Supporting information for

Permanently Porous Single Molecule H-Bonded Organic Framework for Selective CO₂ Capture

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1. Material and Methods:

All the chemicals were bought from Sigma Aldrich and used without further purification. 4,4',4"- nitrilotribenzoic acid was synthesized according previous report^(S1) with slight modification.



SchemeS1. Schematic representation of ligand formation reaction.

1.18g (10 mmol) of 4-aminobenzonitrile was dissolved in 50 ml dry DMF. Then 6.04 g (40.0 mmol) of CsF was added slowly to the solution with continuous stirring followed by the addition of 2.66 g (22 mmol) of 4-Fluorobenzonitrile. The total reaction mixture was then refluxed at 140°C for 48 hrs. After cooling, the reaction mixture was poured into ice cold water to precipitate out the product (4,4 ',4 ''-tricyanotriphenylamine). The precipitate was filtered and washed with plenty of water and finally dried in a hot air oven to yield 2.94g (91%) of 4,4 ',4 ''-tricyanotriphenylamine.

In the second step, 2g of 4,4',4"-tricyanotriphenylamine was dissolved in a mixture containing 20 ml ethanol and 60 ml 6M KOH solution. The mixture was then refluxed for 48 hrs. After cooling down to room temperature the mixture was acidified with 3N HCl. The pH of the solution was adjusted to 3 to get a white precipitate. Finally the precipitate was filtered and washed with plenty of water, dried in an oven to obtain 2.1 g (~90%) of the desired product.

(S1) G.-S. Liou, N.-K. Huang, Y.-L. Yang, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2006, 44, 4095–4107.

Crystallization:

About 1.0 g of 4,4',4"-tricarboxytriphenylamine was dissolved in 5 ml of acetic acid. This solution was transferred to a Teflon lined stainless steel autoclave and heated to 150°C for 3 days. After cooling to room temperature needle-shaped colourless crystals were isolated by filtration, washed with distilled water and then dried. All the physical characterization was carried out using this sample.



Figure S1. A stick representation of the IISERP-HOF1 showing the organic molecule reduced to a tripod. The central core is nitrogen and the three lines emerging out are the benzoic acid moiety. The channels are along the a-axis. The molecules run up and down and in and out.



Figure S2. The -COOH...HOOC- dimeric hydrogen bonds extending along all three orthogonal directions owing to the propeller like shape of the organic molecule. This is due to the benzoic acid moieties being attached to a sp^3 N-centre.

Туре	Donor	,	Hydrogen	Acceptor	[ARU]	DH	HA	DA	D - HA
2	O(2)		H(2)	O(1)	[3356.02]	0.84	1.78	2.619(8)	176
2	O(4)		H(4)	O(9)	[4555.02]	0.84	1.8	2.622(7)	167
2	O(8)		H(8)	0(13)	[2855.01]	0.84	1.77	2.612(8)	175
2	O(10)		H(10)	O(3)	[4454.02]	0.84	1.78	2.602(7)	167
1	O(14)		H(14)	0(7)	[2845.02]	0.84	1.81	2.646(7)	173
1	O(23)		H(23)	O(24)	[3355.01]	0.84	1.84	2.643(7)	160
2	C(21)		H(22)	0(1)	[1655.02]	0.95	2.55	3.288(10)	135
Т	ranslatio	on of	ARU-code to Equi	valent Positi	on Code				
[4	4555]	=	1/2+x, 1/2-y, 1/2+	⊦z					
[2	2845]	=	7/2-x, -1/2+y, 1/2	-Z					
[]	1455]	=	-1+x, y, z						
[]	1655]	=	1+x, y,z						
[4	4454]	=	-1/2+x, 1/2-y, -1/2+z						
[3	3355]	=	-2-x,-y,-z						
[3	3356]	=	-2-x, -y, 1-z	-2-x, -y, 1-z					
[2	2855]	=	7/2-x, 1/2+y, 1/2-z						

Table S1. Selected hydrogen bonds in IISERP-HOF1:

2. Analytical characterization:

Single crystal structure determination:

Single-crystal data was collected on a Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector (Bruker Systems Inc.) and with a Cu K α radiation (1.5418 Å). The incident X-ray beam was focused and monochromated using Micro focus (I μ S). Crystal of IISERP-HOF1 was mounted on nylon Cryo loops with Paratone-N oil. Data was collected at 153(2) K. Data was integrated using Bruker SAINT software and was corrected for absorption using SADABS. Structure was solved by Intrinsic Phasing module of the Direct methods and refined using the SHELXTL 97 software suite. All non-hydrogen atoms were located from iterative examination of difference F-maps following which the structure was refined using least-squares method. Hydrogen atoms were placed geometrically and placed in a riding model.

Powder X-ray diffraction:

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

Thermo gravimetric Analysis:

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

IR spectroscopy:

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



Figure S3.*Top:* A comparative PXRD plot showing the scalability of the synthesis to gram scales. *Bottom:* A PXRD comparison of the sample which was activated at 120°C followed by resolvation against the simulated one. Note that the peak at $2\theta = 3.6$ which was not present in the as synthesized sample can be observed now. Thus indicating its sensitivity towards solvation.

