Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Inexpensive polyphenylene network polymers with enhanced microporosity

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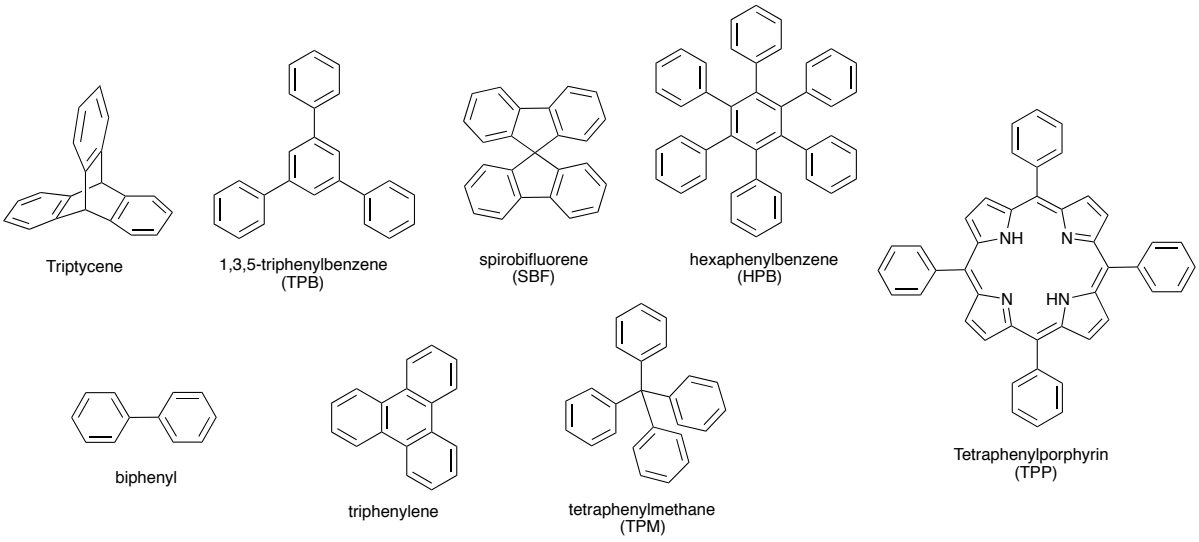


monomers	polymer	Reaction	solvent	SA_{BET} ($m^2 g^{-1}$)	V_{total} ($cm^3 g^{-1}$)	CO_2 Uptake[a] (mmol g^{-1})	
Triptycene	THPS	FC: FDA, $FeCl_3$, 80 °C, 24 h.	DCE	1426	820	3.1	[1]
Triptycene	Polymer4	FC: FDA, $FeCl_3$, 80 °C, 24 h.	DCE	1252	550	-	[2]
Triptycene-Br_3	STP-1	Yamamoto	DMF	1305	800	3.4	[3]
Triptycene-I_3	STP-2	Yamamoto	DMF	1990	950	3.8	[3]
TPB	PAF-48	Scholl: $FeCl_3$, 60 °C, 24 h.	$CHCl_3$	972	380	3.6	[4]
TPB	SMP-1	Scholl: $AlCl_3$, 58 °C, 24 h.	$CHCl_3$	1254	650	4.1	[5]
TPB	Polymer 3	FC: FDA, $FeCl_3$, 80 °C, 24 h.	DCE	1059	450	3.6	[6]
TPB-Br_3	PAF-5	Yamamoto	DMF	1503	1000	-	[7]
TPB-Br_3	COP-3	Yamamoto	DMF	1869	1.4	-	[8]
SBF-Br_4	YSN-1	Yamamoto	DMF	1970	1100	-	[9]
SBF-Br_4	YSN-1	Yamamoto	DMF	1275	750	-	[10]
HPB-Br_6	HP	Yamamoto	DMF	673	300	1.9	[11]
Biphenyl	PAF-45	Scholl: $FeCl_3$, 60 °C, 24 h.	$CHCl_3$	777	180	2.0	[4]
Biphenyl	Polymer 2	FC: FDA, $FeCl_3$, 80 °C, 24 h.	DCE	815	300	3.1	[6]
TPP	SMP-4	Scholl: $AlCl_3$, 58 °C, 24 h.	$CHCl_3$	757	450	3.1	[5]
TPM	PAF-41	Scholl: $AlCl_3$, 60 °C, 24 h.	$CHCl_3$	1119	400	3.5	[12]
TPM	PAF-32	FC: FDA, $FeCl_3$, 45 °C, 72 h.	DCM	1679	700	1.7	[13]

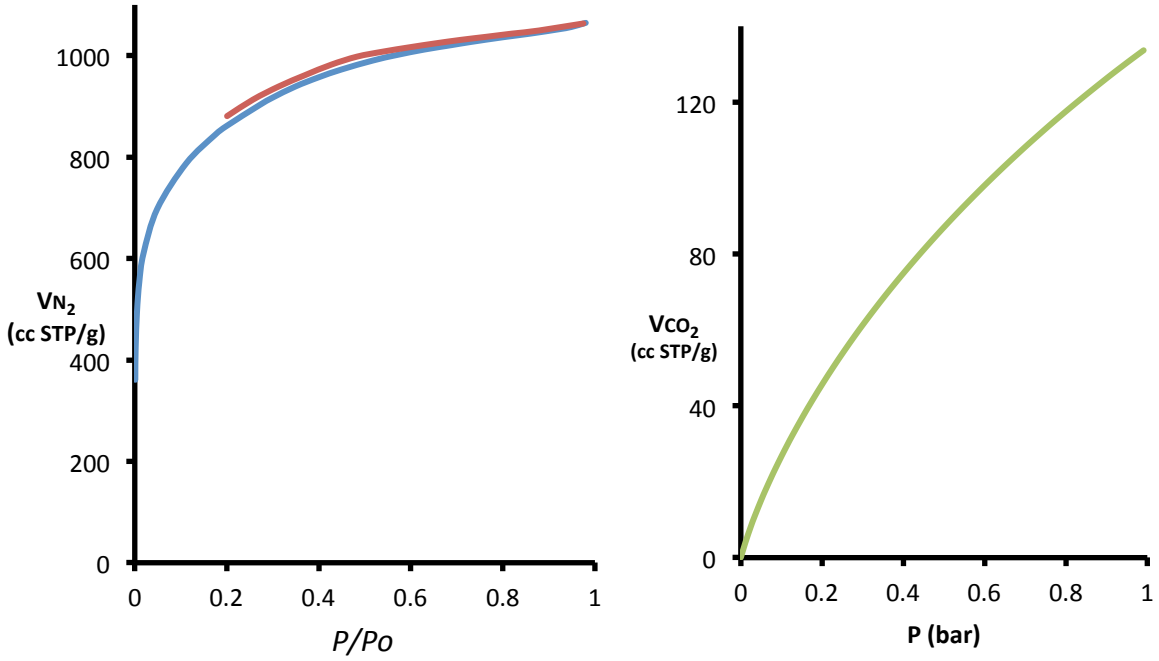
[a]at 273 K/1 bar.

1. Materials. Anhydrous aluminium chloride ($AlCl_3$) (Merck 99%), triptycene (Aldrich 98%), triphenylene (Aldrich 98%), 1,3,5-triphenylbenzene (Aldrich 97%), hexaphenylbenzene (Aldrich 98%), 9,10-diphenylanthracene (Fluka 98%), 9,9'-spirobifluorene (Aldrich 97%), biphenyl (Alfa-Aesar 99%), tetraphenyl methane (Alfa-Aesar 96%), tetraphenylporphyrin (Aldrich 97%), dichloroethane (DCE, Fisher HPLC grade), dichloromethane (DCM; Fisher HPLC grade), chloroform ($CHCl_3$ Fisher HPLC grade), tetrahydrofuran (THF VWR Chemical), ethanol (VWR Chemical) and methanol (Fisher) were all used as supplied.

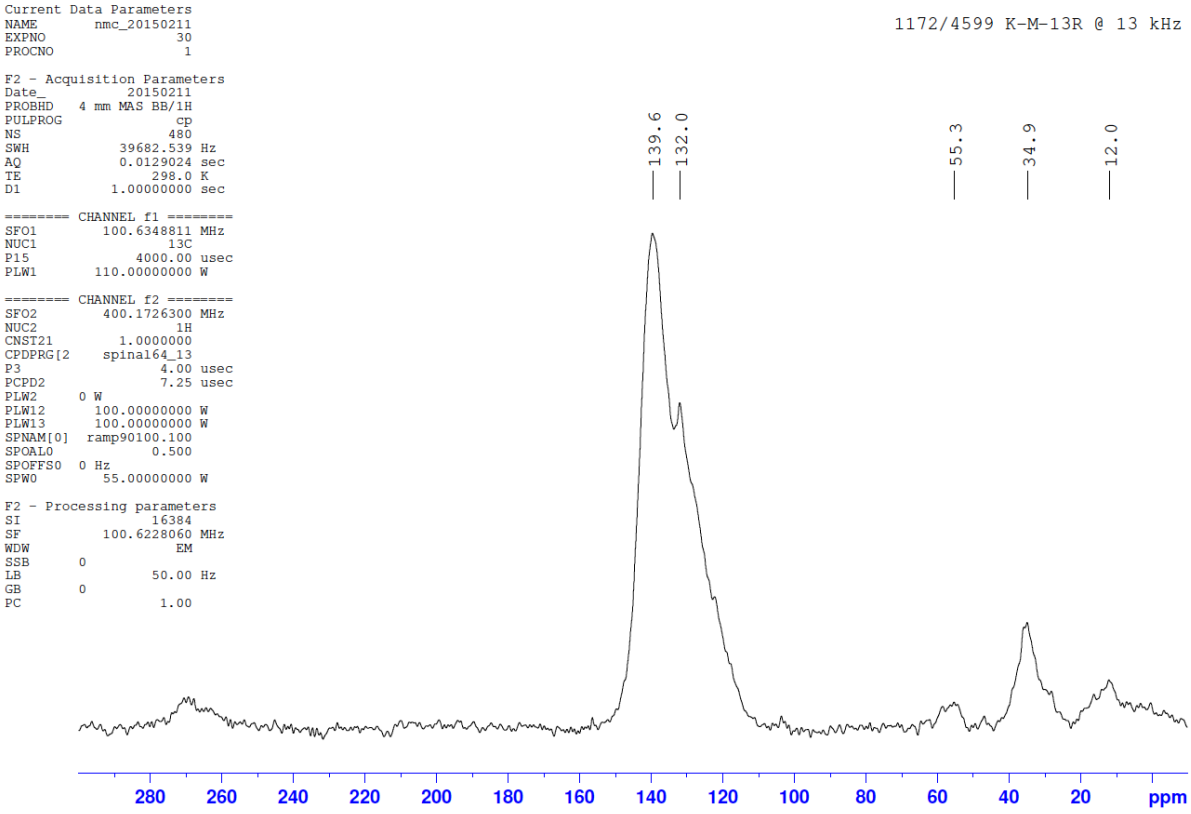
2. Characterization methods. The structures of the polymeric materials were characterized using solid-state ^{13}C-NMR spectroscopy using a Varian VNMRS & Bruker Avance III HD and carried out by the EPSRC UK Solid State NMR Service at Durham University. Thermogravimetric analysis (TGA) was performed using a TA Instruments, model SDT Q600 Analyzer. Surface area was obtained by nitrogen adsorption/desorption at 77 K using a Coulter SA 3100 instrument (with foreline filter to avoid contamination with oil vapour). CO_2 adsorption isotherms were measured using a Quadrasorb Evo instrument at 273 K. Elemental analysis (C, H, N, Cl) was performed by Warwick Analytical Services.

