Electronic Supplementary Information

High Surface Area Amorphous Microporous Poly(aryleneethynylene) Networks using Tetrahedral Carbon- and Silicon-Centred Monomers

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Experimental Procedures

Chemicals. All chemicals were used as received unless stated otherwise. Tetraphenyl methane was received from Alfa Aesar (purity 96 %). Bis[(trifluoroacetoxy)iodo] benzene, carbon tetrachloride, 1,4-dibromobenzene, *n*-butyllithium (2.5M solution in hexane), silicon tetrachloride, bis(triphenylphosphine)palladium(II) dichloride, copper(I) Iodide, toluene, diisopropylamine, triethylamine, and 1,4-diethynylbenzene were received from Sigma-Aldrich. 1,3,5-triethynylbenzene was received from ABCR. Tetrakis(4-iodophenyl) methane was prepared by a literature procedure from tetraphenylmethane[1] with an average isolated yield of 60 % over several syntheses. Tetrakis(4-bromophenyl) silane was prepared in a 75 % isolated yield by a literature procedure via lithiation of dibromobenzene (not isolated) and subsequent reaction with tetrachlorosilane.[2]

Synthesis of E1 and E2 networks. All synthesis reactions were carried out in Radleys 6- or 12-place Carousel reactors using standard Schlenk techniques. All glassware was dried in an oven at approx. 100°C for 12 h prior to the reaction. Tetrakis(4-iodophenyl)methane (1.0 mmol) , 1,4-diethynylbenzene (3.0 mmol) or 1,3,5-triethynylbenzene (2.0mmol), $Pd(PPh_3)_2Cl_2$ (60 mg) and CuI (18 mg) were suspended in a mixture of anhydrous toluene (2.5 mL) and diisopropylamine (2.5 mL). After degassing the mixture was heated to 90 °C under N_2 for 24 h. After cooling to room temperature the polymer was washed with excess methanol and acetone and then Soxhlet extracted with methanol overnight. The porous material was dried in a vacuum oven for 24 hours at 60 ^{o}C. Final gravimetric yields were between 90 and 95 %.

Synthesis of E3 and E4 networks. All synthesis reactions were carried out in Radleys 6- or 12-place Carousel™ reactors using standard Schlenk techniques. All glassware was dried in an oven at approx. 100°C for 12hours prior to the reaction. Tetrakis(4-bromophenyl)silane (2.0 mmol), 1,4-diethynylbenzene (6.0 mmol) or 1,3,5-triethynylbenzene (4 mmol), $Pd(PPh_3)_2Cl_2$ (100 mg) and CuI (30 mg) were suspended in a mixture of anhydrous toluene (2.5 mL) and anhydrous triethylamine (2.5 mL). After degassing three times, the mixture was heated to 90 °C under N_2 for 24 h. After cooling to room temperature, the product was washed with THF, water, aqueous hydrochloric acid, water, ethanol and acetone. Following the Soxhlet extraction with THF, the product was dried in vacuo. Final gravimetric yields were between 75 and 80 %.

Gas Sorption Analysis. Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using either a Micromeritics ASAP 2420 or a Micromeritics ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 110 °C for 15 h under vacuum (10^{-5} bar) before analysis. Hydrogen isotherms were measured at 77.3 K up to 1.13 bar using a Micromeritics ASAP 2420 volumetric adsorption analyzer with the same degassing procedure.

Solid-State NMR. Solid-state NMR experiments were conducted at 9.4 T using a Bruker DSX-400 spectrometer equipped with a 4 mm $^1H/X/Y$ probe head and samples were spun under dry nitrogen in 4mm outer diameter zirconia rotors.

The ^1H-^{13}C cross-polarization (CP) MAS NMR spectra were acquired at 400.16 MHz for ^1H and 100.56 MHz for ^{13}C at MAS rates of 10.0 or 13.0 kHz. A ^1H $\pi/2$ pulse length was 3.0 μs and the recycle delay was 8.0 s. Two Phase Pulse Modulation (TPPM) decoupling was used during acquisition. The CP contact time was 2.0 ms with the Hartman–Hahn matching condition set for both spinning speeds using hexamethylbenzene (HMB). The ^{13}C chemical shifts are quoted in ppm with respect to TMS. Typically 1 to 2K of scans was acquired.

^1H-^{29}Si cross polarization (CP) MAS NMR spectra were acquired at 400.16 MHz for ^1H and 78.5 MHz for ^{29}Si at a MAS rate of 4.0 kHz. A ^1H $\pi/2$ pulse length of 3.1 μs and a recycle delay of 10 s with TPPM decoupling being used during acquisition. The CP contact time was 2.0 ms with the Hartmann–Hahn matching condition set using kaolinite. The ^{29}Si chemical shifts are quoted in ppm with respect to tetramethylsilane (TMS). All data was processed using Bruker Topspin 1.3 software.

Atomistic Simulations. Molecular models for the network fragments were generated using the Materials Studio Modeling 4.0 package (Accelrys Inc., San Diego, CA, 2005). The fragments were constructed by adding the repeating unit for each system in a stepwise manner. All models fully relaxed using the Discover molecular mechanics and dynamics simulation module with the COMPASS force field.[4,5]

SEM. SEM images were recorded using a Hitachi S4800 Type II FE-SEM at 3.0 kV. Samples were sputter-coated with gold prior to analysis.

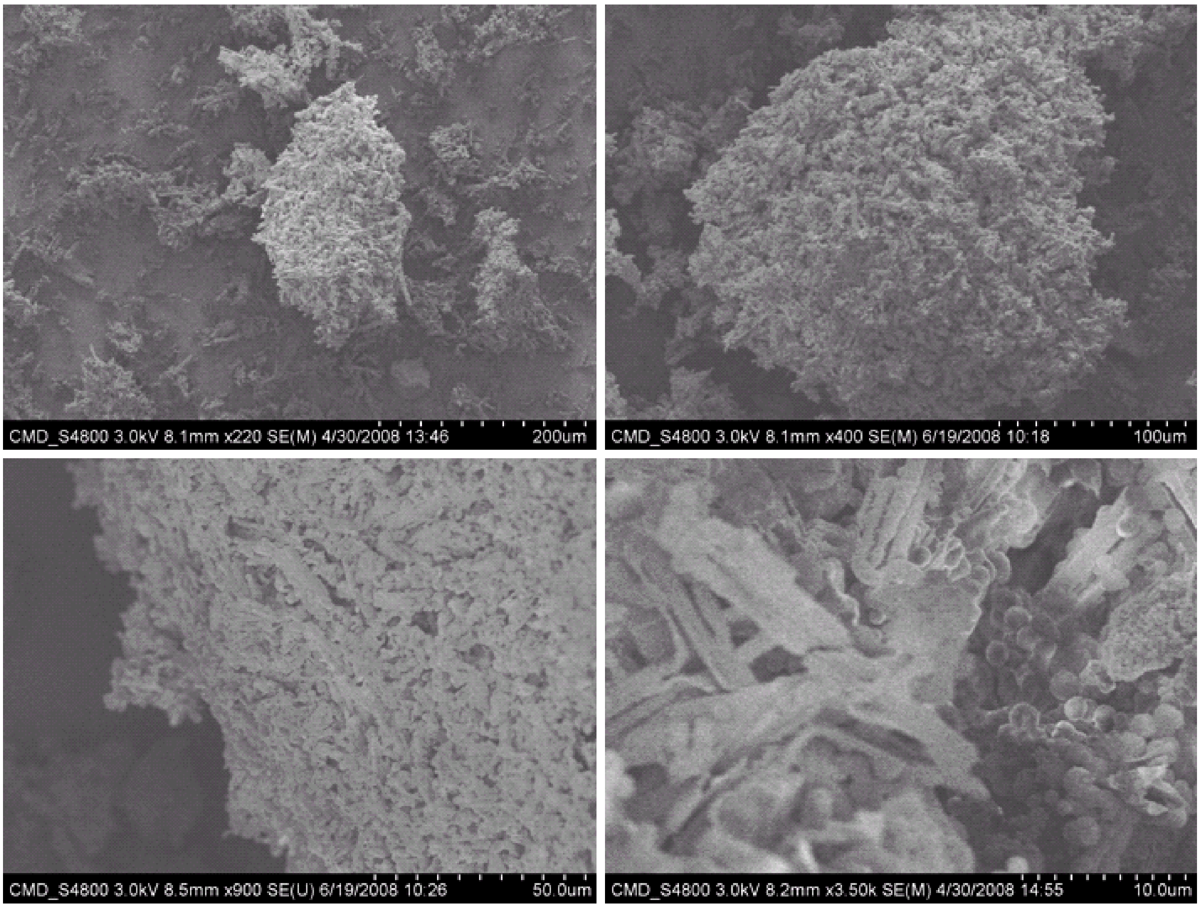

Figure S1. SEM images for network E1 showing 'sphere and tubule' morphology as observed for CMP networks (see ref. 9, main text), possibly suggesting reaction induced liquid-liquid phase separation followed by further polymerisation in the monomer-rich phase.

