Supporting Information for

# A Triazine-Resorcinol based Porous Polymer With Polar Pores and Exceptional Surface Hydrophobicity Showing CO<sub>2</sub> Uptake Under Humid Conditions

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## 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) was synthesized according to previously reported procedure (S1) with slight modification. The hydrophobic standard, Silica Alumina was obtained from Micromeritics.

## Synthesis of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-1,3-diol):

About 2g (10.8mmol) of cyanuric chloride and 3.58g (32.5mmol) of resorcinol were dispersed in 100ml of 1,2-dichloroethane. Contents were dissolved by heating at 70°C, following this, the mixture was cooled to 0°C. To this, about 4.35g (32.5mmol) anhydrous AlCl<sub>3</sub> was slowly added over 30mins. This mixture was refluxed for 36 hrs. The reaction mixture was cooled to room temperture and solvent was removed using a rotaevaporator. The solid was then stirred in 100 ml of 10% HCl for 3 hrs and kept standing for an additional 3 hrs. A yellow solid precipitated, which was filtered under vacuum and washed with about 250ml of diethyl ether to remove any unreacted starting materials. The product was dried in a vacuum oven. About 3.2g (Yield: 88%) of the product was obtained.

## Synthesis of polymer:

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 terephthaldehyde(0.100g; 0.75mmol) in a solution containing 5ml 1,4-dioxane + 3ml tetrahydrofuran (THF) was carried out at 200°C for 96hrs. Yellowish brown color powder was isolated by filtration and was washed with Dimethylformamide (DMF) (15ml) , THF(10ml) and finally with methanol and acetone. The air dried sample gave a yield of ~85%. The PXRD pattern indicated this to be amorphous. CHN analysis (calculated values within brackets): C: 72.88 (72.5128); H: 5.65 (4.7997); N: 6.54 (6.6738)%.

## Steam conditioning experiments:

*Experiment 1:* Silica-rich alumina (used as standard for hydrophobic material) and HKUST-1 were activated according to standard procedures reported in literature, while HPF-1 was activated by heating at 160°C for 12hrs under vacuum. These three samples were then exposed to a flow of humid N<sub>2</sub> (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 CO<sub>2</sub> adsorption was carried out on the wet material.

*Experiment 2:* In another separate experiment, about 1gm of HPF-1 was activated (evacuated at  $160^{\circ}$ C for 12hrs under  $10^{-4}$ Torr) and then was exposed to a stream of CO<sub>2</sub> (100ml/min) over 75% RH solution (saturated NaCl solution maintained at  $60^{\circ}$ C) for 24hrs. This sample was then cut off from the CO<sub>2</sub> stream and was exposed to ambient conditions to release any CO<sub>2</sub> filling the vessel. The adsorbed CO<sub>2</sub> was desorbed by heating the sample at  $60^{\circ}$ C and the evolved CO<sub>2</sub> was captured on to a pre-treated solution of CaO (see below). Brisk bubbling was observed followed by the occurrence of white crystalline precipitate of CaCO<sub>3</sub>, which was extracted by filtration and dried with an acetone wash. This was characterized to be CaCO<sub>3</sub> (ICSD: 18165)

using PXRD and TGA (Fig. S16). Following this, a mass balance was carried out to estimate the  $CO_2$  uptake as being 2.66mmol/g.

Pre-treatment of CaO solution: Cao solution used in the above procedure was made by dissolving 1.5g of CaO in 250ml distilled water. Any insoluble precipitate was filtered. The clear solution was bubbled with  $N_2$  gas to remove any dissolved  $CO_2$  from air. It was then freeze dried and left under  $N_2$  atmosphere.

## Synthesis of Lithiated HPF-1 (Li.HPF-1)

Lithium was loaded into HPF-1 via a solvothermal reaction between LiOH and HPF-1. About 0.235g of HPF-1 was reacted with 0.006g (0.15 mmol) of LiOH.H<sub>2</sub>O in a mixture of 4ml dioxane and 3ml of H<sub>2</sub>O at 180°C for 12 hrs. After cooling the dark brown colour polymer was isolated by vacuum filtration and washed with DMF and water and then dried in a vacuum oven. The dried sample gave a yield of 96%. (Note: This gives a Lithium loading of 16.7% with respect to the number of phenolic -OH groups present in the polymer formed by combining the triazinetriresorcinol and terephthaldehyde in a 2:3 ratio.). Lithium loading was confirmed via Microwave Plasma Atomic Emission Spectrometry (MP-AES).

