Supplementary Material (ESI) for Chemical Science
This journal is (c) The Royal Society of Chemistry 2011

Chemical Tuning of CO_2 Sorption in Robust Nanoporous Organic Polymers

R. Dawson, D.J. Adams and A.I. Cooper*

Supporting Information

Experimental

Materials

1,3,5-Triethynylbenzene was purchased from ABCR. Tetrakis(triphenylphosphine)palladium(0) was purchased from Alfa Aesar. All other chemicals were obtained from Sigma-Aldrich. All chemicals were used as received with no further purification.

Preparation of conjugated microporous polymer networks

CMP networks with no additional functions (R = H, Scheme 1), methyl functionalities (R = CH_3), and hydroxyl (R = OH) functionalities were prepared as previously reported.[1] The carboxylic acid and amine-functionalized CMP networks were synthesised using a analogous method using *N,N'*-dimethylformamide as a solvent.

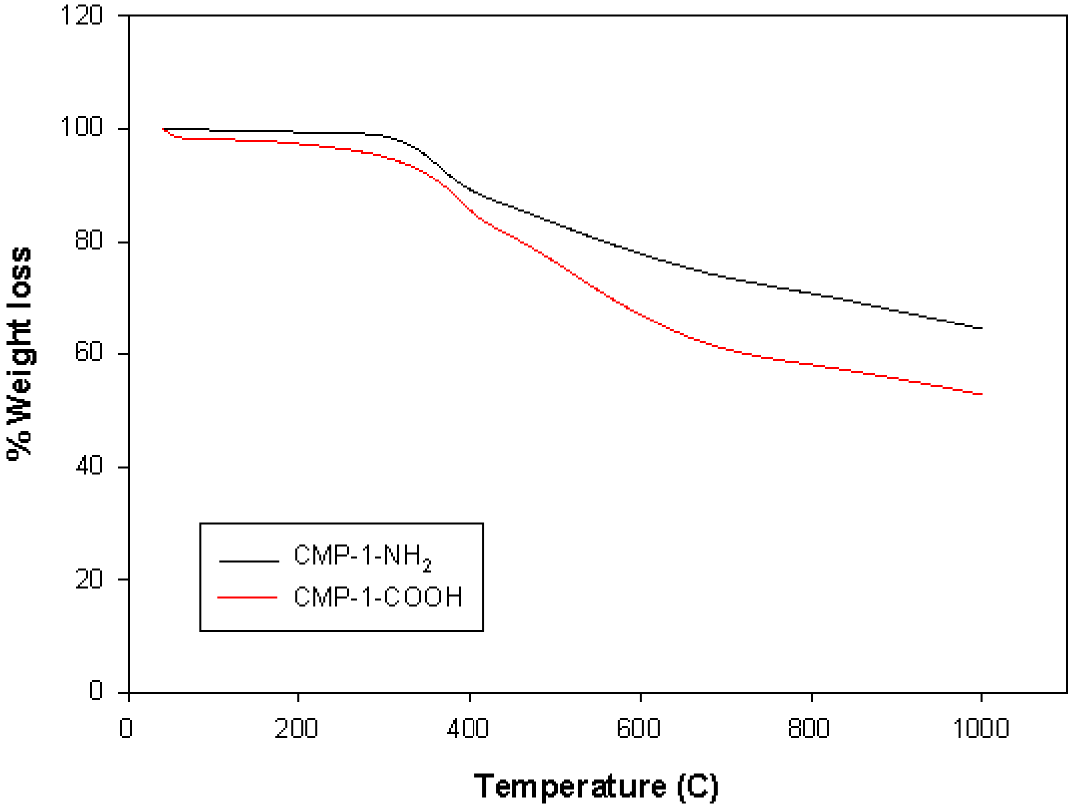
In a typical procedure, the dibromo aromatic monomer (1 mmol) and 1,3,5-triethynylbenzene (1.5 mmol) were degassed and the reaction flask backfilled with nitrogen three times. This molar ratio has been shown to lead to materials with higher surface area.[1,2] Anhydrous *N,N'*-dimethylformamide (1.5 mL) and anhydrous triethylamine (1.5 mL) were added and the solution heated to 100 °C. Tetrakis(triphenylphosphine)palladium(0) (50 mg) and copper(I)iodide (15 mg) were added as a slurry in DMF (1 mL) and the reaction was stirred under nitrogen for 72 hours. The precipitate was collected by filtration, washed with hot DMF and soxhlet extracted with methanol for 18 hours. The product was dried under vacuum at 60 °C for 18 hours.