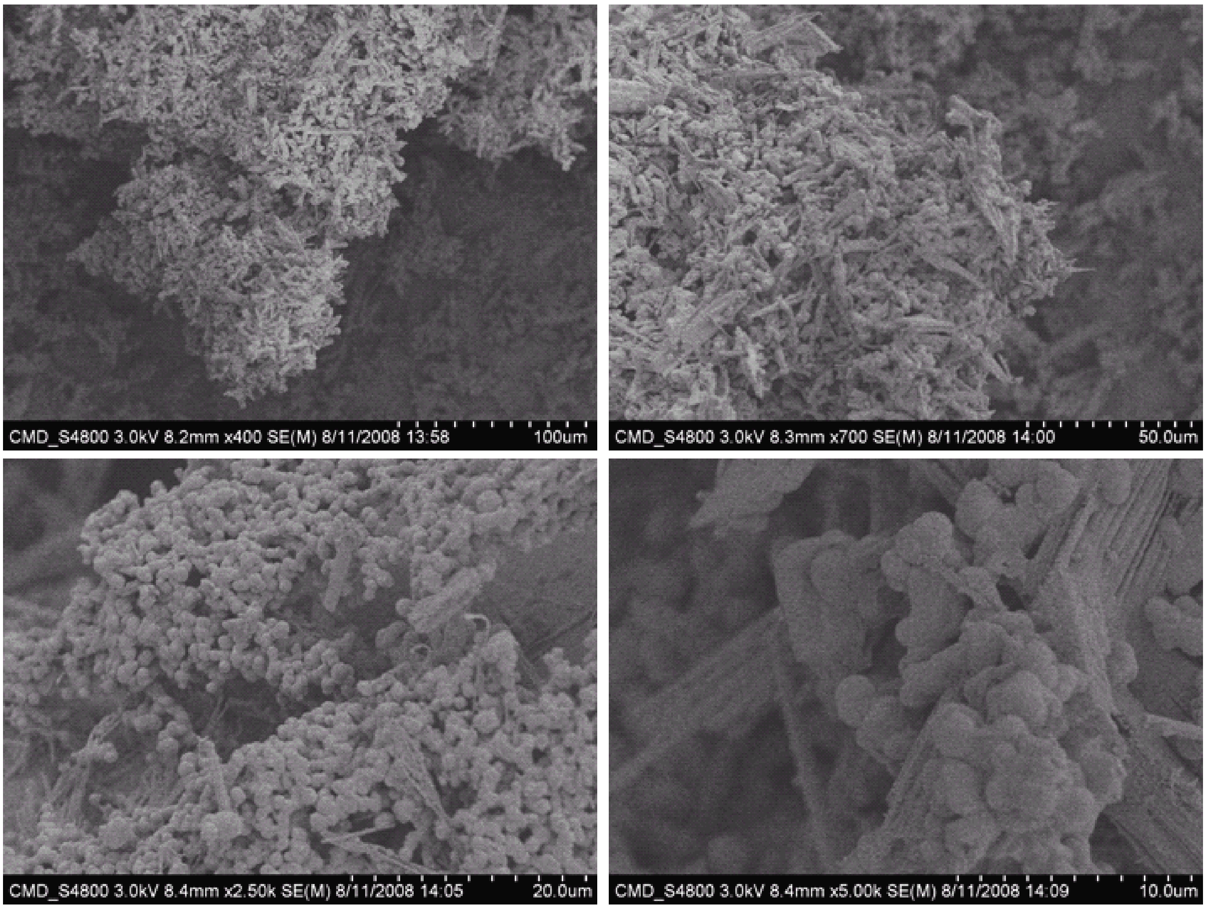

Figure S2. SEM images for network E2; the morphology is similar to that for E1 (Fig. S1).

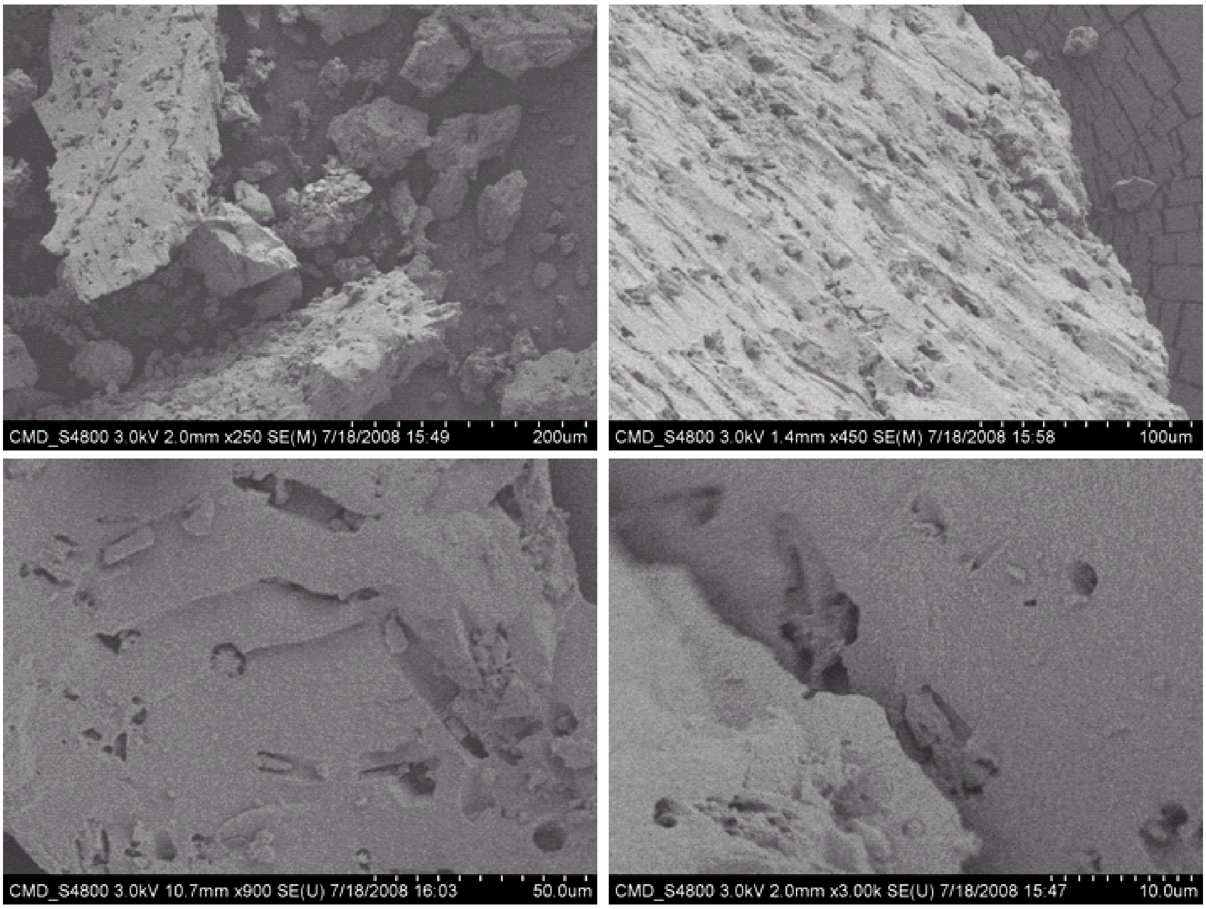

Figure S3. SEM images for network E3; much larger polymer fragments were observed than for E1, E2 with some evidence (see high magnification image) for texture relating to mesopore / small macropores between primary agglomerated particles.

