Synthetic Control of Pore Dimension and Surface Area in Conjugated Microporous Polymer and Copolymer Networks

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SUPPORTING INFORMATION

Experimental

All of the poly(aryleneethynylene) (PAE) networks were synthesized by using palladium−catalyzed Sonogashira−Hagihara cross−coupling polycondensation under a nitrogen atmosphere.

Thermogravimetric Analysis

The thermal properties of the polymer networks were evaluated using a thermogravimetric analysis (TGA)−differential thermal analysis instrument (EXSTAR6000) over the temperature range 50 to 700 °C under a nitrogen atmosphere with a heating rate of 5 °C/min.

Synthesis of CMP-1 networks at various monomer concentrations

All polymer networks in this series (see Table S1) were synthesized at a fixed ratio of ethynyl to halogen functionalities of 1.5:1, a fixed reaction temperature of 80 °C, and a reaction time of 72 h.

CMP-1E: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were dissolved in a mixture of toluene (1.5 ml) and Et₃N (1.5 ml). The reaction mixture was heated to 80 °C, stirred for 72 h under a nitrogen atmosphere in

order to rigorously exclude oxygen and to prevent homocoupling of the alkyne monomers. The mixture was cooled to room temperature and the precipitated network polymer was filtered and washed four times (once each) with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. The further purification of the polymers was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C. (Yield: 68.5%). IR (KBr cm^{-1}): 3297.8 ($-C{\equiv}C-H$), 2201.5 ($-C{\equiv}C-$). Elemental combustion analysis (%) Calcd for $C_{36}H_{18}$: C 95.25, H 4.75; Found: C 86.37, H 4.33.

CMP-1F: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), copper(I) iodide (30 mg), toluene (2.5 ml), and Et$_3$N (2.5 ml) were used in the polymerization. Yield: 66.4%. Elemental combustion analysis (%) Found: C 87.42, H 4.28.

CMP-1G: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), copper(I) iodide (30 mg), toluene (3.3 ml), and Et$_3$N (3.3 ml) were used in the polymerization. Yield: 68.9%. Elemental combustion analysis (%) Found: C 88.25, H 4.54.

CMP-1H: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), copper(I) iodide (30 mg), toluene (5.0 ml), and Et$_3$N (5.0 ml) were used in the polymerization. Yield: 66.9%. Elemental combustion analysis (%) Found: C 87.58, H 4.47.

CMP-1I: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), copper(I) iodide (30 mg), toluene (10 ml), and Et$_3$N (10 ml) were used in the polymerization. Yield: 68.4 %. Elemental combustion analysis (%) Found: C 87.47, H 4.45.

CMP-1J: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), copper(I) iodide (30 mg), toluene (15 ml), and Et$_3$N (15 ml) were used in the polymerization. Yield: 66.9%. Elemental combustion analysis (%) Found: C 87.56, H 4.55.

Table S1. Effect of monomer concentration on the apparent BET surface area for CMP-1.[a]

Polymer	Monomer concentration [mmol/L]	S_{BET} [m^2/g][b]
CMP-1E	666	956
CMP-1F	400	893
CMP-1G	333	881
CMP-1H	200	887
CMP-1I	100	828
CMP-1J	66	870

[a] All reactions were carried out using the same mass of alkyne and halogen monomers (solvent volume was varied) at a fixed reaction temperature of 80 °C for 72 h.

[b] Surface area calculated from the N_2 adsorption isotherm using the BET method.

Synthesis of polymers at different monomer ratios (variation of ratio of alkyne to halogen functionalities)

All polymer networks in this series were synthesized at a fixed total molar concentration of 333 mmol/L, a fixed reaction temperature of 80 °C, and a reaction time of 24 h. The variation in surface area as a function of alkyne to halogen concentration is shown in Table S2.