Gas sorption analysis

Nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2420 gas sorption analyser. Carbon dioxide measurements were measured at 273 and 298 K using a Micromeritics ASAP 2050 extended sorption analyser fitted with a chiller circulator dewar. Samples were degassed under high dynamic vacuum for 16 hours prior to analysis. Isosteric heats were calculated using the standard calculation routines provided with the ASAP 2050 software. Nitrogen NLDFT pore size distributions were calculated from the nitrogen adsorption branch using a cylindrical pore size model for pillared clay provided with the Micromeritics Datamaster software. As with previously described networks the pillared clay model was shown to give the lowest standard deviations of the available models (slits pore - N_2 DFT, cylindrical pores – oxide surface, Tarazona NLDFT and NLDFT for pillared clay).[1-3] Further DFT pore size distributions were calculated from the CO_2 adsorption isotherms using the DFT model for CO_2 on carbon with slit pores provided with the Micromeritics Datamaster software.

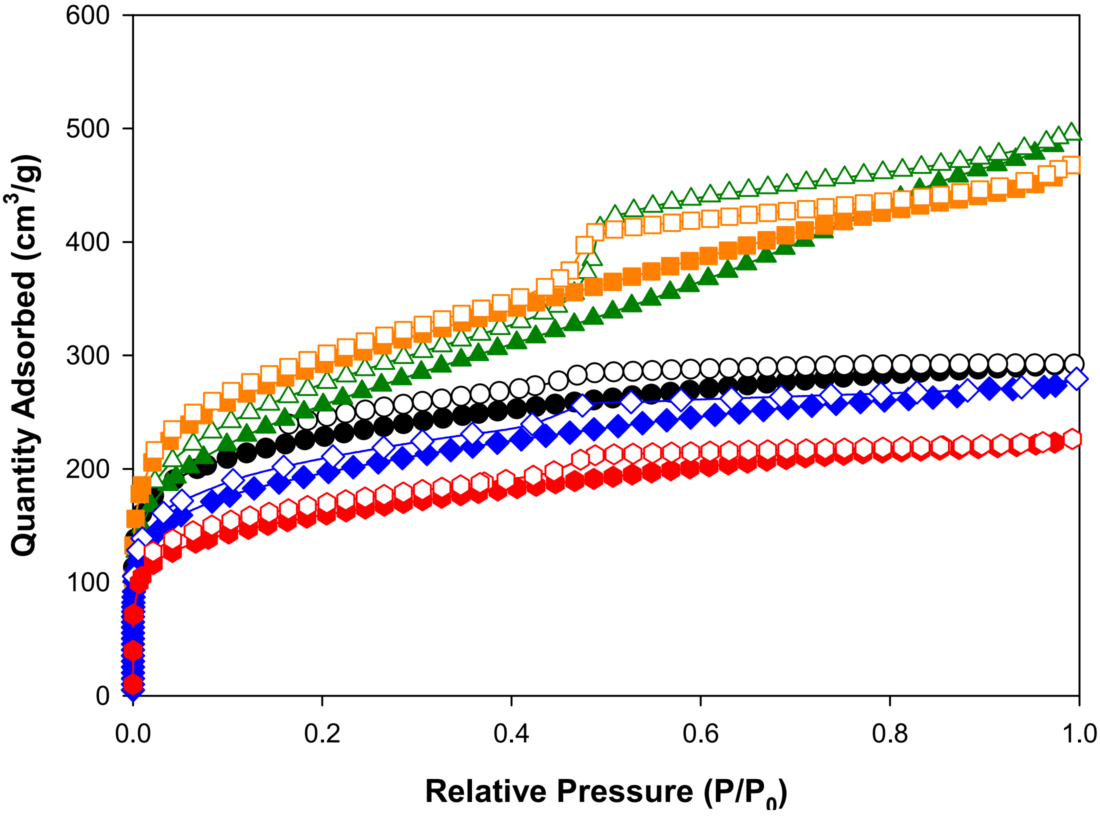
Thermogravimetric analysis

Samples heated at rate of 5 °C/min under nitrogen to 1000 °C.