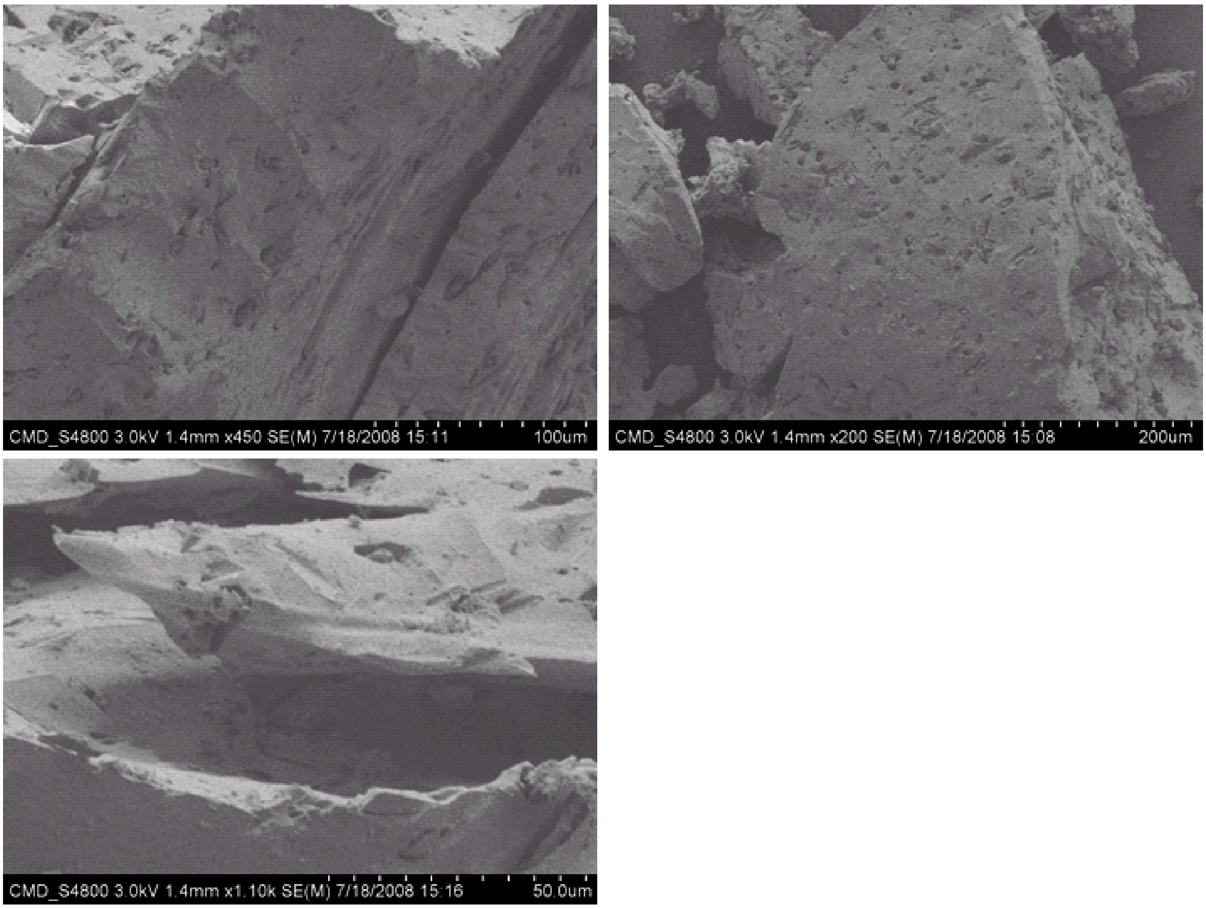

Figure S4. SEM images for network E4, very similar in morphology to E3 (see Fig. S3).

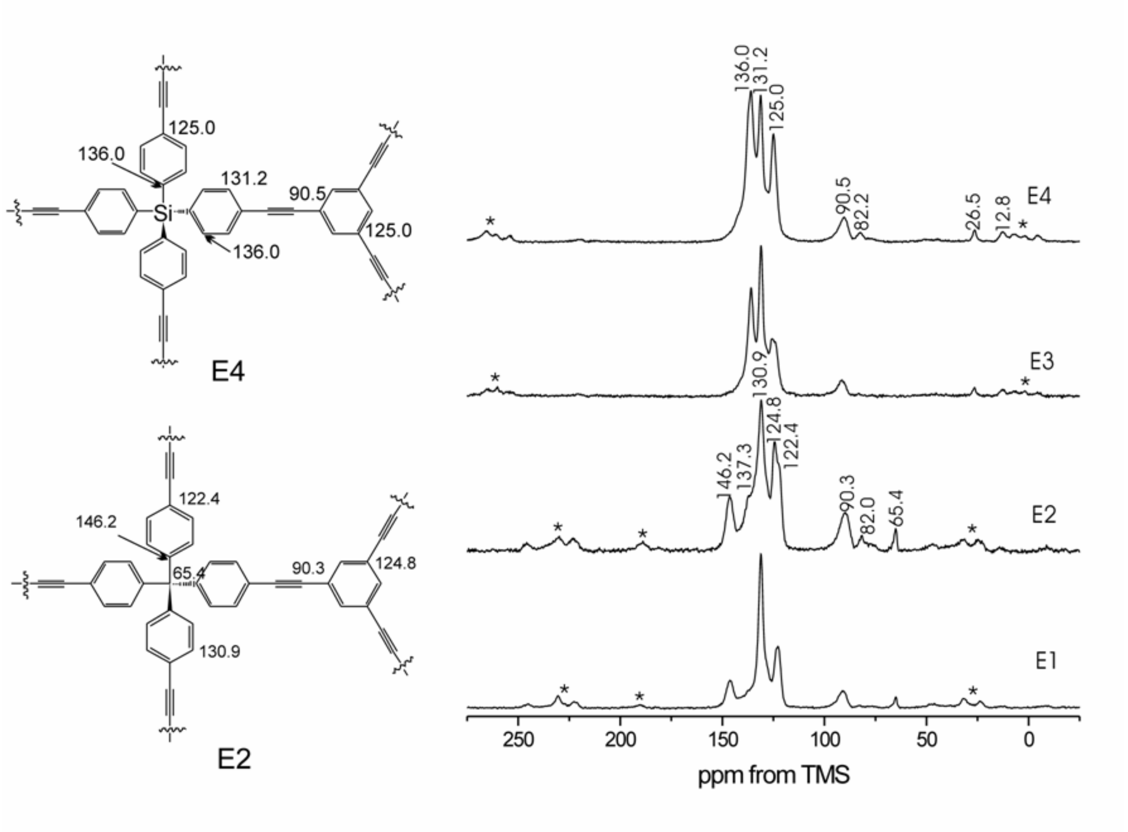

Figure S5. ^1H-^{13}C CP/MAS NMR spectra and peak assignments. The spectra for E1 and E2 were measured at an MAS rate of 10.0 kHz; the spectra of E3 and E4 were measured at an MAS rate of 13.0 kHz. Asterisks denote spinning sidebands.

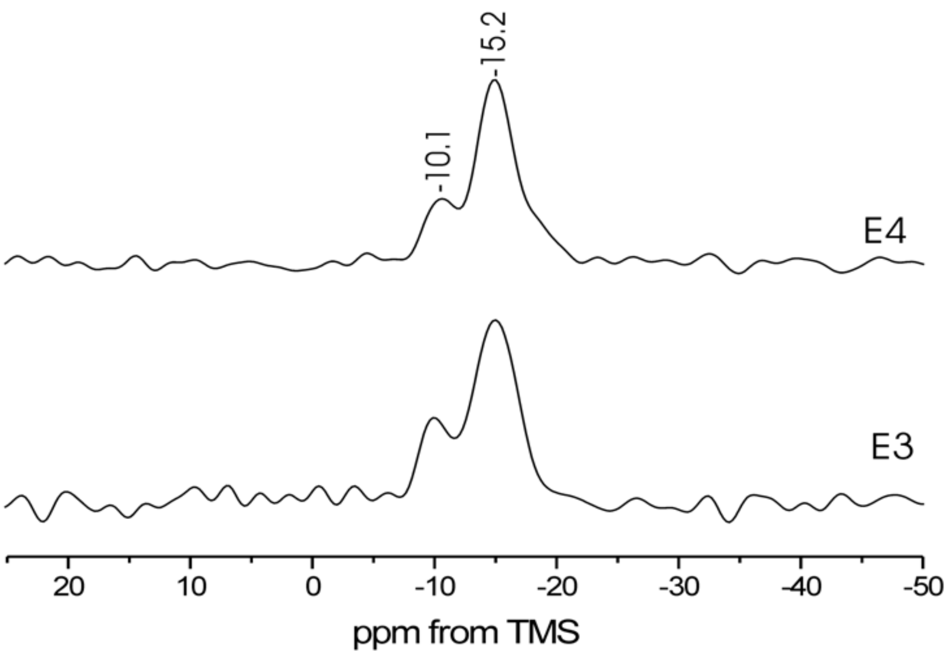

Figure S6. $^1H-^{29}Si$ MAS NMR spectra for networks E3 and E4.