CMP-1A: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (989.7 mg, 3.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were dissolved in the mixture of toluene (5.0 ml) and Et$_3$N (5.0 ml). The reaction mixture was heated to 80 °C, stirred for 24 h under a nitrogen atmosphere in order to rigorously exclude oxygen and to prevent homocoupling of the alkyne monomers. The mixture was cooled to room temperature and the precipitated network polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. The further purification of the polymers was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C. (Yield: 65.6%). IR (KBr cm^{-1}): 3297.8 (–C≡C–H), 2201.5 (–C≡C–). Elemental combustion analysis (%) Calcd for C$_{36}$H$_{18}$: C 95.25, H 4.75; Found: C 87.34, H 4.39.

CMP-1B: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were used in this polymerization. Yield: 67.7%. Elemental combustion analysis (%) Found: C 87.34, H 3.60.

CMP-1C: 1,3,5-triethynylbenzene (225.3 mg, 1.5 mmol), 1,4-diiodobenzene (329.9 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 68.3%. Elemental combustion analysis (%) Found: C 85.07, H 3.43.

CMP-1D: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (329.9 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 65.7%. Elemental combustion analysis (%) Found: C 86.13, H 3.48.

CMP-2A: 1,3,5-triethynylbenzene (150.2 mg, 1.0 mmol), 4,4'-diiodobiphenyl (609 mg, 1.5 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in this case. Yield: 61.4%. Elemental combustion analysis (%) Calcd for $C_{30}H_{15}$: C 96.0, H 4.0; Found: C 84.25, H 4.05.

CMP-2B: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 4,4'-diiodobiphenyl (812 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were used in the polymerization. Yield: 58.3%. Elemental combustion analysis (%) Found: C 85.01, H 4.22.

CMP-2C: 1,3,5-triethynylbenzene (225.3 mg, 1.5 mmol), 4,4'-diiodobiphenyl (406 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 59.5%. Elemental combustion analysis (%) Found: C 86.13, H 4.31.

CMP-2D: 1,3,5-triethynylbenzene (255.3 mg, 1.7 mmol), 4,4'-diiodobiphenyl (406 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 62.4%. Elemental combustion analysis (%) Found: C 87.36, H 4.38.

CMP-3A: 1,4-diethynylbenzene (189.2 mg, 1.5 mmol), 1,3,5-tris-(4'-iodophenyl)benzene (684.1 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 65.6%. Elemental combustion analysis (%) Calcd for $C_{39}H_{21}$: C 95.71, H 4.29; Found: C 85.65, H 4.92.

CMP-3B: 1,4-diethynylbenzene (214.5 mg, 1.7 mmol), 1,3,5-tris-(4'-iodophenyl)benzene (684.1 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 67.7%. Elemental combustion analysis (%) Found: C 82.36, H 3.93.

CMP-3C: 1,4-diethynylbenzene (252.3 mg, 2.0 mmol), 1,3,5-tris-(4'-iodophenyl)benzene (684.1 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. (Yield: 68.3%. Elemental combustion analysis (%) Found: C 85.01, H 4.22.

CMP-3D: 1,4-diethynylbenzene (283.8 mg, 2.25 mmol), 1,3,5-tris-(4'-iodophenyl)benzene (684.1 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 65.7%. Elemental combustion analysis (%) Found: C 86.02, H 4.12.

CMP-3E: 1,4-diethynylbenzene (315.4 mg, 2.5 mmol), 1,3,5-tris-(4'-iodophenyl)benzene (684.1 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 64.2%. Elemental combustion analysis (%) Found: C 87.40, H 4.34.

CMP-3F: 1,4-diethynylbenzene (378.4 mg, 3.0 mmol), 1,3,5-tris-(4'-iodophenyl)benzene (329.9 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (25 mg) were used in the polymerization. Yield: 65.3%. Elemental combustion analysis (%) Found: C 87.64, H 4.45.

CMP-4A: 1,4-diethynylbenzene (189.2 mg, 1.5 mmol), 1,3,5-tribromobenzene (314.8 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 67.3%. Elemental combustion analysis (%) Calcd for $C_{36}H_{18}$: C 95.25, H 4.75; Found: C 78.69, H 3.22.

