Electronic Supplementary Material (ESI) for Polymer Chemistry.

Swellable functional hypercrosslinked polymer networks for the uptake of chemical warfare agents

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SUPPORTING INFORMATION

Monomer	Equivalent FDA	Yield (%)
Toluene	1.5	106
Toluene	1.6	113
Toluene	1.7	111
Toluene	1.9	109
Toluene	2	114
Toluene	2.3	108
Toluene	2.5	107
Toluene	2.7	109
Toluene	3	119
Toluene	4	120
Toluene	5	116
Chlorobenzene	2	91
Chlorobenzene	3	92
Fluorobenzene	2	102
Fluorobenzene	3	93
Anisole	2	97
Anisole	3	98
Phenol	2	70
Phenol	3	92

Fig. S1 Percentage yields for HCPs prepared.

Monomer	Equivalent FDA	Theoretical C (%)	Actual C (%)	Theoretical H (%)	Actual H (%)
Toluene	1.5	91.84	87.94	8.16	6.53
Toluene	1.6	91.76	85.84	8.24	6.47
Toluene	1.7	91.69	86.73	8.31	6.53
Toluene	1.9	91.54	86.25	8.46	6.51
Toluene	2	91.47	85.56	8.53	6.29
Toluene	2.3	91.27	84.43	8.73	6.33
Toluene	2.5	91.88	84.36	8.12	6.27
Toluene	2.7	91.74	84.53	8.26	6.30
Toluene	3	91.55	82.48	8.45	6.00
Toluene	4	91.61	80.61	8.39	5.89
Toluene	5	91.67	76.37	8.33	5.58
Chlorobenzene	2	69.33	66.61	5.09	3.75
Chlorobenzene	3	71.30	65.99	5.32	3.66
Fluorobenzene	2	78.67	76.01	5.78	4.24
Fluorobenzene	3	79.39	72.87	6.66	4.05
Anisole	2	80.56	75.68	7.51	5.55
Anisole	3	81.60	70.68	7.53	5.01
Phenol	2	79.97	71.72	6.71	5.02
Phenol	3	81.17	67.55	6.81	4.71

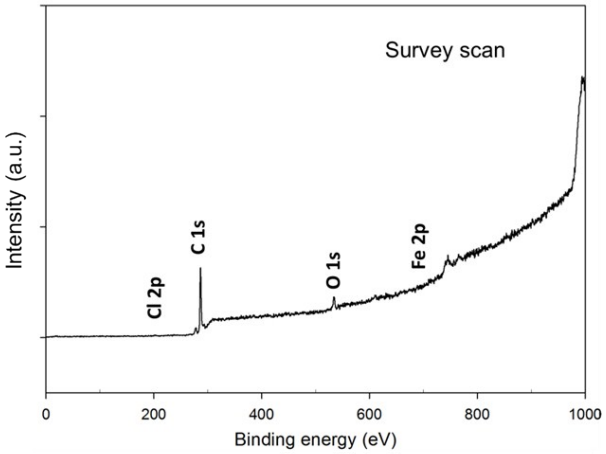
Fig. S2 Microanalysis data for HCPs prepared.

Monomer	Equivalent FDA	Mass loss (wt %)
Toluene	1.5	0.8
Toluene	1.6	1.0
Toluene	1.7	1.5
Toluene	1.9	0.9
Toluene	2	1.0
Toluene	2.3	1.1
Toluene	2.5	0.9
Toluene	2.7	1.0
Toluene	3	2.7
Toluene	4	2.0
Toluene	5	3.1
Chlorobenzene	2	0.5
Chlorobenzene	3	0.5
Fluorobenzene	2	0.5
Fluorobenzene	3	0.9
Anisole	2	1.3
Anisole	3	3.7
Phenol	2	4.6
Phenol	3	7.5

Fig. S3 TGA data for HCPs, showing mass loss (wt%) after heating the polymer to 150 °C and holding at 150 °C for 60 minutes.

(a)

Toluene HCP (2 equivalent FDA)	Atomic %
Fe	0
O	7.5
C	91.9
Cl	0.6
Total	100 %



(b)

Toluene HCP (5 equivalent FDA)	Atomic %
Fe	0.3
O	15.2
C	83.9
Cl	0.6
Total	100 %

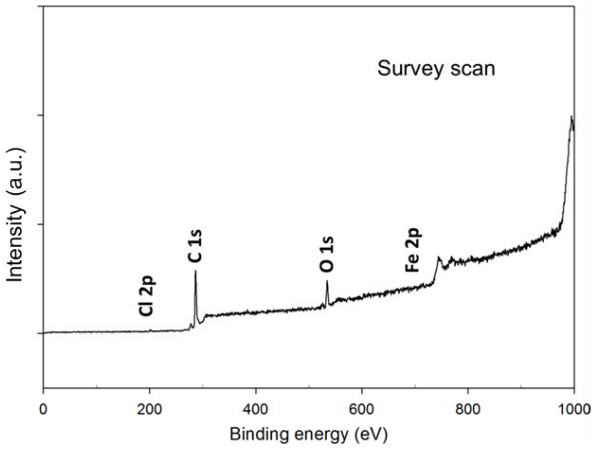


Fig. S4 Atomic composition (%) from XPS analysis for toluene HCPs prepared using (a) 2 equivalents and (b) 5 equivalents of FDA crosslinker.