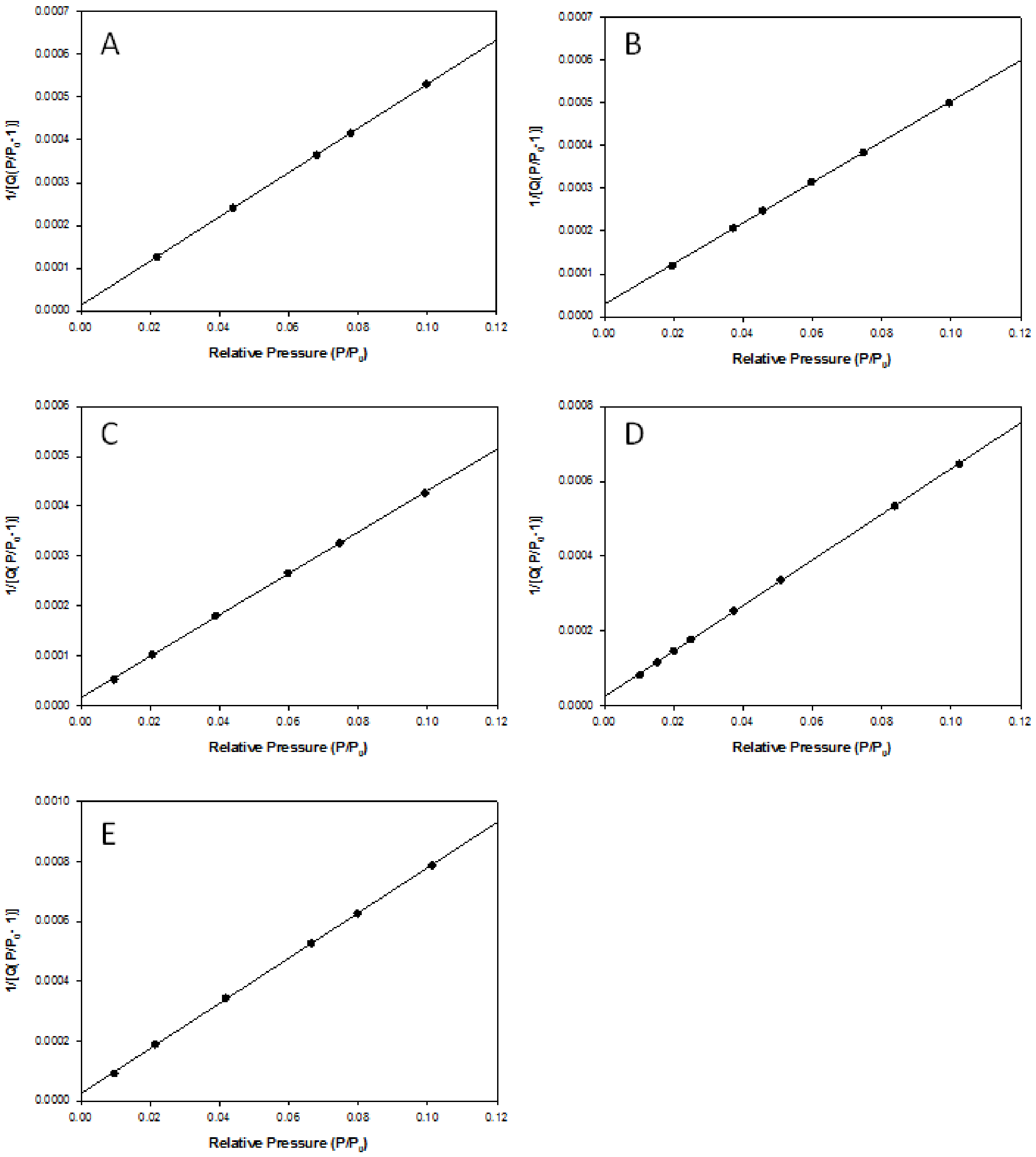
S1. Thermogravimetric analysis (TGA) for CMP-1-NH$_2$ and CMP-1-COOH

