Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

Supporting Information for

Exceptionally Stable Bakelite-type Polymers for Efficient Pre-Combustion CO₂ Capture and H₂ Purification

Shyamapada Nandi,^a Jens Rother,^c Debanjan Chakraborty,^a Rahul Maity,^a Ulrike Werner-Zwanziger,^d Ramanathan Vaidhyanathan^{ab*}

^d Department of Chemistry, IRM, NMR-3, Dalhousie University, 6274 Coburg Road, PO BOX 15000, Halifax, NS B3H4R2, Canada.

E-mail: vaidhya@iiserpune.ac.in

Table of contents:

- 1. Materials and methods
- **2.** Analytical characterizations: Powder diffraction, TGA studies, IR-spectra and Solid State NMR
- 3. Adsorption studies
- 4. Heat of adsorption for CO₂ from Virial and NLDFT models
- 5. Selectivity Calculation; Ideal Adsorption Solution Theory(IAST):
- 6. Contact angle measurement
- 7. TGA cycling experiments (CO₂ adsorption-desorption)
- 8. Steam conditioning experiments:
- 9. Rate of adsorption studies- self-diffusion coefficients calculations and analysis
- 10. Stability study
- 11. Breakthrough (Mixed Gas) Analysis
- 12. Computational details

^a Department of Chemistry, Indian Institute of Science Education and Research, Pune, Dr. Homi Bhabha Rd., Pashan, Pune, MH, India, 411008.

^b Centre for Research in Energy and Sustainable Materials, Centre for Energy Science, Indian Institute of Science Education and Research, Pune, Dr. Homi Bhabha Rd., Pashan, Pune, MH, India, 411008.

^c Rubolab GmbH, Neckarstr. 27, 40219 Düsseldorf, Germany.

1. Materials and Methods:

All the organic chemicals were purchased from sigma aldrich. 4,4',4"-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3-diol) and 4,4',4"-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3,5-triol) was synthesized according to previously reported procedure(S1and 50). S1: Nandi et al., *Adv. Mater. Interfaces* 2015, 2, 1500301.

Synthesis of HPF-3:

A solvothermal reaction between 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3,5-triol) (0.228g; 0.5mmol) and 4-(4-Formylphenoxy)benzaldehyde (0.170g; 0.75mmol) in a solution containing 5ml 1,4-dioxane + 5ml tetrahydrofuran (THF) and 0.25 ml of acetic acid was carried out at 200°C for 72hrs. Yellowish red colored powder was isolated by filtration and was washed with Dimethylformamide (DMF) (20ml), THF(50ml) and finally with plenty of methanol and acetone. The dried sample gave a yield of ~79%. CHN analysis (calculated values within brackets): C: 67.96 (68.29); H: 3.49 (3.27); N: 5.95 (5.69)%. Note: Before the CHN analyses, the samples were washed with hot DMF, exchanged with methanol and then dried under vacuum. Some discrepancies between the calculated and observed values can be attributed to the presence of few unreacted terminal aldehydes, this is consistent with our observations from NMR and IR.

Synthesis of HPF-4:

A solvothermal reaction between 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3-diol)(0.203g; 0.5mmol) and 4-(4-Formylphenoxy)benzaldehyde (0.170g; 0.75mmol) in a solution containing 5ml 1,4-dioxane + 5ml tetrahydrofuran (THF) and 0.25 ml of acetic acid was carried out at 200°C for 72hrs. Bright yellowish colored powder was isolated by filtration and was washed with Dimethylformamide (DMF) (20ml), THF (50ml) and finally with plenty of methanol and acetone. The dried sample gave a yield of ~82%. CHN analysis (calculated values within brackets): C: 76.72 (76.59); H: 3.67 (3.67); N: 6.45 (6.38)%.

Synthesis of HPF-5:

A solvothermal reaction between 2,2',4,4' -Tetrahydroxybenzophenone (0.246g; 1.0mmol) and 4-(4-Formylphenoxy)benzaldehyde (0.226g; 1.0mmol) in a solution containing 5ml 1,4-dioxane + 5ml tetrahydrofuran (THF) and 0.25 ml of acetic acid was carried out at

 200° C for 72hrs. Bright red colored powder was isolated by filtration and was washed with Dimethylformamide (DMF) (20ml), THF (50ml) and finally with plenty of methanol and acetone. The dried sample gave a yield of ~86%. CHN analysis (calculated values within brackets): C: 73.96 (74.31); H: 3.65 (3.70)%.

Note: All three polymers were subjected to a soxhlation as a cleaning procedure.

Table S1. CO₂ uptakes and selectivity at 298K for selected porous polymers.

Polymer	$\operatorname{CO}_2(a)$	Surface	HOA	Reference
	298K	area	(KJ mol ⁻¹)	
	(mmol g^{-1})	$(m^2 g-1)$		
SNU-C1-va	2.31	595		35
TB-MOP	2.57	694		ACS Macro Lett.2013, 2, 660-663
BILP-1	2.97	1172	26.5	36
PSN-DA	2.25	1045	34	J. Mater. Chem. A, 2014,2, 18881-18888
PSN-TAPB	1.5	611	33	J. Mater. Chem. A, 2014,2, 18881-18888
PCN-AD	1.7	843	32.4	37
APOP-1	2.69	1298	26	Polym. Chem., 2013, 4, 4690- 4696
TPI-1	1.25	809	34.4	38
COP-93	2.07	606	25.6	Chem. Mater., 2014, 26, 6729-6733
Network-	1.45	4077	24	27

