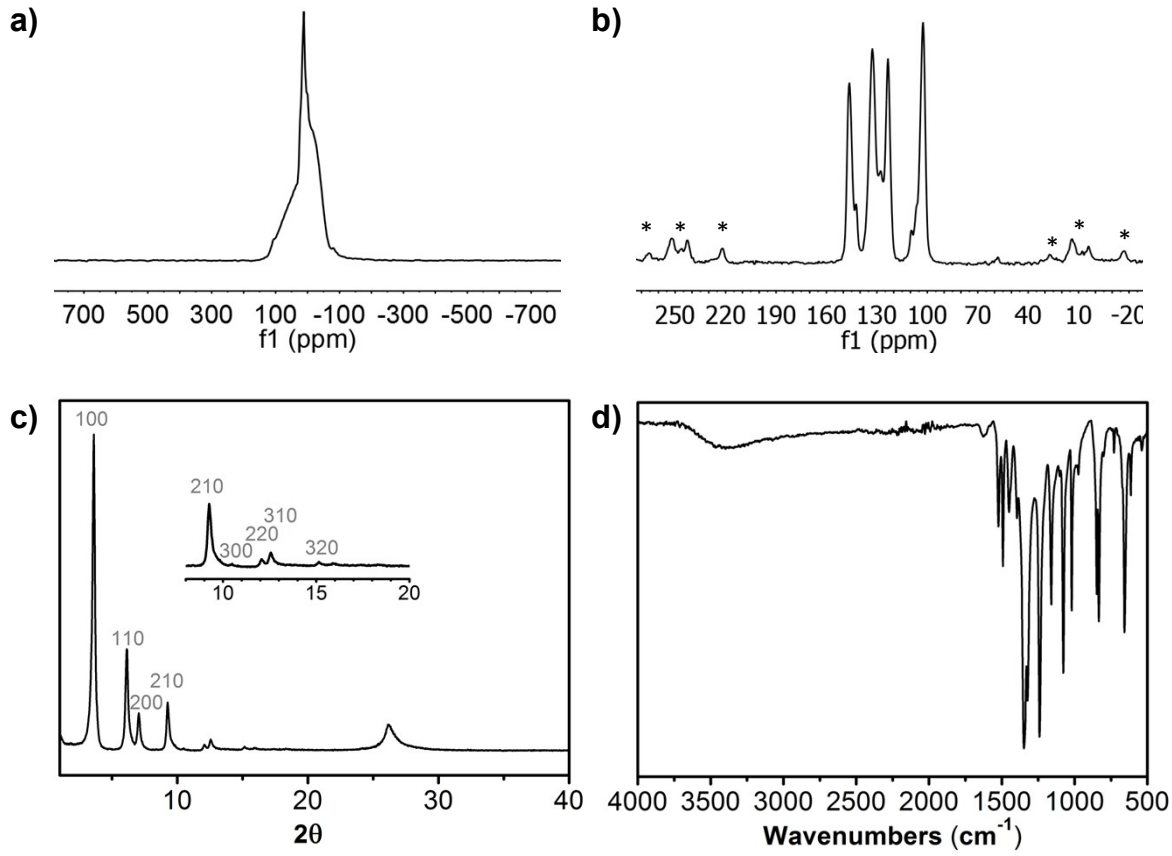

Figure S1 Characterization of COF-5: a) CP/MAS ^{11}B NMR spectrum, b) CP/MAS ^{13}C NMR spectrum, c) powder X-ray diffractogram and d) FT-IR spectrum.