Nitrogen adsorption/desorption isotherms



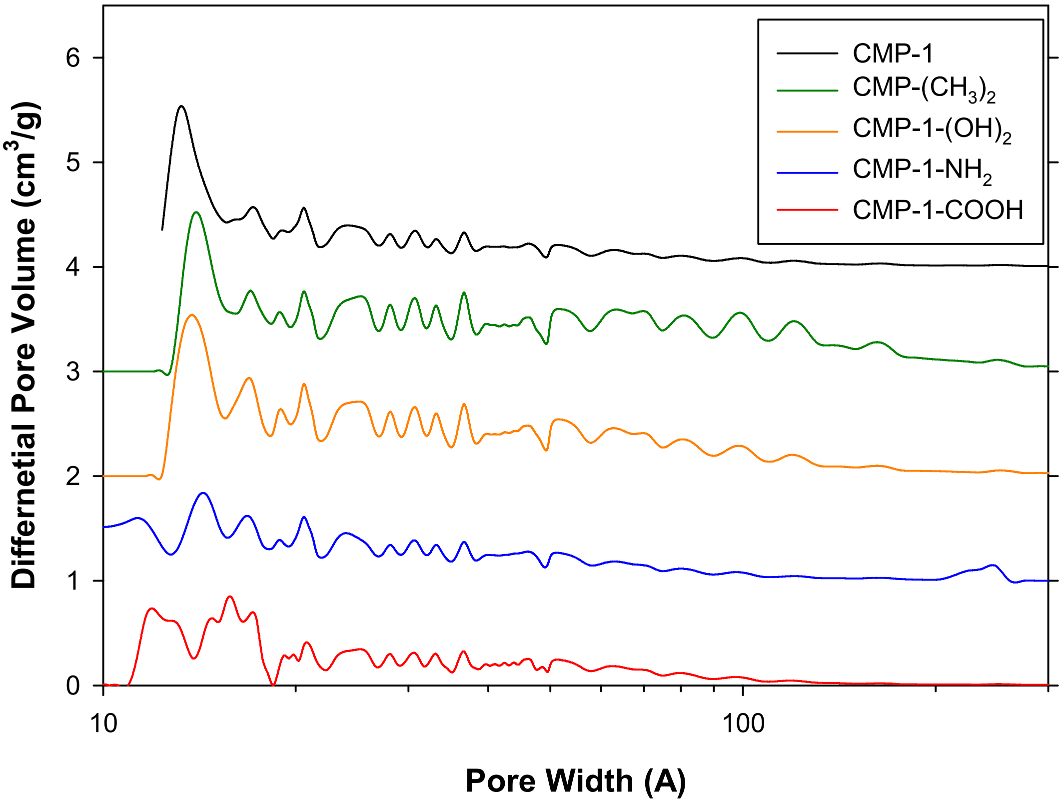
S2. Nitrogen adsorption (closed)/desorption (open) isotherms (77 K) for CMP-1 (black), CMP-1-$(CH_3)_2$ (green), CMP-1-$(OH)_2$ (orange), CMP-1-NH_2 (blue) and CMP-1-COOH (red)

