Electronic Supplementary Material (ESI) for Energy & Environmental Science

Microporous Organic Polymers for Carbon Dioxide Capture

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Contents

Synthetic Procedures

*Synthesis of Network **B**:*

Tetrakis(4-aminophenyl)methane (200 mg, 0.53 mmol) and terephthaldehyde (120 mg, 0.90 mmol) were added to a glass vial with a volume of 30 mL. Anhydrous dioxane (10 mL) and acetic anhydride (3 M, 2 mL) were added and the vial closed with a screw cap. The vial was then placed into an oven and heated at a rate of 1 °C/min to 120 °C for 72 hrs. After cooling the vial was removed and filled with anhydrous THF and left for 2 hrs. The THF was exchanged 3 times the final time overnight after which the gel like material was filtered on a Büchner funnel and dried in vacuo overnight yielding 213 mg (58 % yield) of yellow solid. Elemental analysis expected from COF-300[1]: C, 80.37 %, H, 5.26 %, N, 9.14 %. Found: C, 79.68 %, H, 5.00 %, N, 9.18 %

*Synthesis of Network **E**:*

To a mixture of tetraphenylmethane (3.20 g, 10 mmol) and formaldehyde dimethyl acetal (7.08 mL, 80 mmol) was added 1,2-dichloroethane (20 mL). Iron(III) chloride (12.98 g, 80 mmol) was added and the reaction heated to 80 °C under nitrogen overnight. After cooling the solid product was filtered off and washed with methanol until the filtrate turned clear. The product was then Soxhlet extrated with methanol overnight after which the product was washed again with methanol and diethylether and dried in vacuo yielding 4.40 g (105 % yield) of brown powder. (The higher than expected yield maybe due to iron or water trapped within the pore structure). Elemental analysis expected: C, 93.51 %, H, 6.48 %. Found: C, 80.91 %, H, 5.26 %. Elemental analysis results differ from those calcuated and are similar to those found for similar networks.[2]

Nitrogen Isotherms

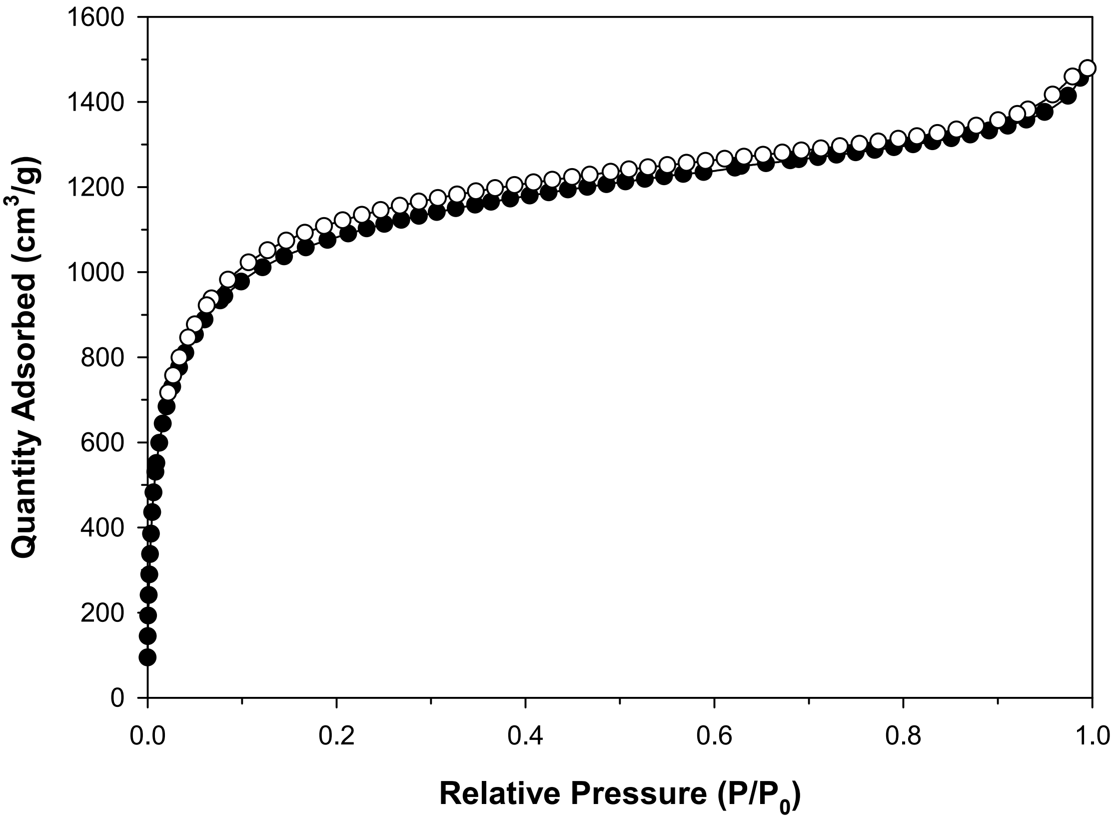

Figure S1 Nitrogen adsorption (closed symbols)/desorption (open symbols) isotherms measured at 77 K for Network **A**

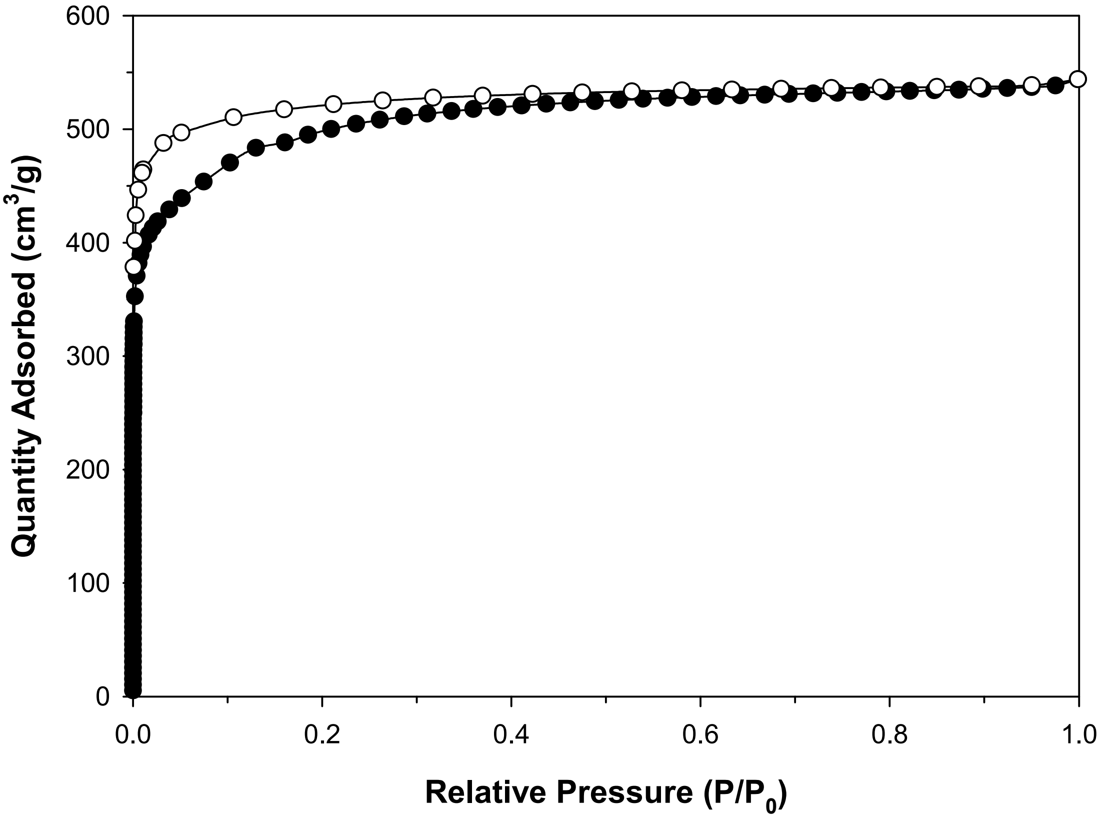

Figure S2 Nitrogen adsorption (closed symbols)/desorption (open symbols) isotherms measured at 77 K for Network **B**