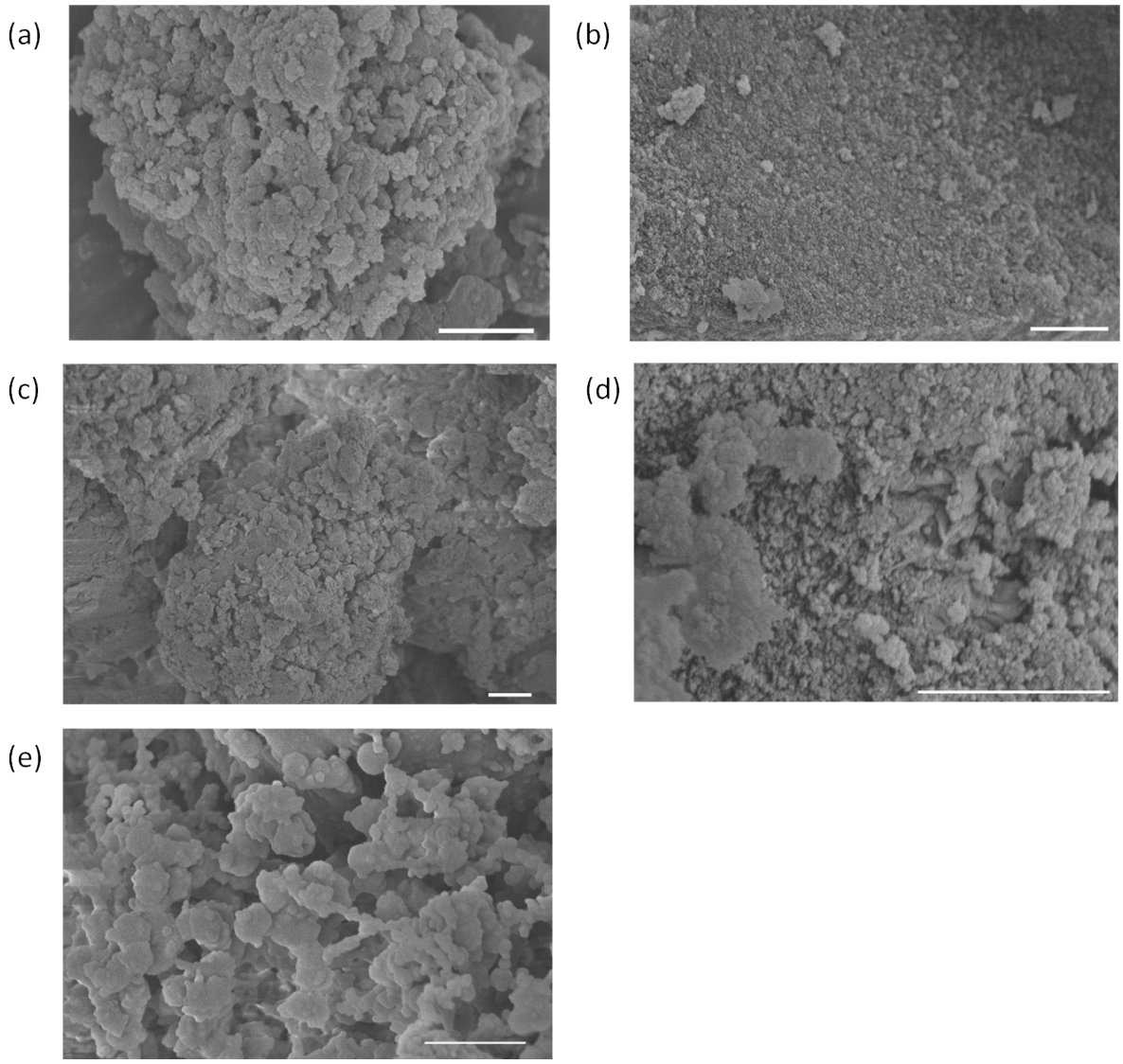


Fig. S5 SEM micrographs obtained for (a) fluorobenzene, (b) toluene, (c) chlorobenzene, (d) anisole, and (e) phenol based HCPs, all prepared with 2 equivalents of the FDA crosslinker.

(scale bar= 1.00 μm)

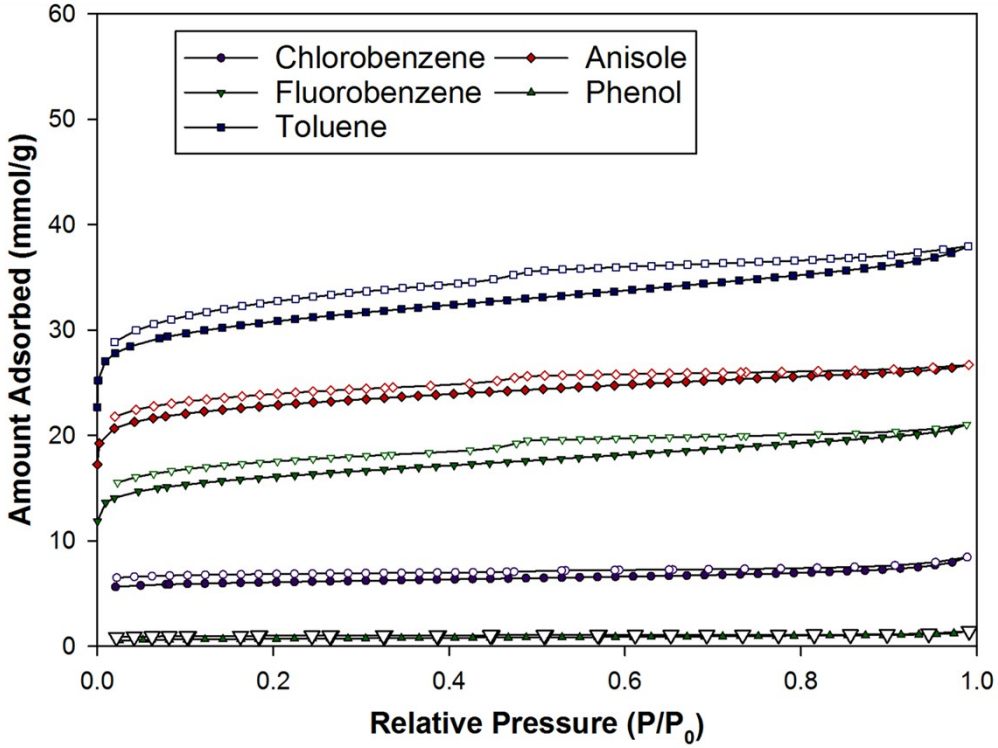


Fig. S6.1 Nitrogen isotherms for HCPs prepared using 2 equivalents of FDA. Adsorption (filled symbols), desorption (empty symbols). Data offset by 20 mmol/g (using 5 mmol/g increments) for clarity.

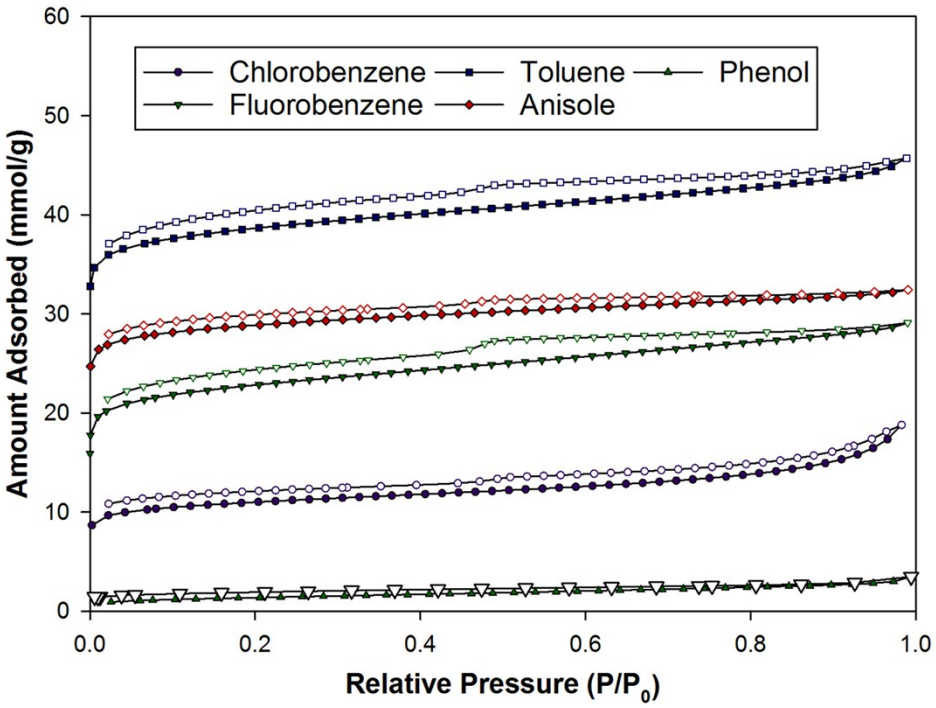


Fig. S6.2 Nitrogen isotherms for HCPs prepared using 3 equivalents of FDA. Adsorption (filled symbols), desorption (empty symbols). Data offset by 20 mmol/g (using 5 mmol/g increments) for clarity.