A/(PAF-1)				
TSP-1	1.9	562.5	28.1	39
TSP-2	2.6	913.0	30.2	39
TCMP-0	1.34	963		Polym. Chem., 2012, 3, 928
TzTz-POP1	1.3	299	32	Chem. Commun., 2014, 50, 15055
TzTz-POP1	1.5	488	30	Chem. Commun., 2014, 50, 15055
PECONF-1	1.34	499	29	40
PECONF-2	1.98	637	31	40
PPN-6-SO ₃ H	3.5	1254	30.4	43
Network-4R	2.21	927	30	J. Am. Chem. Soc.2012, 134, 10741
azo-COP-1	1.47	635	29.3	20
azo-COP-2	1.52	729	24.8	20
COP-3	1.13	413	24.5	41
COP-1	1.36	168		21
COP-2	0.93	158		21

COP-4	1.13	2015		42
P-1	1.29	100	80	74
P-2	0.88	57	50	74
P-3	0.82	50	50	74
HPF-1	2.8(303K)	851	26	50
NUT-1	1.50	100	74	ACS Sustainable Chem. Eng. 2015, 3, 3077-3085
Polymer 1 (phosphonium salt based)	1.6	1015	27.2	Chem. Commun. 2015, 51, 15708-15711
CuPor-BPDC POP	0.96	442		<i>Polym. Chem.</i> 2013, 4, 4566- 4569
ThPOP-1		1050		<i>Polym. Chem.</i> 2016, 7, 5031- 5038
CNF-1	3.35	1730	35.5	44
BATP 1	1.7	700	30	73
PCTF-8	1.6 (293K)	625	37	J. Mater. Chem. A. 2016, 4, 13450-13457
HPF-3	2.50 (303K)	315	27	This Work
HPF-4	3.80 (303K)	525	29	This Work

HPF-5	3.01 (303K)	516	32	This Work

----- = Data not available.

2. Analytical Characterizations:

Powder X-ray diffraction:

Powder XRDs were carried out using a Rigaku Miniflex-600 instrument and processed using PDXL software.

Thermogravimetric Analysis (TGA):

Thermogravimetry was carried out on NETSZCH TGA-DSC system. The conventional TGA experiments were done under N_2 gas flow (20 ml min⁻¹) (purge + protective) and samples were heated from RT to 550°C at 2 K min⁻¹.

Infrared Spectroscopy:

IR spectra were obtained using a Nicolet ID5 attenuated total reflectance IR spectrometer operating at ambient temperature. The anhydrous KBr pellets were used.

Solid State NMR Spectroscopy:

All NMR experiments were carried out on a Bruker Advance NMR spectrometer with a 9.4T magnet (400.24 MHz proton Larmor frequency, 100.64MHz ¹³C Larmor frequency) using our probe head for rotors of 4 mm diameter. The parameters for the ¹³C CP/MAS experiments with TPPM proton decoupling were optimized on glycine, whose carbonyl resonance also served as external, secondary chemical shift standard at 176.06 ppm. For the final ¹³C CP/MAS NMR spectra up to 600 scans were acquired at 3.1 s recycle delay. The sample was spun at 7.0, 8.0, and 13.3 kHz rotation frequencies to separate isotropic shift peaks and spinning sidebands. Spinning sidebands were separated from the isotropic shift peak by a multiple of the rotation frequency. The cross-polarization contact time was chosen to be 2.6 ms, to obtain a good balance between detecting carbons with directly bonded protons and other carbons, for which protons are further removed.

Field Emission-SEM:

Field Emission Scanning Electron Microscope with integral charge compensator and embedded EsB and AsB detectors. Oxford X-max instruments 80mm². (Carl Zeiss NTS, Gmbh), Imagin conditions: 3kV, WD= 2mm, 200kX, SE lens detector. For SEM images sample was

grind nicely and soaked in THF for 12 hrs. Then filtered and dried in hot oven at 90°C. The fine powder was spread over carbon paper and SEM images were taken at different range.



Figure S1. Powder X-ray diffraction patterns of HPF-3 indicating its amorphous character. The big hump at around $2\theta = 20^{\circ}$ is from the polymer and is not from the glass substrate. Plenty of sample was used during the experiment.



Figure S2. Powder X-ray diffraction patterns of HPF-4 showing its amorphous character.



Figure S3. Powder X-ray diffraction patterns of HPF-5 showing the amorphous nature of the sample.



Figure S4. FE-SEM images of (A) HPF-3, (B) HPF-4, (C) HPF-5 microspheres indicating high homogeneity as well as purity of the sample. The sizes of the microspheres are distributed between 0.3 to 5microns.



Figure S5. TGA carried out on the as-synthesized sample of HPF-3, HPF-4, HPF-5. The weight loss observed about 15-20% from room temperature to 200°C can be attributed to the solvent molecules (THF and Dioxan) trapped in the polymer. The materials are thermally stable upto 380°C.



Figure S6. Infra red spectra of HPF-3 showing the various stretching and bending modes present. Selected peaks: IR (KBr pellet, cm⁻¹): v -OH: 3461; v(C-H): 2926; v(CO): 1690; v(CN): 1522 and v(C=C): 1400 to1200. (*Source: Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry, 6th Edition, Kazuo Nakamoto*). Note that peak at 1692cm⁻¹ is due to carbonyl stretching of unreacted aldehyde (very less intense).



Figure S7. Infra red spectra of HPF-4 showing the various stretching and bending modes present. Selected peaks: IR (KBr pellet, cm⁻¹): v(O-H)solvent and -OH: 3472; v(C-H): 2922; v(CO): 1684; v(CN): 1522 and v(C=C): 1400 to1200. (*Source: Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry, 6th Edition, Kazuo Nakamoto*). Note that peak at 1692cm⁻¹ is due to carbonyl stretching of unreacted aldehyde (very less intense).