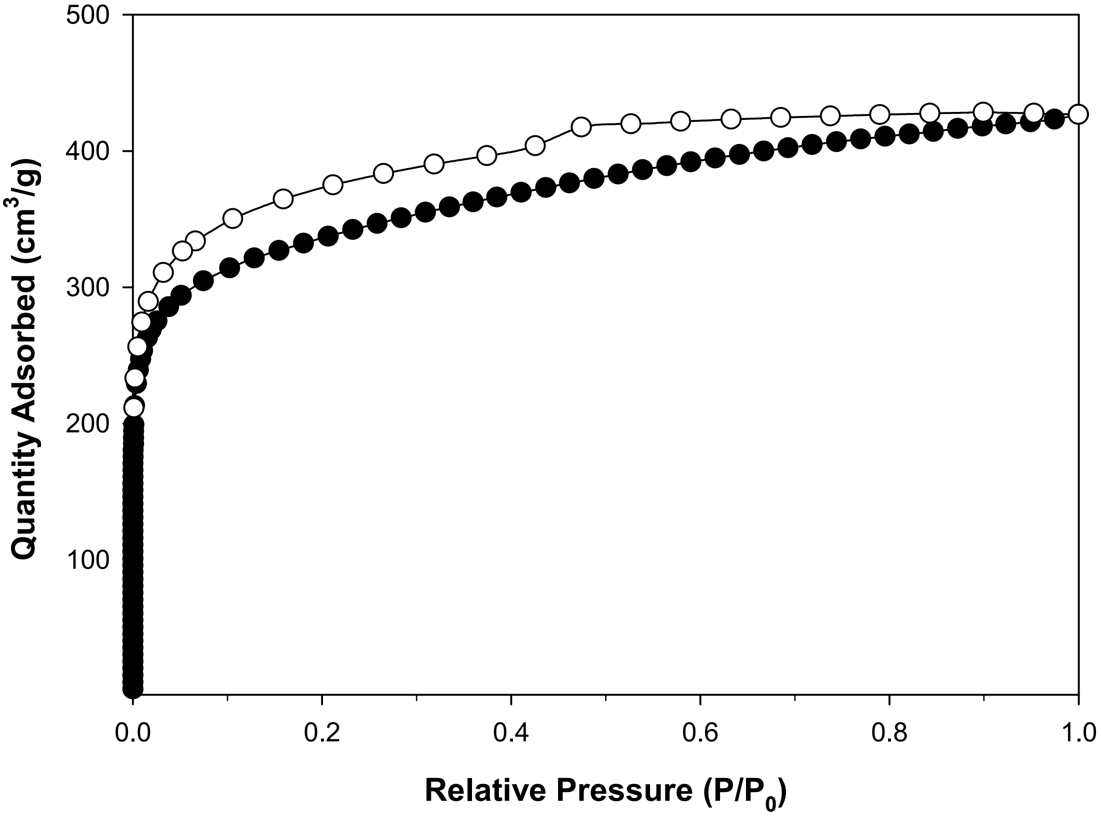

Figure S3 Nitrogen adsorption (closed symbols)/desorption (open symbols) isotherms measured at 77 K for Network **C**

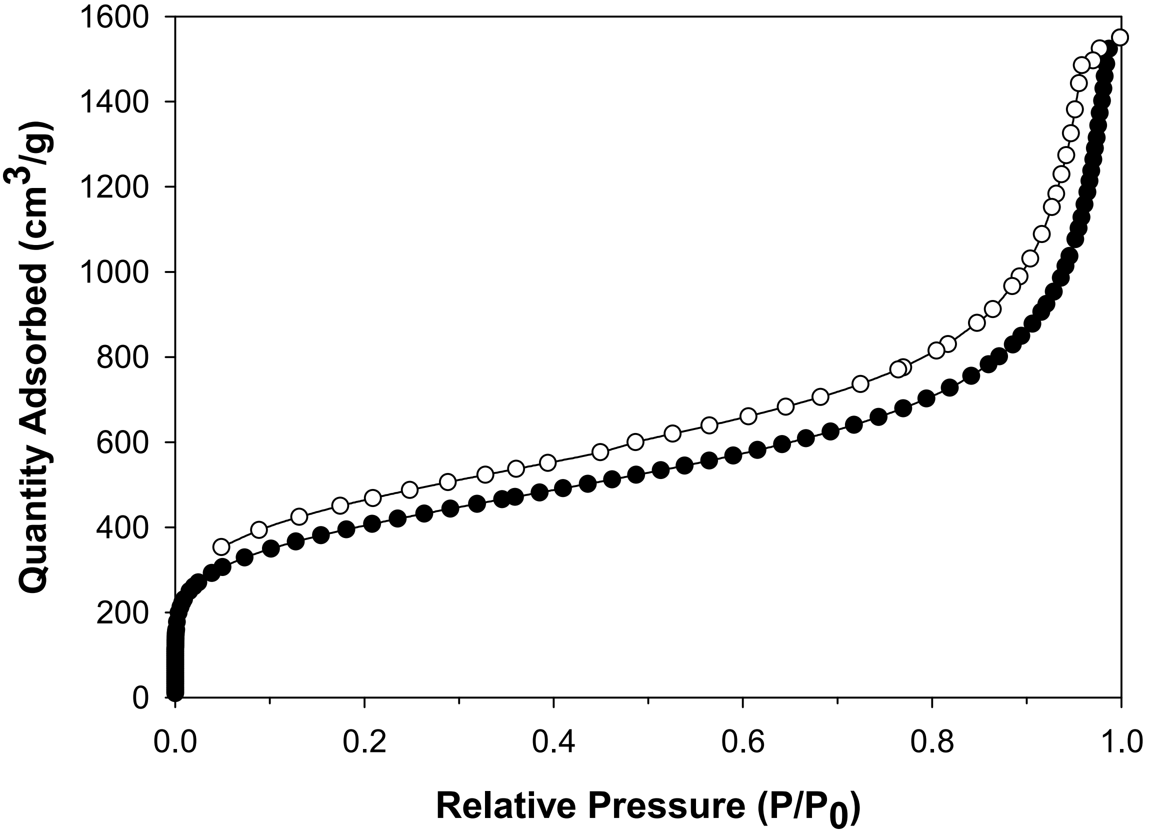

Figure S4 Nitrogen adsorption (closed symbols)/desorption (open symbols) isotherms measured at 77 K for Network **E**