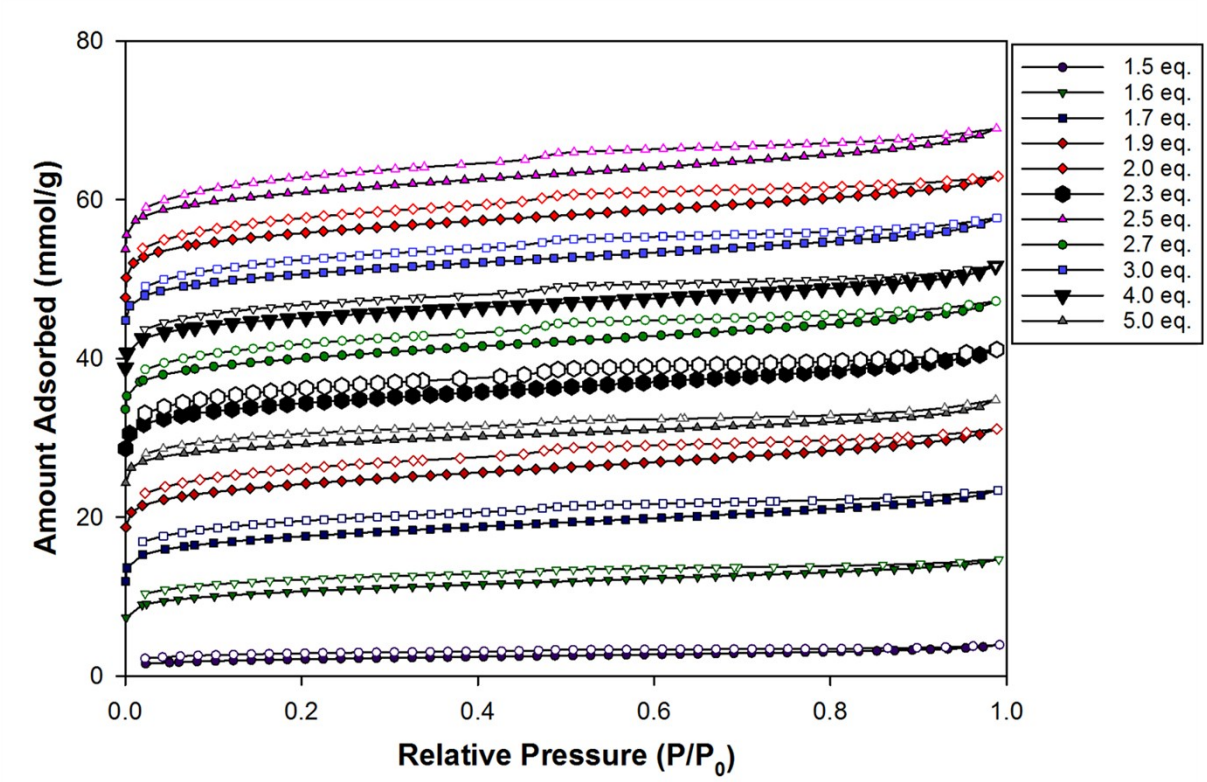


Fig. S6.3 Nitrogen isotherms for toluene HCPs with varying FDA amounts. Adsorption (filled symbols), desorption (empty symbols). Data offset by 50 mmol/g (using 5 mmol/g increments) for clarity.

Monomer	Equivalent FDA	SA_{BET} (m^2 g^{-1})	V_{total} (cm^3/g)
Toluene	1.5	171	0.14
Toluene	1.6	452	0.34
Toluene	1.7	602	0.46
Toluene	1.9	731	0.56
Toluene	2.0	860	0.62
Toluene	2.3	746	0.56
Toluene	2.5	872	0.66
Toluene	2.7	800	0.60
Toluene	3.0	852	0.61
Toluene	4.0	810	0.56
Toluene	5.0	746	0.51
Chlorobenzene	2.0	88	0.12
Chlorobenzene	3.0	319	0.41
Fluorobenzene	2.0	483	0.38
Fluorobenzene	3.0	698	0.52
Anisole	2.0	627	0.41
Anisole	3.0	637	0.40
Phenol	2.0	58	0.05
Phenol	3.0	110	0.12

Fig. S6.4 Summary of the apparent SA_{BET} and total pore volumes (V_{total}) obtained for HCPs prepared. V_{total} calculated from nitrogen isotherm in the range P/P_o=0.89–0.99.

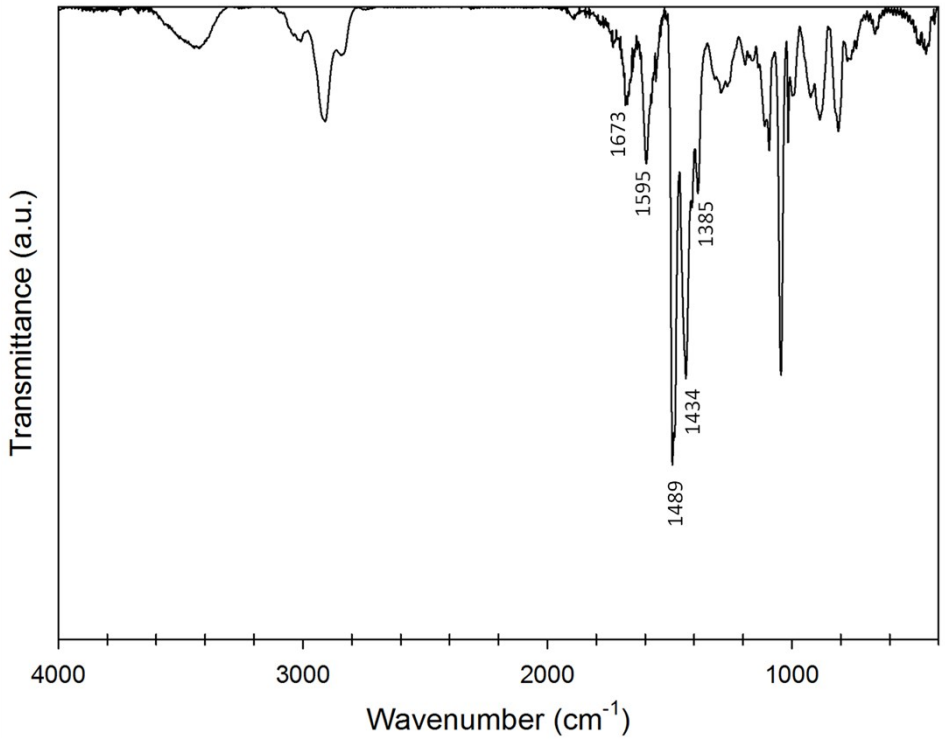


Fig. S7.1 IR spectrum of chlorobenzene based HCP, prepared with 2 equivalents of FDA crosslinker.

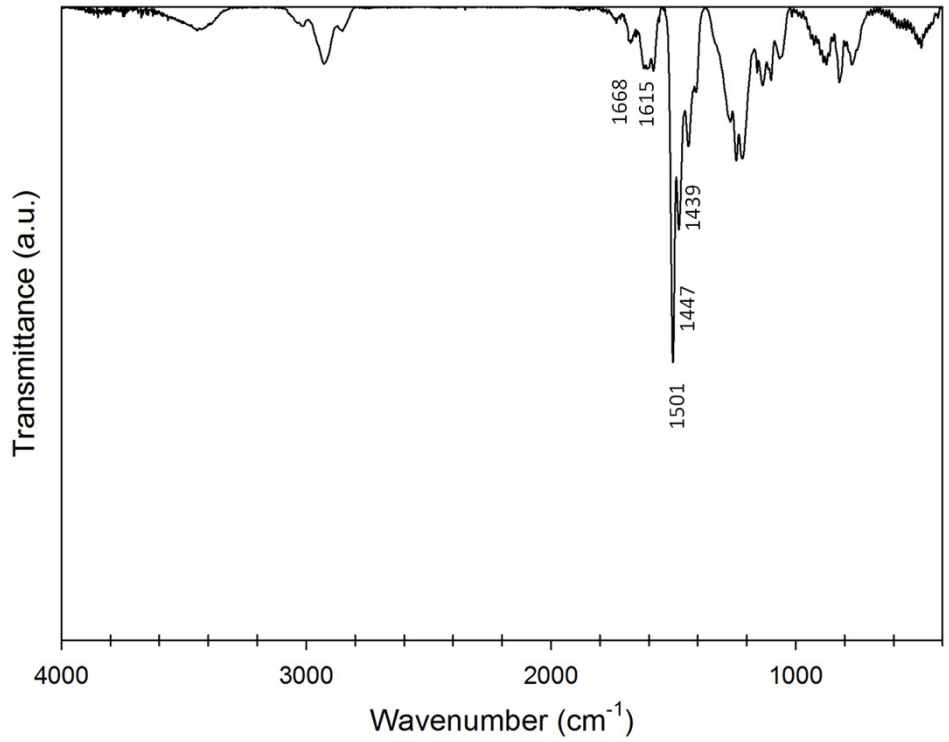


Fig. S7.2 IR spectrum of fluorobenzene based HCP, prepared with 2 equivalents of FDA crosslinker.