Figure S8. Infra red spectra of HPF-5 showing the various stretching and bending modes present. Selected peaks: IR (KBr pellet, cm⁻¹): v(O-H)solvent and -OH: 3486; v(C-H): 2921; v(CO): 1652; v(CN): 1520 and v(C=C): 1400 to1200. (*Source: Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry, 6th Edition, Kazuo Nakamoto*). Note that peak at 1692cm⁻¹ is due to carbonyl stretching of unreacted aldehyde (very less intense).

3. Adsorption Analysis:

All gas sorption isotherms were measured on a Micromeritics ASAP 2020HD or 3-FLEX or Quantachrome-iQ instrument using ultra-high purity gases (\geq 4.8 grade). At least 100mg of each sample was transferred to analysis glass vial and evacuated at 160°C on the degas port for 16hrs (10⁻⁶ mbar), at which point the outgas rate was \leq 2 µbar/min.

The rate of adsorption experiments were carried out on the Micromeritics ASAP2020HD instrument equipped with a ROA software capabilities. Numerous equilibrium points and associated kinetic data were recorded at 273K, however for data analysis regularly spaced 11 CO₂ loading points were picked out in the interval of 0 to 1000mbar.

195K CO ₂			
Adsorption		Desorption	
P(mm Hg)	Q(mmol/g)	P(mm Hg)	Q(mmol/g)
0.32888	1.63926	725.1994	18.77821
0.9962	2.69153	695.4288	18.72208
1.66459	3.29303	667.0587	18.64825
2.77824	3.94309	634.731	18.57842
3.70798	4.32332	605.4498	18.48205
4.63698	4.62649	573.4857	18.35342
8.18004	5.39983	543.8008	18.24035
12.9624	6.04264	513.192	18.09971
15.171	6.27663	481.1546	17.93893
17.26723	6.47816	450.7146	17.75691
21.66501	6.81926	419.542	17.56452
28.90655	7.27948	388.7333	17.3272
36.01192	7.65935	357.9181	17.08595
48.00089	8.19172	327.1488	16.77625
60.04379	8.62045	297.0222	16.44762
70.24181	8.92609	266.445	16.04856
80.17822	9.23056	234.8875	15.48422
90.24131	9.46367	204.5974	14.96045
100.0033	9.76157	189.2091	14.70779
114.3583	10.01621	174.1069	14.40347
128.5819	10.429	142.9198	13.63735
135.8821	10.52772	112.3636	12.76618

Table S2. CO₂ adsorption and desorption data of HPF 4 at 195K and 303K

142.8946	10.62953	81.47445	11.69567
157.2358	10.84248	66.00819	11.06683
171.6117	11.09706	50.70897	10.29001
186.1856	11.36603	35.14199	9.29446
200.3547	11.59078	19.71072	7.89167
214.3728	11.80488	12.03575	6.67772
228.8539	12.03529	8.31857	5.50047
243.4553	12.25036		
271.5838	12.67874		
300.3454	13.09554		
328.9029	13.51604		
343.4845	13.70323		
357.4537	13.88406		
386.5335	14.26722		
414.9891	14.6873		
443.2531	14.97426		
471.692	15.41956		
501.5413	15.7032		
529.0272	16.07014		
557.9059	16.4065		
586.8875	16.90287		
615.549	17.20361		
646.1376	17.97403		
673.4589	18.40966		
702.7596	18.58405		
725.1994	18.77821		

303K CO ₂				
Adsorption		Desorption		
P(mm Hg)	Q(mmol/g)	P(mm Hg)	Q(mmol/g)	
0.33075	0.00554	900.3128	4.01579	
0.66741	0.01134	873.0267	3.97515	
1.00117	0.01705	847.3207	3.935	
1.67254	0.02848	821.8936	3.89511	
2.79113	0.04729	796.4464	3.84814	
3.72462	0.0629	773.8743	3.80883	
4.6535	0.07817	751.2296	3.77064	
6.2062	0.10328	706.7331	3.67574	

7.76351	0.13002	626.2682	3.49958
10.33902	0.15753	590.2872	3.40473
13.09543	0.19436	555.0627	3.30978
15.34408	0.22445	492.1578	3.13274
17.49938	0.25366	436.0129	2.953
19.64794	0.28155	386.6693	2.77102
21.76053	0.31033	342.3257	2.59696
25.51796	0.35593	303.583	2.43304
29.0541	0.39634	269.2248	2.26963
32.60812	0.43514	238.4738	2.113
36.23187	0.47699	211.4889	1.9631
42.23356	0.54833	187.4097	1.81748
48.2729	0.61576	166.2157	1.68153
51.14283	0.6466	147.2541	1.54985
54.1335	0.67924	130.6826	1.42726
60.20168	0.74281	115.8427	1.311
65.40663	0.7948	102.6561	1.20645
70.31162	0.83974	91.00278	1.10643
75.31184	0.8857	80.66891	1.01123
80.3195	0.93222	71.52169	0.92491
90.25084	1.01914	63.36257	0.84436
100.464	1.10495	56.17084	0.76606
110.3869	1.18389	49.77603	0.6941
120.1214	1.25753	18.5325	0.324
131.9006	1.34513	7.0748	0.16173
143.6	1.42847	2.65575	0.07423
157.5587	1.5254	1.00295	0.03021
171.495	1.62267		
188.497	1.7292		
196.5463	1.77831		
204.7115	1.82664		
215.0884	1.88397		
225.1633	1.93762		
234.8855	1.98934		
244.8702	2.04157		
256.926	2.10459		
280.7437	2.21862		
292.8107	2.27112		
307.571	2.33997		
321.7351	2.40347		

336.2827	2.47185	
350.2396	2.53138	
368.3849	2.60436	
385.1534	2.67049	
402.1633	2.73428	
419.0935	2.79141	
460.3385	2.92858	
501.5008	3.0589	
534.381	3.15853	
553.1329	3.21671	
571.0976	3.27463	
609.3105	3.38156	
651.1413	3.48996	
694.2368	3.59145	
718.015	3.64857	
741.622	3.70208	
791.0228	3.80239	
803.5783	3.82589	
817.1663	3.85064	
830.2835	3.88041	
843.9065	3.91357	
873.381	3.96467	
900.3128	4.01579	



Figure S9. BET fits of HPF-3 from the 77K N₂ data. Blue squares- experimental; red line- fit.