CO_2 Isotherms

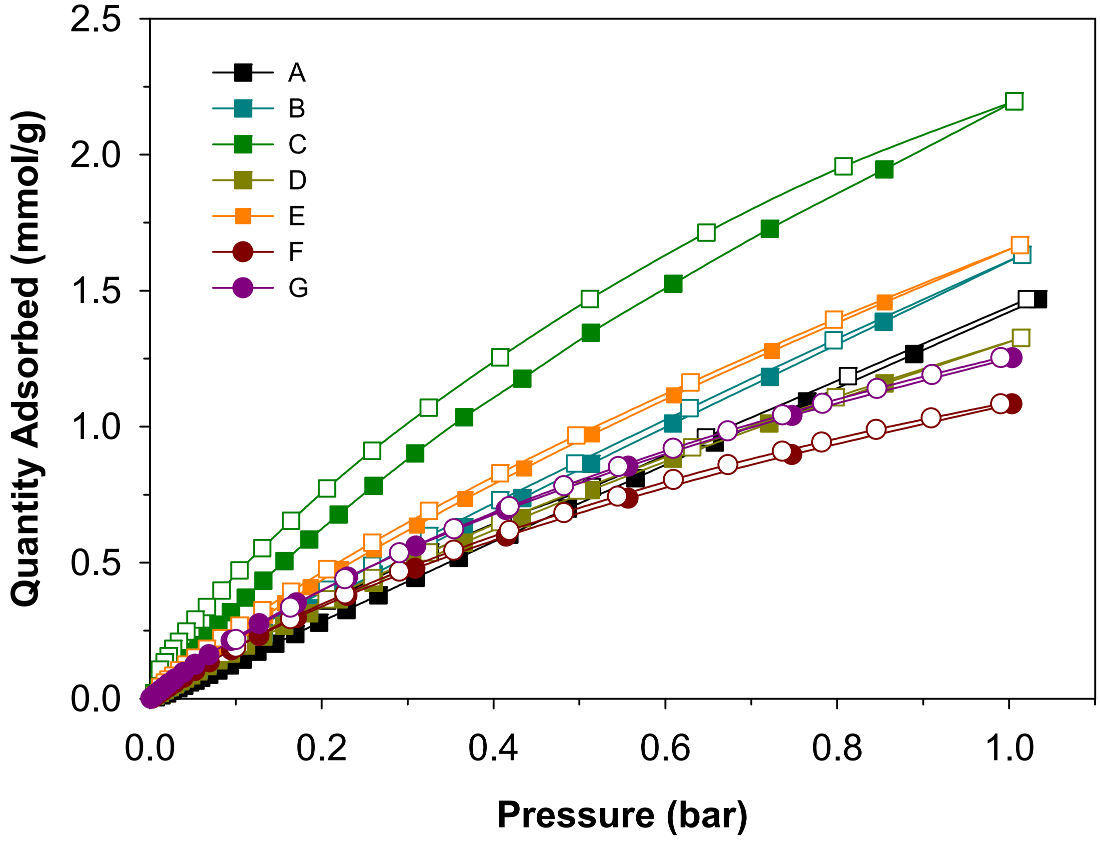

Figure S5 CO_2 adsorption (filled symbols) and desorption (open symbols) isotherms measured at 298 K for Networks **A – G.**

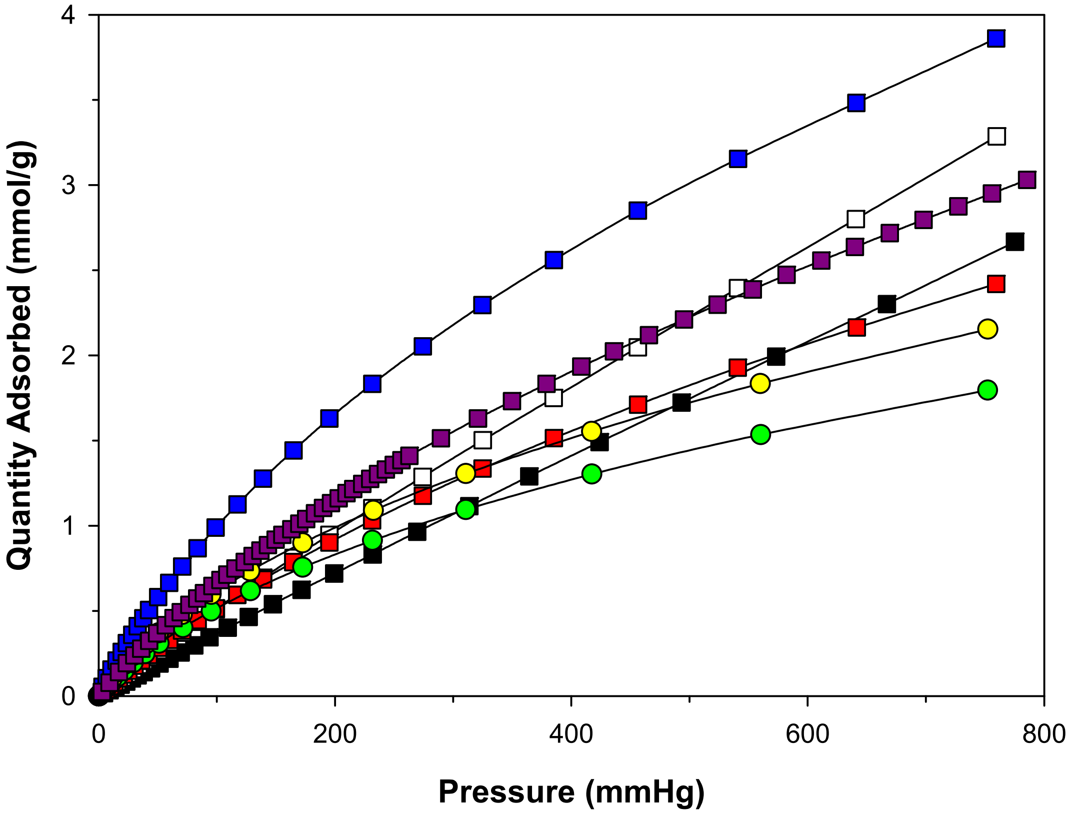

Figure S6 CO_2 isotherms measured at 273 K for Networks **A** (black), **B** (white), **C** (blue), **D** (red), **E** (purple), **F** (green) and **G** (yellow)

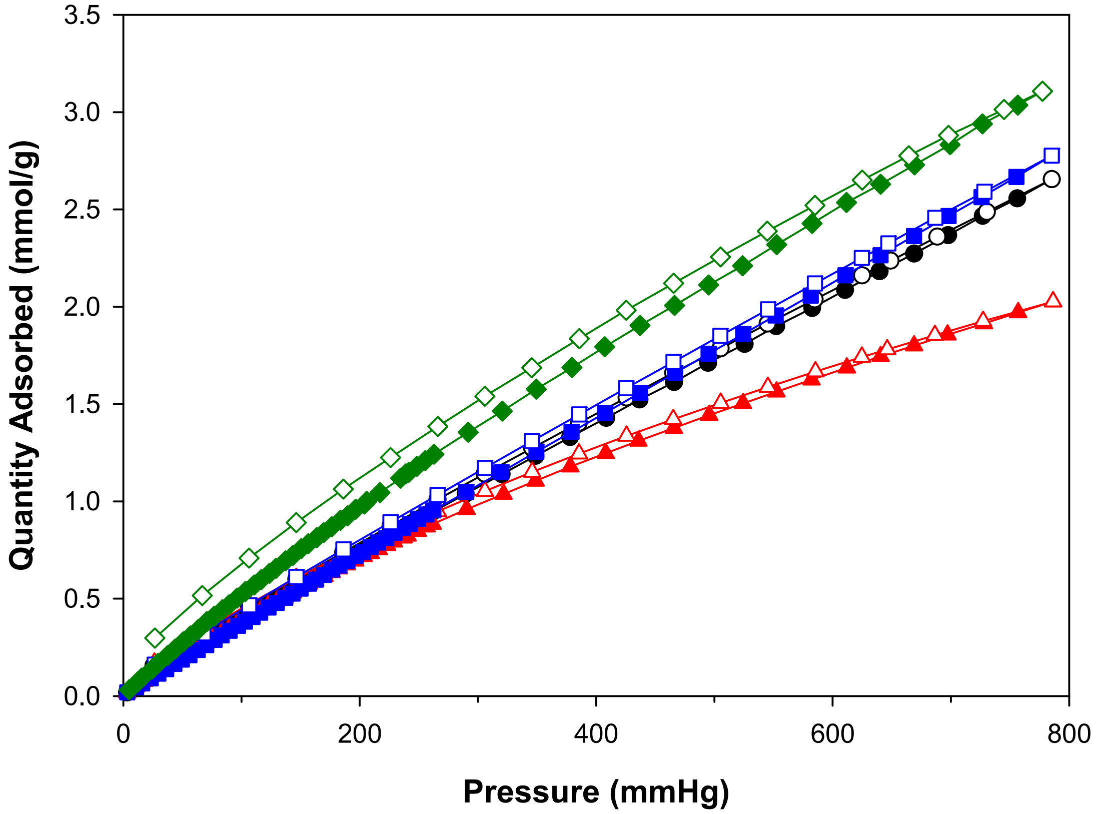

Figure S7 CO_2 isotherms measured at 273 K for Networks **1** (black), **2** (red), **3** (blue) and **4** (green) from as synthesised by Holst *et al.*[3]

Powder X-ray Diffraction

Powder X-ray diffraction data was collected on a PANalytical X'Pert pro multi-purpose diffractometer in transmission mode operating with a Cu anode at 40 kV 40 mA. Samples were mounted as a loose powder onto a transparent film in a 96 well HT plate. The PXRD pattern was collected in a 30 min scan with a step size of 0.0131 degrees 2θ and a scan time of 130 s/step over 2 – 50 deg 2θ. The incident X-ray beam was conditioned with 0.04 rad Soller slits and an anti-scatter slit of ½ deg and focusing mirror with a 4 mm mask. The diffracted beam passed through 0.04 rad Soller slits before processing by the PIXcel detector operating in scanning mode.