3. General procedure for polymer preparation.

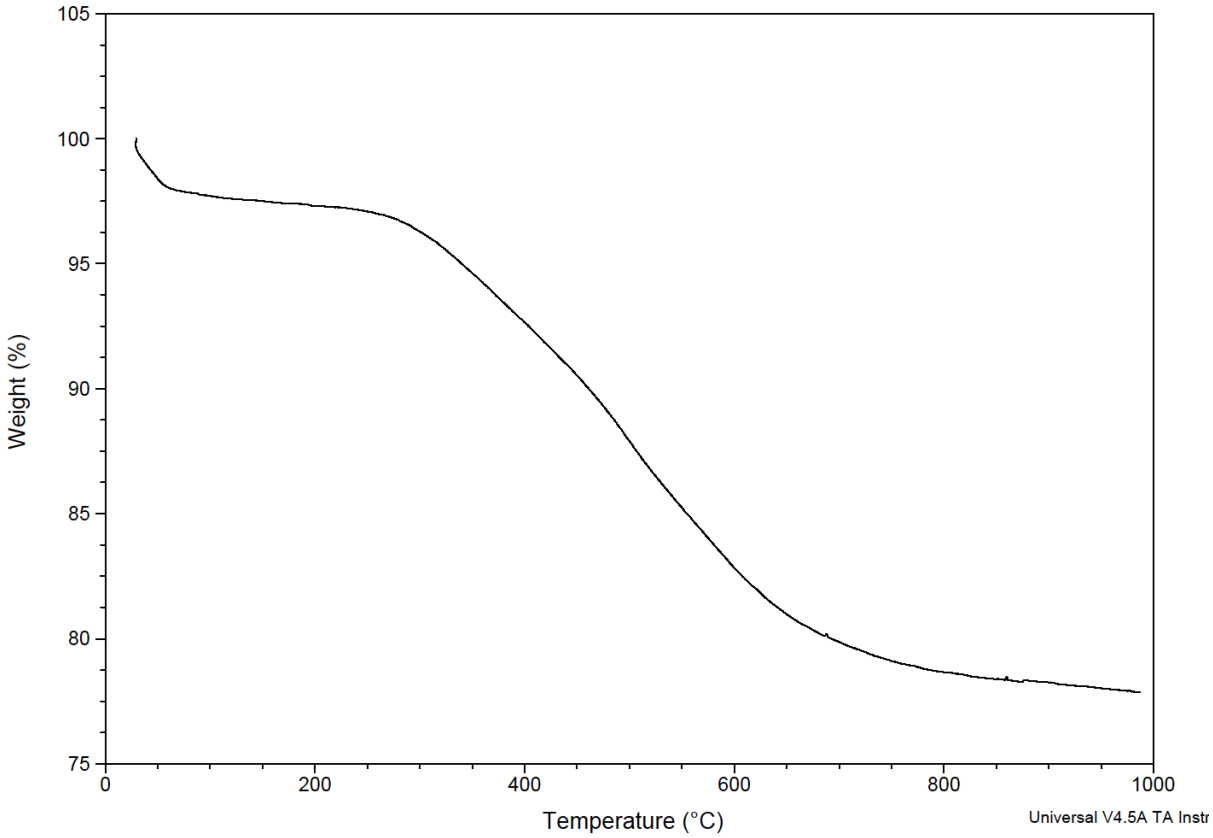
a. Polymer from 1,3,5-triphenylbenzene/DCM. Under a nitrogen atmosphere, anhydrous aluminium chloride (4.9 g, 36.8 mmol) was added to a solution of 1,3,5-triphenylbenzene (1.51 g, 4.9 mmol) in refluxing DCM (60 ml) and the mixture was stirred at reflux for 18-24 h. The resulting brown precipitate was collected by filtration and washed with water then ethanol. The polymer was then dispersed sequentially in the following solvents at reflux for six hours: ethanol, chloroform, THF, acetone and methanol. The brown product was then ground into a fine powder and dried in a vacuum oven at 80 °C for 18 h. Yield: 112% based on ideal structure. Solid-state ^{13}C NMR (100.5 MHz): δ ppm 139.6, 132.0, 55.3, 34.9. N_2 adsorption (77 K): SA_{BET} = 2518 m^2 g^{-1}, total pore volume =1.7 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 5.9 mmol g^{-1}, at 295 K/1 bar = 3.6 mmol g^{-1}; TGA: Thermal degradation commences at 280 °C. Elemental analysis: calculated for ideal repeat unit [$C_{24}H_{15}$]: C 95.02, H 4.98, Cl 0.0 %; found: C 77.00, H 4.21, Cl 0.83 %.



ESI Fig. 1 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from TPB.



ESI Fig. 2 SSNMR of the network polymer derived from TPB. The peaks at 12.0 and 270 ppm are spinning side-bands.

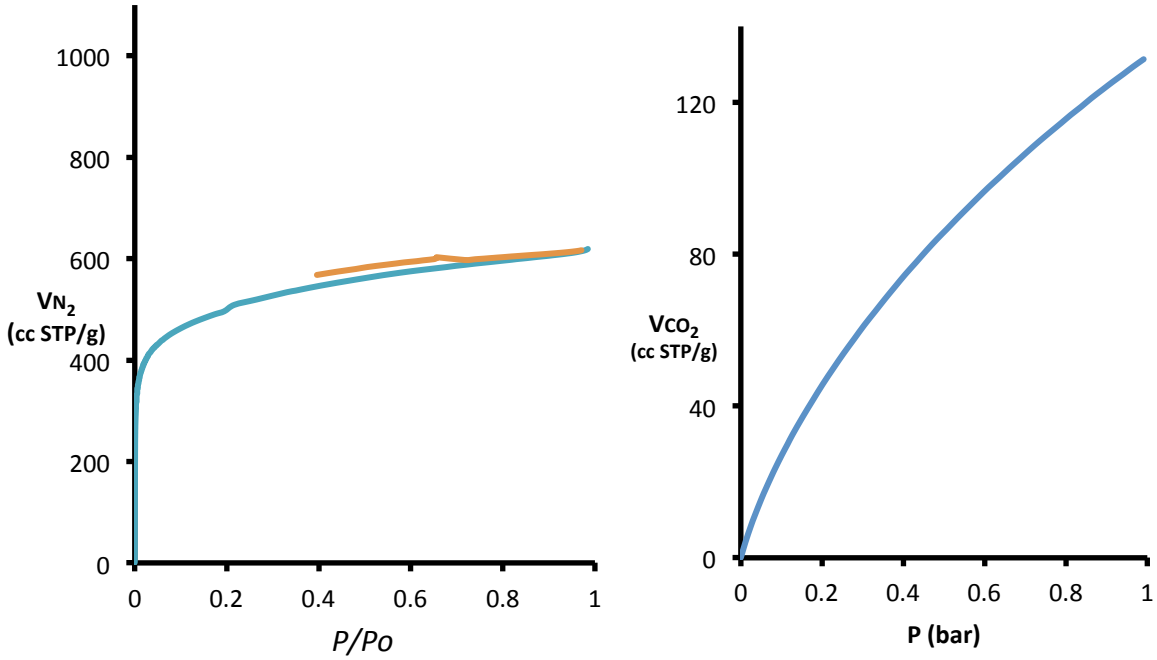


ESI Fig. 3 TGA of the network polymer derived from TPB.

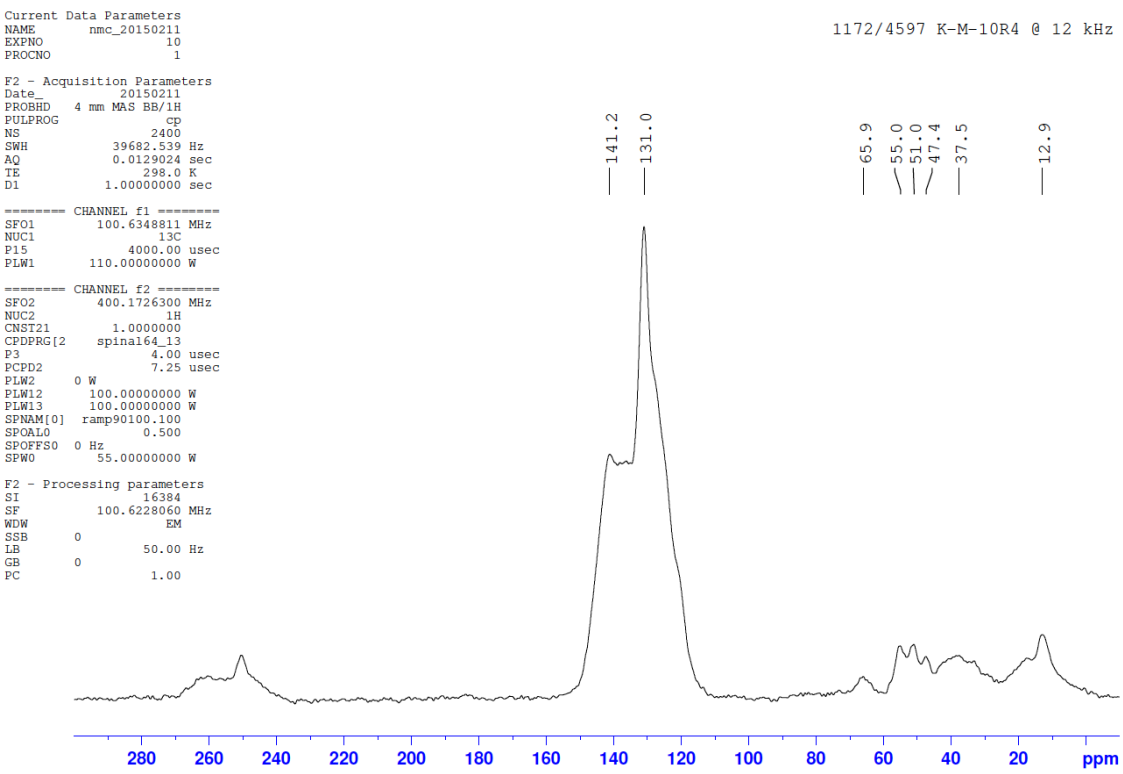
b. Polymer from 1,3,5-triphenylbenzene/chloroform. A brown powder was obtained using the general procedure from 1,3,5-triphenylbenzene (1.5 g, 4.89 mmol) with $AlCl_3$ (6.4 g, 48 mmol) in chloroform (60 ml). Yield: 105%. Solid-state ^{13}C NMR (100.5MHz): δ ppm 190.4, 140.3, 127.4, 74.0, 64.0, 54.3. N_2 adsorption (77 K): SA_{BET} = 1414 $m^2\ g^{-1}$ (literature value = 1254 $m^2\ g^{-1}$)[5]; total pore volume = 0.73 ml g^{-1}; CO_2 adsorption (273 K/1 bar,) = 5.0 mmol g^{-1} (literature value = 4.1 mmol g^{-1})[5] CO_2 adsorption (295 K/1 bar = 3.2 mmol g^{-1}); TGA: thermal degradation commences at 288 °C. Elemental analysis: calculated for ideal repeat unit [$C_{24}H_{15}$]: C 95.02, H 4.98 Cl 0.0 %; found: C 71.81, H 3.66, Cl 5.4 %.

c. From 1,3,5-triphenylbenzene/DCE. A brown powder was obtained using the general procedure from 1,3,5-triphenylbenzene (1.07 g, 3.5 mmol) with $AlCl_3$ (5 g, 37.5 mmol) in DCE (60 ml). Yield: 99%. Solid-state ^{13}C NMR (100.5MHz): δ ppm 137.7, 37.1, 14.6. N_2 adsorption (77 K): SA_{BET} = 725 $m^2\ g^{-1}$, total pore volume = 0.68 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 1.7 mmol g^{-1}, at 295 K/1 bar = 1.2 mmol g^{-1}; TGA: thermal degradation commences at 334 °C. Elemental analysis: calculated for ideal repeat unit [$C_{24}H_{15}$]: C 95.02, H 4.98, Cl 0.0%; found: C 79.99, H 5.83, Cl 1.01%.