3. Aza-CMP Characterization

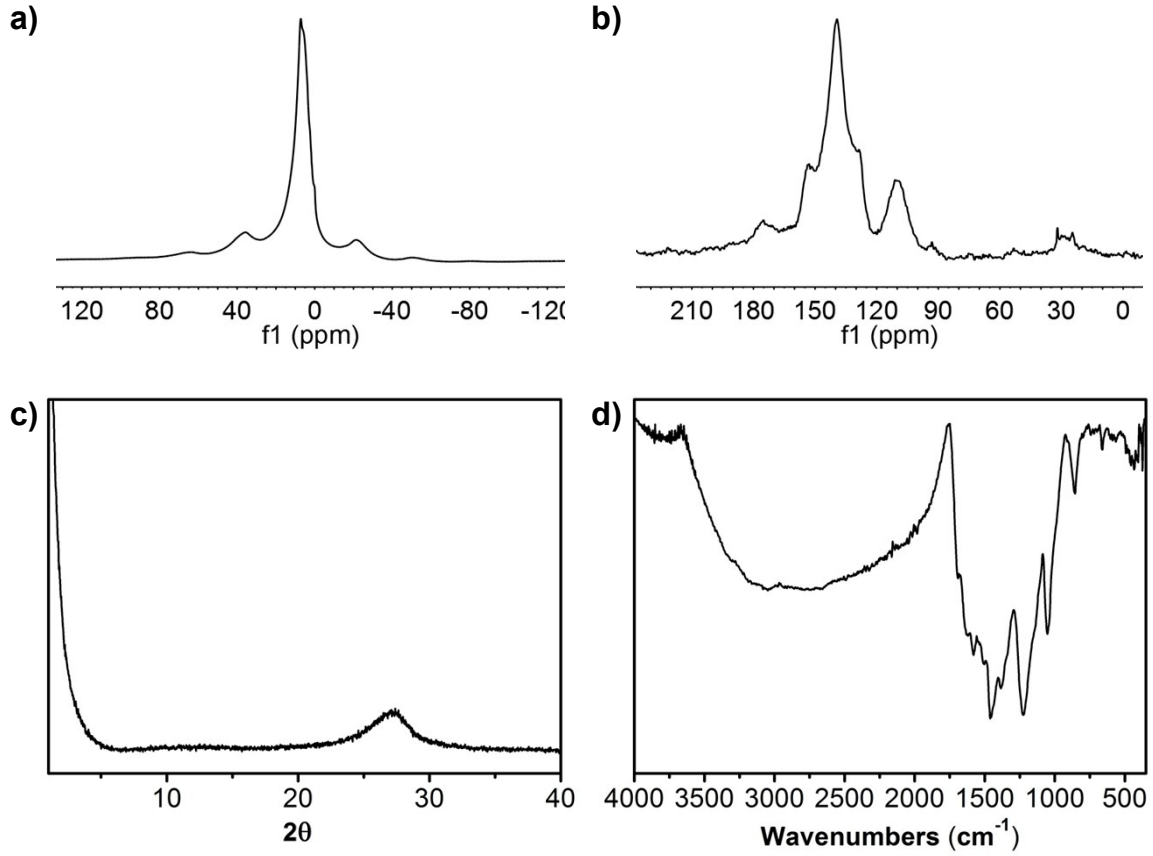

Figure S2 Characterization of Aza-CMP, a) CP/MAS ^{1}H NMR spectrum, b) CP/MAS ^{13}C NMR spectrum, c) powder X-ray diffractogram and d) FT-IR spectrum.

4. Simultaneous iterative reconstruction technique:

See videos V2, V4, V5, V6.