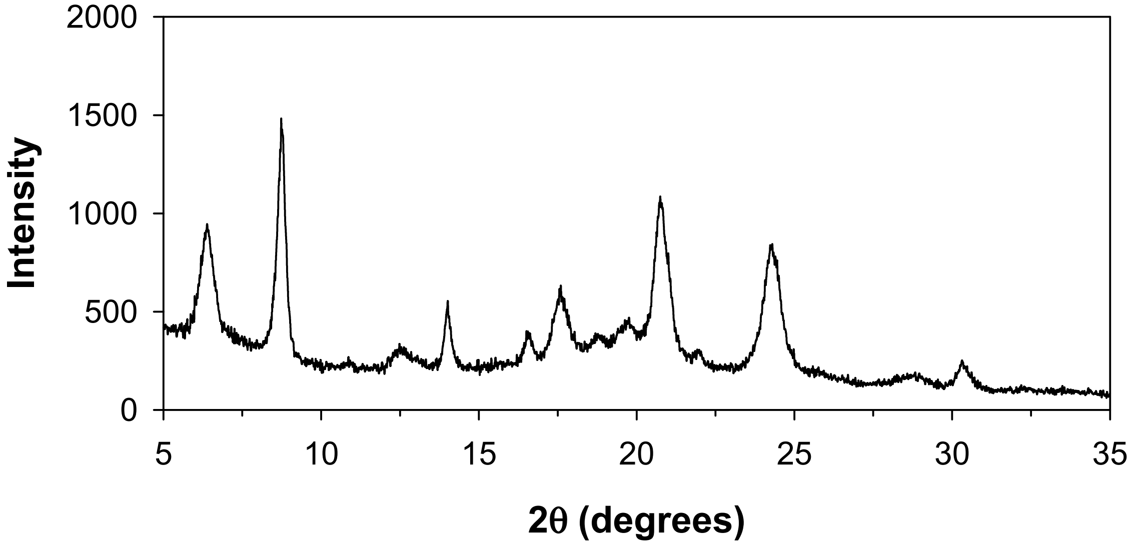

Figure S8 PXRD of as synthesised Network **E**

The PXRD of network **E** shows similar peak positions to that of the previously reported COF-300[1] although some peak heights are different to those reported possibly due to differences in particle morphology.

BET plots

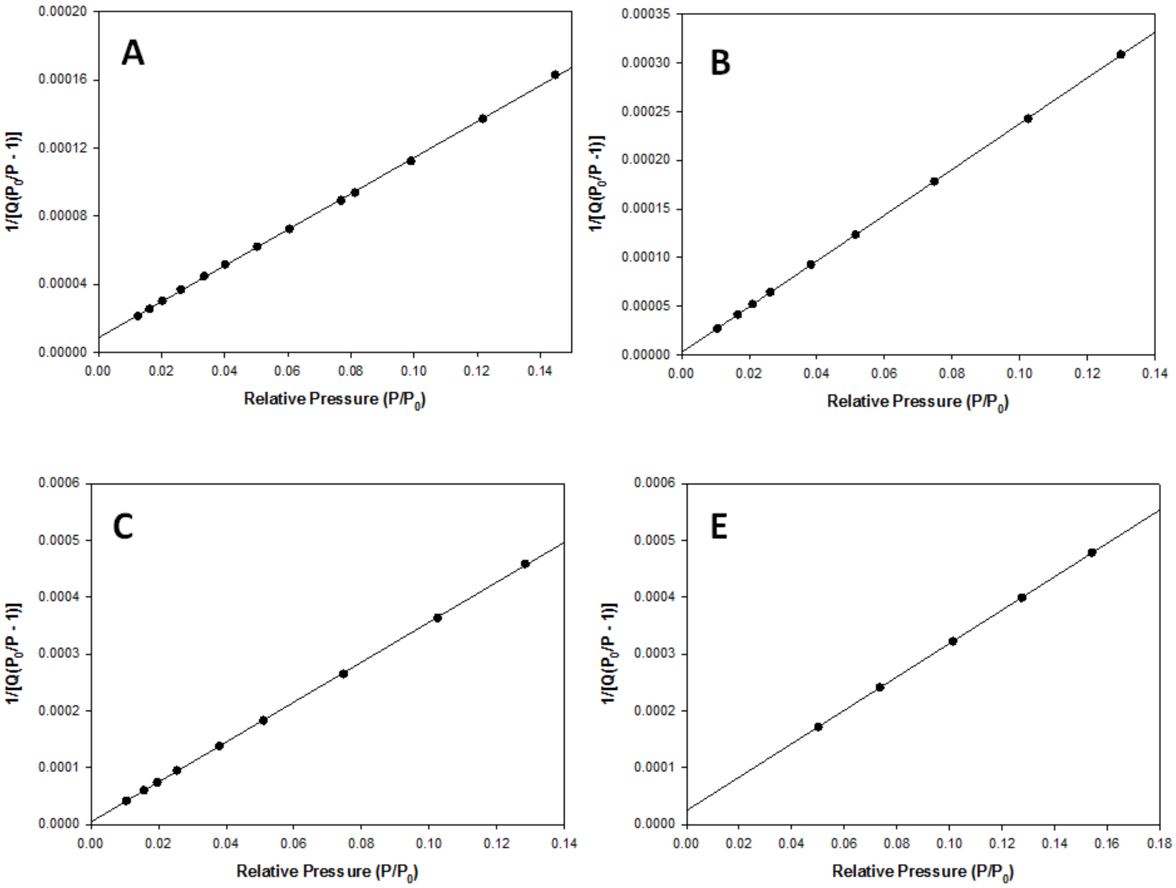

Figure S9 BET plots for Networks **A**, **B**, **C** and **E**

Pore Size Distributions

NL-DFT pore sizes were calculated using the Micromeritcs Datamaster software version 4.03.01 using the nitrogen adsorption branch with the cylindrical pore model for pillared clay