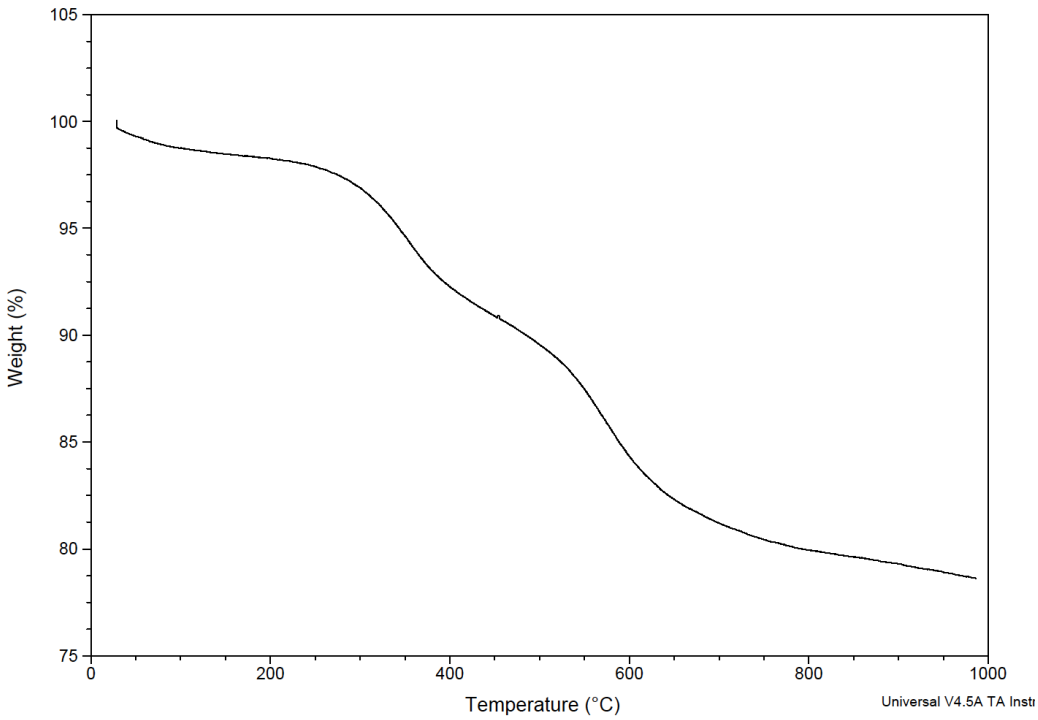
d. Polymer from triptycene/DCM. A brown powder was obtained using the general procedure from triptycene (1.11 g, 4.36 mmol) with $AlCl_3$ (5.7 g, 42.8 mmol) in DCM (40 ml). Yield = 109%. Solid-state ^{13}C NMR (100.5 MHz): δ ppm 140.6, 131.0, 65.9, 55.0, 51.0, 37.5. N_2 adsorption (77 K): SA_{BET} = 1750 m^2 g^{-1}, total pore volume = 1.0 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 5.8 mmol g^{-1}, at 295 K/1 bar = 3.1 mmol g^{-1}; TGA: Thermal degradation commences at 265 °C. Elemental analysis: calculated for ideal repeat unit $[C_{20}H_{11}]$: C 95.6, H 4.4, Cl 0.0 %; C 81.46, H 4.51, Cl 2.77 %.



ESI Fig. 4 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from triptycene.

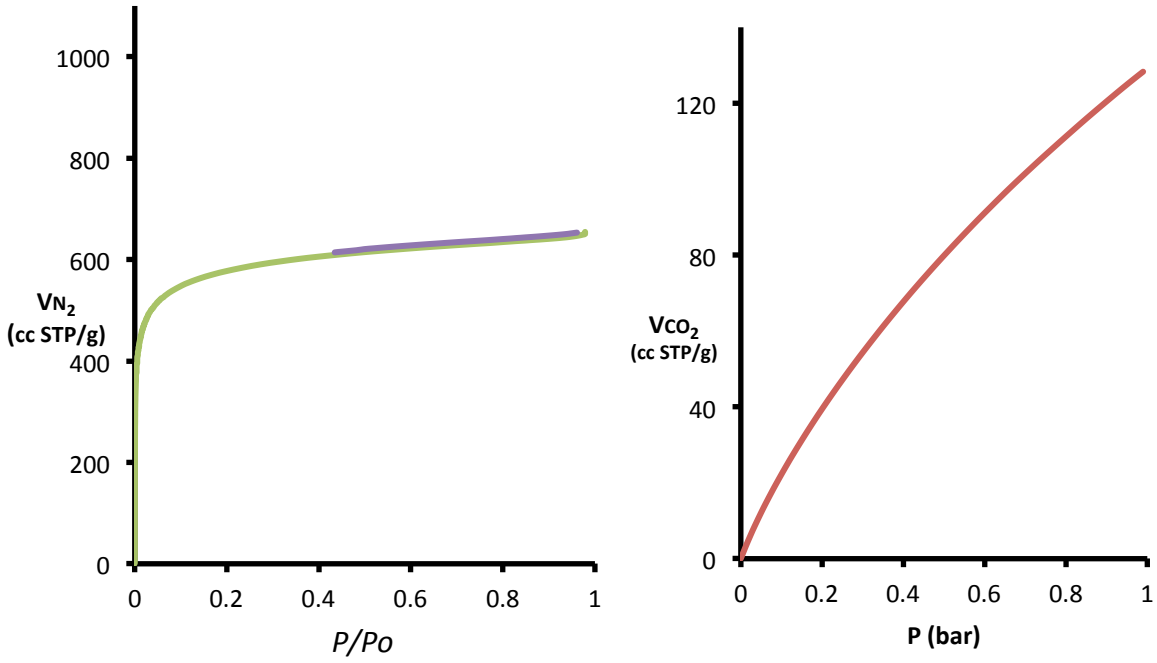


ESI Fig. 5 SSNMR of the network polymer derived from triptycene. The broad peaks at 12.9 and 250 ppm are spinning side-bands.

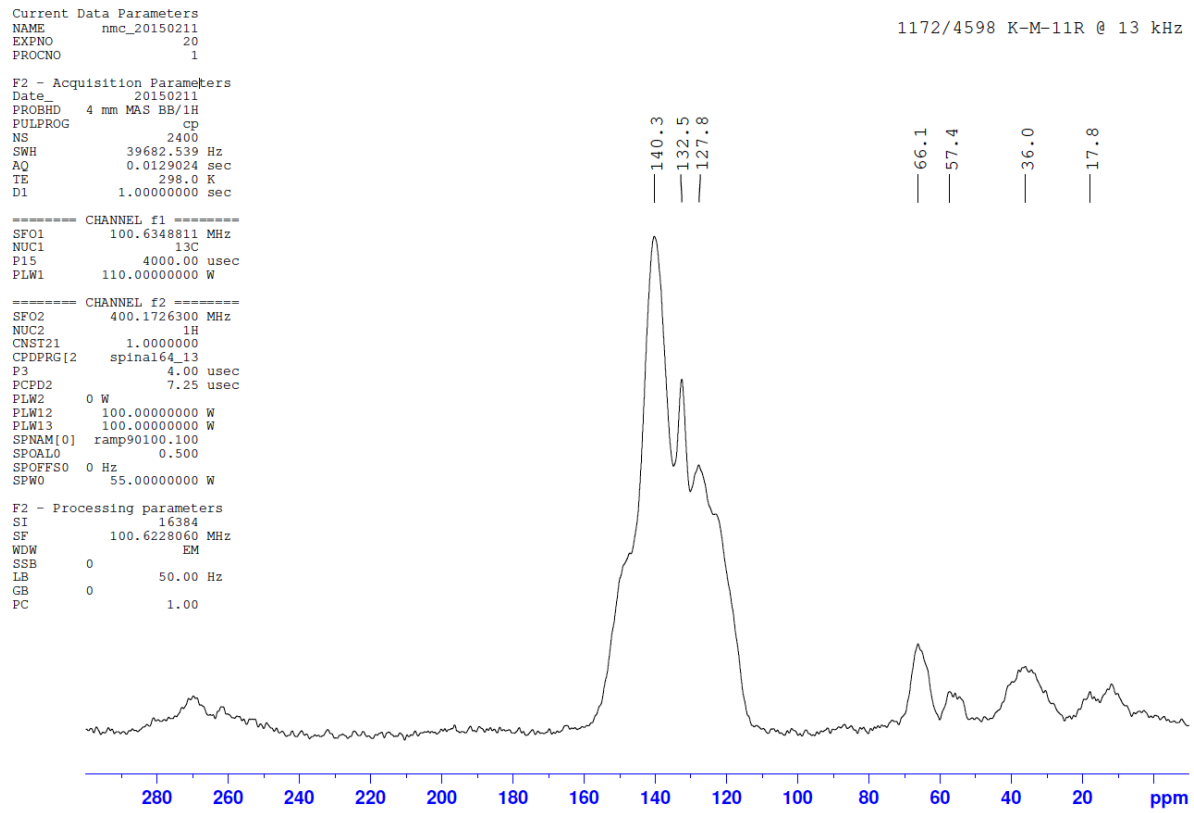


ESI Fig. 6 TGA of the network polymer derived from triptycene.

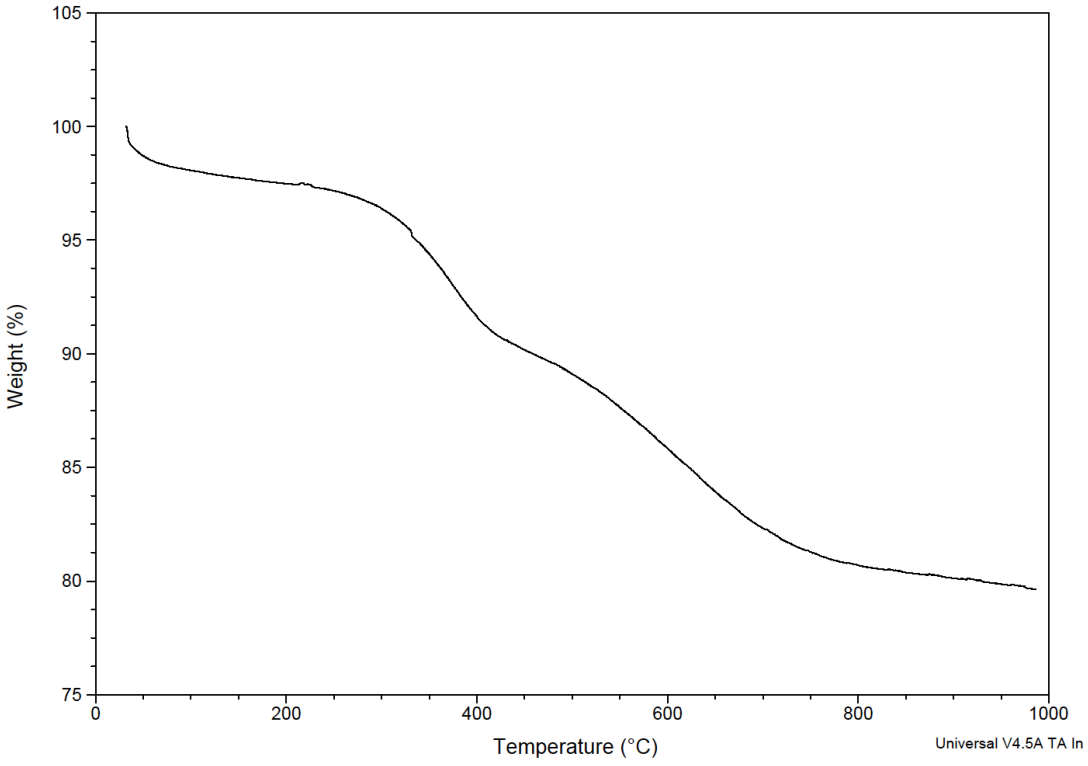
e. Polymer from 9,9'-spirobifluorene/DCM. A brown powder was obtained using the general procedure from 9,9'-spirobifluorene (0.88 g, 2.8 mmol) with $AlCl_3$ (3.88 g, 29.13 mmol) in DCM (30 ml). Yield: 109%. Solid-state ^{13}C NMR (100.5 MHz): δ ppm 140.3, 132.5, 127.8, 66.0, 57.4, 36.0. N_2 adsorption (77 K): SA_{BET} = 2036 m^2 g^{-1}, total pore volume = 1.0 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 5.8 mmol g^{-1}, at 295 K/1 bar = 3.0 mmol g^{-1}; TGA: Thermal degradation commences at 305 °C. Elemental analysis: calculated for ideal repeat unit [$C_{25}H_{12}$]: C 96.12, H 3.82 Cl 0.0 %; found: C 79.36, H 4.09, Cl 1.97 %.