CMP-4B: 1,4-diethynylbenzene (214.5 mg, 1.7 mmol), 1,3,5-tribromobenzene (314.8 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 65.2%. Elemental combustion analysis (%) Found: C 80.19, H 3.20.

CMP-4C: 1,4-diethynylbenzene (252.3 mg, 2.0 mmol), 1,3,5-tribromobenzene (314.8 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 66.4%. Elemental combustion analysis (%) Found: C 84.12, H 3.50.

CMP-4D: 1,4-diethynylbenzene (283.8 mg, 2.25 mmol), 1,3,5-tribromobenzene (314.8 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 62.2%. Elemental combustion analysis (%) Found: C 87.35, H 3.87.

CMP-4E: 1,4-diethynylbenzene (315.4 mg, 2.5 mmol), 1,3,5-tribromobenzene (314.8 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 65.7%. Elemental combustion analysis (%) Found: C 90.98, H 3.92.

CMP-4F: 1,4-diethynylbenzene (378.4 mg, 3.0 mmol), 1,3,5-tribromobenzene (314.8 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (80 mg), and copper(I) iodide (20 mg) were used in the polymerization. Yield: 66.6%. Elemental combustion analysis (%) Found: C 88.38, H 3.86.

Table S2. Effect of the molar ratio of alkyne and halogen monomers on the BET surface area and H_2 uptakes for polymer networks CMP-1 – CMP-4 (maximum surface area conditions shown in **bold** for each of the four networks, in all cases the optimum molar ratio of alkyne to halogen was in the range 1.5–1.66)

polymer	Molar ratio[a]	Ratio of ethynyl to halogen groups	S_{BET} (m^2/g)[b]	H_2 uptake (wt%)[c]
CMP-1A	1:1.5	1	703	0.95
CMP-1B	**1:1**	**1.5**	**778**	**1.01**
CMP-1C	1.5:1	2.25	627	0.99
CMP-1D	2:1	3	609	0.98
CMP-2A	1:1.5	1	257	0.59
CMP-2B	**1:1**	**1.5**	**678**	**0.91**
CMP-2C	1.5:1	2.25	615	0.87
CMP-2D	1.7:1	2.55	535	0.82
CMP-3A	1.5:1	1	167	0.66
CMP-3B	1.7:1	1.13	325	0.53
CMP-3C	2:1	1.33	503	0.76
CMP-3D	**2.25:1**	**1.5**	**568**	**0.85**
CMP-3E	2.5:1	1.66	426	0.62
CMP-3F	3:1	2	467	0.70
CMP-4A	1.5:1	1	403	0.66
CMP-4B	1.7:1	1.13	465	0.73
CMP-4C	2:1	1.33	640	1.04
CMP-4D	2.25:1	1.5	681	1.07
CMP-4E	**2.5:1**	**1.66**	**747**	**1.10**
CMP-4F	3:1	2	457	0.71

[a] The molar ratio based on the alkyne to halogen monomers.
[b] Surface area calculated from the N_2 adsorption isotherm using the BET method.
[c] Data were obtained at 1.13 bar and 77.3 K.

Synthesis of PAE networks using monomers with varying "strut" lengths

To ensure consistency between syntheses and to exclude, for example concentration effects, networks CMP-0, CMP-1, CMP-2, CMP-3, and CMP-5 were synthesized at a fixed molar monomer concentration of 400 mmol/L, a fixed reaction temperature and time of 80 °C/72 h, and a constant molar ratio of ethynyl to halogen functionalities of 1.5:1. A typical experimental procedures for CMP-0 – CMP-5 are given below.