Synthesis of HKUST: The HKUST-1 was synthesized according to the literature procedures.(S2)

Polymer	CO <sub>2</sub> @	Surface	$S(CO_2/N_2)$	HOA	Reference
	298K	area		$(KJ mol^{-1})$	
	$(\text{mmol g}^{-1})$	$(m^2 g-1)$			
SNU-C1-va	2.31	595	262		83
TB-MOP	2.57	694	50.6		84
BILP-1	2.97	1172	70(initial slope method)	26.5	85
PSN-DA	2.25	1045	40	34	86
PSN-TAPB	1.5	611	65	33	<b>S6</b>
PCN-AD	1.7	843	112(initial slope method)	32.4	S7
APOP-1	2.69	1298	23	26	<b>S8</b>
TPI-1	1.25	809	30.9	34.4	89
COP-93	2.07	606	36.4	25.6	S10
Network- A/(PAF-1)	1.45	4077	13	24	S11
TSP-1	1.9	562.5	32	28.1	S12
TSP-2	2.6	913.0	38	30.2	S12

Table S1. CO<sub>2</sub> uptakes and selectivity at 298K for selected porous polymers.

TCMP-0	1.34	963	9.6		S13
TzTz-POP1	1.3	299	54(initial slope)	32	S14
TzTz-POP1	1.5	488	35(initial slope)	30	S14
PECONF-1	1.34	499	51	29	S15
PECONF-2	1.98	637	44	31	S15
PPN-6- SO <sub>3</sub> H	3.5	1254	150	30.4	S16
Network-4R	2.21	927		30	S17
CMP	1.61	772			S18
azo-COP-1	1.47	635	96	29.3	S19
azo-COP-2	1.52	729	130	24.8	S19
COP-3	1.13	413	105	24.5	S20
COP-1	1.36	168			S21
COP-2	0.93	158			S21
COP-4	1.13	2015	6.1		S22
P-1	1.29	100		80	S23

P-2	0.88	57	2500	50	S23
P-3	0.82	50	2500	50	S23
HPF-1	2.8(303K)	576	120	26	Present WORK
DBT	1.47	493	80	41.9	S24

----- = Data not available.

#### 2. Analytical characterizations

#### Powder X-ray diffraction:

Powder XRDs were carried out using a Rigaku Miniflex-600 instrument and/or on a Bruker D8 Advance instrument.

#### Thermogravimetric Analysis (TGA):

Thermogravimetry was carried out on NETSZCH TGA-DSC system. The conventional TGA experiments were done under N<sub>2</sub> gas flow (20 ml min<sup>-1</sup>) (purge + protective) and samples were heated from RT to  $550^{\circ}$ C at 2 K min<sup>-1</sup>.

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-1 was loaded on to the Pt pans and evacuated for 6hrs prior to the runs. TGA and DSC calibration and corrections runs were done just prior to carrying out the cycling experiments. This seemed to be critical to obtain accurate data from these cycling experiments. Without these systematic preparations, the data were found to be highly over estimated.

## Microwave Plasma Atomic Emission Spectrometer (MP-AES):

Lithium loading was quantified using an MP-AES analysis carried out on a 4100MP-AES Agilent system. For this purpose a calibration curve of Li standard in the concentration range of 3-20ppm was created. Using this calibration curve the lithium content present in 100gm of Li.HPF-1 was measured using an acid digestion procedure.

## 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 <sup>13</sup>C Larmor frequency) using our probe head for rotors of 4 mm diameter. The parameters for the <sup>13</sup>C 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 <sup>13</sup>C 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 are 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, which I found previously to be a good compromise between detecting carbons with directly bonded protons and other carbons, for which protons are further removed.

#### Field Emission-SEM:

Ultra Plus Field Emission Scanning Electron Microscope with integral charge compensator and embedded EsB and AsB detectors. Oxford X-max instruments 80mm<sup>2</sup>. (Carl Zeiss NTS, Gmbh), Imagin conditions: 2kV, WD= 2mm, 200kX, Inlens detector. For SEM images sample was grind nicely and soaked in MeOH for overnight. Then filtered and dried in hot oven at 80°C. The fine powder was nicely spread over carbon paper and SEM images were taken at different range. Beautiful homogeneous micro spheres were obtained.