Figure S10. Langmuir fits of HPF-3 from the 77K N₂ data. Blue squares- experimental; red line- fit.



Figure S11. BET fits of HPF-4 from the 77K N₂ data. Blue squares- experimental; red line- fit.



Figure S12. Langmuir fits of HPF-4 from the 77K N₂ data. Blue squares- experimental; red line- fit.



Figure S13. BET fits of HPF-5 from the 77K N₂ data. Blue squares- experimental; red line- fit.



Figure S14. Langmuir fits of HPF-5 from the 77K N_2 data. Blue squares- experimental; red line- fit.



Figure S15. QSDFT fits for the 273K CO_2 and 77K N_2 isotherms obtained using a Carbon model.



Figure S16. Pore size distribution in HPF-3 obtained by fitting the Non Localized Density Functional Theory (NLDFT) model to the 77K N_2 adsorption branch. Note the majority of the porosity is due to 5.5Å sized pore in the material.



Figure S17. Pore size distribution in HPF-4 obtained by fitting the Non Localized Density Functional Theory (NLDFT) model to the 77K N_2 adsorption branch. Note the majority of the porosity is due to 9.5Å and 14.6 Å sized pore in the material.



Figure S18. Pore size distribution in HPF-5 obtained by fitting the Non Localized Density Functional Theory (NLDFT) model to the 77K N_2 adsorption branch. Note the majority of the porosity is due to 5.7Å sized pore in the material.

4. Heat of adsorption for CO₂ from Virial and NLDFT models:

The CO₂ adsorption data for all the three polymers were measured from 0- 1bar at 248, 273, 303K and were fitted by the virial equation (1).

$$ln(P) = ln(Va) + (A0 + A1 * Va + A2 * Va^{2} \dots + A6 * Va^{6})/T + (B0 + B1 * Va) \dots (1)$$

Where P is pressure, Va is amount adsorbed, T is temperature, and A0, A1, A2 ..., A4 and B0,

B1

are temperature independent empirical parameters

A0	-3145.987948	B0	14.99726767
A1	241.0188984	B1	0.430359937
A2	-150.7942683	B2	-0.103743696
A3	51.97476338	B3	
A4	-10.91954458		

Table S3: Summary of the fitted Virial parameters(CO₂) for HPF-3.



Figure S19. Comparison of experimental isotherms to the ones obtained from virial modeling carried out using CO_2 isotherms collected at $0^{\circ}C$, +30°C and -25°C for HPF-3.



Figure S20. Virial plots carried out using CO₂ isotherms collected at 0°C, +30°C and -25°C for HPF-3.

A0	-3329.501669	B0	15.33498207
A1	-263.2342745	B1	1.24768008
A2	29.83406661	B2	-0.112843932
A3	0.361805081		
A4	-0.031896591		

Table S4: Summary of the fitted Virial parameters(CO₂) for HPF-4



Figure S21. Comparison of experimental isotherms to the ones obtained from virial modeling carried out using CO_2 isotherms collected at $0^{\circ}C$, +30°C and -25°C for HPF-4.



Figure S22. Virial plots carried out using CO₂ isotherms collected at 0°C, +30°C and -25°C for HPF-4.

Table S5: Summary of	the fitted Virial	parameters(CO ₂) for HPF-5.
----------------------	-------------------	----------------------------	--------------

A0	-3674.679853	B0	16.95870985
A1	226.2432093	B1	0.002974733
A2	-82.41970269	B2	-0.174674631
A3	39.01690367		
A4	-10.12526733		
A5	1.260969137		



Figure S23. Comparison of experimental isotherms to the ones obtained from virial modeling carried out using CO_2 isotherms collected at $0^{\circ}C$, +30°C and -25°C for HPF-5.



Figure S24. Virial plots carried out using CO₂ isotherms collected at 0°C, +30°C and -25°C for HPF-5.

A0	-10431.88245	B0	28.77813374
A1	3521.322573	B1	-2.637644719
A2	-773.2662505	B2	-1.990529606
A3	211.0338766	B3	0.465026047
A4	-35.95388903		
A5	2.298304647		

Table S6: Summary of the fitted Virial parameters(toluene) for HPF-3



Figure S25. Virial plots carried out using water isotherms collected at +25°C and +35°C for HPF-3.

A0	-10402.19379	B0	27.89899548
A1	379.6048987	B1	2.738091842
A2	261.3025532	B2	-1.703546217
A3	-11.91991164	B3	0.125615738
A4	-1.307962347		
A5			

Table S7: Summary of the fitted Virial parameters(toluene) for HPF-4



Figure S26. Virial plots carried out using water isotherms collected at +25°C and +35°C for HPF-4.

Table S8: Summary of the fitted Virial parameters(toluene) for H	PF-5
--	------

A0	-9169.517361	B0	23.3334306
A1	684.5924201	B1	2.505867035
A2	97.84135297	B2	-1.5126849
A3	12.76732157	B3	0.112948228
A4	-3.202179048		
A5			



Figure S27. Virial plots carried out using water isotherms collected at +25°C and +35°C for HPF-5.

Table S9: Summar	y of the fitted	Virial parameters	(Water)) for HPF-3
------------------	-----------------	-------------------	---------	-------------

A0	-5557.334612	B0	17.90471422
A1	106.0990556	B1	2.851214141
A2	-61.98277468	B2	-2.446088567
A3	18.80785699	B3	0.985661022
A4	-29.51765718		
A5	6.642661404		



Figure S28. Virial plots carried out using water isotherms collected at +25°C and +35°C for HPF-3.