CMP-0: 1,3,5-triethynylbenzene (450 mg, 3 mmol), 1,3,5-tris-(4'-iodophenyl)benzene (1368 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were dissolved in a mixture of toluene (2.5 ml) and Et_3N (2.5 ml). The reaction mixture was heated to 80 °C and stirred for 72 h under a nitrogen atmosphere in order to rigorously exclude oxygen and to prevent homocoupling of the alkyne monomers. The mixture was cooled to room temperature and the precipitated polymer network was filtered and washed four times (once each) with chloroform, water, methanol, and acetone, respectively, to remove any unreacted monomer or catalyst residues. Further purification of the polymers was carried out by Soxhlet extraction with methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C. (Yield: 67.3%). IR (KBr cm^{-1}): 3297.6 (–C≡C–H), 2201.7 (–C≡C–). Elemental combustion analysis (%) Calcd for $C_{36}H_{18}$: C 95.25, H 4.75; Found: C 86.15, H 4.41.

CMP-1: This network was produced from 1,3,5-triethynylbenzene (300 mg, 2.0 mmol), 1,4-diiodobenzene (660 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium (100 mg), and copper iodide (30 mg). (Yield, 65.4%). IR (KBr cm^{-1}): 3298.2 (–C≡C–H), 2200.9 (–C≡C–). Elemental combustion analysis (%) Calcd for $C_{21}H_9$: C 96.55, H 3.45; Found: C 83.62, H 3.66.

CMP-2: This network was synthesized from 1,3,5-triethynylbenzene (300 mg, 2.0 mmol), 4,4′-diiododiphenyl (812 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium (120 mg), and copper iodide (35 mg). (Yield, 60.5%). IR (KBr cm^{-1}): 3297.3 (–C≡C–H), 2206.7 (–C≡C–). Elemental combustion analysis (%) Calcd for $C_{30}H_{15}$: C 96.0, H 4.0; Found: C 87.40, H 4.00.

CMP-3: This network was synthesized from 1,4-diethynylbenzene (284 mg, 2.25 mmol), 1,3,5-tris(4′-iodophenyl)benzene (684 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium (100 mg), and copper iodide (30 mg). (Yield, 55.7%). IR (KBr cm^{-1}): no peak observed from (–C≡C–H), 2207.5 (–C≡C–). Elemental combustion analysis (%) Calcd for $C_{39}H_{21}$: C 95.71, H 4.29; Found: C 85.78, H 4.34.

CMP-5: 4,4'-diethynylbiphenyl (454 mg, 2.25 mmol), 1,3,5-tris(4′-iodophenyl)benzene (684 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium (100 mg), and copper iodide (25 mg) were employed in this polymerization. (Yield, 65.4%). IR (KBr cm^{-1}): no peak observed from (−C≡C−H), 2207.5 (−C≡C−). Elemental combustion analysis (%) Calcd for $C_{48}H_{27}$: C 95.52, H 4.48; Found: C 87.57, H 4.52.

Synthesis of polymer networks CPN-1-6

Each of the copolymer networks was synthesized at a fixed ratio of ethynyl to halogen functionalities of 1.5:1, a fixed molar concentration of 400 mmol/L, a reaction temperature of 80 °C, and a reaction time of 72 h.

CPN-1: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (659.8 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were dissolved in a mixture of toluene (2.5 ml) and Et_3N (2.5 ml). The reaction mixture was heated to 80 °C, stirred for 72 h under a nitrogen atmosphere in order to rigorously exclude oxygen and to prevent homocoupling of the alkyne monomers. The mixture was cooled to room temperature and the precipitated polymer network was filtered and washed four times (once each) with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. The further purification of the polymers was carried out by Soxhlet extraction with methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C. Yield: 66.9%. Elemental combustion analysis (%) Found: C 87.24, H 4.59.

CPN-2: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (527.8 mg, 1.6 mmol), 4,4'-diiodobiphenyl (162.4 mg, 0.4 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were used in this case. Yield: 68.4%. Elemental combustion analysis (%) Found: C 86.46, H 4.47.

CPN-3: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (395.8 mg, 1.2 mmol), 4,4'-diiodobiphenyl (324.8 mg, 0.8 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were used in the polymerization. Yield: 65.8%. Elemental combustion analysis (%) Found: C 88.73, H 4.52.