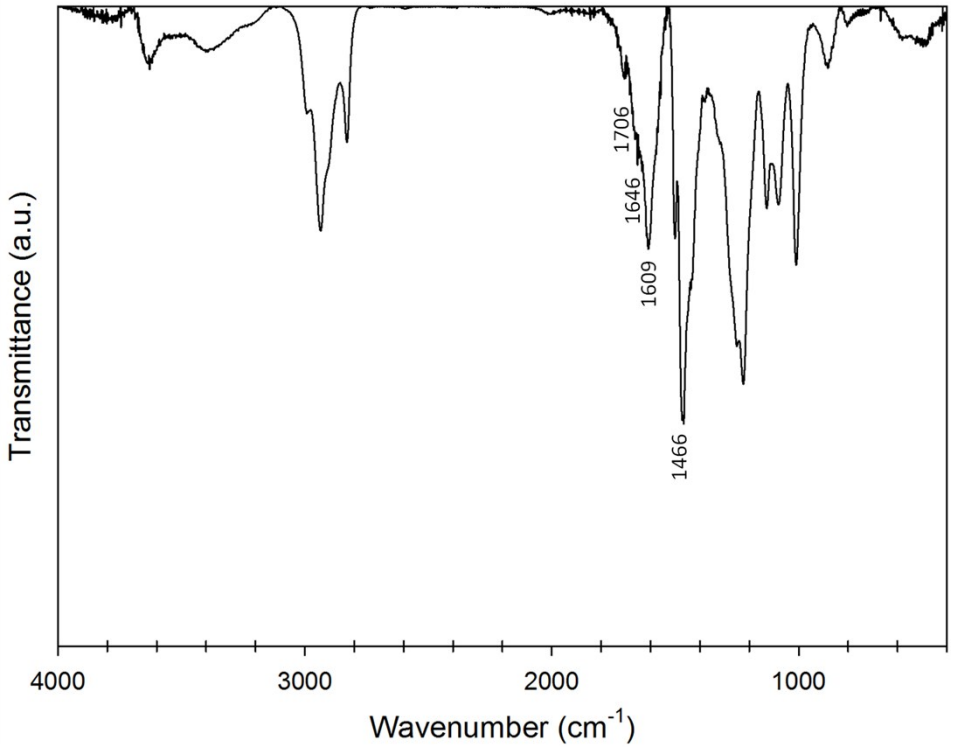


Fig. S7.3 IR spectrum of anisole based HCP, prepared with 2 equivalents of FDA crosslinker.

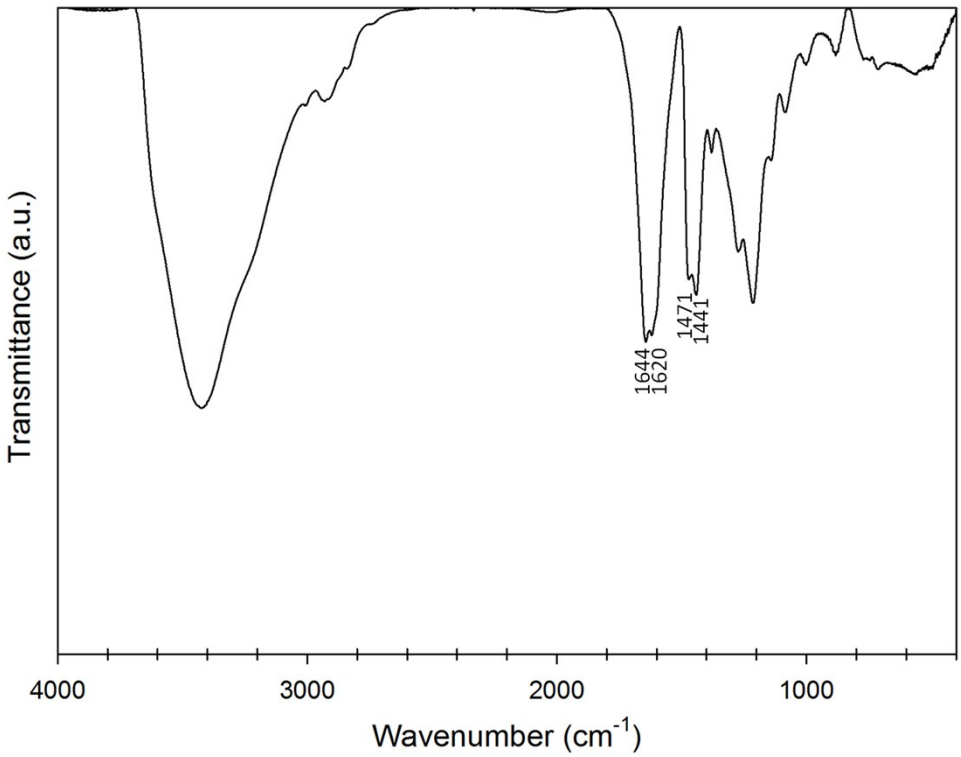


Fig. S7.4 IR spectrum of phenol based HCP, prepared with 2 equivalents of FDA crosslinker.

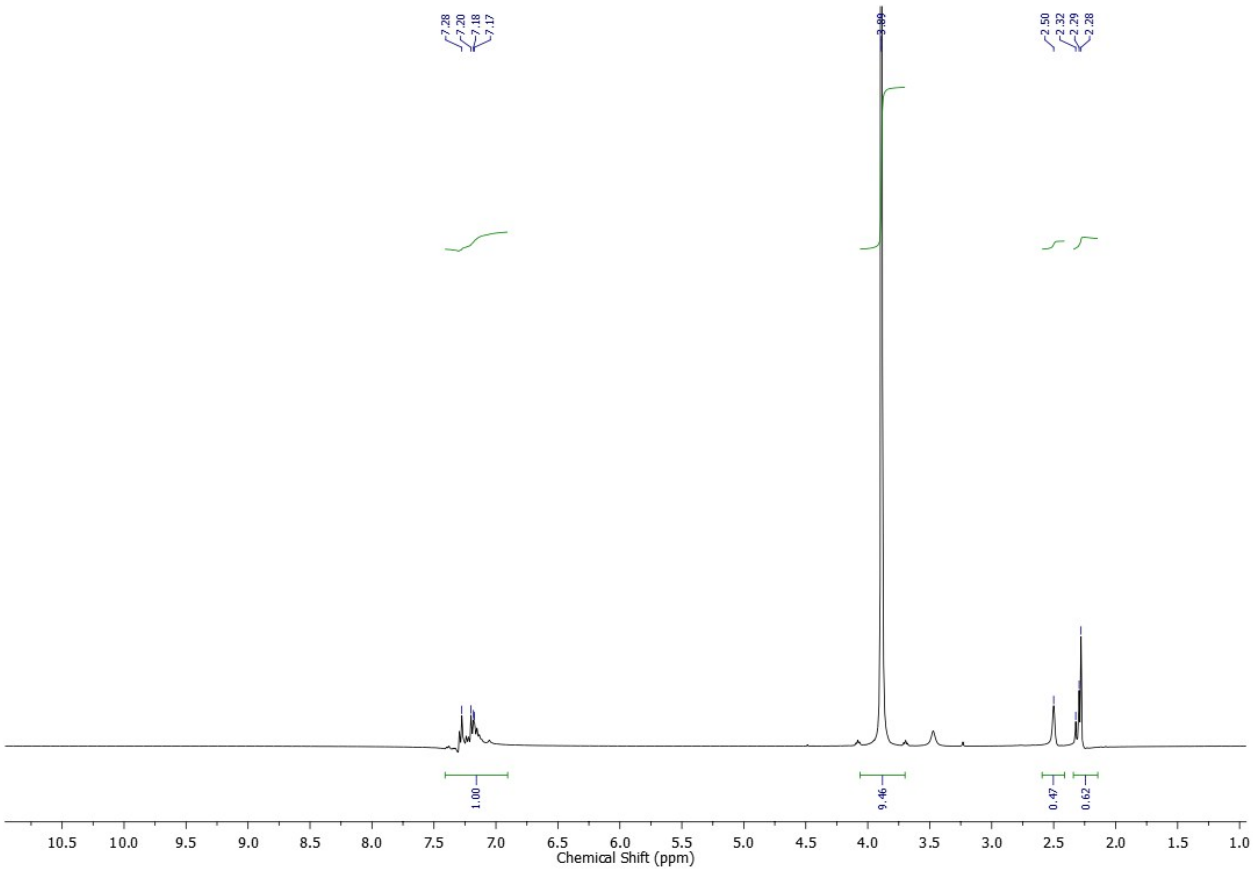


Fig. S8 ^{1}H-NMR spectrum (in dimethyl sulfoxide-d_6) obtained for the toluene oxidation test reaction, showing the absence of any aldehyde peak at ca. 9–10 ppm.