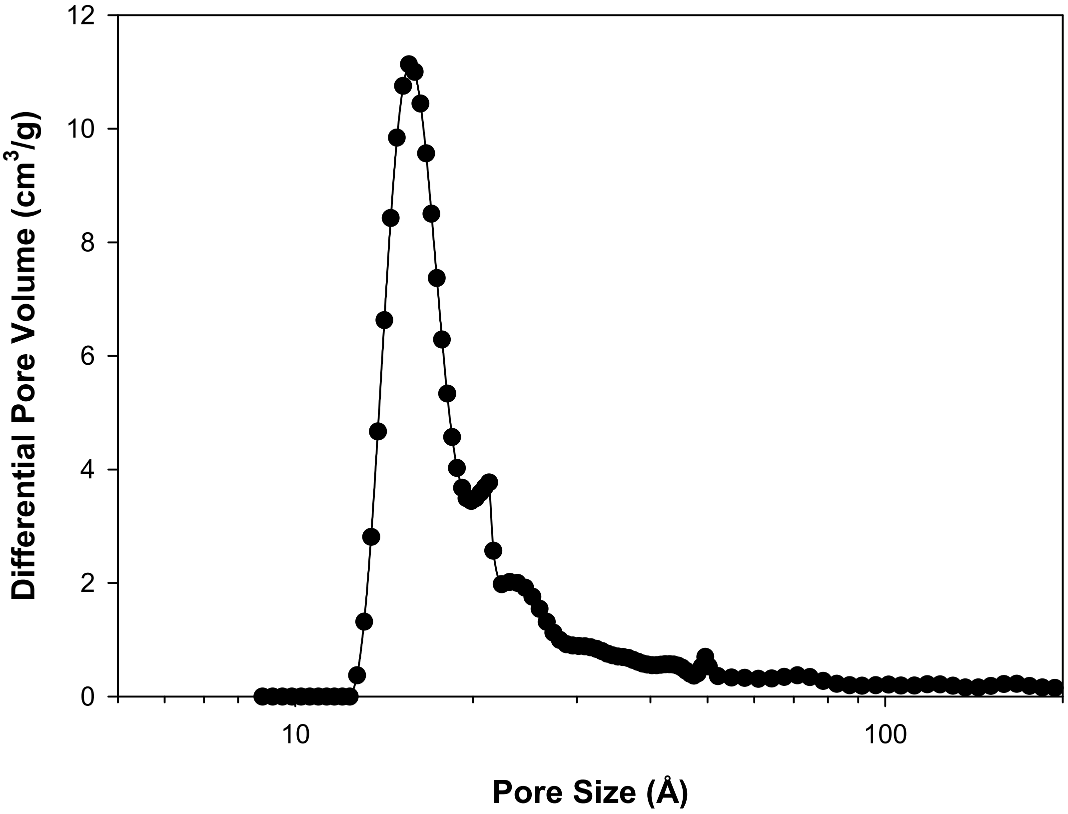

Figure S10 NL-DFT pore size distribution for Network **A**

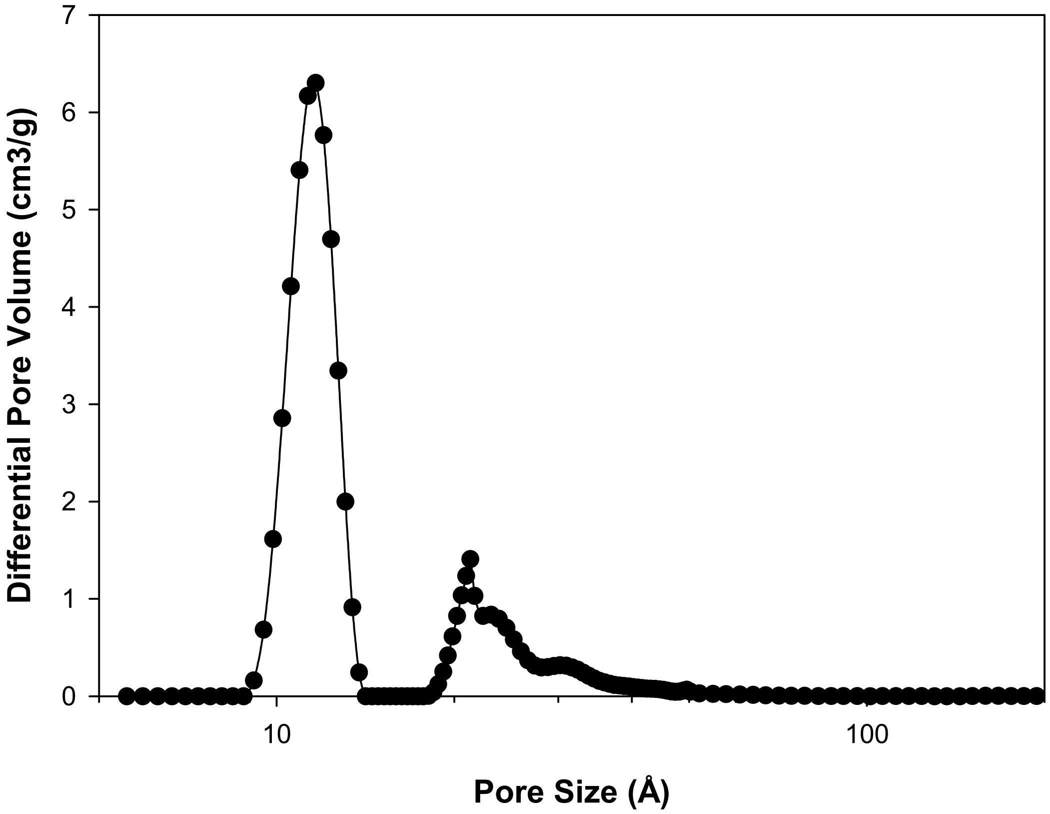

Figure S11 NL-DFT pore size distribution for Network **B**

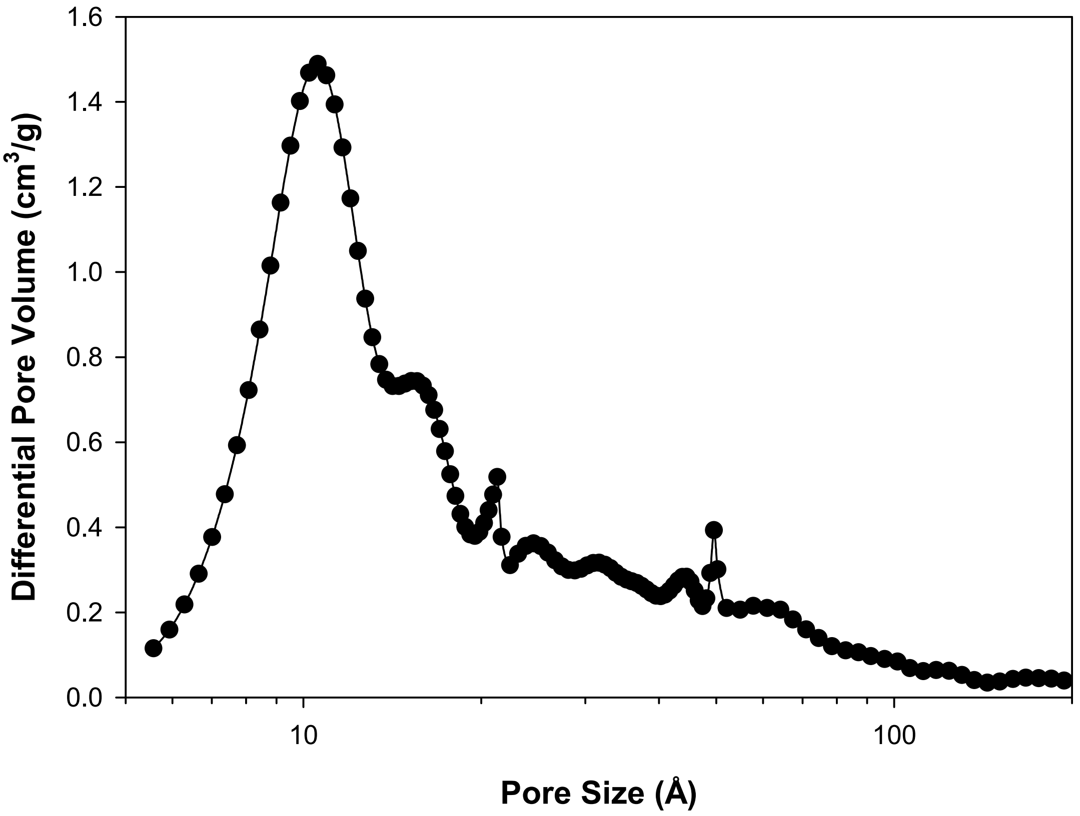

Figure S12 NL-DFT pore size distribution for Network **C**