CPN-4: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (263.9 mg, 0.8 mmol), 4,4'-diiodobiphenyl (487.2 mg, 1.2 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were used in the polymerization. Yield: 66.8%. Elemental combustion analysis (%) Found: C 89.24, H 4.47.

CPN-5: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 1,4-diiodobenzene (131.9 mg, 0.4 mmol), 4,4'-diiodobiphenyl (649.6 mg, 1.6 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were used in the polymerization. Yield: 68.8%. Elemental combustion analysis (%) Found: C 86.36, H 4.35.

CPN-6: 1,3,5-triethynylbenzene (300.3 mg, 2.0 mmol), 4,4'-diiodobiphenyl (812 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (100 mg), and copper(I) iodide (30 mg) were used in the polymerization. Yield: 67.6%. Elemental combustion analysis (%) Found: C 86.85, H 4.51.

Effect of monomer concentration on micropore structure: To evaluate the effect of monomer concentration on the porosity of these polymers, we synthesized a series of CMP-1 networks varying the monomer concentration over a broad range from 66 to 666 mmol/L (Table S1). The ratio of ethynyl to halogen functionalities was kept constant at 1.5:1; that is, at the ratio which gave rise to maximum BET surface area at 333 mmol/L (Table S1). The resulting polymers all showed quite similar apparent BET surface areas in the range 870–956 m^2/g (slightly higher than the CMP-1 sample referred to in the main text, possibly because of the more extended reaction time). The phase behavior varied with monomer concentration; powder precipitates were formed at lower concentrations while macroscopic gelation of the reaction solution was observed at higher concentrations (>300 mmol/L) in the first few minutes of the polymerization. The micropore size distributions for the polymer networks were investigated using nitrogen sorption analysis and application of NL-DFT models. Figure S1a shows the N_2 adsorption and desorption isotherms for the polymer formed at the highest monomer concentration (CMP-1E, 666 mmol/L) and at the lowest monomer concentration (CMP-1J, 66 mmol/L). Both polymers gave rise to similar Type I nitrogen gas sorption isotherms indicating that the materials are predominantly microporous. Figure S1b shows the NL-DFT pore size distribution curves for CMP-1E and CMP-1J. Both polymers exhibited very similar pore size distributions in the micropore range with a median pore diameter of 1.2 nm, and micropore volumes of 0.37 (CMP-1E) and 0.35 cm^3/g (CMP-1J), respectively. This was also confirmed by plots of cumulative NL-DFT pore volume for the two polymers (Figure S1a, inset).
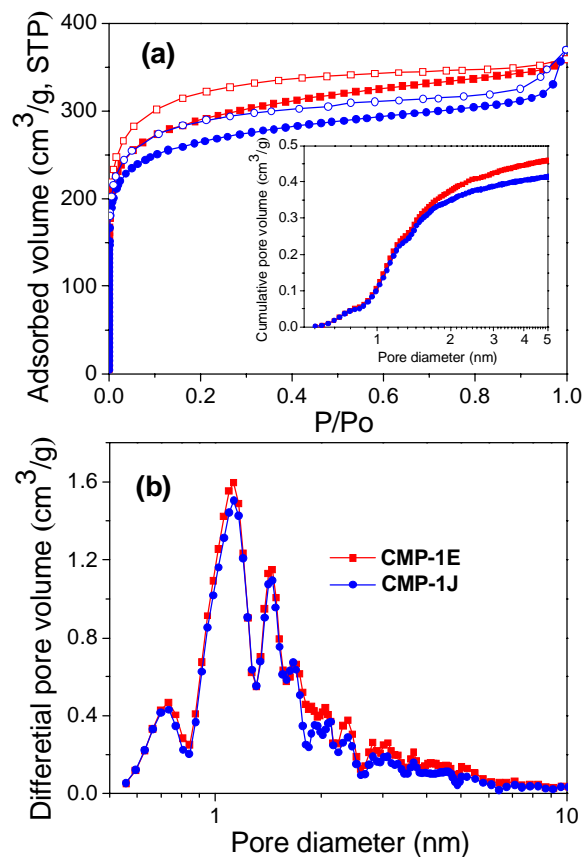
Figure S1. (a) N$_2$ adsorption-desorption isotherms measured at 77.3 K (adsorption branch is labelled with filled symbols). The inset shows the cumulative pore volume curves calculated by NL-DFT; (b) Pore size distribution curves for CMP-1E and CMP-1J calculated using NL-DFT.