A0	-4820.596012	B0	15.6093044
A1	-374.2549545	B1	2.393596768
A2	-29.00072028	B2	-0.379841125
A3	24.40820317	B3	0.005396482
A4	-2.159657046		

Table S10: Summary of the fitted Virial parameters (Water) for HPF-4



Figure S29. Virial plots carried out using water isotherms collected at +25°C and +35°C for HPF-4.

A0	-7150.906388	B0	23.11851189
A1	603.4940537	B1	-0.471299064
A2	-7.320758651	B2	-0.677172212
A3	7.528813204	B3	0.135519672
A4	-6.08168734		
A5	0.405792751		

Table S11: Summary of the fitted Virial parameters (Water) for HPF-5



Figure S30. Virial plots carried out using water isotherms collected at +25°C and +35°C for HPF-5.

5. Selectivity Calculations- Ideal Adsorption Solution Theory(IAST):

Langmuir Fits:

In all the cases the isotherms were fit to the Single-Site Langmuir (SSL) equation. It is widely known that even small fitting errors will have a devastating impact on selectivity calculations. So, we fitted the Isotherms using all the model (SSL, DSL). The isotherms were fit by solving the Langmuir equation using the solver function in Microsoft Excel following a similar protocol to Keller *et al.*^(S2) Utilizing this routine circumvents some of the problems associated with favoring either high or low pressure regions when linearizing the Langmuir equation and offers a balanced approach. A more in depth discussion is available elsewhere.^(S3)

Single-Site Langmuir (SSL):

$$q_i = q_m \frac{K_i P}{1 + K_i P}$$

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1 P}{1 + K_1 P} + q_{m,2} \frac{K_2 P}{1 + K_2 P}$$

(S2) Kemmer, G.; Keller, S. *Nat. Protoc.* 2010, *5*, 267–81.
(S3) Nandi *et al. Sci. Adv.* 2015;1:e1500421

IAST fitting parameters for HPF-3 (CO_2/H_2):303KGas A = CO_2 Gas B = H_2 Gas Mixture

YA =	0.2
YB =	0.8

(G	а	S	А	
	\sim	_		~+~	

Constants	G	as B Consta	ants	
qA1 =	5.409391985	q	A1 =	0.25658189
qA2 =	0	q	A2 =	0
kA1 =	0.002664792	k	A1 =	3.4392E-05
kA2 =	0	k	A2 =	0
na1 =	0.816592186	n	ia1 =	1.0000025
na2 =	0	n	ia2 =	0
HA1 =	0.014414906	н	IB1 =	8.8244E-06
HA2 =	0	H	1B2 =	0

Gas	Mixture	2
		1

YA =	0.4
YB =	0.6

Gas	А
000	

Constants		Gas B Constants
qA1 =	5.409391985	qA1 = 0.25658189
qA2 =	0	qA2 = 0
kA1 =	0.002664792	kA1 = 3.4392E-05
kA2 =	0	kA2 = 0
na1 =	0.816592186	na1 = 1.0000025
na2 =	0	na2 = 0
HA1 =	0.014414906	HB1 = 8.8244E-06
HA2 =	0	HB2 = 0

LAST fitting part 273K Gas A = CO_2 Gas B = H_2 Gas Mixture	ameters for HPF-3 (0	C O ₂ /H ₂):	
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B C	Constants
qA1 =	6.405576353	qA1 =	2.96845074
qA2 =	0	qA2 =	0
kA1 =	0.0082542	kA1 =	6.7233E-06
kA2 =	0	kA2 =	0
na1 =	0.724235043	na1 =	1.00003705
na2 =	0	na2 =	0
HA1 =	0.05287291	HB1 =	1.9958E-05
HA2 =	0	HB2 =	0

Gas Mixture	
YA =	0.4
YB =	0.6

0

0

0

0

Gas B Constants Constants qA1 = 6.405576353 2.96845074 qA1 = qA2 = qA2 = 0 kA1 = 0.0082542 kA1 = 6.7233E-06 kA2 = kA2 = 0 0.724235043 1.00003705 na1 = na1 = na2 = 0 na2 = HA1 = 0.05287291 HB1 = 1.9958E-05 HA2 = 0 HB2 =

Gas A



Figure S31. IAST fit for HPF-3 using CO₂ and H₂ isotherms collected at 273 and 303K.

LAST fitting parameters for HPF-4 (CO_2/H_2): 303K Gas A =CO₂ Gas B = H₂

na2 =

HA1 =

HA2 =

Gas Mixture			
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	6.005634529	qA1 =	0.01514213
qA2 =	0	qA2 =	0
kA1 =	0.001603973	kA1 =	0.0018418
kA2 =	0	kA2 =	0
na1 =	1	na1 =	1.00000025
na2 =	0	na2 =	0
HA1 =	0.009632877	HB1 =	2.7889E-05
HA2 =	0	HB2 =	0
Gas Mixture			
YA =	0.4		
YB =	0.6		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	6.005634529	qA1 =	0.01514213
qA2 =	0	qA2 =	0
kA1 =	0.001603973	kA1 =	0.0018418
kA2 =	0	kA2 =	0
na1 =	1	na1 =	1.00000025

0

0

0.009632877

na2 =

HB1 =

HB2 =

0

0

2.7889E-05

$\frac{2}{3\Lambda}$ Gas A = CO ₂			
Gas $B = H_2$			
Gas Mixture			
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	11.0101008	qA1 =	2.96853656
qA2 =	0	qA2 =	0
kA1 =	0.00687708	kA1 =	1.7306E-05
kA2 =	0	kA2 =	0
na1 =	0.779016471	na1 =	1.00003705
na2 =	0	na2 =	0
HA1 =	0.075717343	HB1 =	5.1373E-05
HA2 =	0	HB2 =	0
Gas Mixture			
YA =	0.4		
YB =	0.6		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	11.0101008	qA1 =	2.96853656
qA2 =	0	qA2 =	0
kA1 =	0.00687708	kA1 =	1.7306E-05
kA2 =	0	kA2 =	0
na1 =	0.779016471	na1 =	1.00003705
na2 =	0	na2 =	0
HA1 =	0.075717343	HB1 =	5.1373E-05
HA2 =	0	HB2 =	0



Figure S32. IAST fit for HPF-4 using CO₂ and H₂ isotherms collected at 273 and 303K.