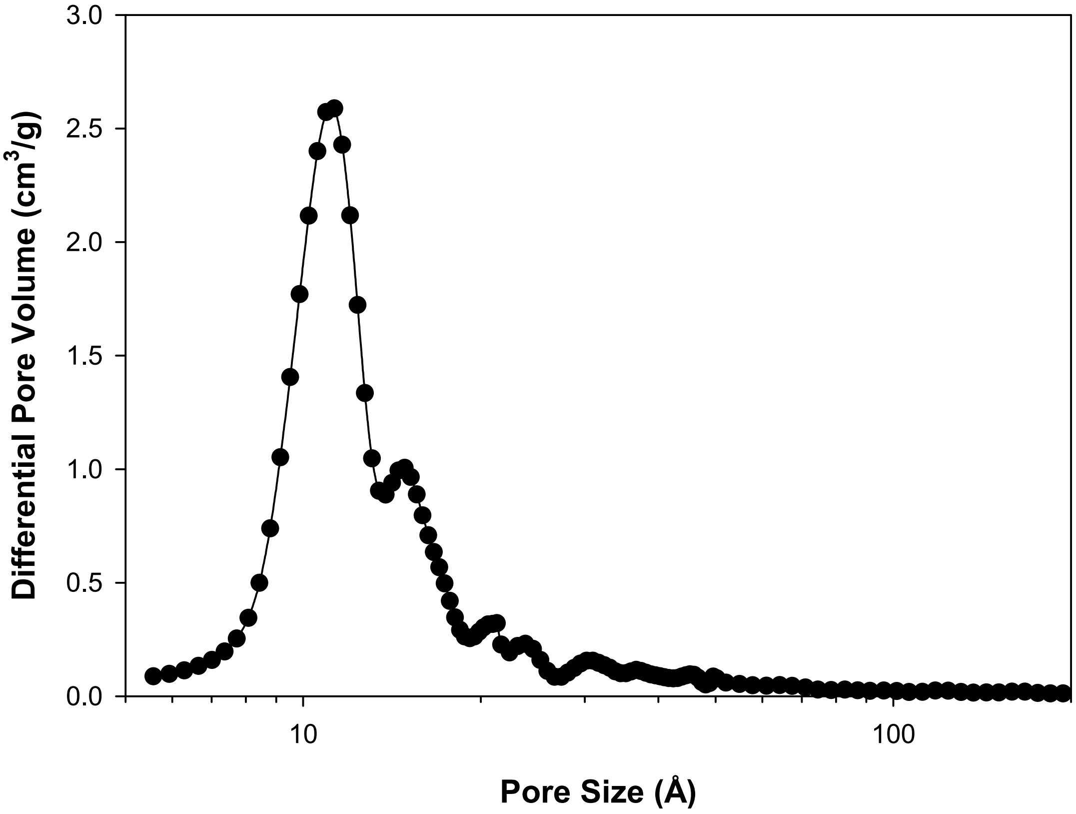

Figure S13 NL-DFT pore size distribution for Network **D**

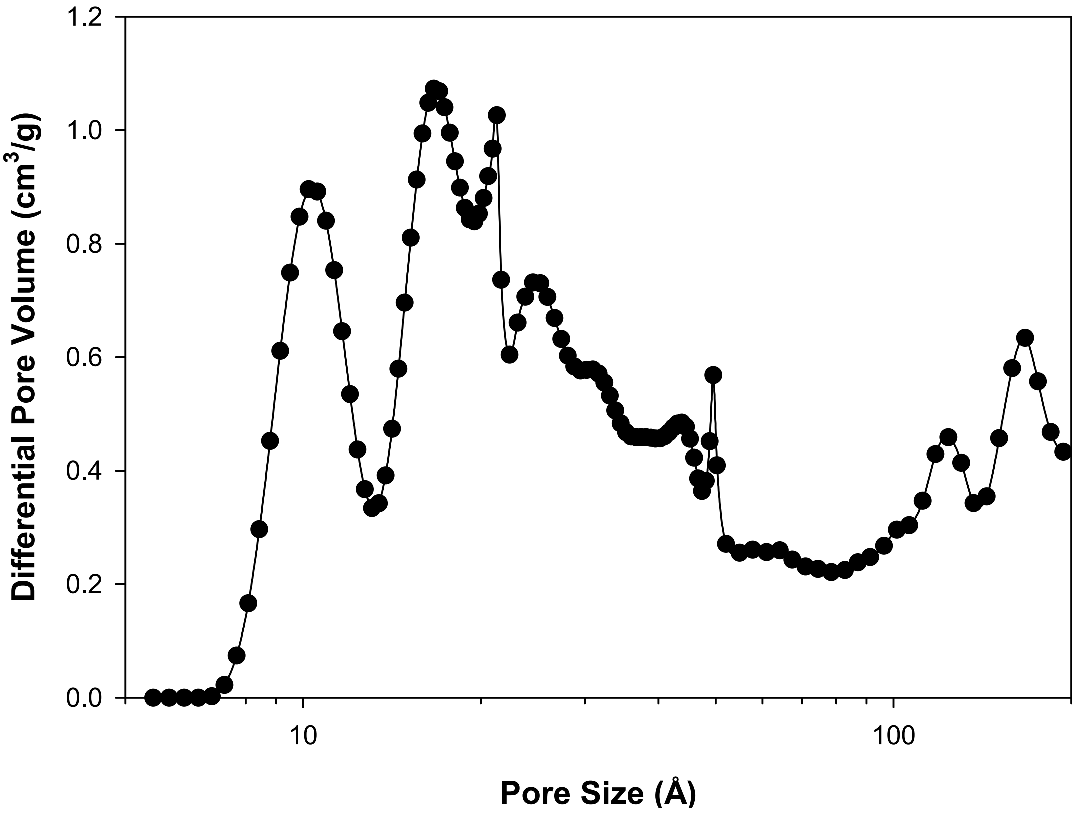

Figure S14 NL-DFT pore size distribution for Network **E**

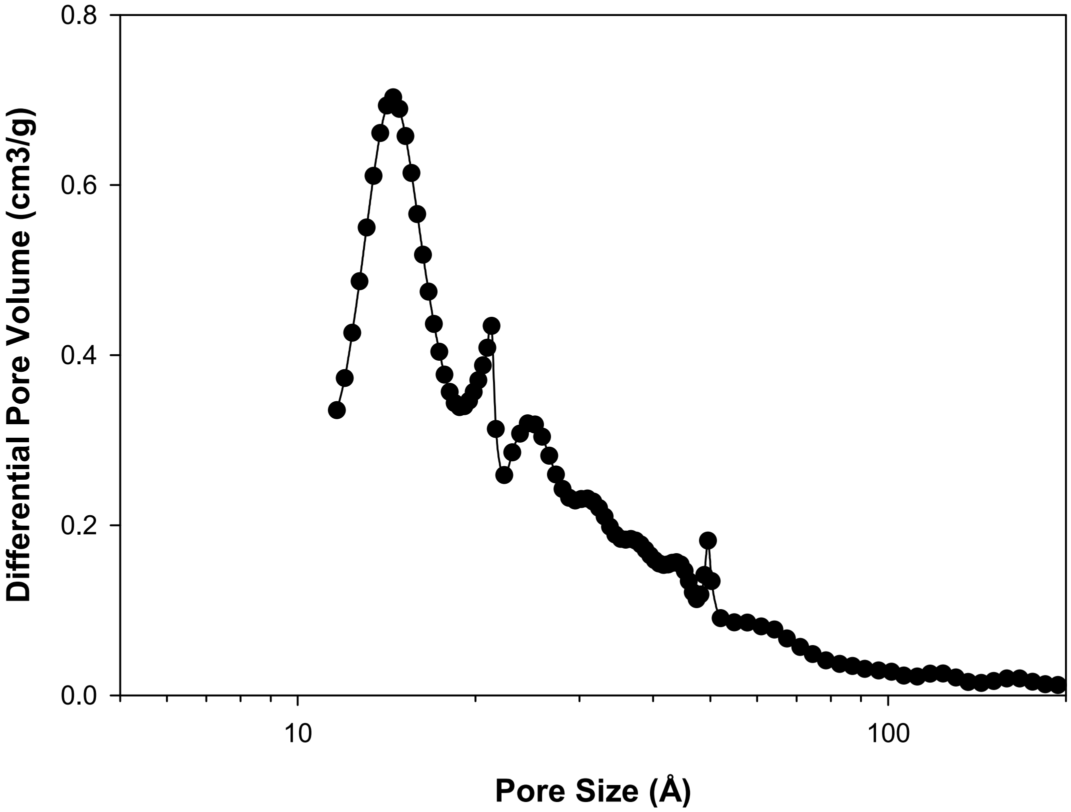

Figure S15 NL-DFT pore size distribution for Network **F**