Effect of ethynyl-to-halogen ratio on polymer surface area: Table S2 summarizes the apparent BET surface areas and H$_2$ uptakes (1.13 bar, 77.3 K) for the resulting polymer networks. The results demonstrate that the monomer ratio has a significant effect on both the apparent BET surface area and the H$_2$ uptake. For all networks, the maximum surface area and H$_2$ uptake were observed when the molar ratio of ethynyl to halogen functionalities was in the range 1.5–1.66. In principle, one might expect the network connectivity (and perhaps therefore the surface area) to be maximized at an equimolar ratio of these two reactive functionalities. However, complete network condensation may be hard to achieve on steric grounds at any molar ratio, and indeed there is NMR evidence for the presence of both ethynyl end groups and

halogen-bearing end groups in the networks. The rationale for requiring an excess of the ethynyl monomer is currently

unclear and is under further investigation. For subsequent materials in this study a fixed molar ratio of 1.5:1 ethynyl to

halogen functionalities was used.

Correlation between BET surface area and H$_2$ uptake: Figure S2a shows a plot of the maximum H$_2$ uptake observed

(1.13 bar / 77.3 K) *versus* the apparent BET surface area for the CMP-0−5 samples. In general, the H$_2$ sorption was found

to increase quite systematically with the apparent BET surface area, unlike hypercrosslinked polymers where this

correlation was weak.[1] Again, this is consistent with the much tighter, synthetically-determined micropore size

distribution observed for these PAE materials. Zhao *et al.*[2] demonstrated that linear Langmuir graphs for H$_2$ on activated

carbon at 77.3 K in the pressure range 0.15–1.0 bar. Here, we have also obtained linear Langmuir graphs for the five

samples at 77.3 K over a similar range of hydrogen pressures, as observed for hypercrosslinked materials.[1] Figure S2b

shows the strong correlation between the maximum H$_2$ uptake (1.13 bar/77.3 K) and the Langmuir surface area, as

calculated from the H$_2$ adsorption isotherms (0.15−1.13 bar) for samples CMP-0−5.
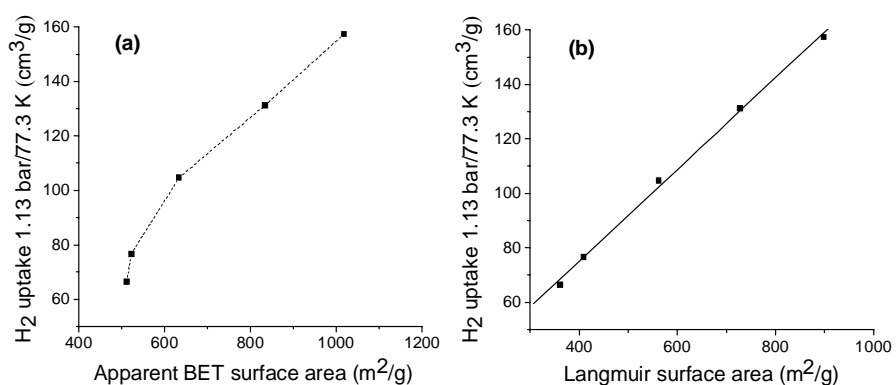