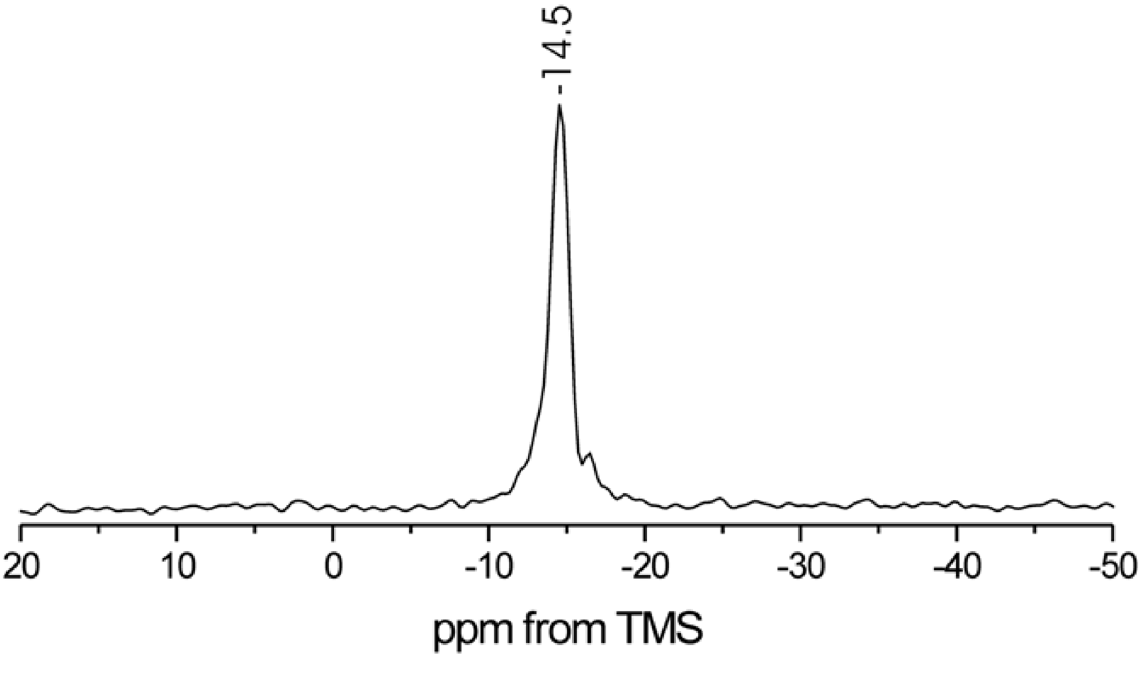

Figure S7. $^1H-^{29}Si$ CP/MAS NMR spectrum for $Si(C_6H_4Br)_4$ monomer – only one main peak is observed in contrast to polymer networks E3 and E4 (Fig. S6).

Nitrogen Adsorption / Desorption Isotherms

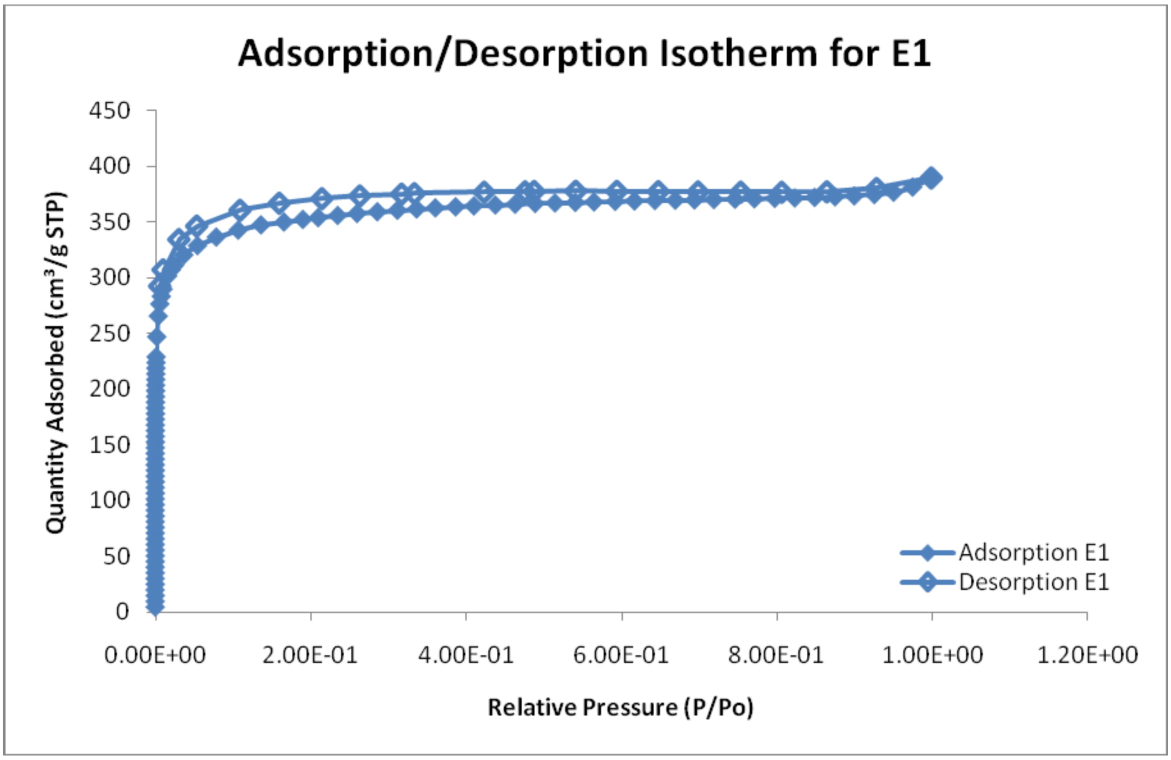

Figure S8. Nitrogen isotherm for network E1: the sorption plateau is more horizontal than observed for most microporous amorphous polymers and is reminscent of COF-1 (ref. 6, main text).

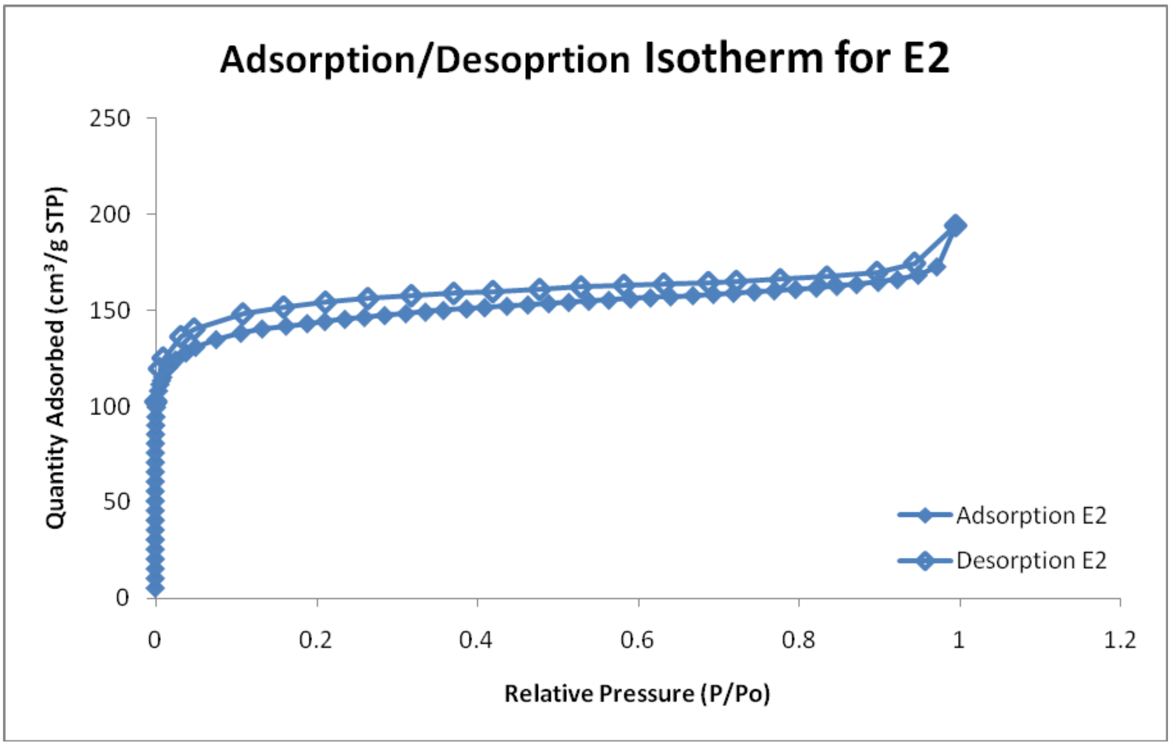

Figure S9. Nitrogen isotherm for network E2.