Procedure for toluene oxidation test reaction;

Toluene (10 mmol) was added to anhydrous 1,2-dichloroethane (10 mL) under a flow of nitrogen. Iron (III) chloride (20 mmol) was added and the reaction mixture heated to 80 °C for 18 hours. After such time a crude ^{1}H NMR was taken in dimethyl sulfoxide-d_6.

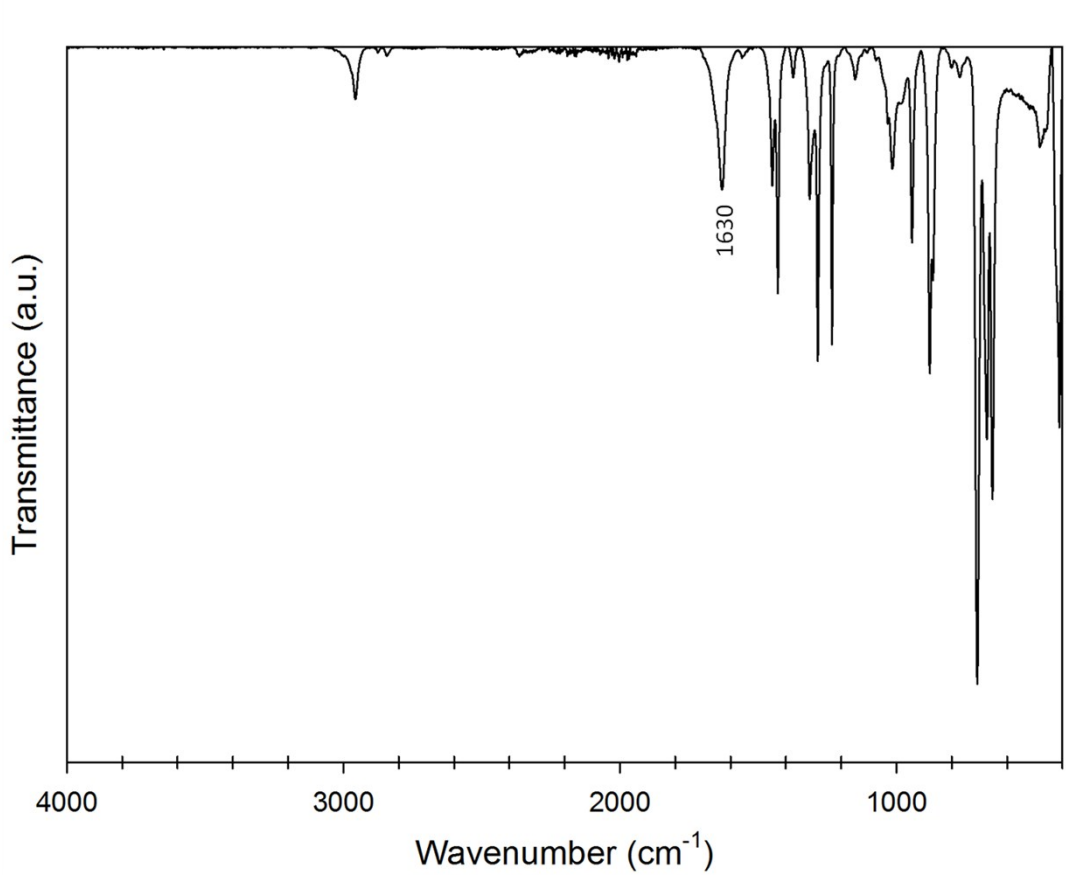


Fig. S9 IR spectrum for formaldehyde dimethyl acetal (FDA) test reaction, indicating the absence of any carbonyl peaks in the 1670-1760 cm^{-1} region.

Procedure for FDA test reaction;

Formaldehyde dimethyl acetal (20 mmol) was added to anhydrous 1,2-dichloroethane (10 mL) under a flow of nitrogen. Iron (III) chloride (20 mmol) was added and the reaction mixture heated to 80 °C for 18 hours. After such time, an ATR IR spectrum was recorded.

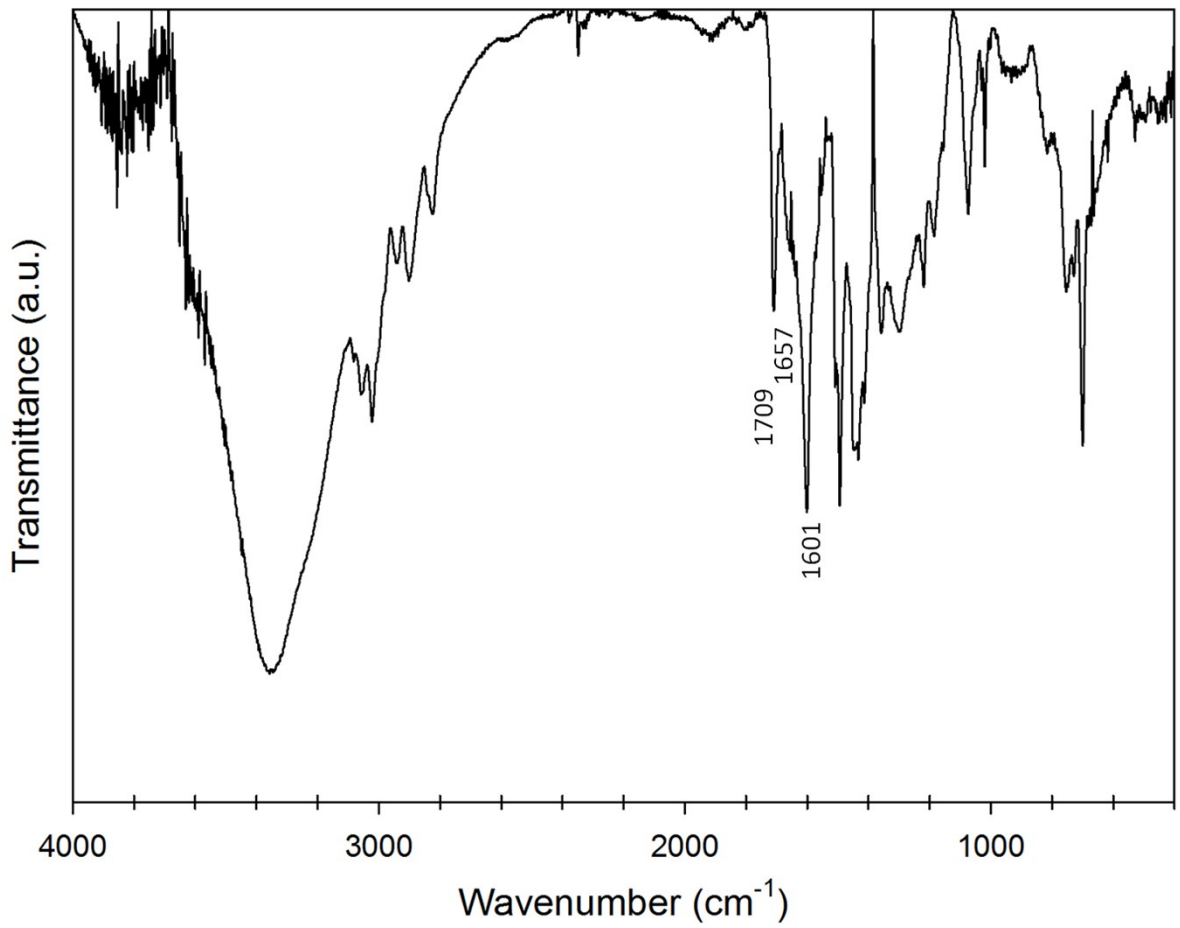


Fig. S10 IR spectrum for benzyl methyl ether test reaction.