**Figure S1.** Powder X-ray diffraction patterns of HPF-1 indicating its amorphous nature. The big hump at around  $2\theta = 20^{\circ}$  is inherent to the polymer. Note: It is not from the glass substrate as plenty of sample was used during the experiment.



**Figure S2.** FE-SEM images of the polymer microspheres indicating high homogeneity as well as purity of the sample. Though the microspheres shape and texture looks homogeneous the size is distributed between 0.3 to 15microns.



**Figure S3.** TGA carried out on the as synthesized sample. The weight loss observed about 20% from room temperature to 200°C can be attributed to the solvent (THF and Dioxan) molecules trapped in the polymer. The decomposition of the material does not set in until about 380°C.



**Figure S4.** Infra red spectra of the polymer, showing the various stretching and bending modes present. Selected peaks: IR (KBr pellet, cm<sup>-1</sup>): v(O-H)solvent and -OH: 3431; v(C-H): 2930; v(CO): 1692; 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<sup>-1</sup> is due to carbonyl stretching of unreacted aldehyde (very less intense).

#### 3. Adsorption studies

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). Samples were transferred to a glass tube for analysis, with dual stage activation: The as-made samples were solvent exchanged by soaking 200mg in 7ml methanol (reagent grade) for 24 hours, with the solvent being replenished every 6hrs. Following this ~ 100mg of the solvent exchanged sample was transferred to analysis glass vial and evacuated at 160°C on the degas port for 16hrs (10<sup>-6</sup> mbar), at which point the outgas rate was  $\leq 2 \mu bar/min$ .

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  $CO_2$  loading points were picked out in the interval of 0 to 1000mbar.

#### **Langmuir Fits:**

In most cases the isotherms were fit to the Dingle-Site Langmuir (DSL) equation. The two exceptions,  $N_2$  at 273 K (Single-Site Langmuir) and  $N_2$  at 303 K (Single-Site Langmuir). It is widely known that even small fitting errors will have a devastating impact on selectivity calculations.

The isotherms were fit by solving the Langmuir equation using the solver function in Microsoft Excel following a similar protocol to Keller *et al.*(S24) Utilizing this routine circumvents some of the problems associated with favoring either high or low pressure regions when linearizing the Langmuir equation<sup>3</sup> and offers a balanced approach. A more in depth discussion will be published elsewhere.

Single-Site Langmuir (SSL):

$$q_i = q_m \frac{K_i P}{1 + K_i P}$$
 Eq.S1

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1 P}{1 + K_1 P} + q_{m,2} \frac{K_2 P}{1 + K_2 P}$$
 Eq.S2

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1 P}{1 + K_1 P} + q_{m,2} \frac{K_2 P}{1 + K_2 P}$$
 Eq.S3

## **IAST Fitting parameters:**

303K

Gas Mixture			
YA =	0.15		
YB =	0.85		
Gas A			
Constants		Gas B Cor	nstants
qA1 =	9.146200123	qA1 =	0.12049249
qA2 =	2.677579358	qA2 =	0
kA1 =	8.50277E-05	kA1 =	0.00083347
kA2 =	0.003860592	kA2 =	0
na1 =	1	na1 =	1.000061
na2 =	1.000004074	na2 =	0
HA1 =	0.000777681	HB1 =	0.00010043
HA2 =	0.010337041	HB2 =	0
273K			
Gas Mixture			
YA =	0.15		
YB =	0.85		
Gas A			
Constants		Gas B Cor	nstants

1.98589172	qA1 =	10.08659267	qA1 =
0	qA2 =	3.088424317	qA2 =
0.00018174	kA1 =	0.000125694	kA1 =
0	kA2 =	0.003613829	kA2 =
1.000061	na1 =	1	na1 =
0	na2 =	1.000004074	na2 =
0.00036091	HB1 =	0.001267828	HA1 =
0	HB2 =	0.011161038	HA2 =

 $Gas A = CO_2$  $Gas B = N_2$ 

Table S2.  $CO_2$  adsorption and desorption data for 195K and 303K

Adsorption		Desorption		
P(mm Hg)	Q(mmol/g)	P(mm Hg)	Q(mmol/g)	
195K				
0.32356	1.42406	702.217	9.34134	
0.99973	2.33655	695.3358	9.35461	
1.66425	2.82893	666.1895	9.3518	
2.78706	3.40061	635.5768	9.34357	
3.71226	3.72889	605.1062	9.32978	
4.64654	3.98898	574.4381	9.31195	
8.38361	4.71327	542.8259	9.28589	
13.03725	5.23184	513.0055	9.25613	
15.13743	5.39821	481.2696	9.22389	
17.25901	5.54225	450.4792	9.17923	