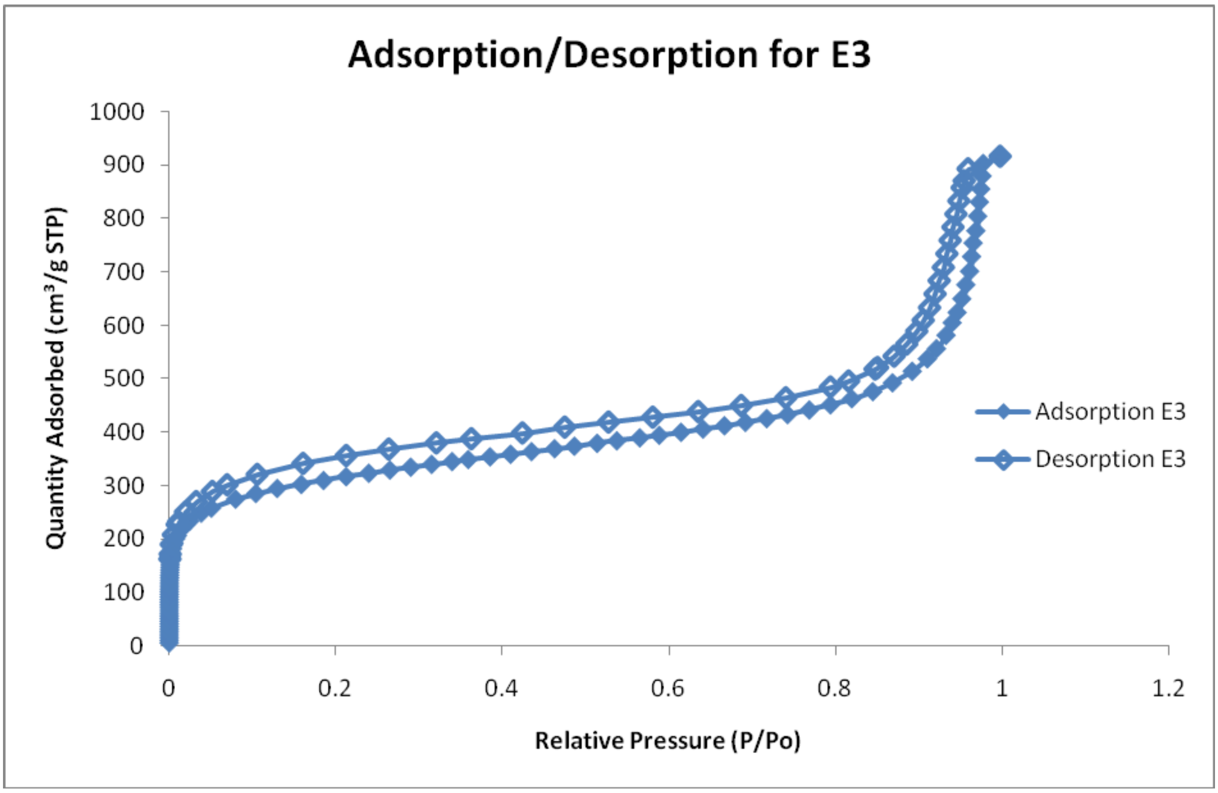

Figure S10. Nitrogen isotherm for network E3.

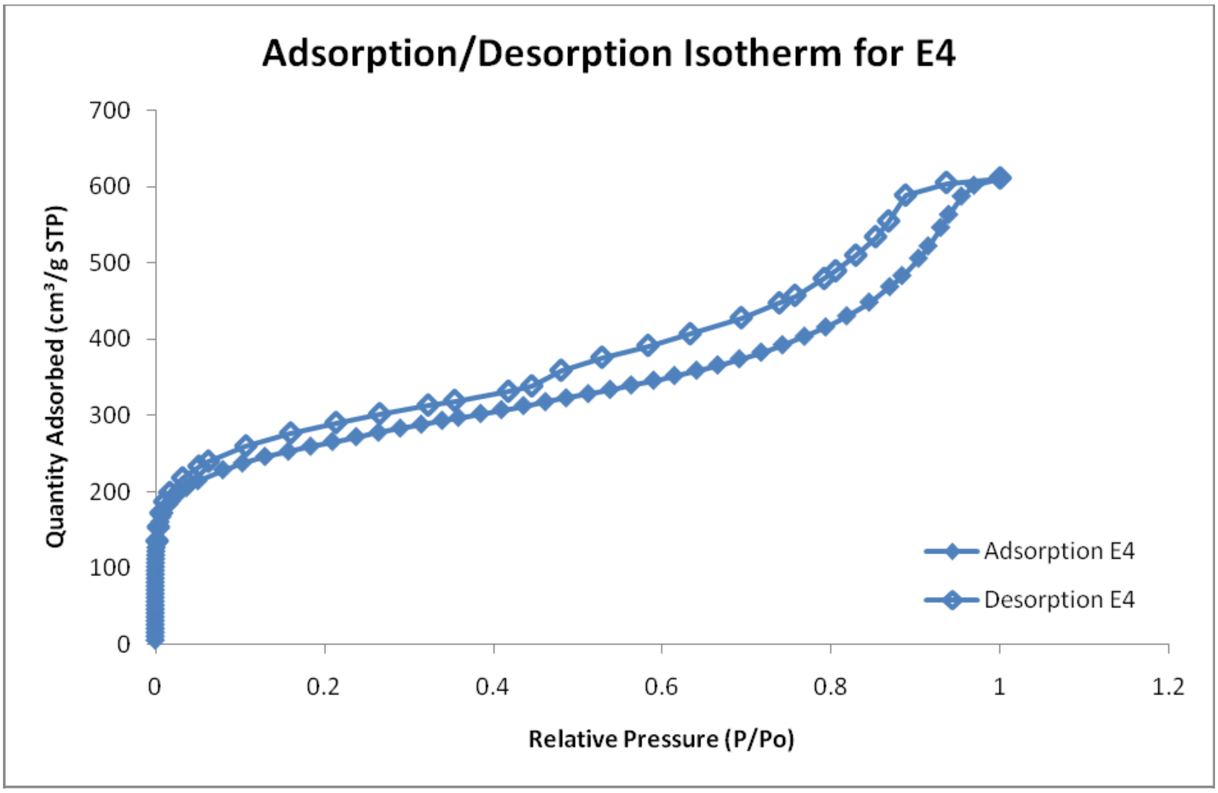

Figure S11. Nitrogen isotherm for network E4 showing hysteresis upon desorption.

NL-DFT Micropore Size Distributions

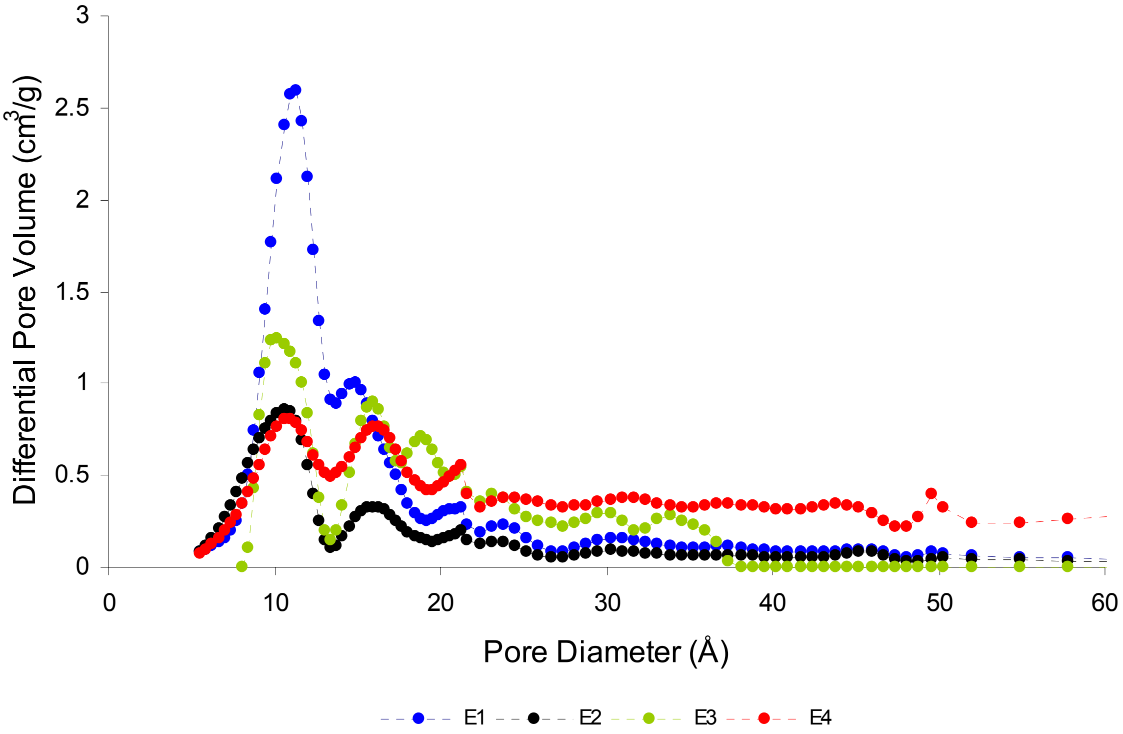

Figure S12. Stacked NL-DFT micropore size distributions up to 6 nm.