Figure S2. (a) Hydrogen uptake at 1.13 bar/77.3 K as a function of apparent BET surface area for CMP-0−5; (b) Hydrogen uptake at 1.13 bar/77.3 K as a function of Langmuir surface area as calculated from the H$_2$ isotherm for CMP-0−5. Solid line shows linear fit ($r^2 = 0.9989$) for the five samples.
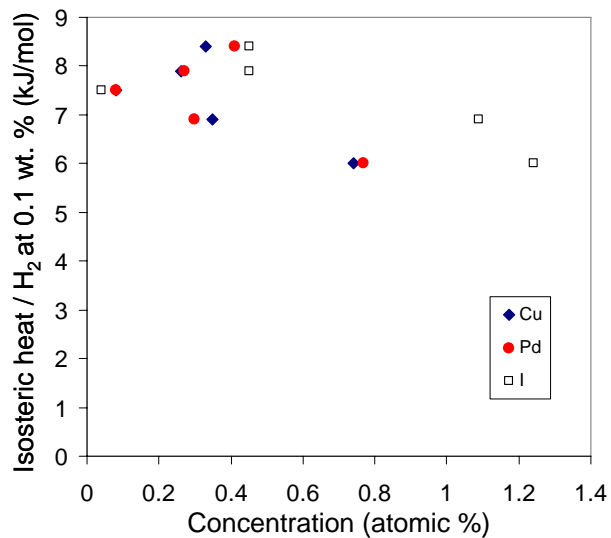
Figure S3. Variation of isosteric heat of sorption in polymers CMP0–CMP5 as a function of residual metal and halogen concentration, as determined by EDX analysis. The isosteric heat refers to the value measured at 0.1. wt. % H_2 uptake in each case.
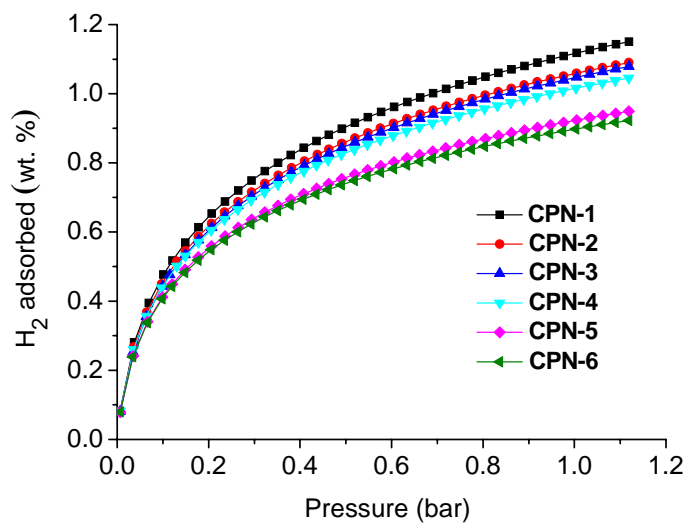

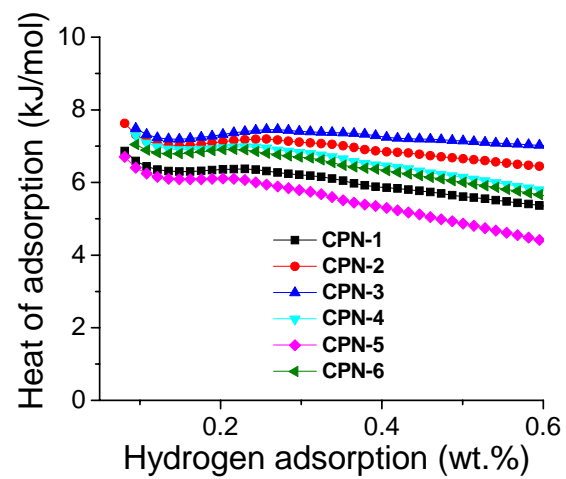**Figure S4.** Volumetric H_2 adsorption for polymer networks CPN-1-6 at 77.3 K.