21.74	5.79585	420.5535	9.13384
28.82916	6.10707	389.5824	9.07722
36.17385	6.35173	357.7842	9.00509
48.17046	6.6528	327.5363	8.93616
60.15596	6.8848	296.8089	8.85341
70.15409	7.03966	265.75	8.75257
80.40269	7.17951	234.7805	8.62024
90.36143	7.29526	204.5061	8.48769
100.3568	7.40019	188.6329	8.40349
114.303	7.53411	174.1234	8.31719
129.0467	7.66421	143.1163	8.10066
135.9099	7.718	112.2321	7.84707
143.1306	7.77694	81.53052	7.4875
157.2044	7.86982	66.17602	7.24918
171.8376	7.96734	50.7402	6.94648
186.2317	8.04599	35.30672	6.52646
200.1606	8.11911	19.99541	5.84362
214.3002	8.1906	10.53423	5.28882
228.6847	8.25762		
242.9166	8.32214		
271.5904	8.44588		
300.6142	8.55437		
328.9263	8.63598		

343	.5976	8.6868		
358	.3952	8.73635		
387	.0398	8.8029		
414	.8864	8.86456		
443	.8797	8.9298		
472	.5877	8.98983		
501	.2255	9.05761		
529	.2346	9.096		
558	.7052	9.14508		
587	.5902	9.18825		
616	5.426	9.22499		
645	.3116	9.26689		
674	.6436	9.30524		
702	2.217	9.34134		
30	)3K			
0.3	2897	0.00481	900.04	3.0264
0.9	9801	0.01555	796.5862	2.92533
1.6	7073	0.02733	707.2197	2.81624
2.7	9167	0.047	626.7273	2.69663
4.6	5633	0.07866	554.4988	2.57579
7.9	9951	0.13356	492.1299	2.45457
12.9	93494	0.19943	435.3777	2.32979

17.38812	0.25981	386.7478	2.20635
21.86311	0.31648	342.6381	2.08688
29.02614	0.39999	303.3881	1.968
36.23599	0.48085	269.2047	1.85071
48.35517	0.60176	238.8232	1.73791
60.16658	0.7098	211.6892	1.62574
70.27207	0.79306	187.561	1.51707
80.40591	0.86918	166.2111	1.41474
90.35298	0.94203	147.389	1.31669
100.406	1.01211	131.0325	1.22444
110.1314	1.07503	115.9829	1.13375
119.9965	1.13604	102.7714	1.04889
131.6809	1.20367	91.10788	0.9693
143.4531	1.26869	80.7356	0.89275
157.4205	1.34332	71.66833	0.82303
171.0625	1.41383	63.49024	0.75765
188.4524	1.49603	56.30807	0.69168
205.4504	1.5709	50.00063	0.63248
225.1051	1.65175	31.44394	0.44825
245.185	1.73079	19.81118	0.31077
269.6362	1.81882	9.99444	0.18041
293.6971	1.90031		
321.7879	1.99228		

349.794	2.07709	 
384.8517	2.17023	 
420.0388	2.25625	 
460.571	2.34692	 
480.7376	2.39108	 
500.8984	2.43141	 
534.2066	2.49806	 
569.8571	2.56239	 
609.7858	2.6306	 
650.4791	2.69677	 
693.7511	2.7641	 
741.0284	2.83357	 
789.9896	2.89686	 
843.6656	2.96095	 
900.04	3.0264	 



**Figure S5.** Pure component  $CO_2$  and  $N_2$  isotherms of HPF-1 collected at (a) 195K, (b) 273K and (c) 303K. Note that the 195K isotherm represents the saturation uptake of HPF-1, while the 303K uptake represents the capacity of interest for applications.



Figure S6. BET and Langmuir fits from the 77K N<sub>2</sub> data.



**Figure S7.** Pore size distribution in HPF-1 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 pore in the material.



Figure S8: DFT fitting comparision obtained using the 77K N<sub>2</sub> adsorption branch.



**Figure S9.** Pore size distribution in HPF-1 obtained by fitting the Non Localized Density Functional Theory (NLDFT) model to the 273K  $CO_2$  adsorption branch. Note the majority of the porosity is due to 5.5Å pore in the material.