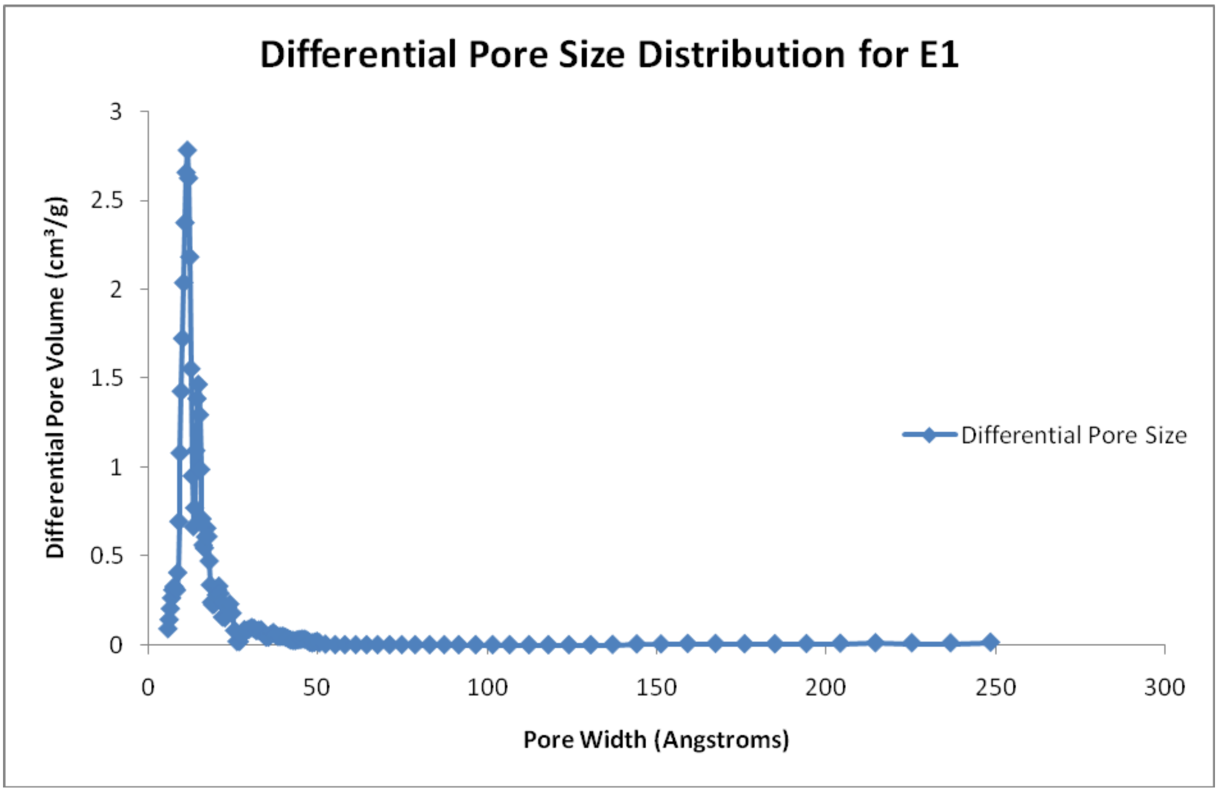

Figure S13. NL-DFT differential pore size distribution for network E1.

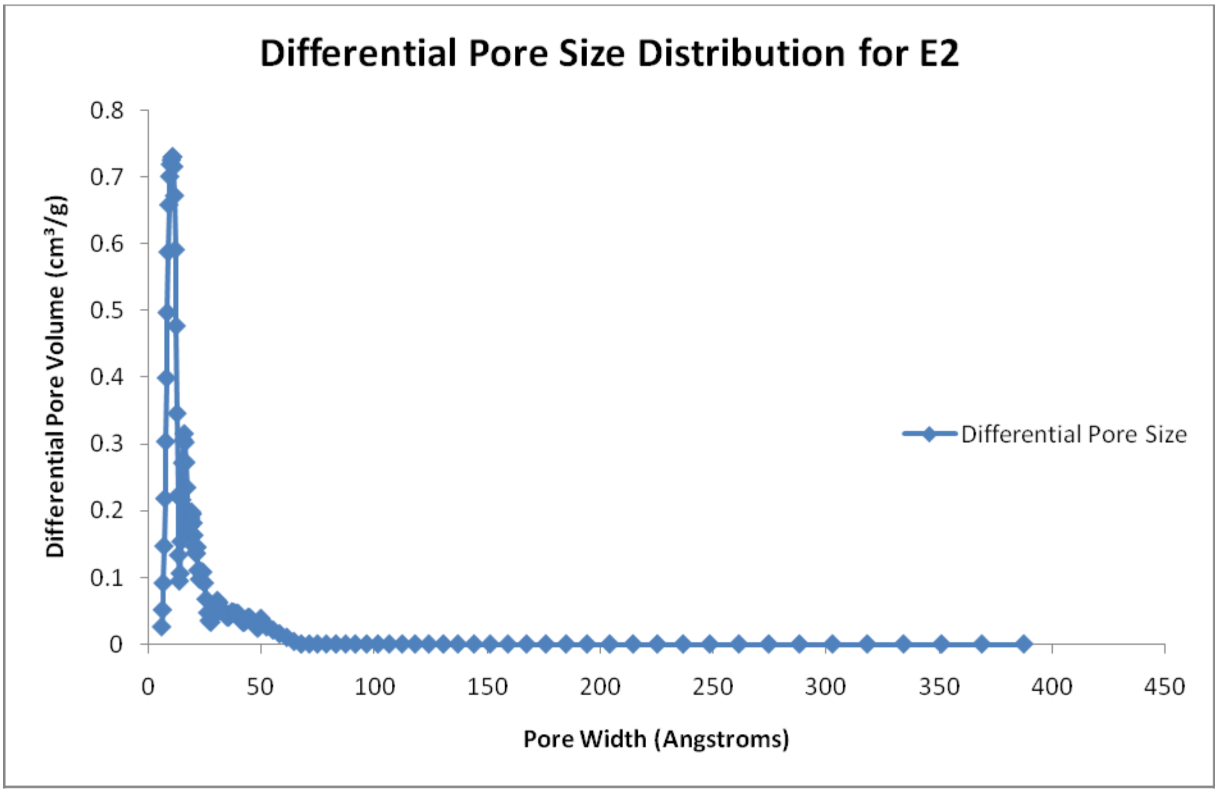

Figure S14. NL-DFT differential pore size distribution for network E2.

Hydrogen Physisorption Isotherms at 77.3 K.

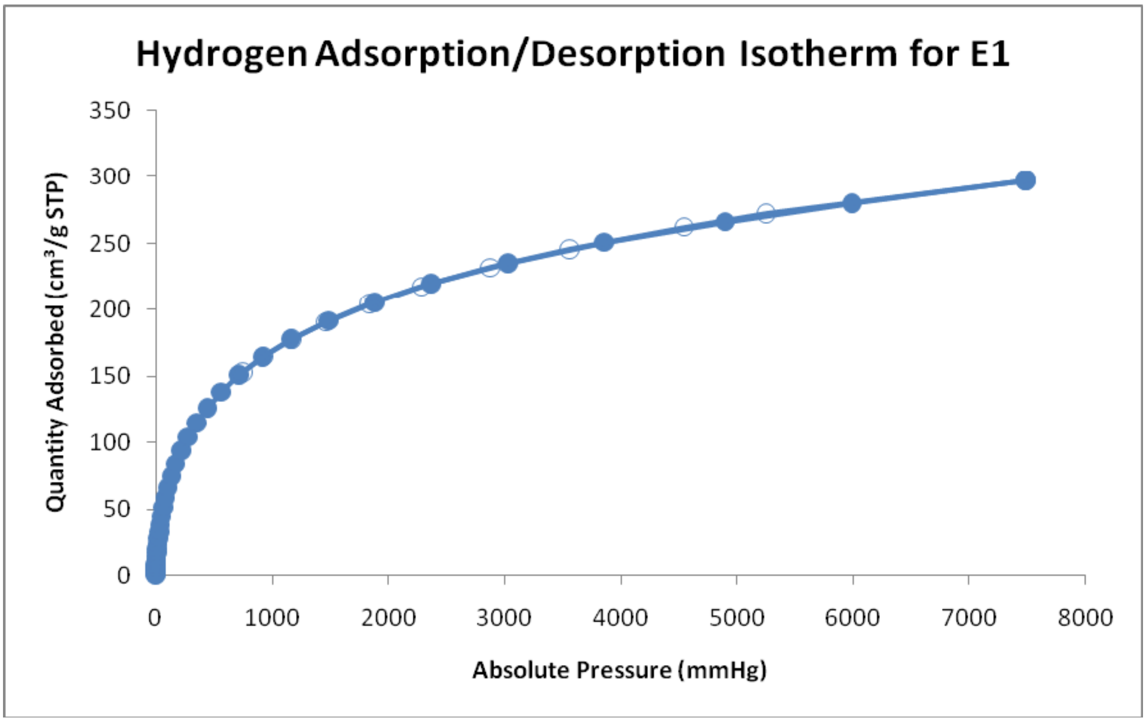

Figure S15. Hydrogen adsorption (closed sybols) and desorption (open symbols) isotherms for E1 up to 8 bar / 77.3 K. Maximum H_2 uptake at 8 bar = 2.66 wt. %.