Procedure for benzyl methyl ether test reaction;

Benzyl methyl ether (10 mmol) was added to anhydrous 1,2-dichloroethane (10 mL) under a flow of nitrogen. Iron (III) chloride (20 mmol) was added and the reaction mixture heated to 80 °C for 18 hours. The solid product was removed by filtration and washed with methanol several times. The product was then further purified by Soxhlet extraction in methanol for 18 hours, followed by drying *in vacuo* at 60 °C for 18 hours. FTIR and gas sorption analysis (conducted using the same procedure detailed in the experimental section) was recorded on the obtained black solid.

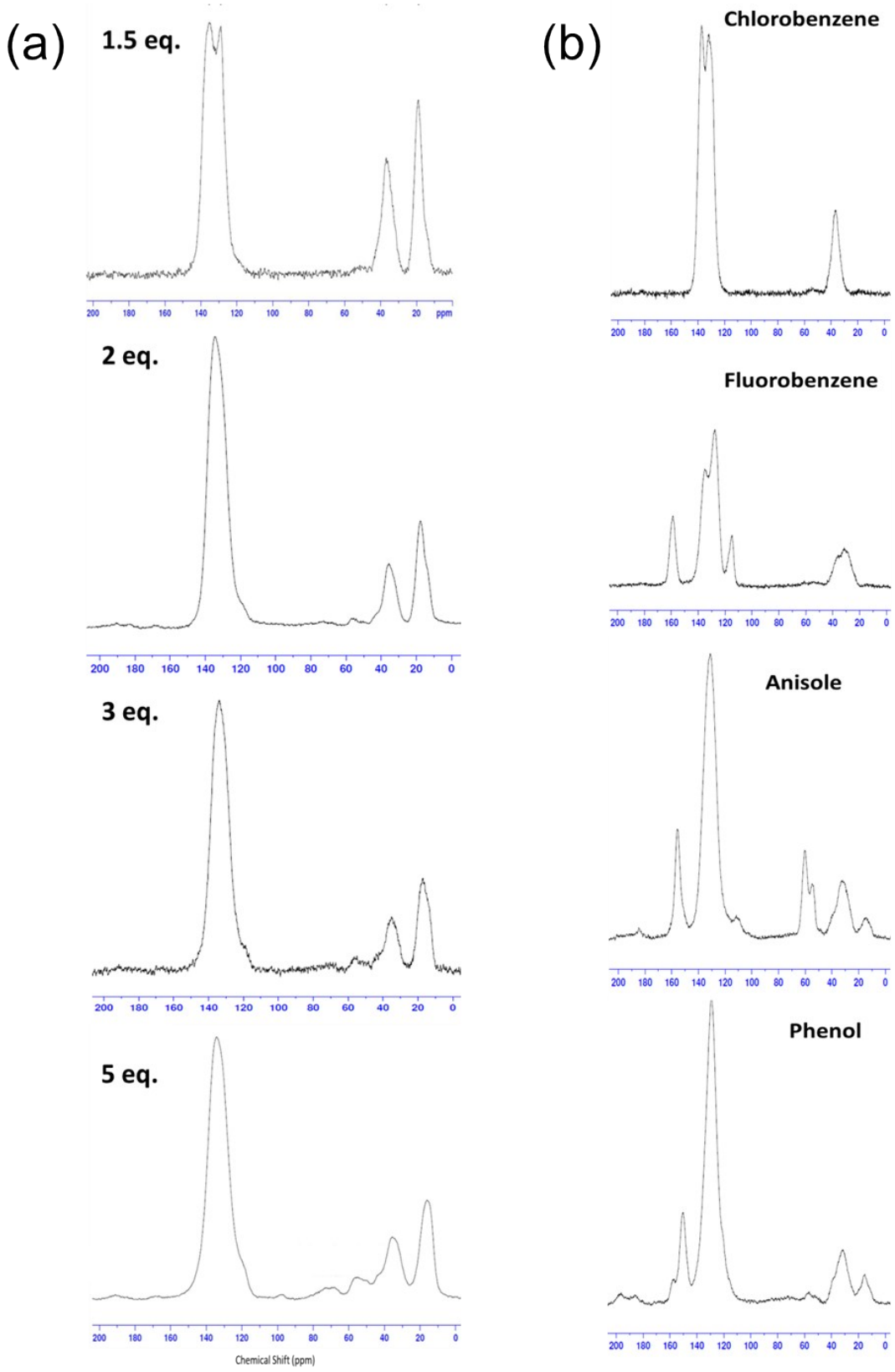


Fig. S11 Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of (a) toluene based HCP samples prepared with 1.5, 2.0, 3.0 and 5.0 equivalents of FDA and (b) for the HCPs prepared with other monomers using 2 equivalents of FDA in each case.

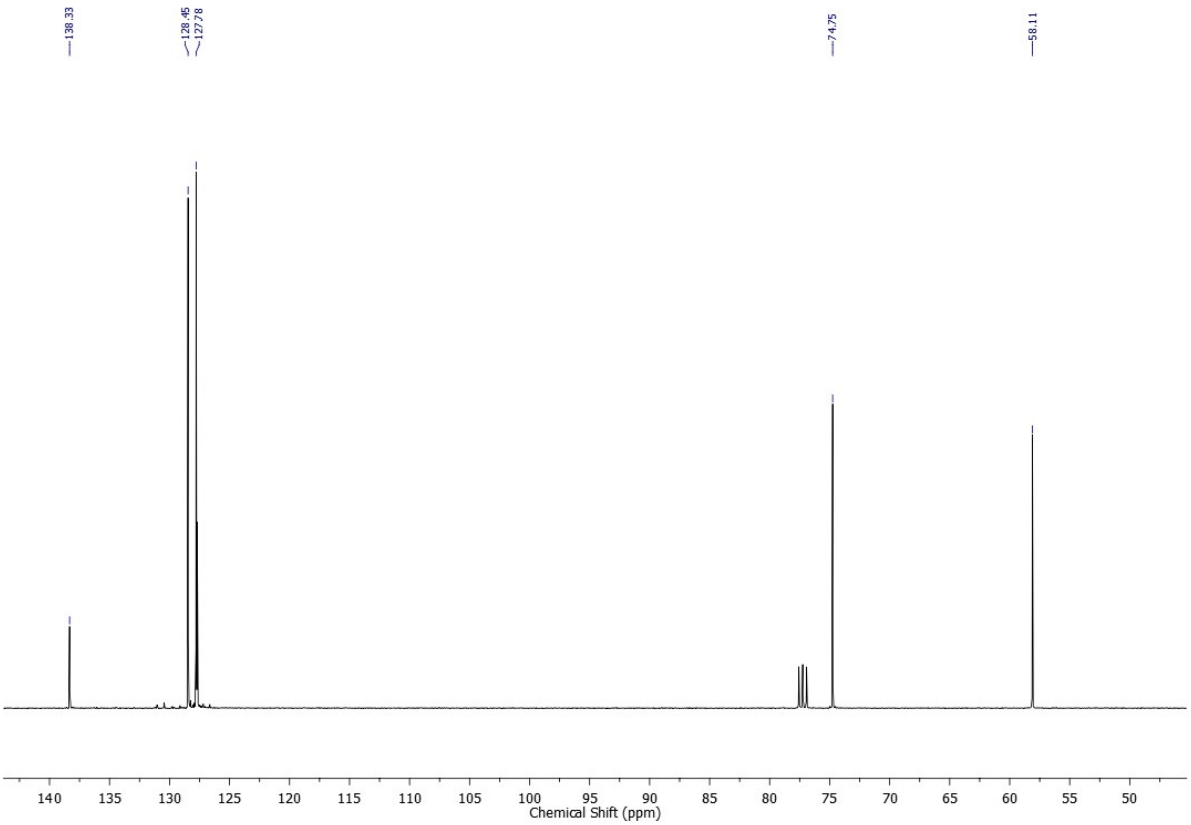


Fig. S12 ^{13}C NMR for benzyl methyl ether, in $CDCl_3$.