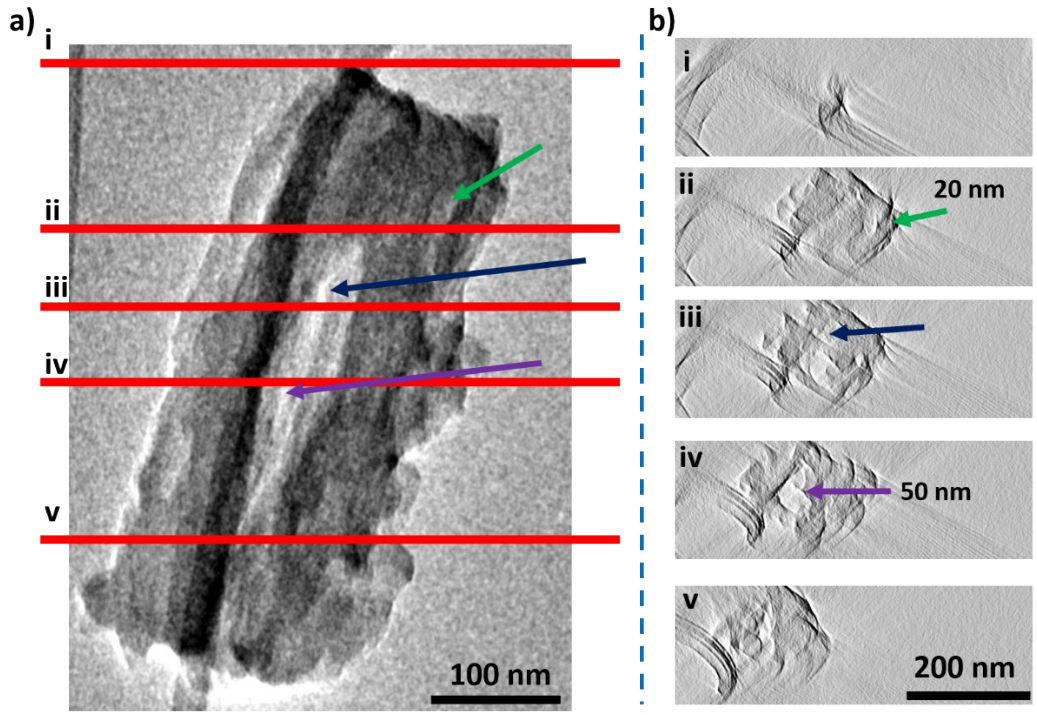

Figure S3: HRTEM image (panel a) and corresponding images (panel b) showing a reconstruction of the cross section of the COF particle. Each of the horizontal red lines in (a) (i-v) relate to the position of which the stills in (b) correspond to, for example line (i) shows the reconstruction taken just above the CMP particle, line (ii) bisects the small pore (green arrow) and this is visible in the reconstruction. The large void in the centre of the particle is demonstrated at positions (iii) and (iv) with the blue and purple arrows and is clearly seen in the corresponding reconstructions.

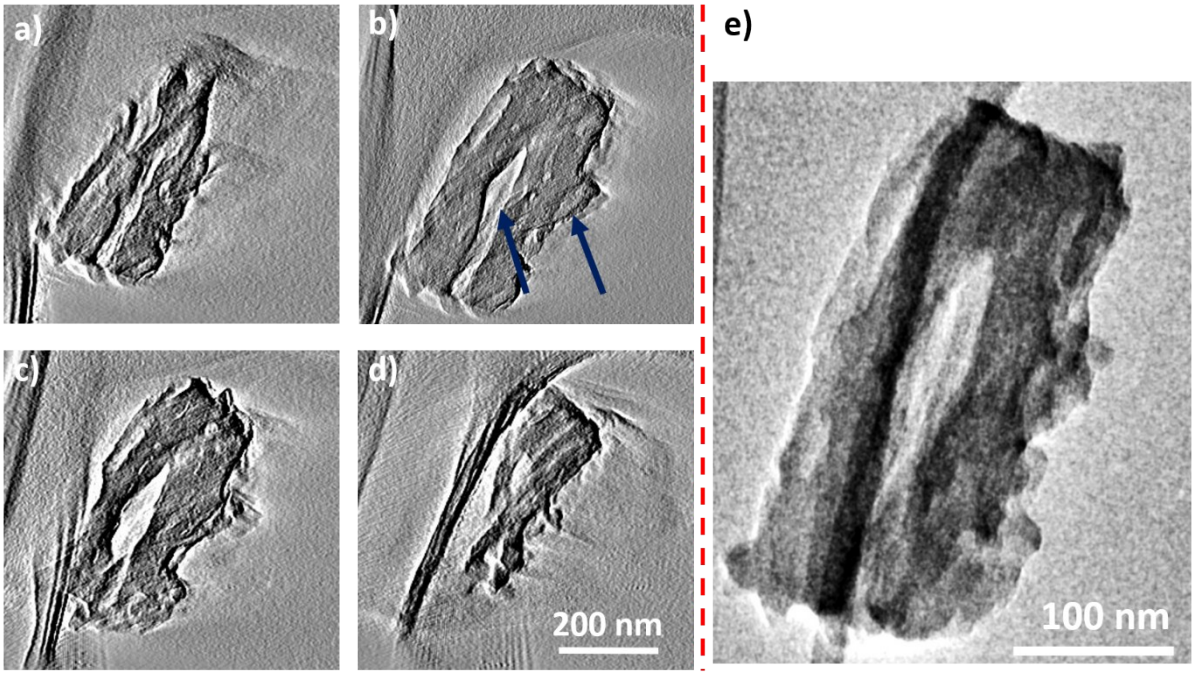

Figure S4: (a-d) a series of SIRT images revealing the internal pores (blue arrows) of the particle from a lateral perspective, demonstrating that the changes in contract observed in the HR-TEM (e) are due to cavities within the structure.