BET plots



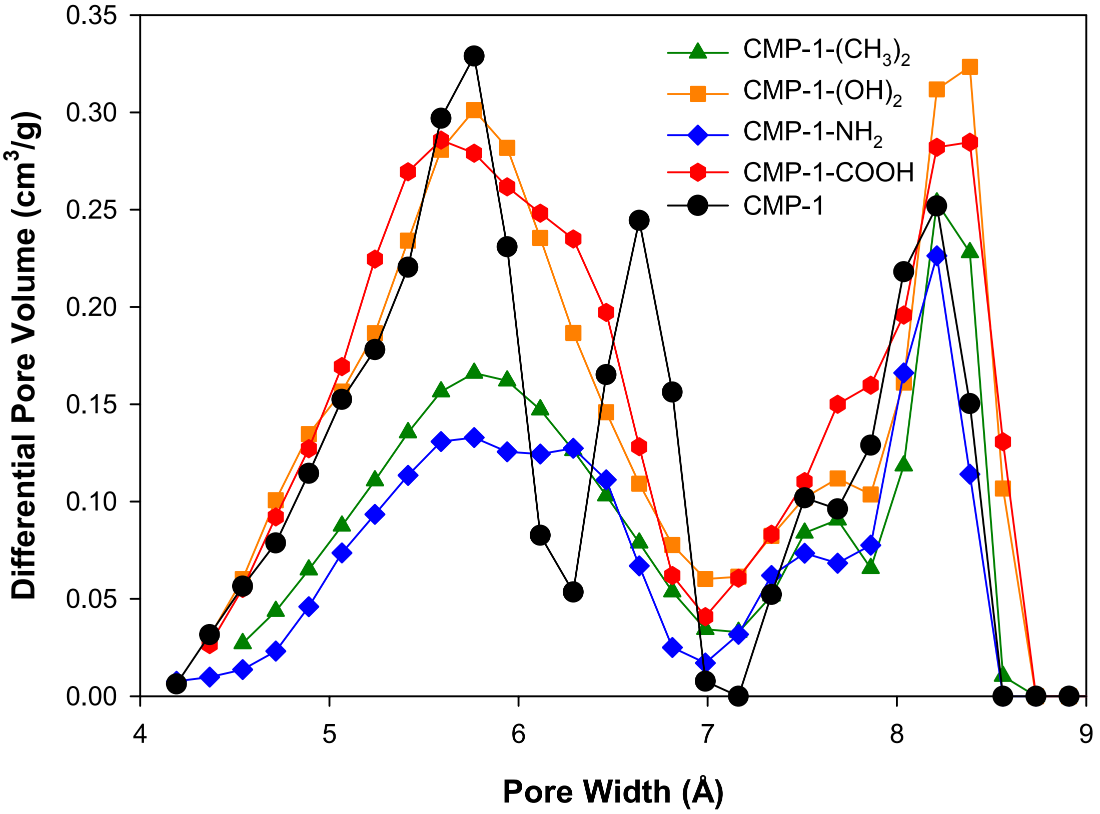
S3. BET plots for: (A) CMP-1, (B) CMP-1-$(CH_3)_2$, (C) CMP-1-$(OH)_2$, (D) CMP-1-NH_2 and (E)CMP-1-COOH

NL-DFT pore size distribution



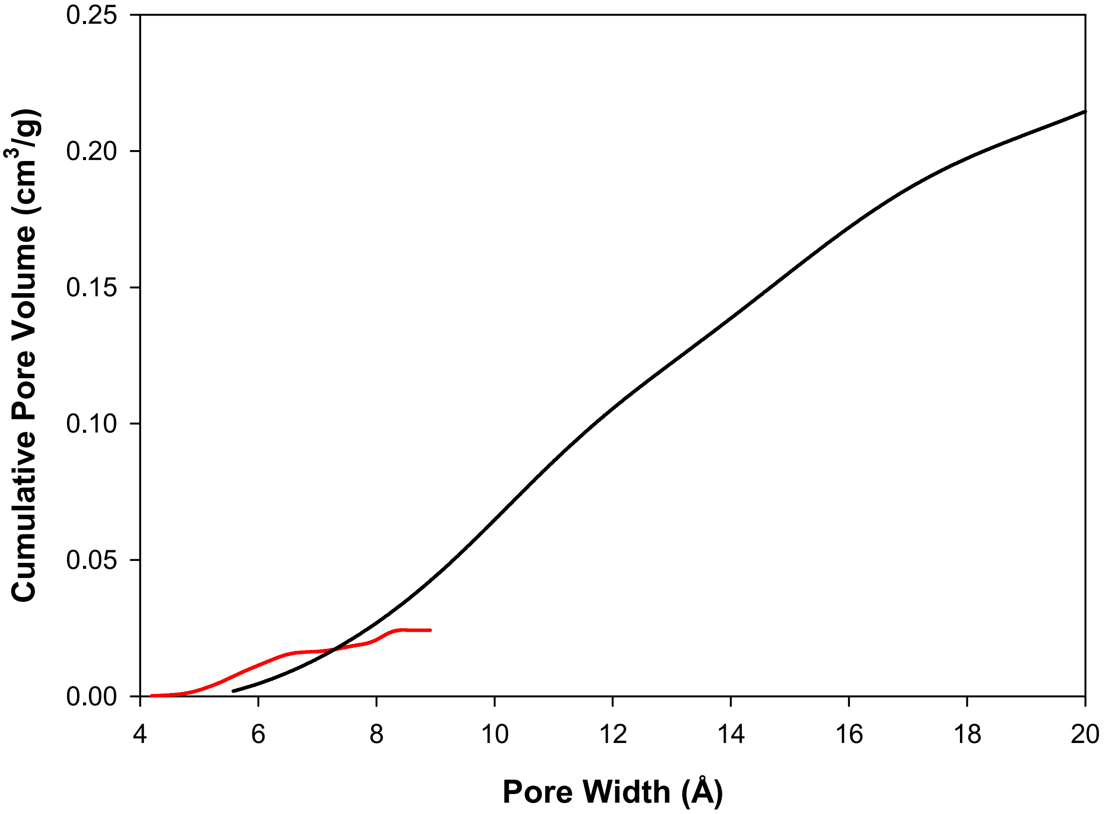
S4. NL-DFT pore size distributions for CMP networks