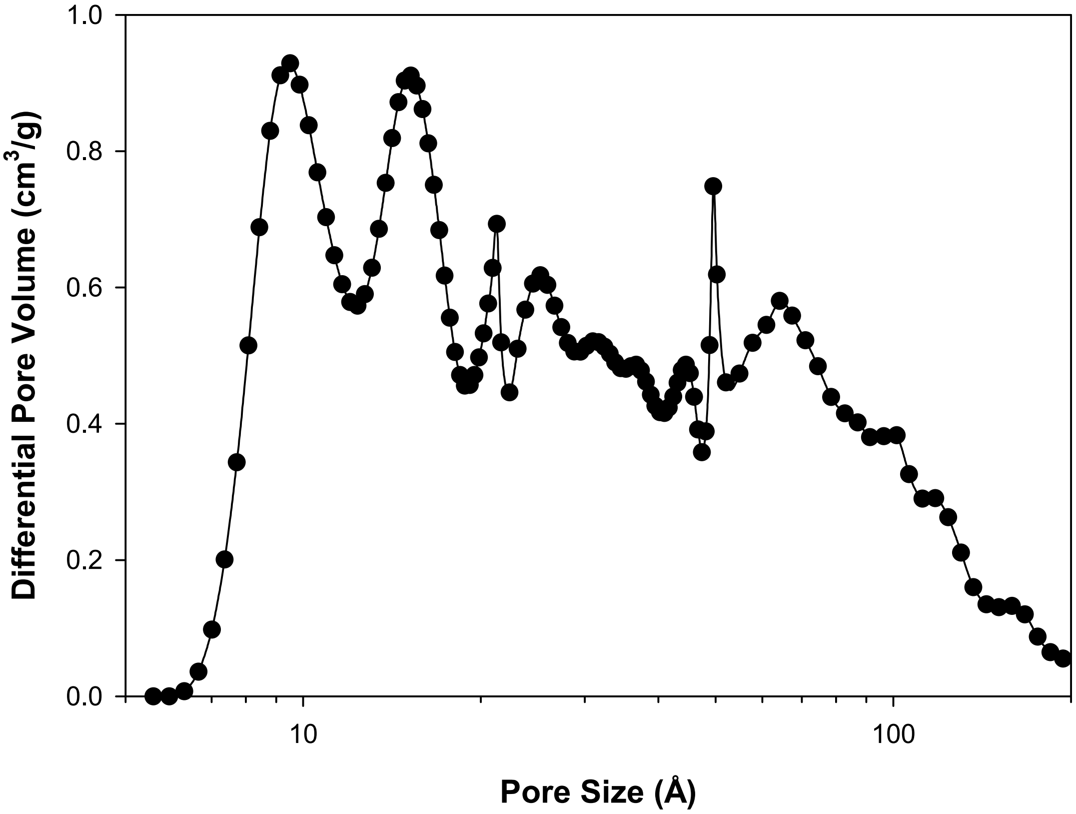

Figure S16 NL-DFT pore size distribution for Network **G**

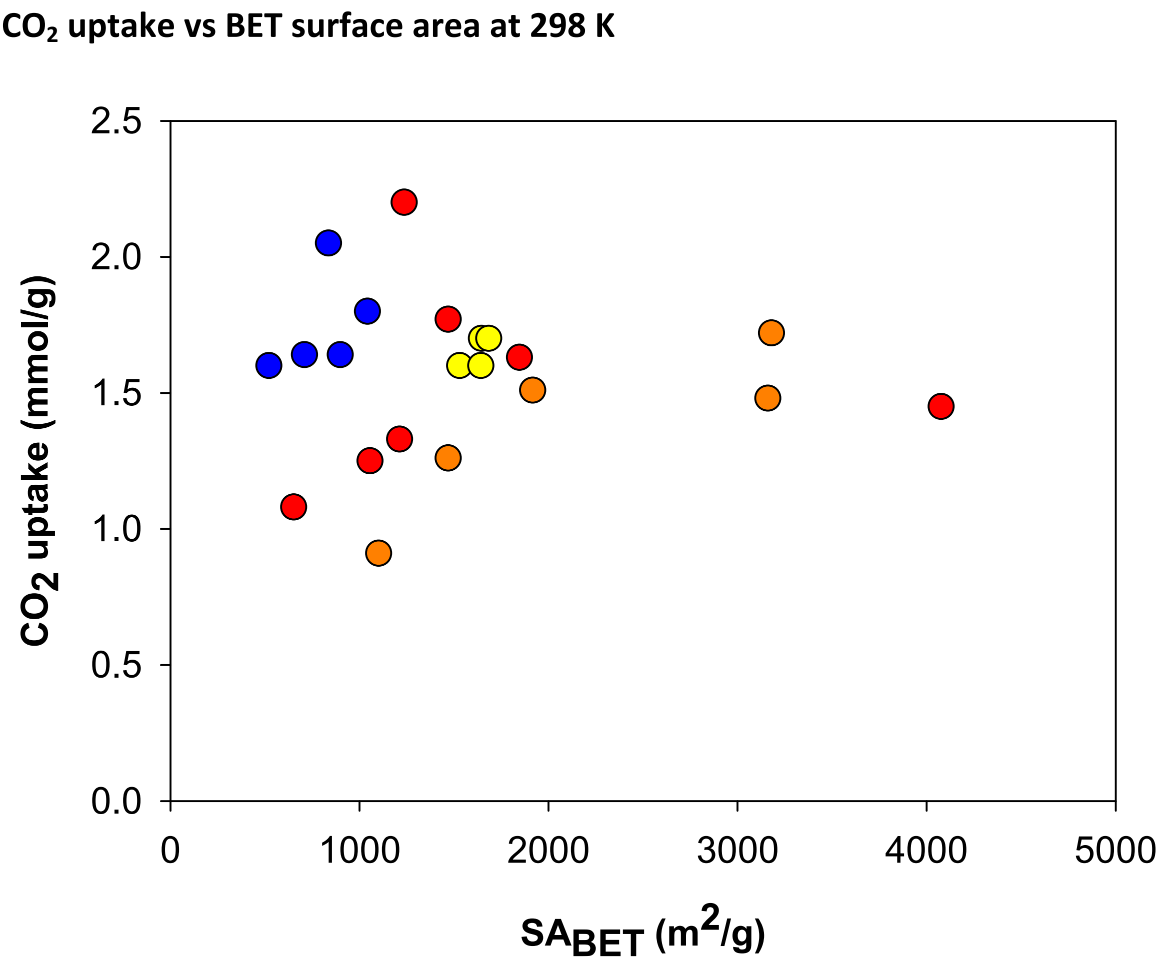

Figure S17 CO_2 uptake vs BET surface area at 298 K. Networks **A-G** (red), COFs (blue) DCX (yellow) and tetrahedral networks (orange).