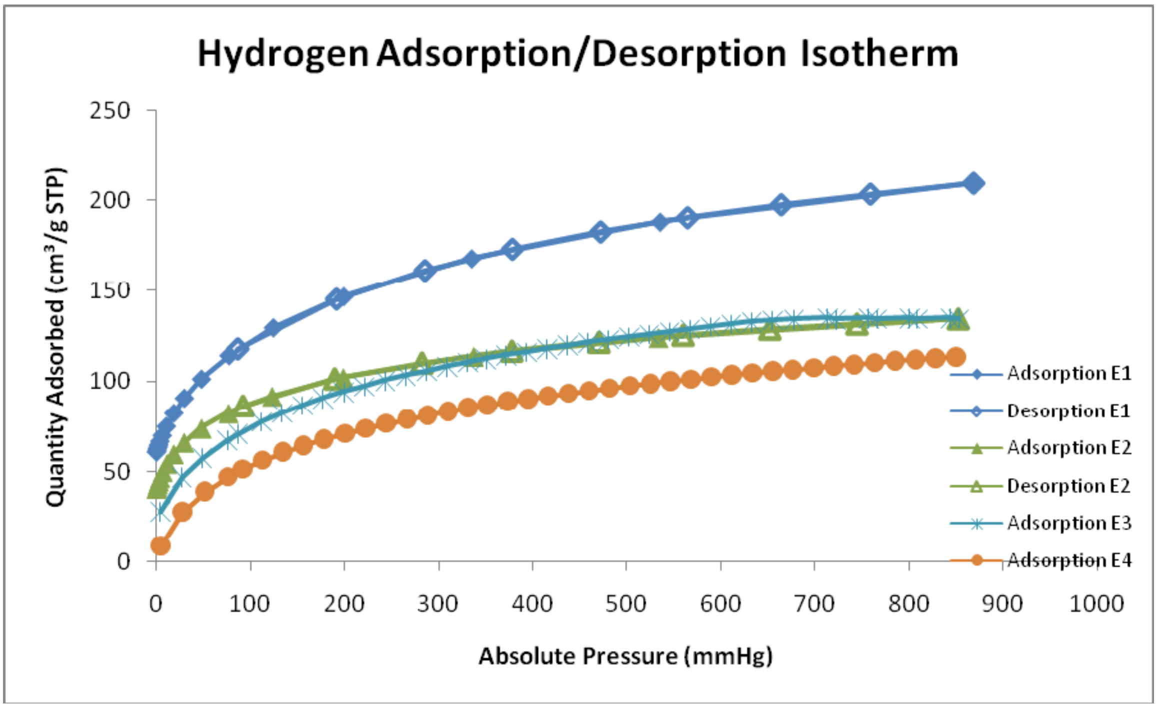

Figure S16. Hydrogen isotherms for networks E1–E4 up to 1 bar, offset by 20 cm^3/g for clarity. Maximum H_2 uptakes at 1 bar are: E1: 1.33 wt. %; E2: 0.84 wt. %; E3: 1.03 wt. %; E4: 1.01 wt. %.

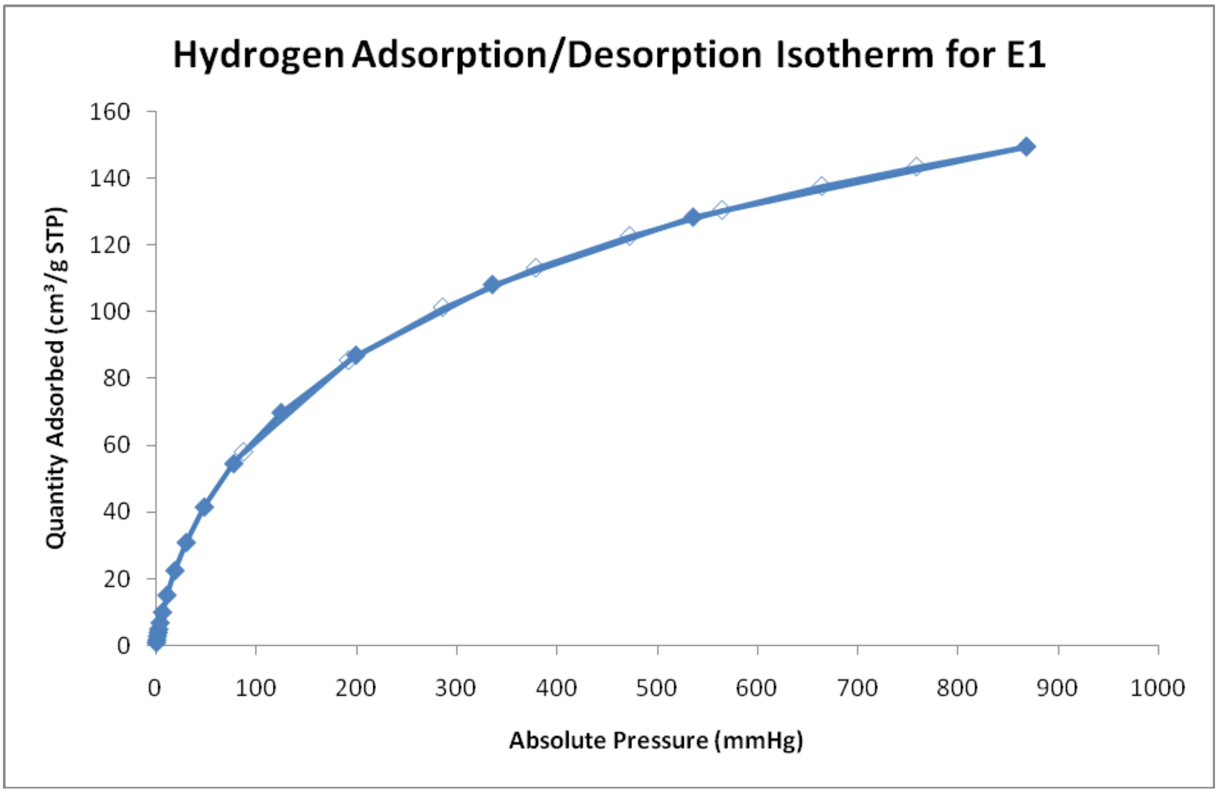

Figure S17. Hydrogen adsorption (closed sybols) and desorption (open symbols) isotherms for E1 up to 1 bar / 77.3 K.