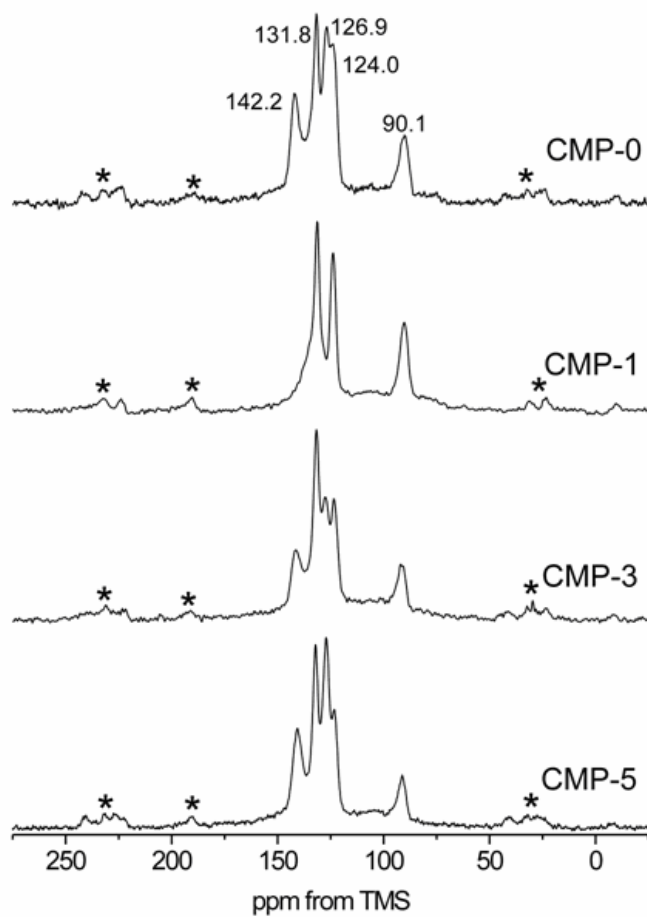**Figure S5.** Isosteric heat of sorption for H_2 as measured for copolymer networks CPN-1 to CPN-6.

Figure S6. Solid-state $^{13}C/^{1}H$ MAS NMR spectra NMR for conjugated microporous PAE networks recorded at MAS rate of 10 kHz, asterisks denote spinning sidebands.
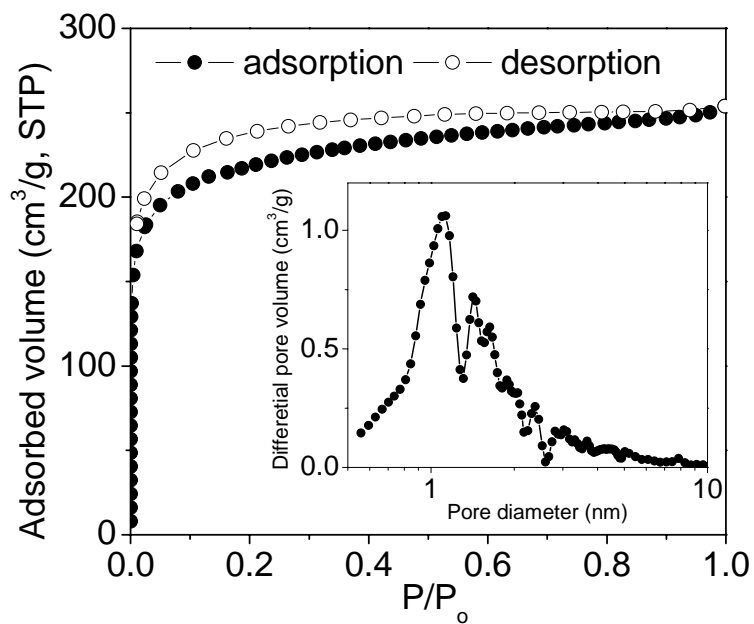
Figure S7. Nitrogen sorption data for microporous PAE network CMP-4. Inset shows micropore size distribution as calculated by NL-DFT.

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