ESI Fig. 7 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from spirobifluorene.

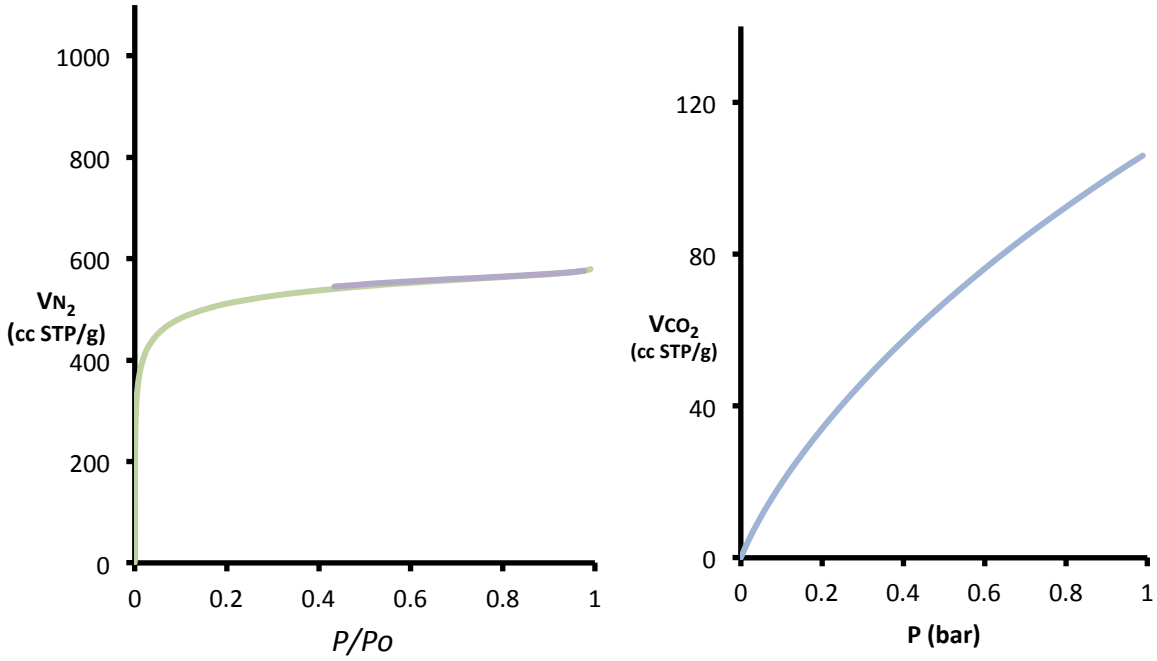


ESI Fig. 8 SSNMR of the network polymer derived from spirobifluorene. The broad peaks at 12.0 and 270 ppm are spinning side-bands.

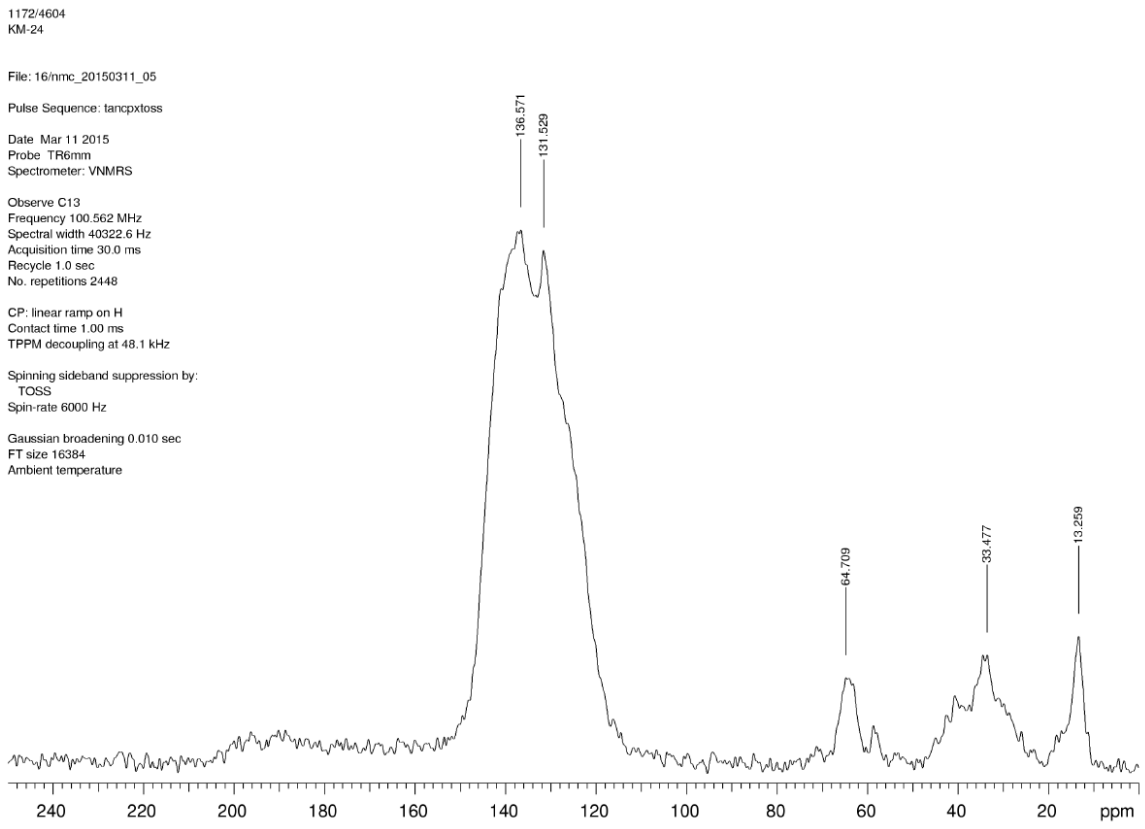


ESI Fig. 9 TGA of the network polymer derived from spirobifluorene.

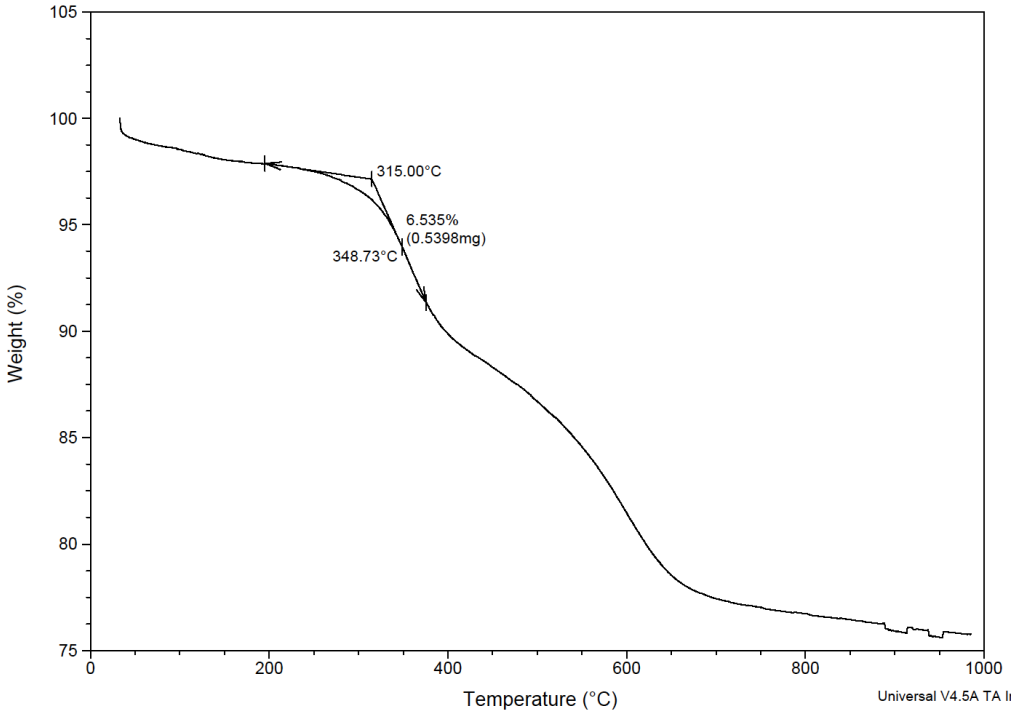
f. Polymer from hexaphenylbenzene/DCM. A brown powder was obtained using the general procedure from hexaphenylbenzene (0.9 g, 1.68 mmol) with $AlCl_3$ (3 g, 22.5 mmol) in DCM (40 ml). Yield: 110% Solid-state ^{13}CNMR (100.5 MHz): δ ppm 136.5, 131.5, 67.0, 33.7. N_2 adsorption (77 K): SA_{BET} = 1791 m^2 g^{-1}, total pore volume = 0.9 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 4.5 mmol g^{-1}, at 295 K/1 bar = 2.7 mmol g^{-1}; TGA: Thermal degradation commences at 270 °C. Elemental analysis: calculated for ideal repeat unit [$C_{42}H_{24}$]: C 95.42, H 4.57, Cl 0.0 %; found: C 78.6, H 4.43, Cl 2.36 %.



ESI Fig. 10 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from HPB.

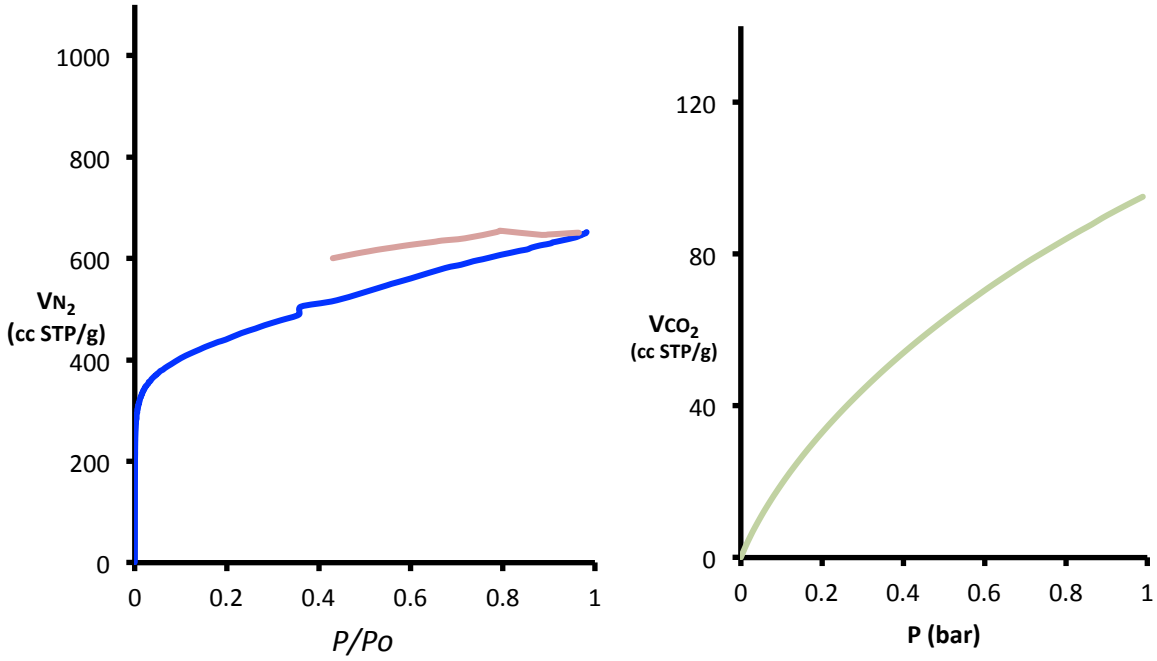


ESI Fig. 11 SSNMR of the network polymer derived from HPB. The peaks at 13.0 ppm is a spinning side-band.