CO_2 DFT pore size distributions



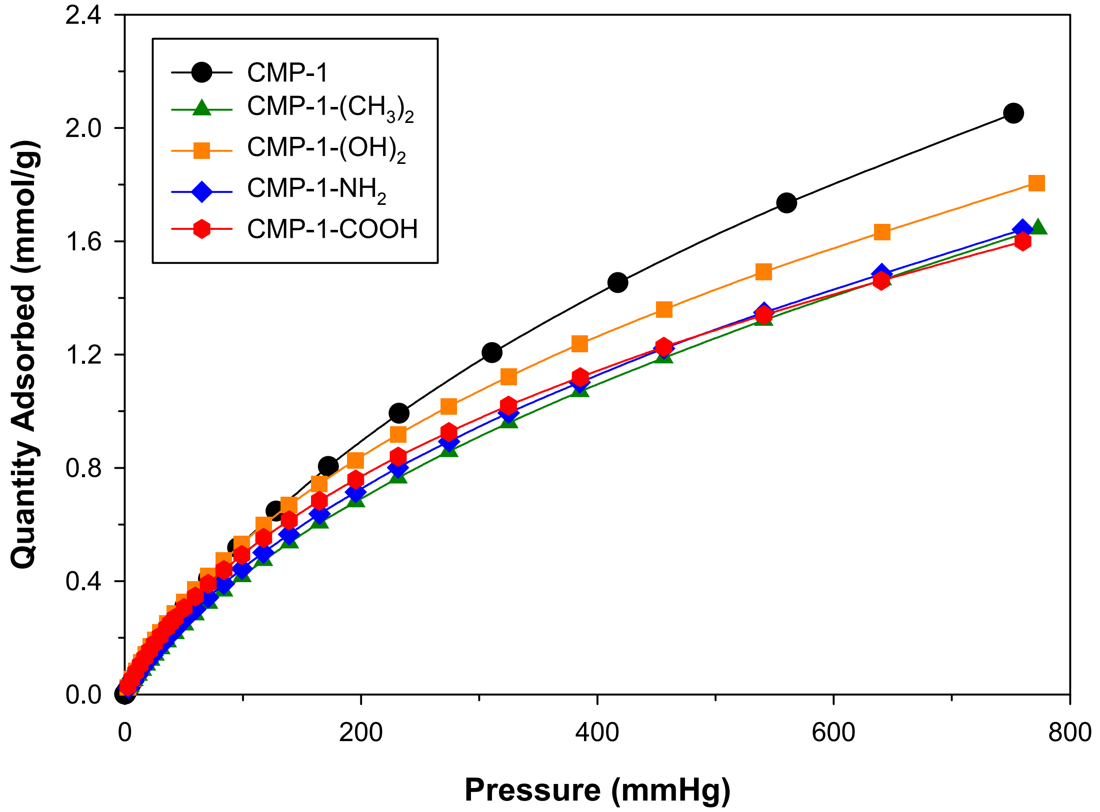
S5. DFT pore size distributions for CMP networks calculated from the CO_2 adsorption isotherm at 273 K

DFT cumulative pore volumes



S6. DFT cumulative pore volume for network CMP-1-NH_2 calculated from the N_2 adsorption isotherm (black) and CO_2 adsorption isotherm (red)