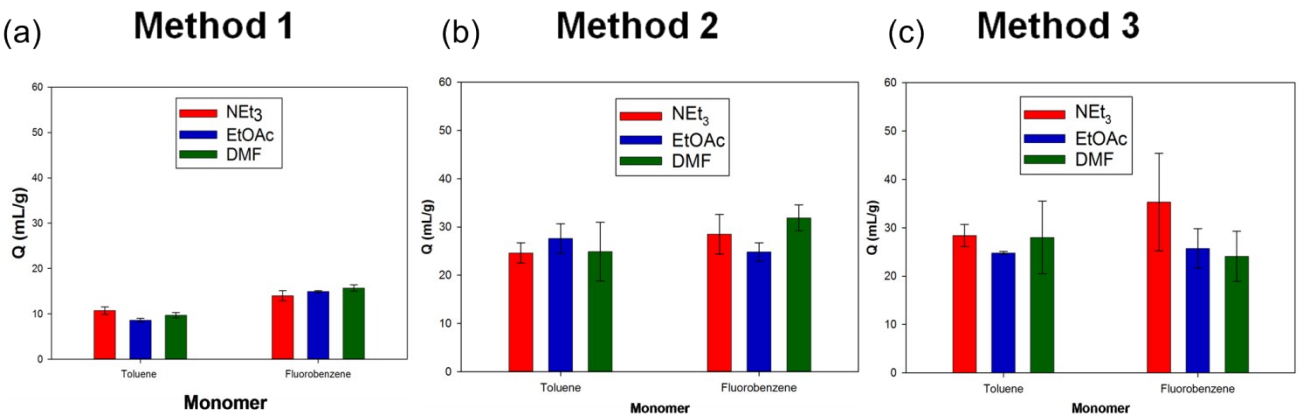


Fig. S13 Swellability (Q) data obtained for three HCPs on exposure to the three CWA simulants triethylamine (NEt_3), ethyl acetate (EtOAc), and dimethylformamide (DMF) using (**a**) Method 1, (**b**) Method 2, and (**c**) Method 3.

Simulant	Simulant added (mL)	Recovered simulant (mL)	Simulant lost (mL)
EtOAc	5.0	4.3	0.7
EtOAc	4.9	4.3	0.6
EtOAc	5.0	4.3	0.7
NEt_3	5.0	4.3	0.7
NEt_3	2.0	1.5	0.5
NEt_3	2.0	1.5	0.5
DMF	5.1	4.4	0.7
DMF	5.0	4.6	0.4
DMF	5.1	4.5	0.6
AcCl	1.7	1.2	0.5
AcCl	1.7	1.3	0.4
AcCl	4.6	4.2	0.4

Fig. S14 Summary of experiments to determine the residual loss on filtering different volumes of the CWA simulants EtOAc, NEt_3, DMF, and AcCl, using the Method 2 procedure.

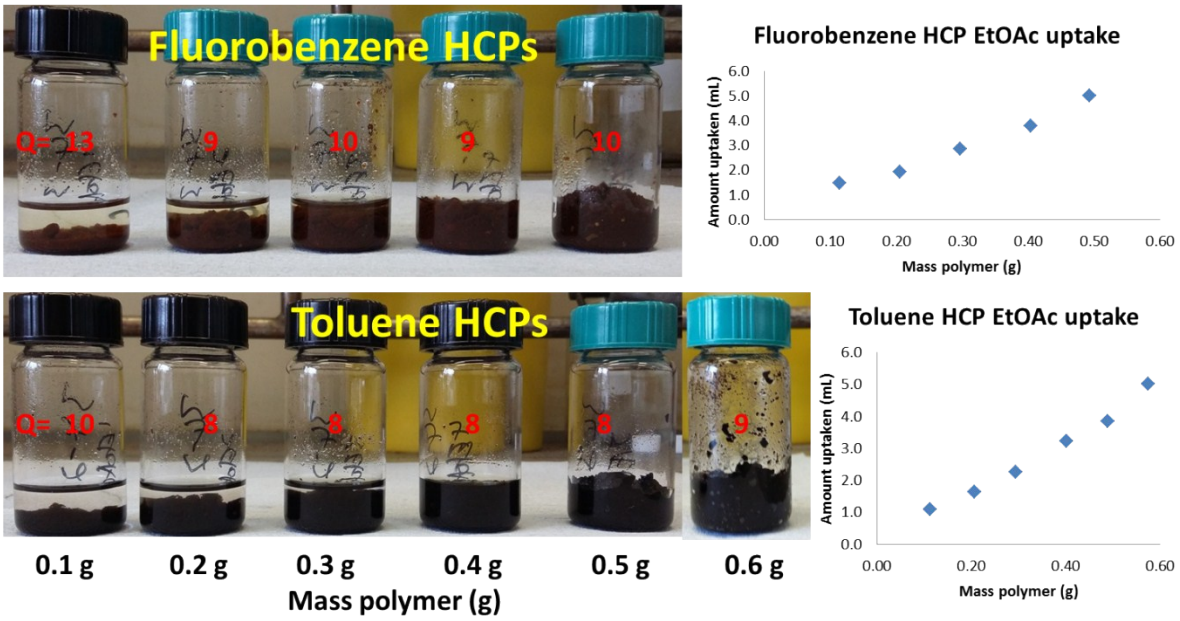


Fig. S15 Scale-up experiments using Method 2 to determine the swelling of the fluorobenzene and toluene based HCPs on exposure to the simulant ethyl acetate.

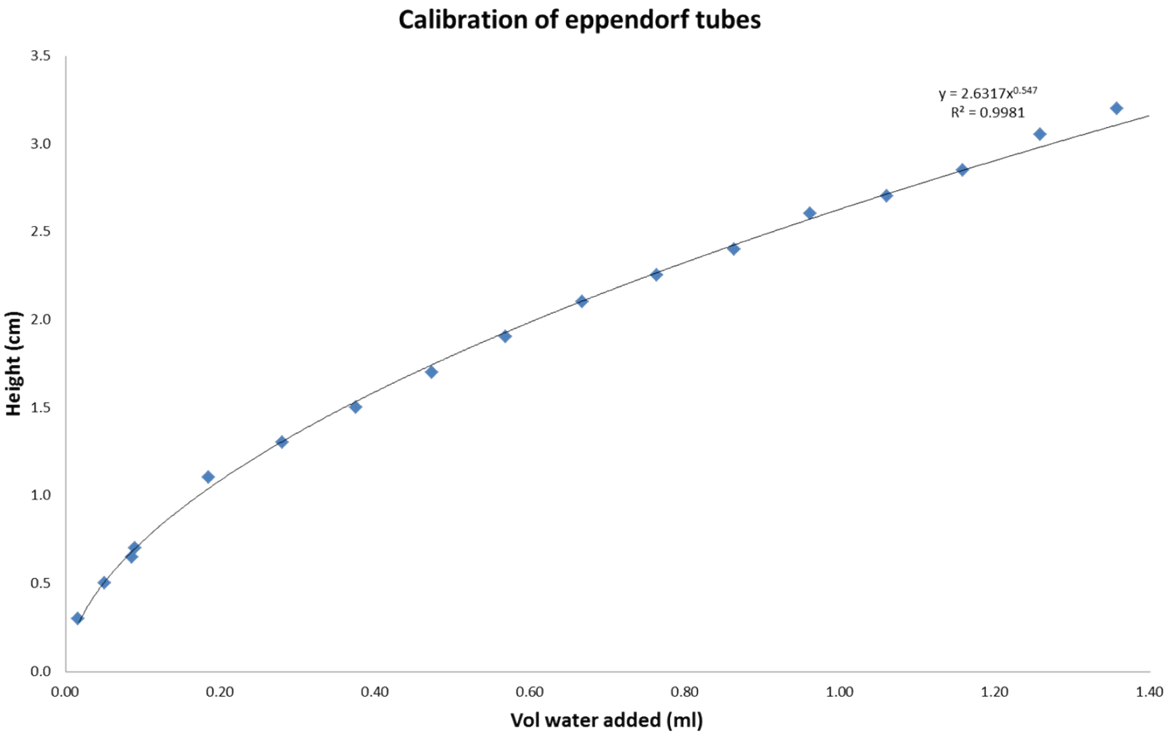
Each vial contains 5 mL of ethyl acetate with the indicated mass of polymer added.