5. Supplementary TEM Images of Aza-CMP

See video V5 for the tomographic series of the Aza-CMP particle shown in Figure 2.

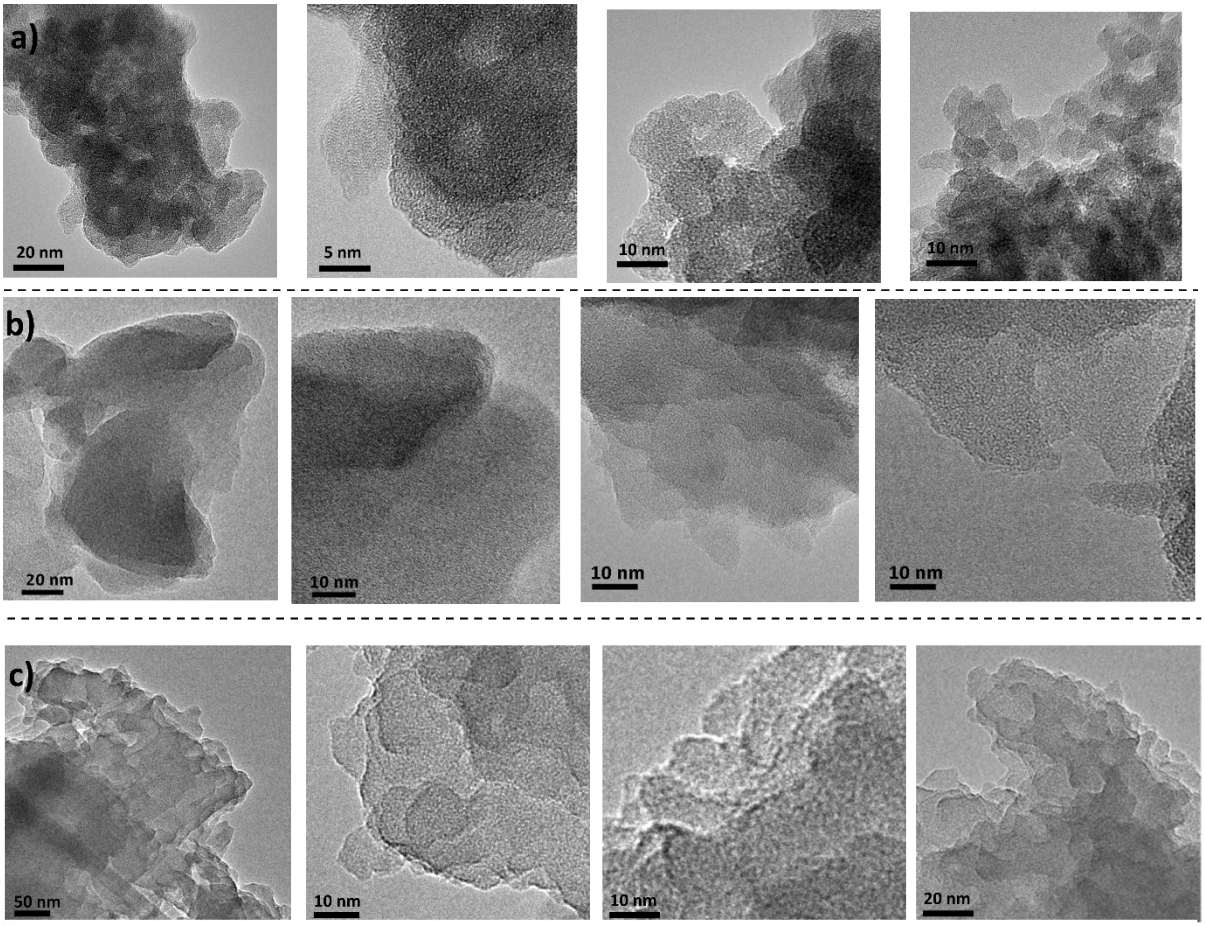

Figure S5: HR-TEM images of various particles of Aza-CMP prepared via different methods, dry deposition (a), dispersion in either propan-2-ol (b), or acetone (c). Regardless of method of TEM sample preparation, terraces are still present, in addition to features of differing contrast which can be attributed to mesopores.