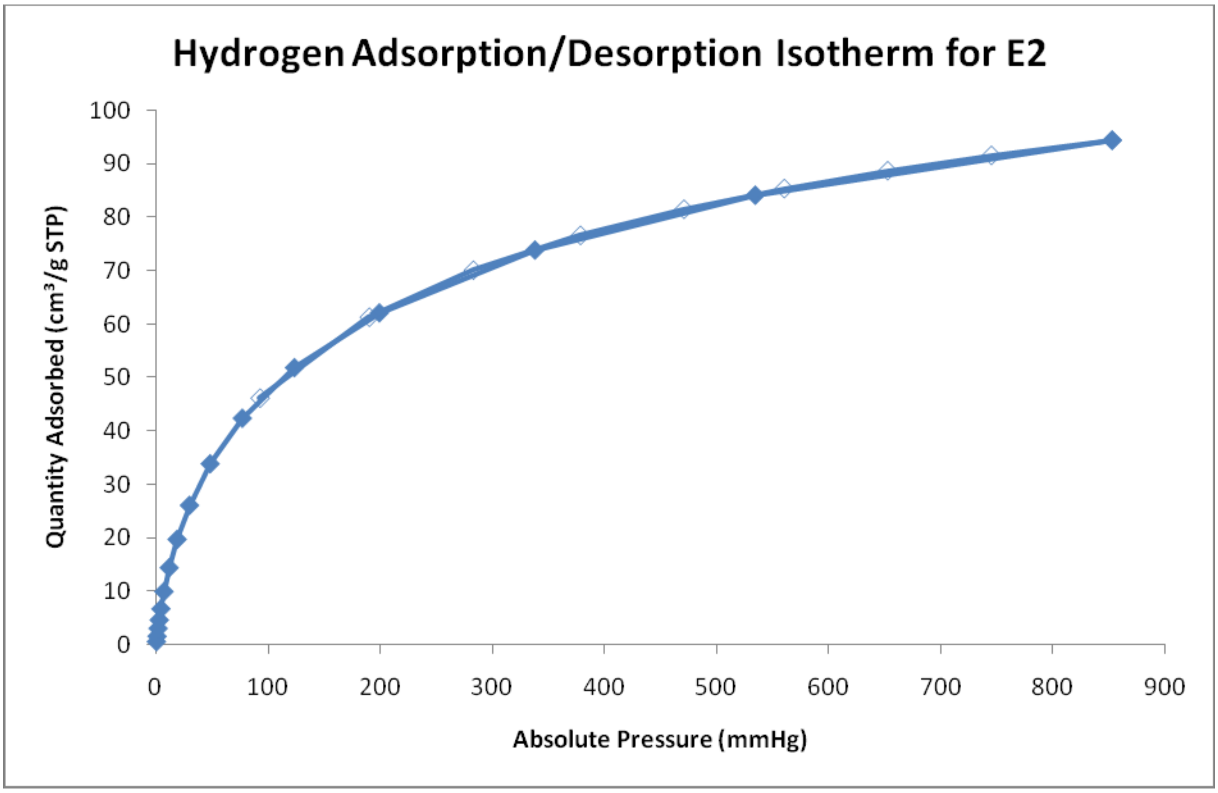

Figure S18. Hydrogen adsorption (closed sybols) and desorption (open symbols) isotherms for E2 up to 1 bar / 77.3 K.

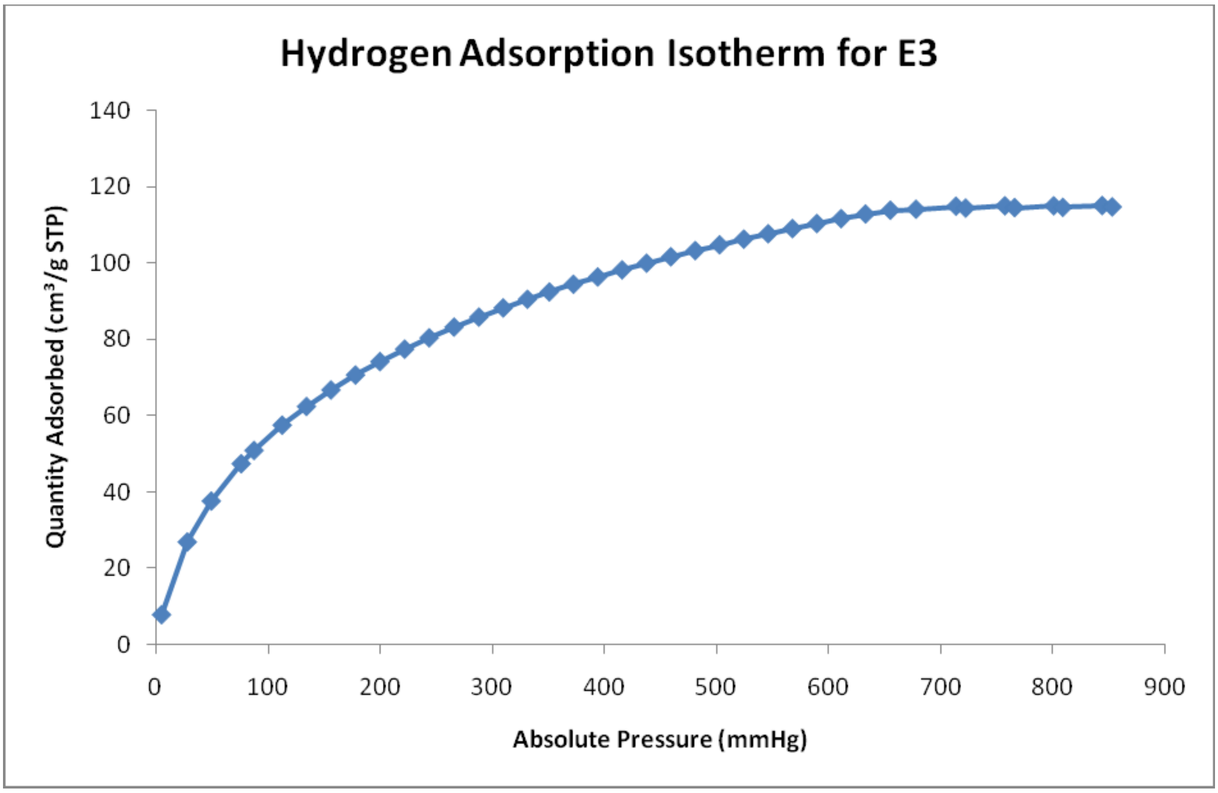

Figure S19. Hydrogen adsorption isotherm for E3 up to 1 bar / 77.3 K..

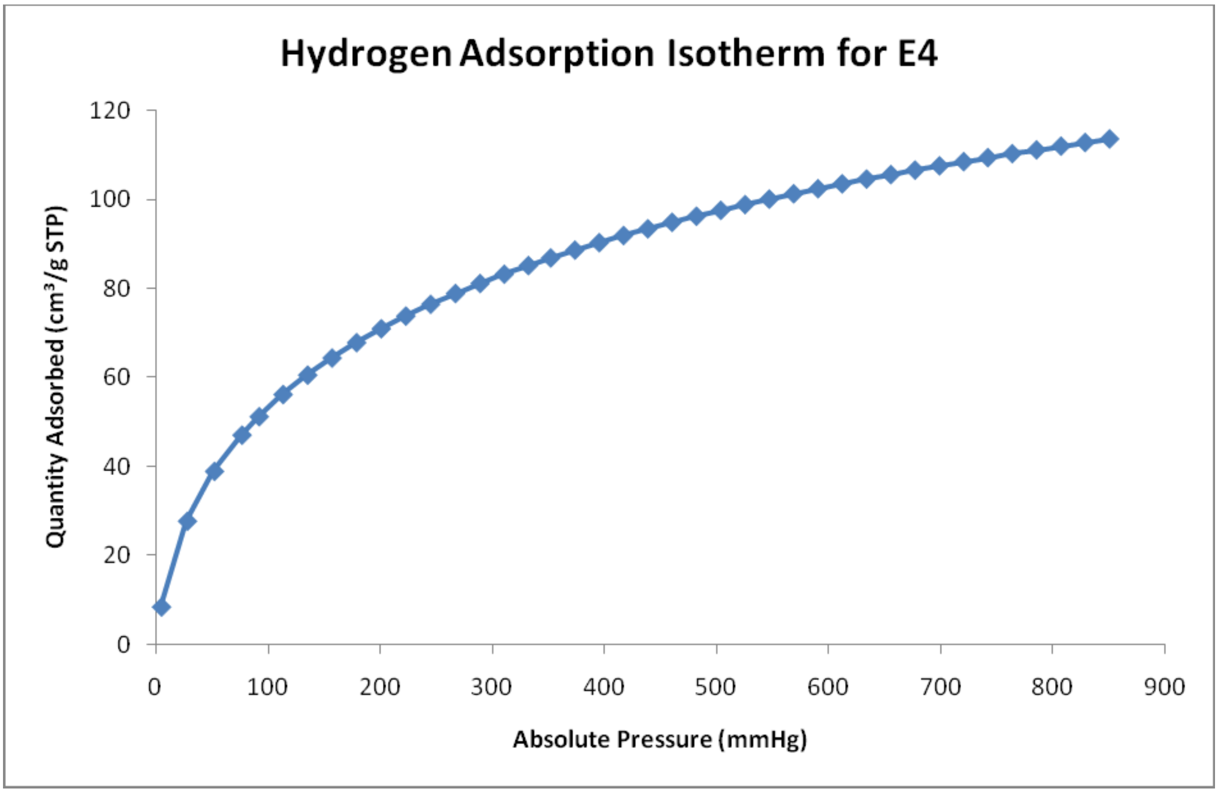

Figure S20. Hydrogen adsorption isotherm for E4 up to 1 bar / 77.3 K..

References

1. D. Su and F. M. Menger, *Tetrahedron Lett.*, 1997, **38**, 1485-1488.
2. Y. Liao, M. Baskett, P.M. Lahti and F. Palacio, *Chem. Commun.* 2002, 252-253.
3. A. E. Bennett, C. M. Rienstra, M. Auger, K. V. Lakshmi and R. G. Griffin, *J. Phys. Chem.* 1995, **103**, 6951–6958.
4. H. Sun, *J. Phys. Chem. B* 1998, **102**, 7338–7364.
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