IAST fitting parameters	for HPF-5 (CO ₂ /H ₂):
303K	

Gas A = CO_2			
Gas $B = H_2$			
Gas Mixture			
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	5.416903051	qA1 =	0.02214416
qA2 =	0	qA2 =	0
kA1 =	0.001170108	kA1 =	0.00130854
kA2 =	0	kA2 =	0
na1 =	1	na1 =	1.0000025
na2 =	0	na2 =	0
HA1 =	0.00633836	HB1 =	2.8976E-05
HA2 =	0	HB2 =	0

Gas	Mixture

YA =	0.4
YB =	0.6

Gas A

Constants		Gas B Constants	
qA1 =	5.416903051	qA1 =	0.02214416
qA2 =	0	qA2 =	0
kA1 =	0.001170108	kA1 =	0.00130854
kA2 =	0	kA2 =	0
na1 =	1	na1 =	1.00000025
na2 =	0	na2 =	0
HA1 =	0.00633836	HB1 =	2.8976E-05
HA2 =	0	HB2 =	0

IAST fitting para $273K$ Gas A =CO2Gas B = H2Gas Mixture	meters for HPF-5 (CO ₂ /H	<i>[</i> ₂):	
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B Cor	istants
qA1 =	8.596375223	qA1 =	2.96854993
qA2 =	0	qA2 =	0
kA1 =	0.00529283	kA1 =	1.5007E-05
kA2 =	0	kA2 =	0
na1 =	0.801439785	na1 =	1.00003705
na2 =	0	na2 =	0
HA1 =	0.045499155	HB1 =	4.4548E-05
HA2 =	0	HB2 =	0

Gas Mixture			
YA =	0.4		
YB =	0.6		

Constants	Gas B Constants		stants
qA1 =	8.596375223	qA1 =	2.96854993
qA2 =	0	qA2 =	0
kA1 =	0.00529283	kA1 =	1.5007E-05
kA2 =	0	kA2 =	0
na1 =	0.801439785	na1 =	1.00003705
na2 =	0	na2 =	0
HA1 =	0.045499155	HB1 =	4.4548E-05
HA2 =	0	HB2 =	0



Figure S33. IAST fit for HPF-5 using CO₂ and H₂ isotherms collected at 273 and 303K.

IAST fitting para	meters for HPF-3 (CO ₂ /H	I2) at high press	ure:
303K			
Gas $A = CO_2$			
$Gas D = \Pi_2$			
Gas Mixture			
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	11.77210626	qA1 =	1.39221583
qA2 =	0	qA2 =	0
kA1 =	0.00010896	kA1 =	1.9058E-06
kA2 =	0	kA2 =	0
na1 =	1	na1 =	1.12129683
na2 =	0	na2 =	0
HA1 =	0.000320484	HB1 =	2.6534E-06
HA2 =	0	HB2 =	0
Gas Mixture			
YA =	0.4		
YB =	0.6		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	11.77210626	qA1 =	1.39221583
qA2 =	0	qA2 =	0
kA1 =	0.00010896	kA1 =	1.9058E-06
kA2 =	0	kA2 =	0
na1 =	1	na1 =	1.12129683
na2 =	0	na2 =	0
HA1 =	0.001282688	HB1 =	2.6534E-06
HA2 =	0	HB2 =	0



Figure S34. IAST fit for HPF-3 using CO₂ and H₂ isotherms collected at 303K.

IAST fitting parameters for HPF-4 (CO_2/H_2) at high pressure:

303K			
Gas A = CO_2			
Gas $B = H_2$			
Gas Mixture			
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B Cor	istants
qA1 =	22.42795427	qA1 =	19.1445384
qA2 =	0	qA2 =	0
kA1 =	0.002660991	kA1 =	5.0231E-07
kA2 =	0	kA2 =	0
na1 =	0.632156772	na1 =	1.00000025
na2 =	0	na2 =	0
HA1 =	0.059680592	HB1 =	9.6165E-06
HA2 =	0	HB2 =	0

Gas Mixture			
YA =	0.4		
YB =	0.6		
Gas A			
Constants		Gas B Cor	istants
qA1 =	22.42795427	qA1 =	19.1445384
αA2 =	0	αA2 =	0

Ũ	9/1=	0	97.1
5.0231E-07	kA1 =	0.002660991	kA1 =
0	kA2 =	0	kA2 =
1.0000025	na1 =	0.632156772	na1 =
0	na2 =	0	na2 =
9.6165E-06	HB1 =	0.059680592	HA1 =
0	HB2 =	0	HA2 =



Figure S35. IAST fit for HPF-4 using CO₂ and H₂ isotherms collected at 303K.