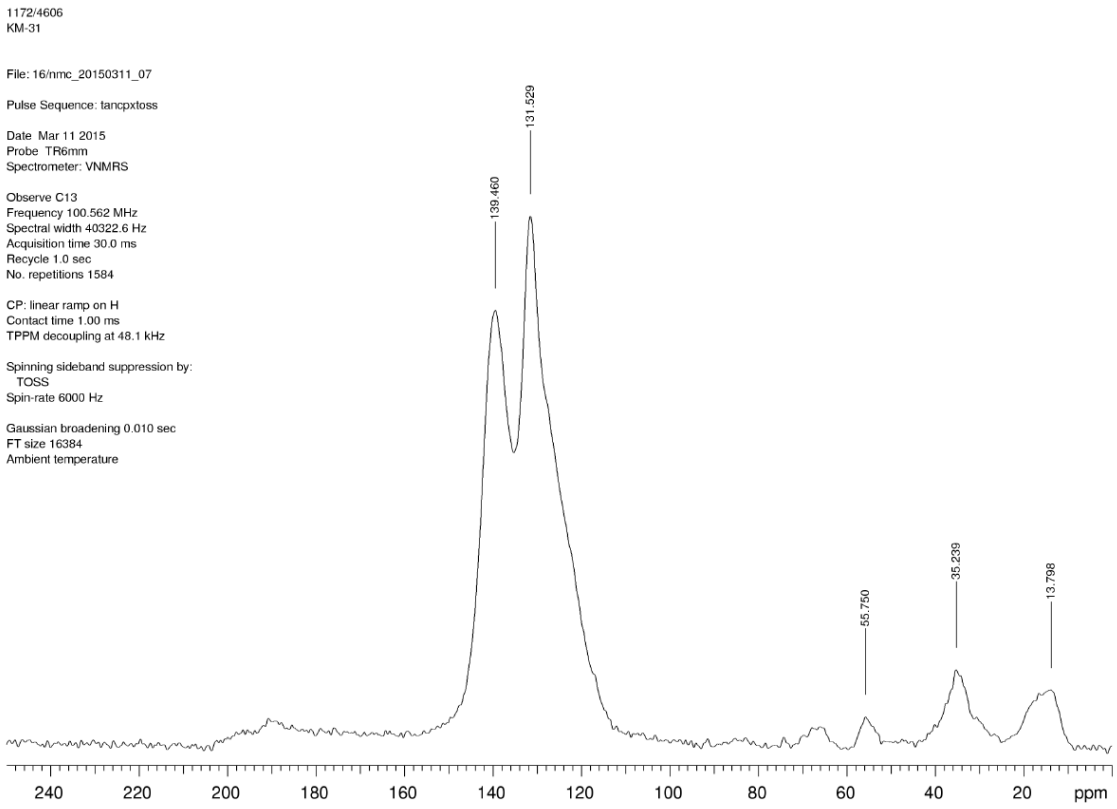


ESI Fig. 12 TGA of the network polymer derived from HPB.

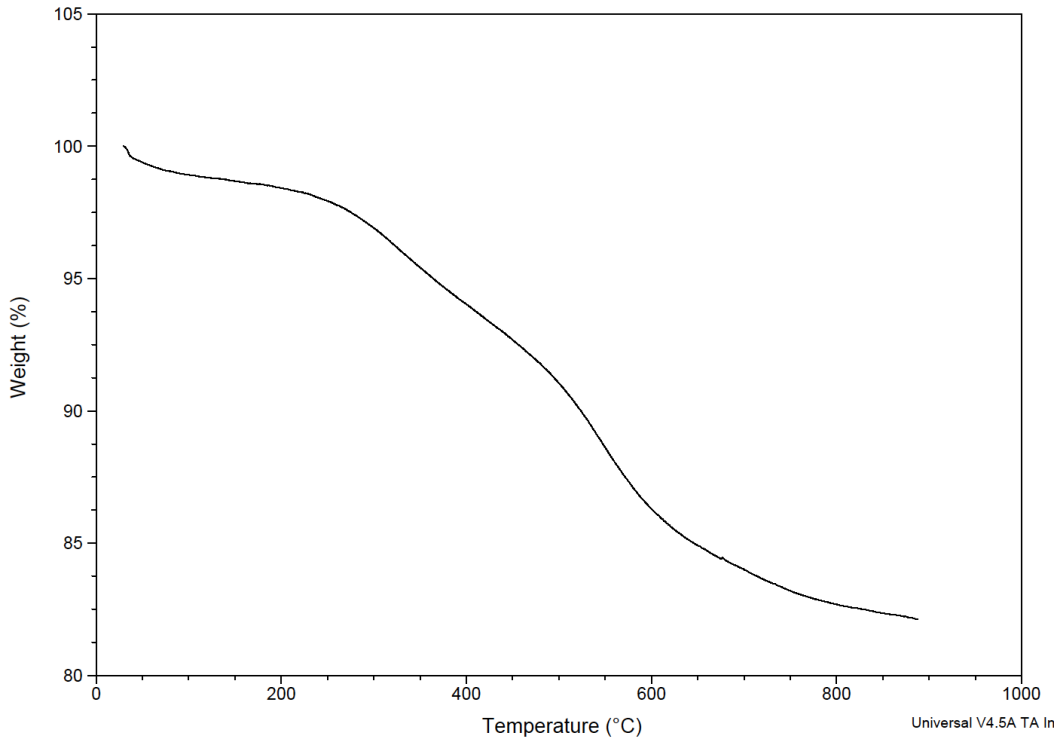
g. Polymer from biphenyl/DCM. A brown powder was obtained using the general procedure from biphenyl (1.18 g, 7.65 mmol) with $AlCl_3$ (4.8 g, 36 mmol) in DCM (30 ml). Yield = 106%. Solid-state ^{13}C NMR (100.5MHz): δ ppm 139.5, 131.5, 55.0, 35.2. N_2 adsorption (77 K): SA_{BET} = 1552 m^2 g^{-1}; total pore volume = 1.0 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 4.0 mmol g^{-1}, at 295 K/1 bar = 2.7 mmol g^{-1}; TGA: Thermal degradation commences at 270 °C. Elemental analysis: calculated for ideal repeat unit [$C_{12}H_8$]: C 94.7, H 4.4, Cl 0.0 %; found: C 83.66, H 4.7, Cl 1.51%.



ESI Fig. 13 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from biphenyl.



ESI Fig. 14 SSNMR of the network polymer derived from biphenyl. The broad peak at 13.0 is a spinning side-band.

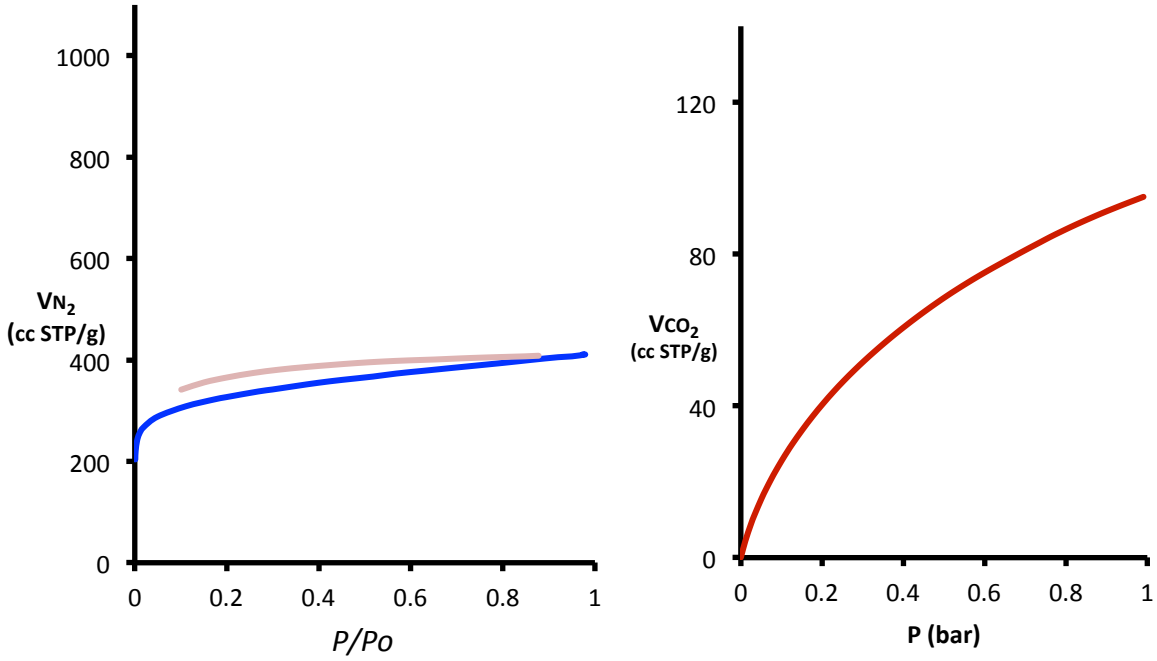


ESI Fig. 15 TGA of the network polymer derived from biphenyl.

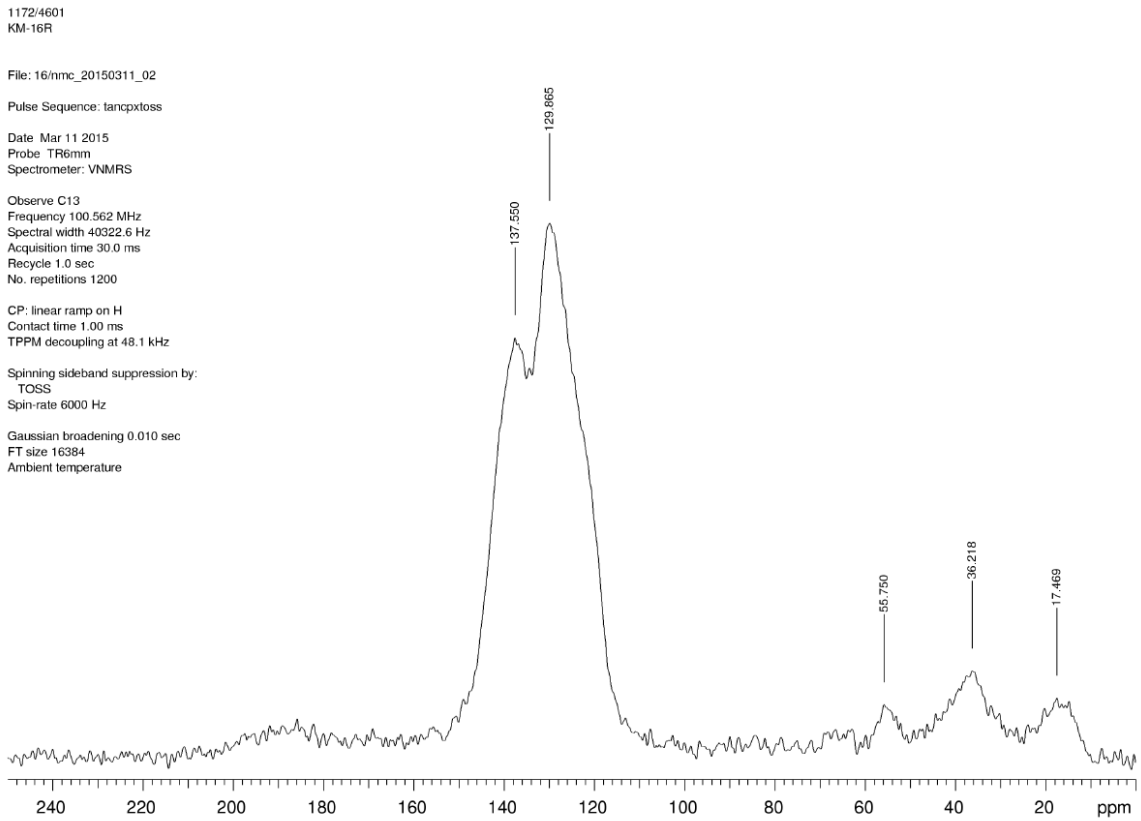
i. Polymer from biphenyl/chloroform. A brown powder was obtained using the general procedure from biphenyl (1.19 g, 7.71 mmol) with $AlCl_3$ (5.3 g, 39 mmol) in chloroform (35 ml). Yield =108%. Solid-state ^{13}C NMR (100.5 MHz): δ ppm 190.1, 140.3, 126.4, 82.6, 54.8. N_2 adsorption (77 K): SA_{BET} = 799 m^2 g^{-1} (literature value = 777 m^2 g^{-1})[4]; total pore volume = 0.45 ml g^{-1}; CO_2 adsorption (1 bar, 273 K) = 3.3 mmol g^{-1} (literature value = 3.3 mmol g^{-1})[4] at 295 K/1 bar = 2.4 mmol g^{-1}; TGA: Thermal degradation commences at 338 °C. Elemental analysis: calculated for ideal repeat unit [$C_{12}H_8$]: C 94.7, H 4.4, Cl 0.0 %; found: C 68.03, H 3.55, Cl 10.44 %.

j. Polymer from biphenyl/DCE. A brown powder was obtained using the general procedure from biphenyl (1.52g, 9.85 mmol) with $AlCl_3$ (7g, 52 mmol) in DCE (55 ml). Yield = 90%. Solid-state ^{13}C NMR (100.5MHz): δ ppm 136.7, 35.3, 15.1. N_2 adsorption (77 K): SA_{BET} = 453 m^2 g^{-1}; total pore volume= 0.3 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 1.7 mmol g^{-1}, at 295 K/1 bar = 1.0 mmol g^{-1}; TGA: Thermal degradation commences at 280 °C. Elemental analysis: calculated for ideal repeat unit [$C_{12}H_8$]: C 94.7, H 4.4, Cl 0.0 %; found: C 77.85, H 5.83, Cl 1.1%.