Q (mL/g) calculated as volume of simulant absorbed (mL)/mass polymer used (g).

Procedure for larger scale swelling experiments

The polymer (x g) was weighed into an empty vial and the simulant of interest (5 mL) added. The polymer was allowed to stand in the simulant for 18 hours. After such time, the mass of excess simulant was obtained by filtration of the polymer/simulant solution (using a funnel fitted with a plug of glass wool) into an empty pre-weighed vial. Calculating the volume of recovered agent (mL) allowed the volume of simulant absorbed (mL) by the polymer to be calculated. The swellability (Q) of the polymer could be defined by the amount of simulant absorbed (mL) divided by the mass of polymer used (g).

Increasing amounts of polymer was added to each vial until no excess simulant was observed.



Height of polymer in tube (cm)	Volume (ml)
0.3	0.02
0.4	0.03
0.5	0.05
0.6	0.07
0.7	0.09
0.8	0.11
0.9	0.14
1.0	0.17
1.1	0.20
1.2	0.24
1.3	0.28
1.4	0.31
1.5	0.36
1.6	0.40
1.7	0.45
1.8	0.50
1.9	0.55

Fig. S16 Calibration of the Eppendorf tubes with water, in order to determine the volume of swollen polymer inside the tube for Method 1.

Material	Swellability, Q (mL/g)			
	NEt_3	EtOAc	DMF	AcCl
AC-2	4.1 (+/- 0.6)	4.0 (+/- 0.3)	4.5 (+/- 0.3)	4.3 (+/- 0.3)
Y-Z	4.7 (+/- 0.8)	4.9 (+/- 0.6)	2.3 (+/- 1.3)	2.9 (+/- 0.8)
MS	1.5 (+/- 0.2)	1.6 (+/- 0.1)	1.3 (+/- 0.1)	1.9 (+/- 0.2)
CMP-1	3.4 (+/- 0.3)	3.5 (+/- 0.4)	3.4 (+/- 0.4)	3.6 (+/- 0.1)
F-HCP	16.4 (+/- 0.3)	12.3 (+/- 0.3)	15.1 (+/- 0.1)	11.0 (+/- 0.2)

Fig. S17.1 Swellability (Q) for activated charcoal 100–400 mesh (AC-2), molecular sieves 3 Å (MS), y-zeolite (Y-Z), CMP-1 and fluorobenzene derived HCP (F-HCP) prepared using 3 equivalents of FDA against triethylamine (NEt_3), ethyl acetate (EtOAc), dimethylformamide (DMF), and acetyl chloride (AcCl).

Q values calculated as an average of three measurements, with error (shown in brackets) calculated as the standard deviation.

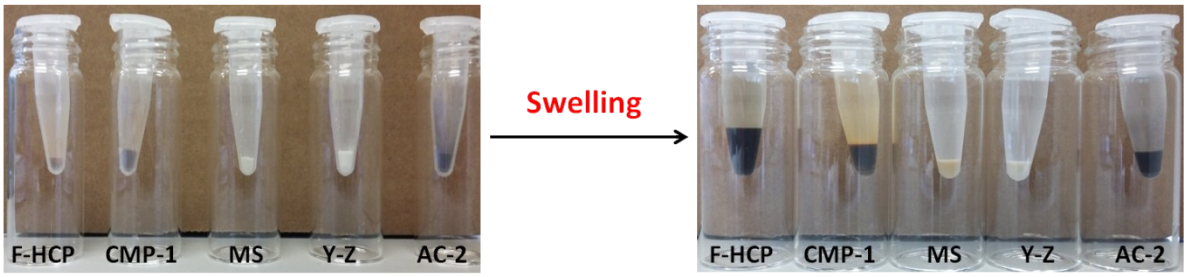
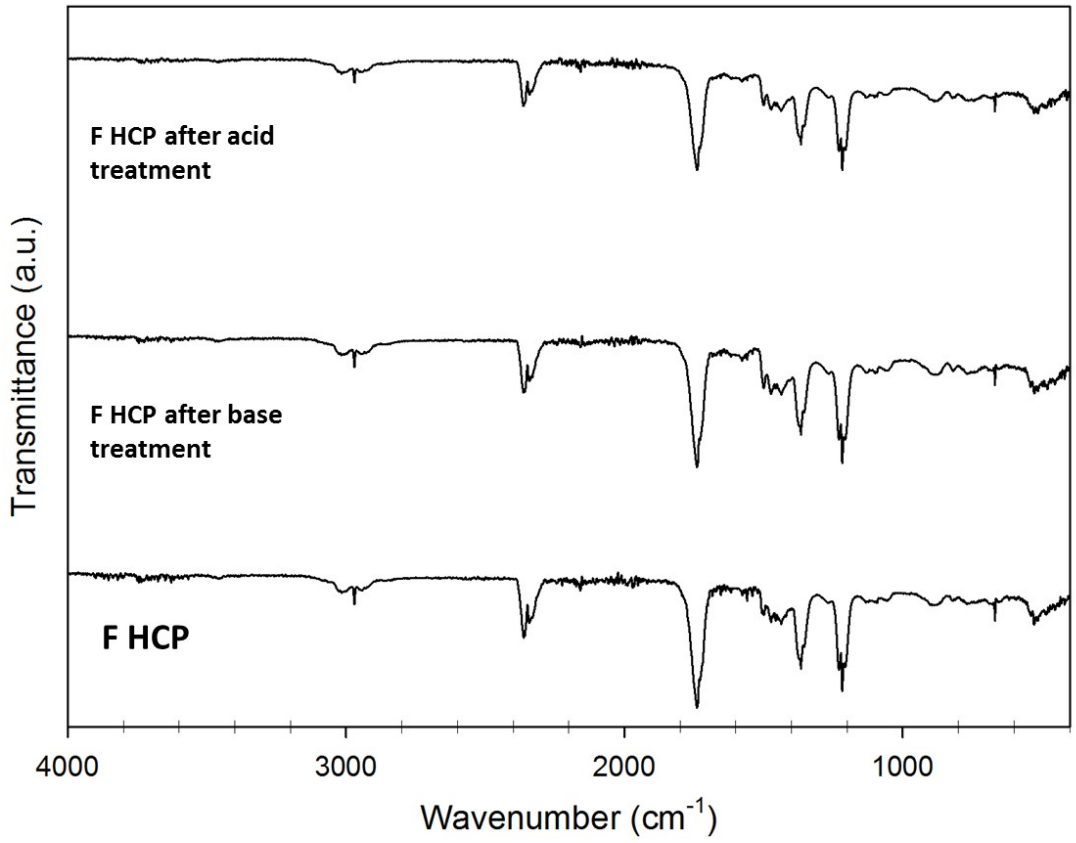


Fig. S17.2 Before and after swelling of the materials against acetyl chloride (AcCl).



HCP	Actual Carbon (%)	Actual Hydrogen (%)
F-HCP (prior to treatment)	73.11	4.05
F-HCP (after base treatment)	72.46	4.04
F-HCP (after acid treatment)	74.73	4.16

HCP	Prior to treatment		After base treatment		After acid treatment	
	SA_{BET}	V_{total} (cm^3/g)	SA_{BET}	V_{total} (cm^3/g)	SA_{BET}	V_{total} (cm^3/g)
Fluorobenzene derived (3 equivalents FDA)	633	0.45	602	0.39	669	0.46

Fig. S18 IR spectrum, elemental analysis, SA_{BET}, and total pore volume obtained for the HCP derived from fluorobenzene (prepared using 3 equivalents of FDA) after stirring of the HCP in acid (1 M aqueous sulfuric acid) or base (1 M aqueous sodium hydroxide) for a period of 24 hours, including a 1 hour reflux followed by wash with deionised water, then methanol and vacuum dried. V_{total} calculated from nitrogen isotherm in the range P/P_o=0.89–0.99.