IAST fitting para	meters for HPF-5 (CO2/H	I ₂) at high press	ure:
303K			
Gas $A - CO_2$			
$Gas D = \Pi_2$			
Gas Mixture			
YA =	0.2		
YB =	0.8		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	24.52078493	qA1 =	19.1445384
qA2 =	0	qA2 =	0
kA1 =	0.003601205	kA1 =	5.6128E-07
kA2 =	0	kA2 =	0
na1 =	0.548456239	na1 =	1.00000025
na2 =	0	na2 =	0
HA1 =	0.088304376	HB1 =	1.0745E-05
HA2 =	0	HB2 =	0
Gas Mixture			
YA =	0.4		
YB =	0.6		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	24.52078493	qA1 =	19.1445384
qA2 =	0	qA2 =	0
kA1 =	0.003601731	kA1 =	5.6128E-07
kA2 =	0	kA2 =	0
na1 =	0.548456258	na1 =	1.00000025
na2 =	0	na2 =	0
HA1 =	0.088304376	HB1 =	1.0745E-05
HA2 =	0	HB2 =	0



Figure S36. IAST fit for HPF-5 using CO₂ and H₂ isotherms collected at 303K.

6. Contact angle measurement:

Contact angles were measured on the polymers surfaces using computerized camera technique and processed with ImageJ software.

For the measurement the polymer powder was spreaded homogeniously on the glass slide. Then droplet of water slowly placed on the top of the polymer surface with a syringe needle. The camera was focused to the particular region and images were recorded. Note: The surface hydrophobicity of the sample is sensitive to the reaction condition and this is because of the texture of the final product. However, the intrinsic hydrophobicity remains the same even when the synthesis conditions (time 3 days vs. 4 days, or solvent amounts) are varied. This is confirmed from the solvent sorption experiments.



Figure S37. Contact angle measured using water droplet for the HPF-3 showing hydrophobic nature of the polymer. By fitting the image using Image J, contact angle was found to be $\sim 148^{\circ}$.



Figure S38. Contact angle measured using water droplet for the HPF-4 showing hydrophobic nature of the polymer. By fitting the image using Image J, contact angle was found to be $\sim 149^{\circ}$.



Figure S39. Contact angle measured using water droplet for the HPF-5 showing hydrophobic nature of the polymer. By fitting the image using Image J, contact angle was found to be $\sim 152^{\circ}$.

7. TGA Cycling Experiment:

For the cycling experiments, no protective gas was used, and the gas flows were systematically switched between CO_2 and He on the purge lines. The methanol exchanged and activated (150°C, 6 hrs) sample of HPF-3, HPF-4 and HPF-5 were loaded on to the Pt pans and evacuated for 6hrs prior to the runs. TGA and DSC calibration and corrections runs were done prior to carrying out the cycling experiments.

8. Steam Conditioning Experiments:

The materials were activated by heating at 160° C for 12hrs under vacuum. These three samples were then exposed to a flow of humid N₂ (100ml/min over a 75%RH, saturated NaCl solution maintained at 60°C) for a period of 24hrs. This steam conditioned materials were loaded on to the adsorption cell and without any further activation (no heating or evacuation), a CO₂ adsorption was carried out on the wet material.



Figure S40. Comparative CO_2 (273K) adsorption isotherms of as-synthesized and steam-conditioned phases of HPF-3 (A), HPF-4 (B) and HPF-5 (C). Note in all three cases the steam condition phases were not subjected to any activation prior to the analysis.

9. Rate of Adsorption Studies- Self-diffusion Coefficients Calculations and Analysis:

<u>Self-diffusion coefficient CO₂ in powder and pelletized form of the material:</u>

Diffusion coefficient determination from Rate of Adsorption (ROA) measurements: An extremely high resolution rate of adsorption measurement was carried out using the ASAP2020HD instrument at 273K in the pressure range of 0-1bar. The diffusion coefficient was calculated as a function of CO_2 loading. For this purpose, 10 different loading points were used and each of the ROA data was fitted to a spherical pore model[¥]:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \operatorname{Exp} (-n^2 \pi^2 \tau)$$

F = fractional uptake; τ = non-dimensional time given by τ = Dt/R², where R= particle size; t= time (secs); D = apparent diffusivity.

[¥] Kourosh Malek and Marc-Olivier Coppensa), *J. Chem. Phys.*, Vol. 119, 2801 (*2003*); Adsorption analysis and equilibria and kinetics, D. D. Do, Imperial College Press, Ed. 2008.



Figure S41. Representative plot of the adsorbate fractional filling vs time showing the fit between the spherical model (line) and the collected data (spheres) obtained from the single component CO_2 isotherm of HPF-3. Note 10 such fittings were considered to obtain the average diffusion coefficient.



Figure S42. Representative plot of the adsorbate fractional filling vs time showing the fit between the spherical model (line) and the collected data (spheres) obtained from the single component CO_2 isotherm of HPF-4. Note 10 such fittings were considered to obtain the average diffusion coefficient.



Figure S43. A plot of the adsorbate fractional filling vs time showing the fit between the spherical model (line) and the collected data (spheres) obtained from the single component CO_2 isotherm of HPF-5. Note 10 such fittings were considered to obtain the average diffusion coefficient.

10. Stability Studies:

Mentioned in this section are some of the important requirements for any porous material when it comes to its potential industrial application. These porous polymers are quite interesting owing to their good stability to solvent removal as compare to the large pore MOFs which in many cases require highly demanding moisture free handling and in spite of that tend to show partial to complete loss of porosity. This polymer has excellent shelf-life and they retain complete porosity even after 6-8 months. Additionally, the hydrolytic stability of the material was confirmed by exposing the material to boiling solvent like water, wet DMF, wet THF, wet DMA etc. (from CO_2 isotherms) and no further loss was observed even after 5 days of boiling. Also in the adsorption cycling experiments the samples did not show any loss in uptake across the cycles. Most of this stability can be attributed to the polymers framework being constructed from exceptionally stable C-C bonds.



Figure S44. Stability of HPF-3 in boiling DMF displayed from 273K CO₂ isotherms.



Figure S45. Stability of HPF-4 in boiling DMF confirmed from 273K CO₂ isotherms.



Figure S46. Stability of HPF-5 in boiling DMF confirmed from 273K CO₂ isotherms.