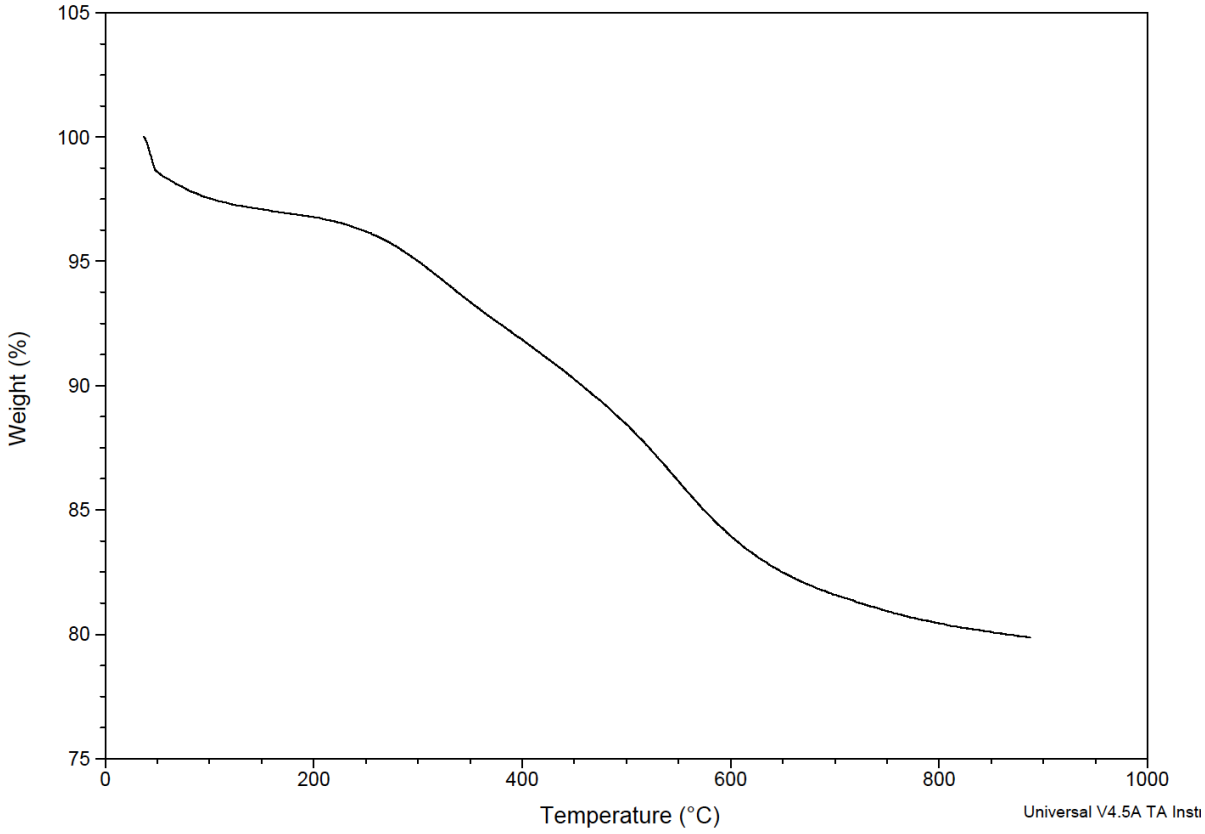
k. Polymer from triphenylene/DCM. A brown powder was obtained using the general procedure from triphenylene (1.15 g, 5.06 mmol) with $AlCl_3$ (4.5 g, 33.7 mmol) in DCM (30 mL). Yield: 102%. Solid-state ^{13}C NMR (100.5 MHz): δ ppm 137.6, 129.9, 36.2. N_2 adsorption (77 K): SA_{BET} = 1181 ml g^{-1}, total pore volume = 0.66 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 4.0 mmol g^{-1}, at 295 K/1 bar = 2.9 mmol g^{-1}; TGA: Thermal degradation commences at 345 °C. Elemental analysis: calculated for ideal repeat unit [$C_{18}H_9$]: C 95.97, H 4.02, Cl 0.0 %; found: C 78.72, H 3.84, Cl 1.47 %.



ESI Fig. 16 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from triphenylene.

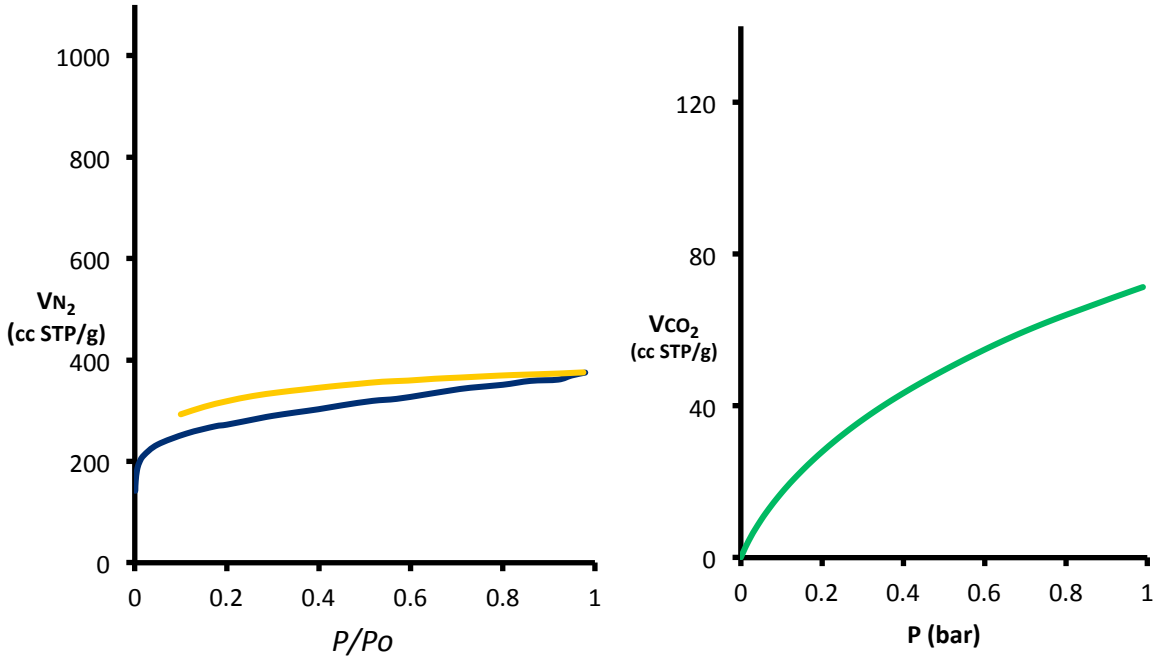


ESI Fig. 17 SSNMR of the network polymer derived from triphenylene. The broad peak at 17.0 is a spinning side-band.

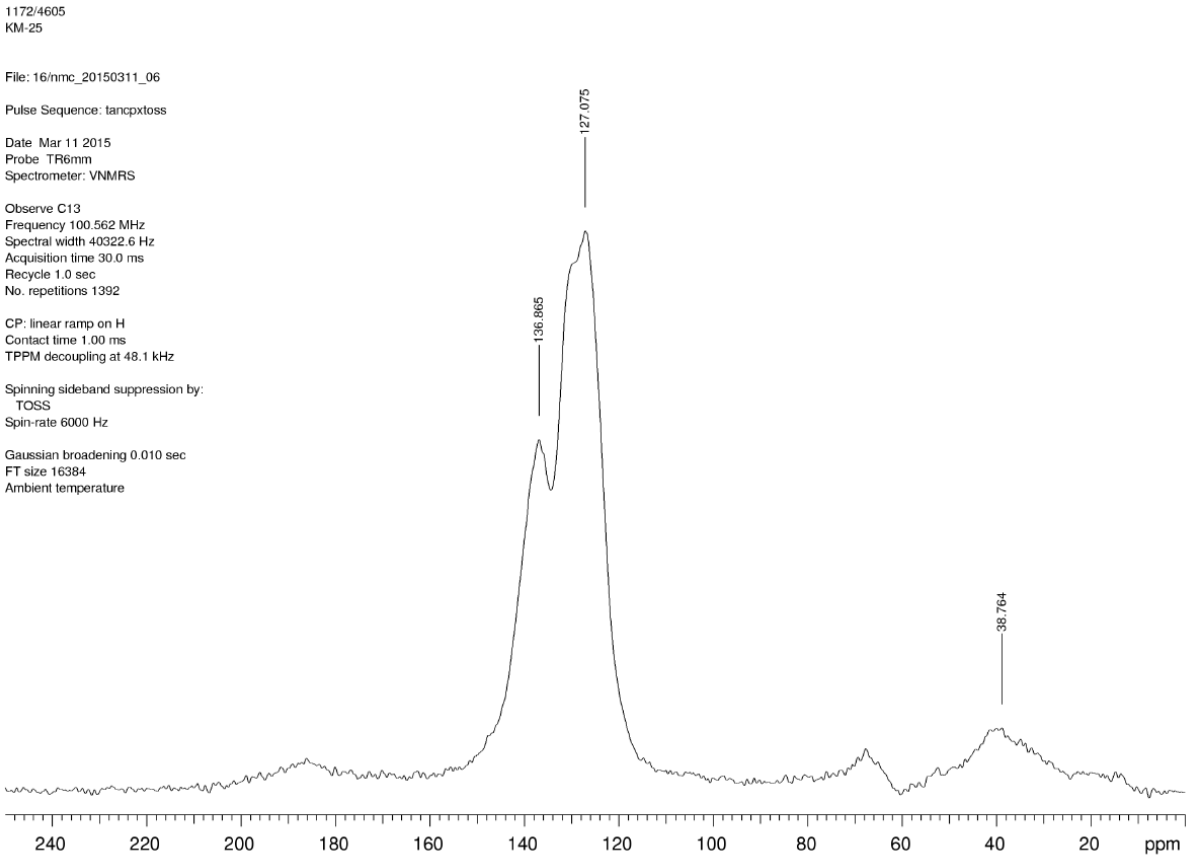


ESI Fig. 18 TGA of the network polymer derived from triphenylene.