CO_2 uptake at 273 K



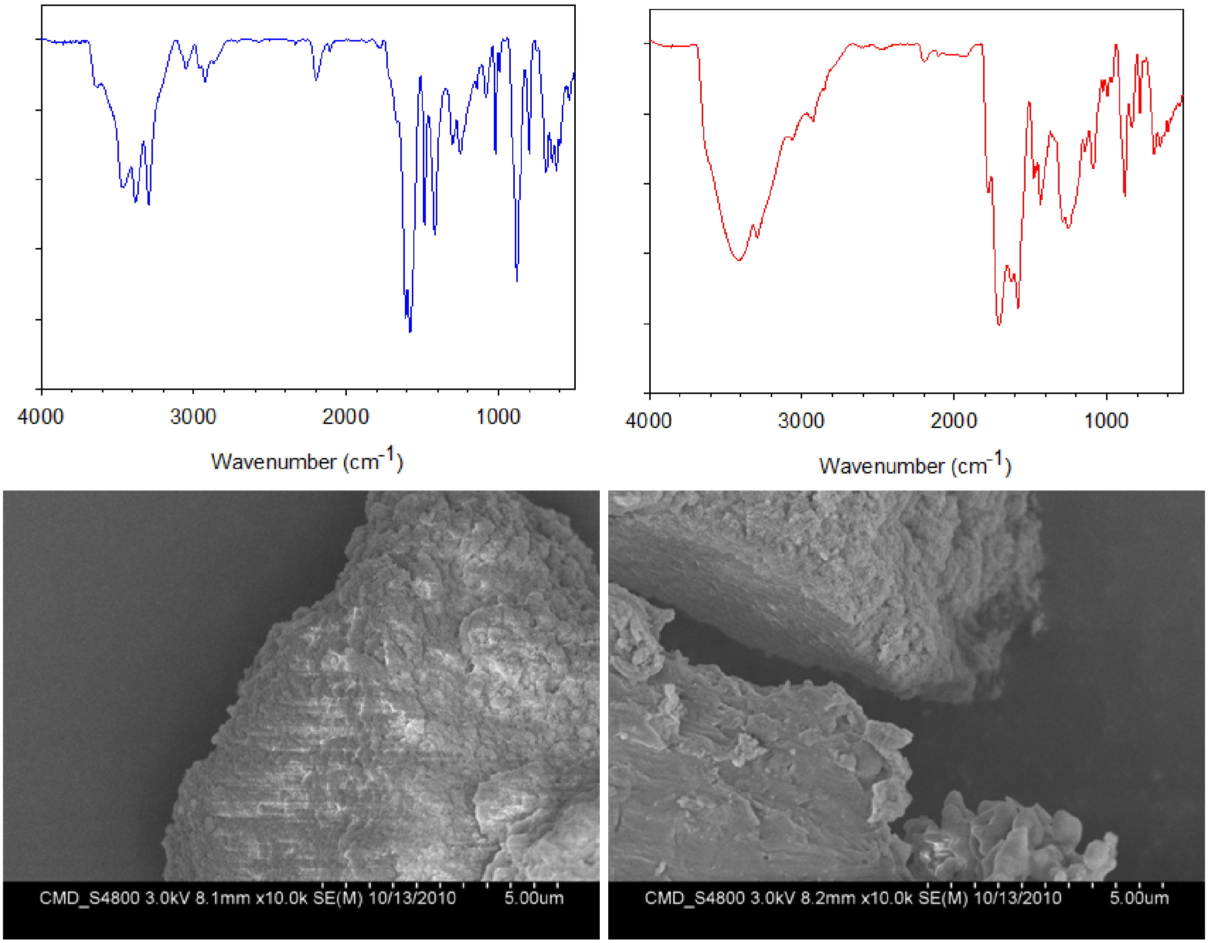
S7. CO_2 adsorption isotherms at 273 K.

Infrared spectroscopy

IR spectra were collectetd on a Bruker Tensor 27 using KBr discs.

Scanning Electron Microscopy

High resolution imaging of the polymer morphology was achieved using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM). The dry samples were prepared on 15 mm Hitachi M4 aluminium stubs using either silver dag or an adhesive high purity carbon tab. The samples were then coated with a 2 nm layer of gold using an Emitech K550X automated sputter coater. The FE-SEM measurement scale bar was calibrated using certified SIRA calibration standards. Imaging was conducted at a working distance of 8 mm and a working voltage of 3 kV using a mix of upper and lower secondary electron detectors.



S8. IR and SEM of CMP-1-NH2 (left) and CMP-1-COOH (right)

References

1. J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper, *J. Am. Chem. Soc.*, 2008, **130**, 7710-7720.

2. R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Macromolecules*, 2010, **43**, 8524-8530.

3. J. R. Holst, E. Stöckel, D. J. Adams, A. I. Cooper, *Macromolecules* 2010, **43**, 8531-8538