Infra-Red Spectra

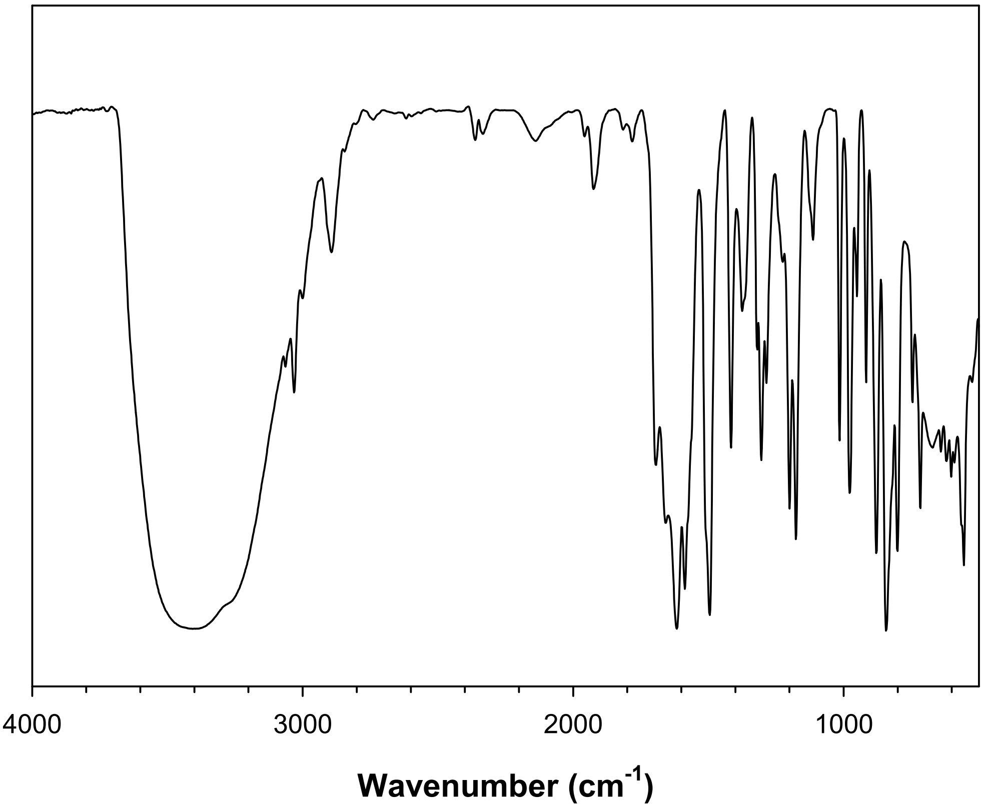

Figure S18 FT-IR spectrum of Network **B**

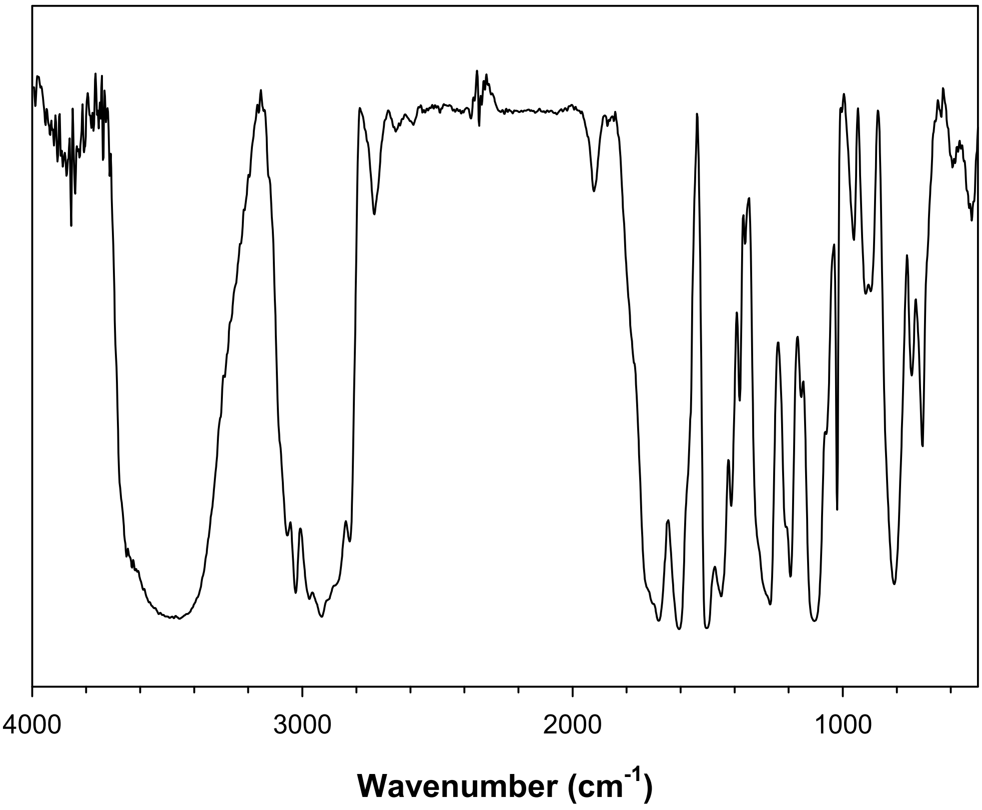

Figure S19 FT-IR spectrum of Network **E**

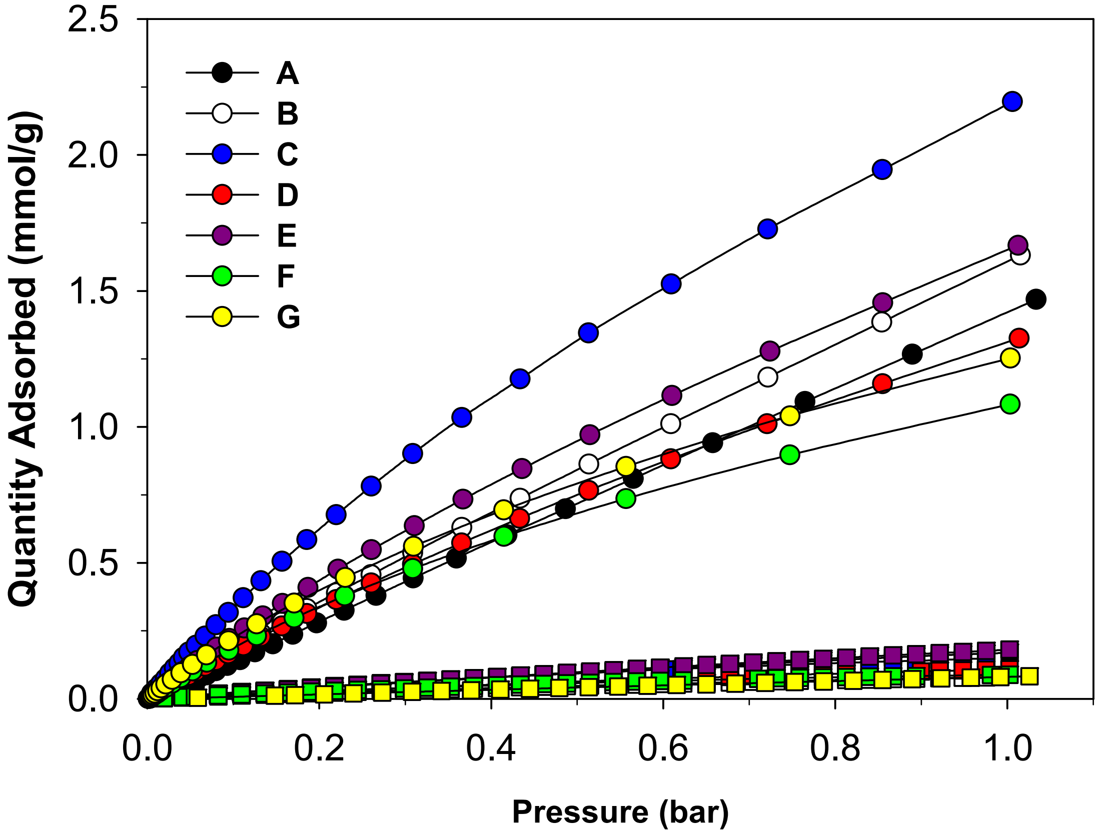

Figure S20 CO_2 (circles) and Nitrogen (squares) isotherms at 298 K for Networks **A-G**

Selectivities

Network	**CO_2/N_2 selectivity**
A	8.7
B	19.5
C	14.2
D	12.2
E	9.2
F	12.2
G	15.1

References

1. F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klock, M. O'Keeffe and O. M. Yaghi, *Journal of the American Chemical Society*, 2009, **131**, 4570-4571.
2. B. Li, R. Gong, W. Wang, X. Huang, W. Zhang, H. Li, C. Hu and B. Tan, *Macromolecules*, 2011, **44**, 2410-2414.
3. J. R. Holst, E. Stöckel, D. J. Adams and A. I. Cooper, *Macromolecules*, 2010, **43**, 8531-8538.