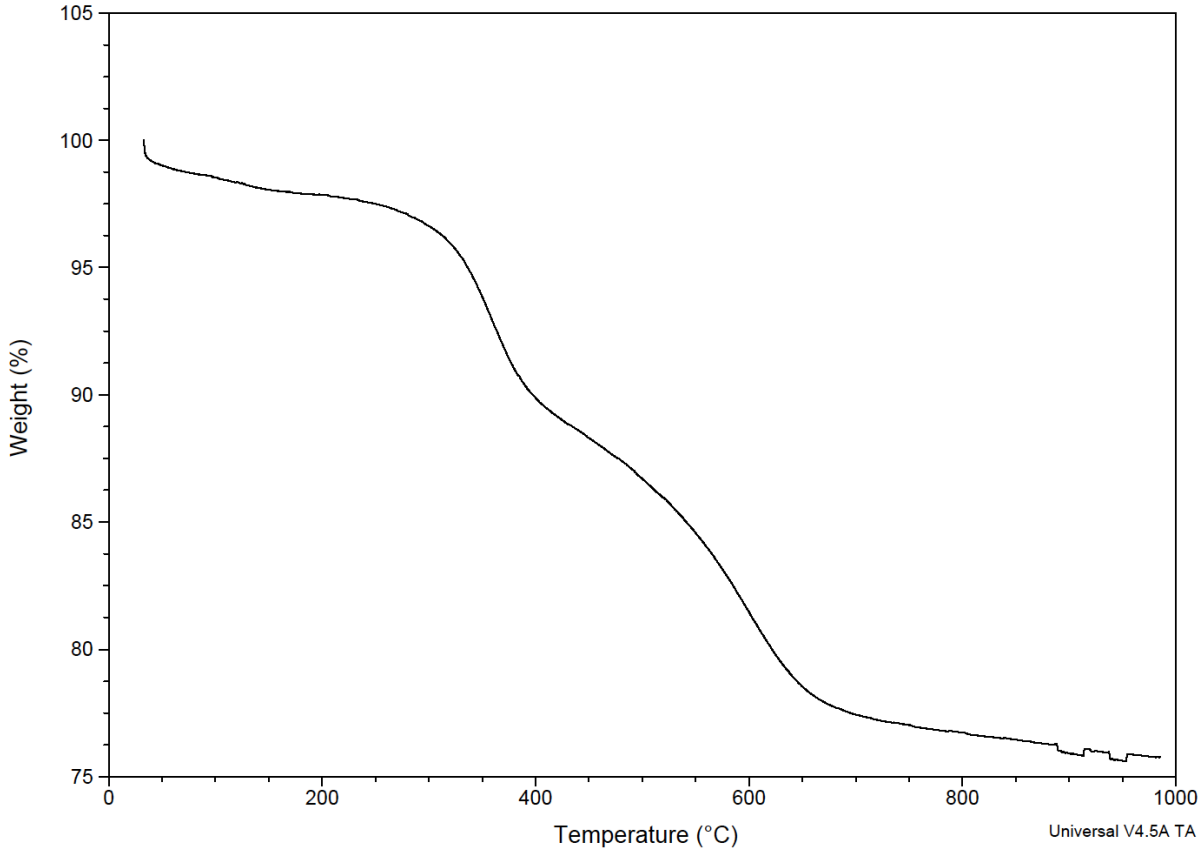
l. Polymer from 9,10-diphenyl anthracene/DCM. A brown powder was obtained using the general procedure from 9,10-diphenyl anthracene (1.07 g, 3.23 mmol) with $AlCl_3$ (4.1 g, 30 mmol) in DCM (30 ml). Yield:100%. Solid-state ^{13}C NMR (100.5 MHz): δ ppm 136.8, 127.1, 38.7. N_2 adsorption (77 K): SA_{BET} = 1018 m^2 g^{-1}, total pore volume = 0.6 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 3.2 mmol g^{-1}, at 295 K/1 bar = 2.0 mmol g^{-1}; TGA: thermal degradation commences at 408 °C. Elemental analysis: calculated for ideal repeat unit $[C_{26}H_{12}]$: C 96.27, H 3.72, Cl 0.0 %; found: C 86.1, H 4.5, Cl 0.69.



ESI Fig. 19 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from 9,10-diphenylanthracene.

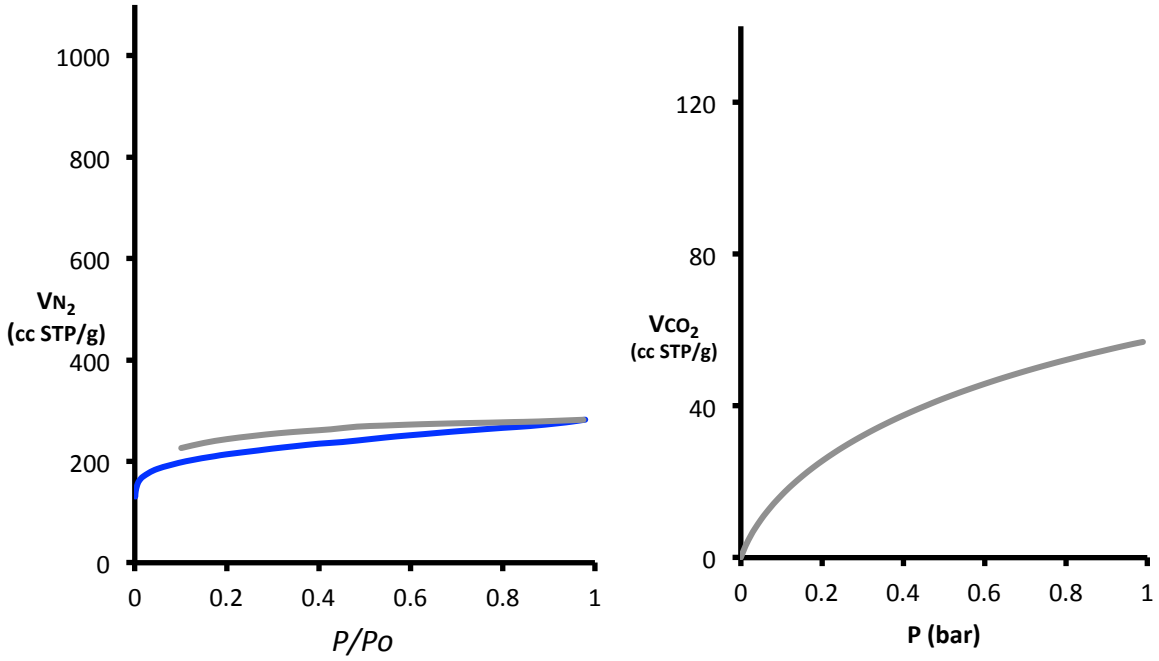


ESI Fig. 20 SSNMR of the network polymer derived from 9,10-diphenyl anthracene.

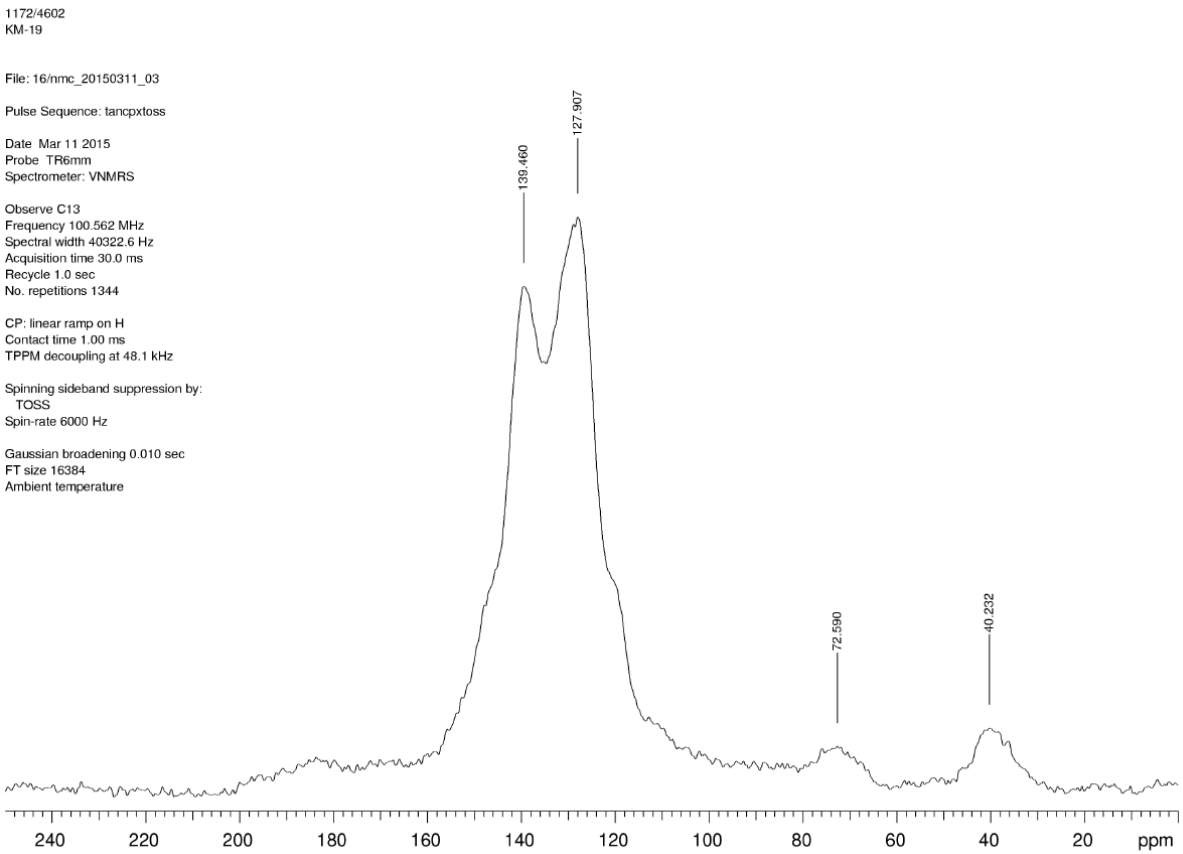


ESI Fig. 21 TGA of the network polymer derived from 9,10-diphenylanthracene.

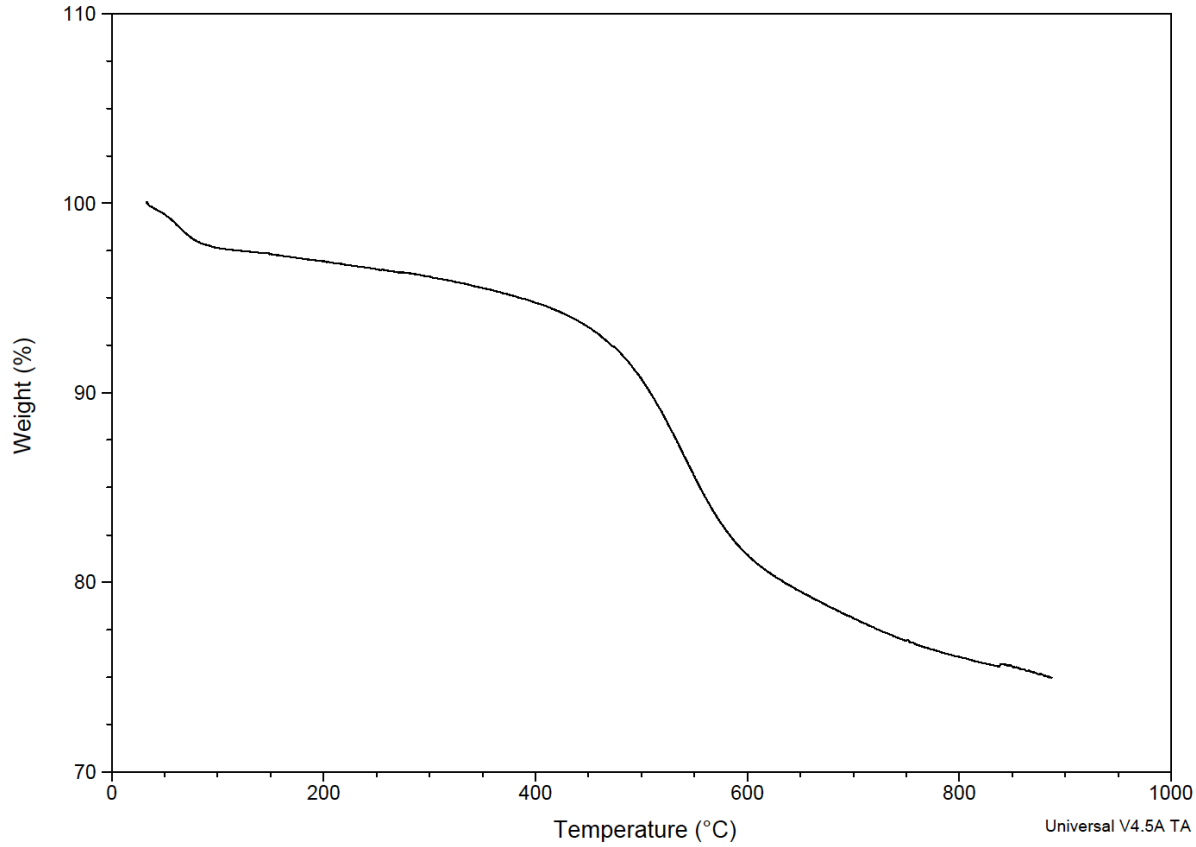
m. Polymer from tetraphenylporphyrin/DCM. A black powder was obtained using the general procedure from 5,10,5,20-tetraphenylporphyrin (1.19 g, 1.94 mmol) with $AlCl_3$ (4.4 g, 33 mmol) in DCM (35 ml). Yield: 101%. Solid-state ^{13}C NMR (100.5MHz): δ ppm 139.5, 127.9, 72.0, 40.2. N_2 adsorption (77 K): SA_{BET} = 907 ml g^{-1}, total pore volume = 0.44 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 2.5 mmol g^{-1}, at 295 K/1 bar = 2.0 mmol g^{-1}; TGA: thermal degradation commences at 420 °C. Elemental analysis: calculated for ideal repeat unit $[C_{44}H_{30}N_4]$: C 86, H 4.91, N 9.1, Cl 0.0%; found: C 68.03, H 3.66, N 6.61, Cl 1.51%.