<u>Acid stability study:</u> about 250 mg of each polymer was dispersed in 3ml of H₂O and 0.5 ml of MeOH were taken in three different small vials. In three different bigger vials a mixture of ClSO₃H (2ml) and HNO₃ (2ml) was taken. Now the smaller vials containing the dispersions of different polymers were kept inside the bigger vials and screw capped in such a way that enough of acidic vapours goes in to the smaller vials but the acid did not directly touch the polymers. These vial-in-a-vial set-ups were placed at ~50°C. After 6 hrs the smaller vials containing the polymers were taken out and pH of the solution was found to be in between 2 to 2.5. The polymer samples were filtered and washed thoroughly with water, methanol and finally with plenty of THF. These polymers were then dried under vacuum and used for gas adsorption analysis. Only <2% drops in CO₂ capacity was observed in each case after this treatment.



Figure S47. Comparison of the pore sizes between the as-made and the acid treated samples. Note: The pore sizes are estimated from the 273K CO_2 adsorption isotherms.

Stability of the pelletized material: About 250 mg of powder HPF-4 was subjected to 15 ton of pressure for 30 minutes using a hydraulic pelletizer. After that the pellet was subjected to pre treatment prior to gas adsorption under similar conditions employed for the powder samples. The thickness of the pellet before and after gas adsorption remains unchanged (Figures S48). This lack of swolling in a polymer is highly desirable for practical gas separation applications.



Figure S48. (A) Photographic image of HPF-4 in powder and pellet form. Thickness of the pellet before (B) and after(C) the adsorption study.



Figure S49. FE-SEM images of the pellet showing lack of any cracks or rupture on the surface upon subjecting to even liquid nitrogen temperatures. This is critical for an all-organic sorbent material.

11. Breakthrough (Mixed Gas) Analysis:

<u>Column Breakthrough Test Set-up, Procedure:</u> About 0.9 gm of HPF 4 was loaded onto a stainless column fitted with mass flow controllers and pressure gauges to control the inlet and outlet pressures. The material was subjected to a pre-treatment by heating at 170° C under vacuum for 24 hours within the adsorption column. The CO₂/H₂ and CO₂/He breakthrough experiments were carried out using the RuboLab / Rubotherm VariPSA system. This instrument allows the measurement of breakthrough curves (BTC) on solid sorbent materials. Based on the sorbent the system settings were optimized. The adsorber column was designed to be approx. 1.5 ml in volume. To measure the sorption based temperature (adsorption front), three temperature sensors were integrated to measure the temperature at two/three different positions within the adsorber bed. (Thermocouple type K, 3 mm diameter of temperature sensor). The gas flow across the column was controlled using a micro-metering valve. All measurements were performed by using a gas flow of 50 or 100 ml/min. While the adsorption of CO_2 was indicated by its retention time on the column, the complete breakthrough of CO_2 was indicated by the downstream gas composition reaching that of the feed gas. Using the formula,

Number of mole adsorbed, $n = F * C_i * t$,

Where F = molar flow, $C_i = concentration of ith component and t = retention time.$

The CO₂ uptake was calculated to be 2.48mmol/g for the $20CO_2/80He$ mixture and this uptake closely matched with the uptake obtained for the $20CO_2/80H_2$ (2.42 mmol/g) mixture. This suggest almost negligible amount of H₂ is being adsorbed by the polymer. Similarly CO₂ uptake was calculated to be 3.52 mmol/g for $40CO_2/60H_2$ mixture.

12. Computational and Molecular Modelling Details:

Structure solution: In our study HPF-4 is the best performing one. We considered only HPF-4 for all the simulation studies. For structure solution we have adopted our earlier reported strategies.(ref. 50 maintext) In the first step, we created few small oligomers of different length by combining the monomers in a 2:3 ratio and minimized its structure using DFT methods (CASTEP routine) with Materials Studio. Random polymerization of these oligomers yielded longer linear oligomer. These polymers took different configurations depending on the small differences in the geometry of the initial energy minimized smaller oligomers. Three low energy oligomers were chosen based on the energy. These oligomers were then polymerized randomly with branch point at different parts of them. With the lowest energy conformer, amorphous cell was constructed.

Again this amorphous cell was energy and geometry optimized using the tight-binding DFT methods (DFT-TB). This yielded a structure with a triclinic unit cell: P1; a = 48.7804A, b =49.8932A, c = 47.0560A, α = 89.2961 (2)°; β = 90.3408 (4)°, and γ = 90.8990 (4)°. During the entire process complete rotational and torsional freedom was maintained.



Figure S50. Structure of the 2^{nd} lowest energy conformer whose CO_2 isotherms does not match well with the experimental one.

To gain more confidence on the structure solution we simulated the high pressure (0 to 40 bar) CO_2 isotherm using Grand Canonical Monte Carlo (GCMC) method. The simulated and the experimental isotherms matched well (see figure in the main text). From the GCMC calculation it was observed that the material is able to take 209 molecules of CO_2 per unit cell.

To obtain insights on the CO₂ adsorption sites, we extracted the CO₂ positions inside the polymer framework from the GCMC calculations. The lowest energy conformer was subjected to an energy optimization using CASTEP program. It was observed that most of the CO₂ molecules are residing on the top of the π -electron cloud of the aromatic phenyl or triazine ring present in the polymer. Interestingly, it was observed that despite the presence of lone pair carrying O-atom from the phenolic groups, the CO₂ molecules chose to interact with the π -electron cloud from the aromatic ring (Figure S51 and 52).



Figure S51. Positions of CO₂ molecules inside the framework extracted from GCMC/DFT methods showing the interactions between the CO₂ molecules and the aromatic π -electron cloud.



Figure S52. Alternate view from the simulated structure showing the interaction of CO_2 molecules and the aromatic π -electron cloud.