6. Supplementary TEM images at varied doses/accelerating voltages

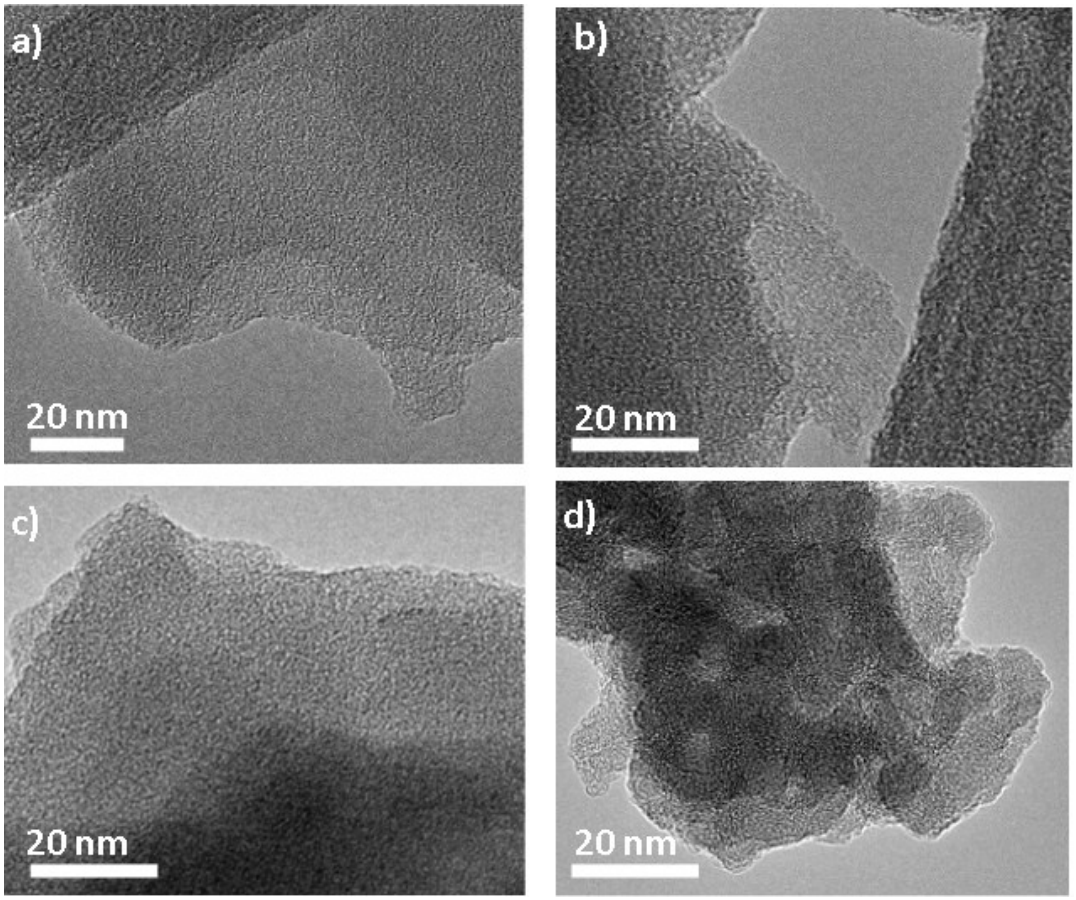

Figure S6: HR-TEM images of various particles of Aza-CMP taken at both differing electron doses and accelerating voltages. Imaging the particles with a LaB_6 source at both 80 kV (a) and 200 kV (b) and also with a FEG source at both 100 kV (c) and 200 kV (d) doesn't alter the morphology of the particles.

7. EDX Quantitative analysis

The atomic ratio of elements in the microporous polymer have been quantified using EDX analysis. This involved taking representative spectra over a variety of different particles and quantitatively evaluating C, N, O atomic percentages compared to the theoretical values expected from the chemical structure.

Table S1: Experimentally obtained atomic percentages of C,N and O within the CMP, compared to those theoretically expected.

Element	Calculated atomic %	Theoretical atomic %
C	74	71
N	19	29
O	7	-