ESI Fig. 22 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from tetraphenylporphyrin.

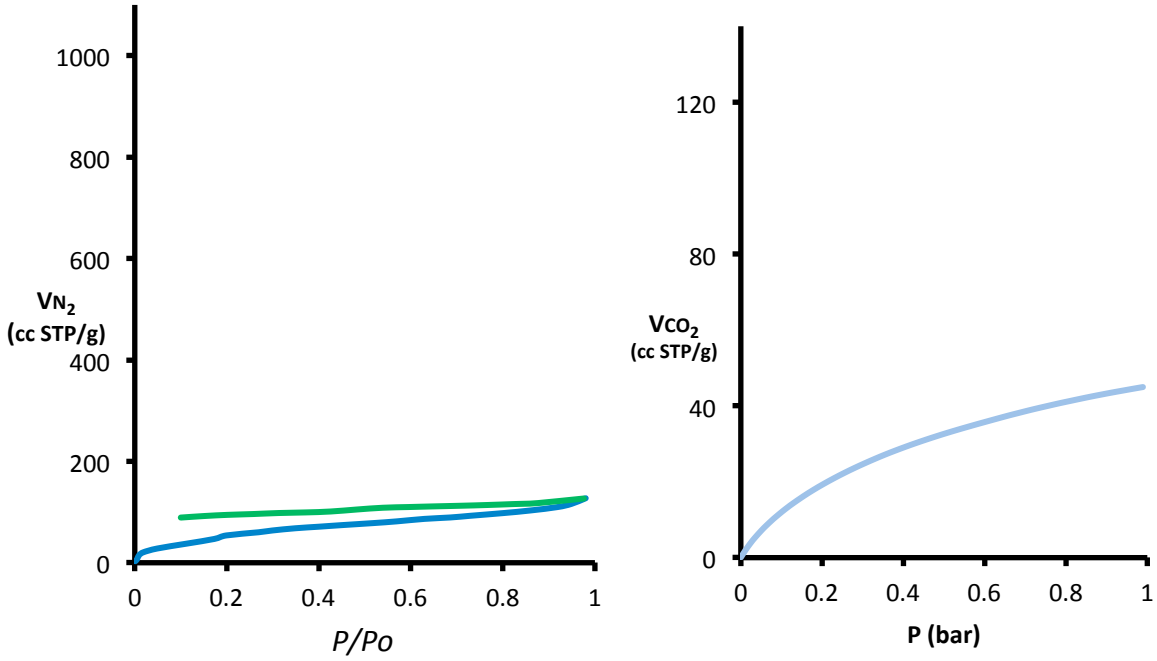


ESI Fig. 23 SSNMR of the network polymer derived from tetraphenylporpyrin.

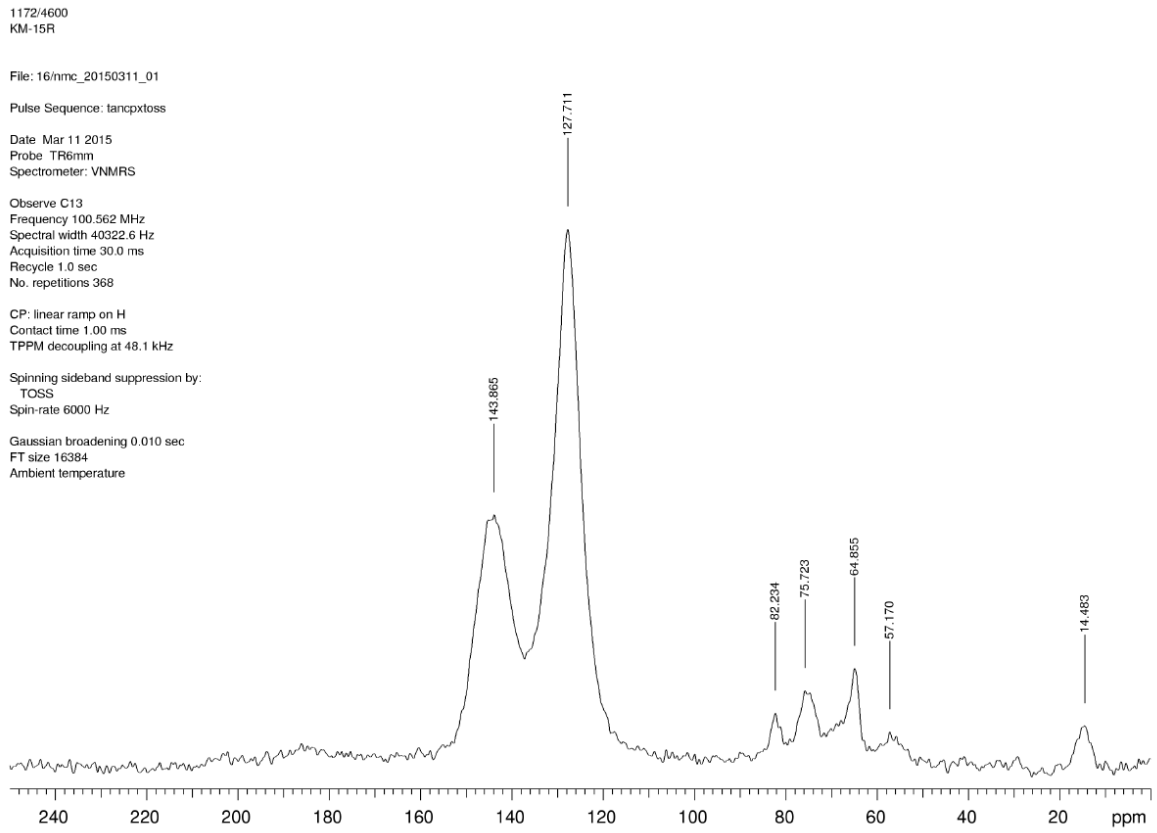


ESI Fig. 24 TGA of the network polymer derived from Tetraphenylporphyrin.

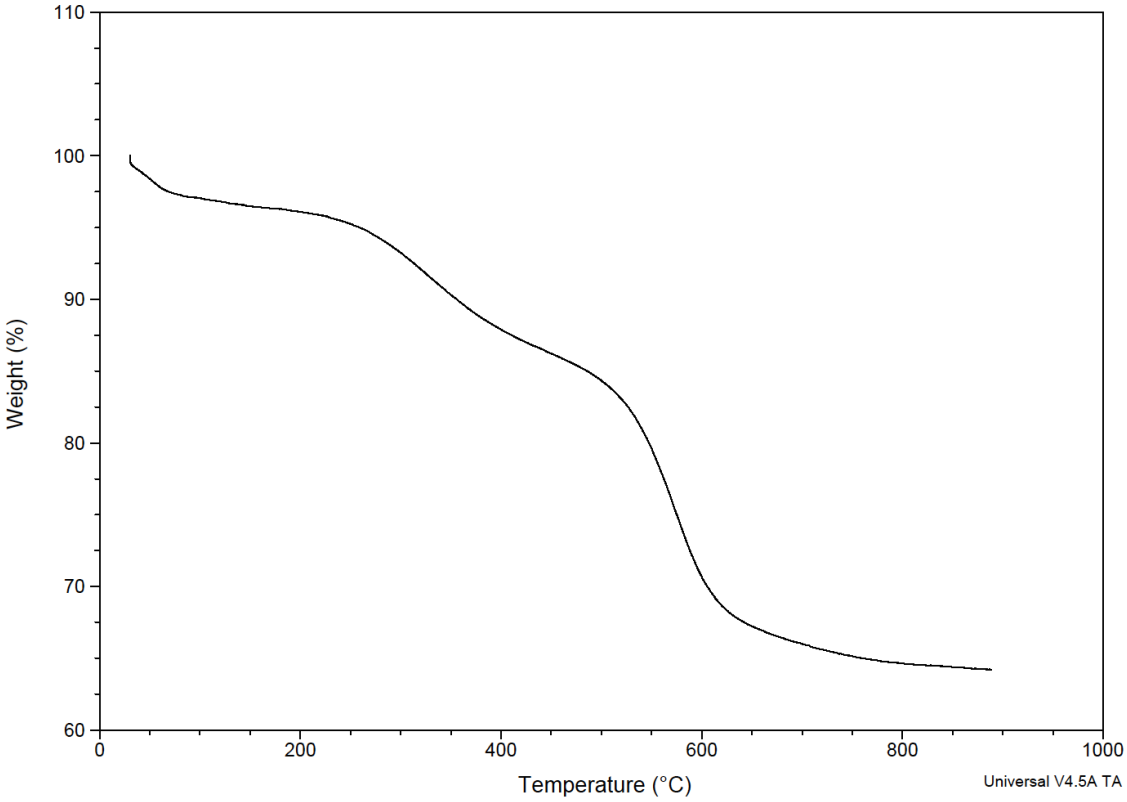
From tetraphenylmethane/DCM. A brown powder was obtained using the general procedure from tetraphenylmethane (1.08 g, 3.37 mmol) with $AlCl_3$ (5.2 g, 39 mmol) in DCM (30 ml). Yield: 49%. Solid-state ^{13}C NMR (100.5MHz): δ ppm 143.9, 127.7, 82.2, 75.7, 64.9. N_2 adsorption (77 K): SA_{BET} = 124 ml g^{-1}, total pore volume = 0.2 ml g^{-1}; CO_2 adsorption at 273 K/1 bar = 2.0 mmol g^{-1}, at 295 K/1 bar = 1.3 mmol g^{-1}; TGA: thermal degradation commences at 281 °C. Elemental analysis: calculated for ideal repeating unit $[C_{25}H_{16}]$: C 94.9, H 5.09, Cl 0.0%; found: C 78.15, H 4.74, Cl 2.46%.



ESI Fig. 25 N_2 (77 K) and CO_2 (273 K) isotherms of the network polymer derived from TPM.



ESI Fig. 26 SSNMR of the network polymer derived from TPM. The peak at 14.0 ppm is a spinning side-band.



ESI Fig. 27 TGA of the network polymer derived from TPM.

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