Figure S10: DFT fitting comparision calculated using 273K CO<sub>2</sub> adsorption branch.

#### 4. Virial Analysis:

The  $CO_2$  adsorption data for **1** were measured from 0- 1bar at 263, 273, 283, 303K and were fitted by the virial equation (Eq.S4).

 $ln(P) = ln(Va) + (A0 + A1 * Va + A2 * Va^{2} ... + A6 * Va^{6})/T + (B0 + B1 * Va)$ Eq.S4

Where P is pressure, Va is amount adsorbed, T is temperature, and A0, A1, A2  $\dots$ , A4 and B0, B1

are temperature independent empirical parameters (Figs. S.15 and S16)

A0	-2509.624613	B0	12.45334868
A1	-511.2213547	B1	1.508359775
A2	232.604966	B2	1.213929088
A3	-98.90127939		
A4	72.27635463		
A5	-22.67075106		

**Table S3:** Summary of the fitted Virial parameters



**Figure S11.** Comparison of the HOA trend obtained from the virial and DFT modeling done using the  $CO_2$  isotherms carried out at  $0^{\circ}C$ ,  $+10^{\circ}C$  and  $+30^{\circ}C$ .



**Figure S12.** Comparison of experimental isotherms to the ones obtained from virial modeling carried out using  $CO_2$  isotherms collected at  $0^{\circ}C$ ,  $+10^{\circ}C$  and  $+30^{\circ}C$ .



**Figure S13.** Virial plots carried out using  $CO_2$  isotherms collected at  $0^{\circ}C$ ,  $+10^{\circ}C$  and  $+30^{\circ}C$ .



Figure S14. Virial plots carried out using water isotherms at 25°C and +35°C.



Figure S15. Virial plots carried out using toluene isotherms collected at 25°C and +35°C.

5. Analytical characterization after steam conditioning experiments



**Figure S16.** (a) Powder pattern and (b) TGA plot corresponding to the CaCO<sub>3</sub> generated by reacting the CO<sub>2</sub> captured by and desorbed from the HPF-1 at room temperature. The PXRD corresponds to the anhydrous CaCO<sub>3</sub> (ICSD: 18165). The 44% weight loss observed on the TGA matches very well with the expected weight loss (cacl. 44%) for CO<sub>2</sub> (2.66 mmol  $g^{-1}$  at room temperature).

## 6. Contact angle measurements



**Figure S17.** Contact angle measured using water droplet for the HPF-1 showing hydrophobic nature of the polymer. A fit to this image yielded a contact angle of ~  $153^{\circ}$ .

#### 7. Computational and Molecular Modelling Details

All computations were carried out using Material Studio software suite (Accelrys). Standard force fields were employed and no constraints were used. Energy minimizations for molecular structures of the building units were carried out using DMOL<sup>3</sup> with a DFT-D correction, while the geometry optimizations for the final polymers in triclinic cell were done using the tight binding DFT routines. Adsorption isotherms were carried out using the default Monte Carlo algorithm (Accelrys).



**Figure S18.** Three low energy configurations for the polymer grown via random polymerization algorithm. They all have been geometry minimized using Tight Binding DFT methods. All the iterations were carried out to ultra-fine cycles.

#### 8. Self-diffusion coefficient CO<sub>2</sub> in HPF-1:

Diffusion coefficient determination from Rate of adsorption 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 (S26, S27):

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \tau)$$
Eq.S5

F = fractional uptake;  $\tau$  = non-dimensional time given by  $\tau$  = Dt/R<sup>2</sup>, where R= particle size; t= time (secs); D = apparent diffusivity.

The single-component diffusion coefficient was estimated to be  $3.70 \times 10^{-9} \text{m}^2 \text{s}^{-1}$  taking the average of these 10 points. Note: the kinetics of the low loadings (<1mmol/g) were extremely hard to model.



**Figure S19.** 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. Note 10 such fittings were considered to obtain the average diffusion coefficient.





**Figure S20:** Comparison of the effect of humidity on the CO<sub>2</sub> adsorption behavior of different samples with varying hydrophobic-hydrophilic character. All isotherms were carried out at 303K. The uptake for the non-humidity treated HKUST-1 matches well with the literature values.(S28) *Important: After the steam conditioning the material was not subjected to any activation*. Note: spheres represent activated phase; squares represent steam conditioned phase.

#### **References for the supporting information:**

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