Remark: Notice that there are few differences in the relative intensities between the simulated and the assynthesized compound (see around 2θ = 3.6 and 10°). We attribute these inconsistencies to a combination of two effects. One, the variation in solvent content between the bulk sample and the single crystal, two, presence of preferred orientation, which is expected considering the fact that the title compound grows as very fine needleshaped crystallites. Also, we had carried out the synthesis several times and compared the relative intensities between the different batches and found that the changes in the relative intensities were consistent suggesting that they are not due to any impurity phases. This was further confirmed by the fact that we could obtain closely reproducible CO_2 uptakes from samples prepared in different batches.



Figure S4. *Top:* TGA plot carried out using the as-synthesized, and 3N HCl treated samples. *Bottom:* TGA with an isothermal step at 120°C to demonstrate the loss of acetic acid (b.p.118°C), followed by stability till 280°C. Inset shows the PXRD of the guest-free sample.



Figure S5. IR spectra of IISERP-HOF1 before and after drying and after soaking in water.



Figure S6. FESEM Image of IISERP-HOF1 showing the needle shaped crystals.

3. Adsorption Analyses:

All gas sorption isotherms were measured on a Quantachrome Autosorb IQ instrument using ultrahigh purity gases (\geq 4.8 grade). Samples were transferred to a glass tube for analysis, with one step activation: about 100 mg of the as-made samples was transferred to analysis cell and evacuated at 120°C on the degas port for 24hrs (10⁻⁶ mbar), at which point the outgas rate was \leq 2 µbar/min.

Langmuir Fits:

In most cases the isotherms were fit to the Single-Site Langmuir (SSL) equation. Also modified Langmuir equations were utilized to account for significant errors in the Langmuir model. 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.*^{s2} Utilizing this routine circumvents some of the problems associated with favoring either high or low pressure regions when linearizing the Langmuir equation^{S3} and offers a balanced approach.

Single-Site Langmuir (SSL):

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

Dual-Site Langmuir (DSL):

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

Dual-Site Langmuir (DSL):

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

Ideal Adsorbed Solution Theory (IAST):

IAST calculations were undertaken as described by Nandi *et al.*^{S4} The selectivity equation is provided below.

Selectivity:

$$S_{1,2} = \frac{q_1/q_2}{P_1/P_2}$$

- (S2) Kemmer, G.; Keller, S. Nat. Protoc. 2010, 5, 267–81.
- (S3) Richter, E.; Schuetz, W.; Myers, A. L. Chem. Eng. Sci. 1989, 44, 1609–1616.
- (S4) Nandi et al. Sci. Adv. 2015, 1 DOI:e1500421.



Figure S7. BET fits from the 77K N_2 data. . Squares- experimental data and line- fit.



Figure S8. Langmuir fits from the 77K N_2 data. . Squares- experimental data and line- fit.



Figure S9. Pore size distribution in IISERP-HOF1 obtained by fitting the NLDFT model to the 77K N_2 adsorption branch. Note the average pore diameter of 11 Å was obtained from the fit. This agrees well with the pore dimension observed in the single crystal structure.



Figure S10. Shows the fitting comparison obtained for the NLDFT fit done to the adsorption branch of the 77K N_2 adsorption data.

Poroisty measuremetns of IISERP-HOF1 treated with 3N HCl for 72hrs:



Figure S11. 77 K N_2 adsorption data for as synthesized sample vs the one obtained from the 3N HCl treatment of the former one. In both the cases amount of gas uptake is nearly comparable indicating the acid stability of the material.

Remark: The N_2 isotherm of the as-synthesized sample shows a step in the uptake @ ~0.15 bar and the N_2 uptake increases gradually with increasing pressure, thus giving a profile characteristic of a mesoporous structure. However, a model independent BJH fit for neither the adsorption nor the desorption branch could give any meaningful fit. This most likely is due to the ill-defined nature of the mesopores. On the contrary, NLDFT fit using Carbon model gives a good fit. Importantly, when an acid treatement (3M HCl for 72hrs) of the assynthesized sample is carried out, as a part of the activation procedure, it helps ordering the pores to more uniform micropores giving rise to a typical type-I isotherm.



Figure S12. BET fits from the 77K N_2 data obtained from 3N HCl treated sample. Squaresexperimental data and line- fit.



Figure S13. Langmuir fits from the 77K N_2 data obtained from 3N HCl treated sample. Squaresexperimental data and line- fit.



Figure S14. BET fits from the CO₂ isotherm data. Squares- experimental data and line- fit.

Note: The surface area obtained from this fit matches exceptionally well with the theoritical surface area calculated from crystal structure.



Figure S15. Pore size distribution of the acid treated sample obtained by fitting the NLDFT model to the 77K N_2 adsorption branch. Note the average pore diameter of 14 Å was obtained from the fit. This agrees well with the pore dimension observed in the single crystal structure.



Figure S16. Shows the fitting comparison obtained for the NLDFT fit done to the adsorption branch of the 77K N_2 adsorption data from the acid treated sample.

Virial analysis:

The CO_2 adsorption data were measured from 0- 1bar at 303, 273 and 195K. For virial fitting the 303 and 273K isotherms were taken and fitted by the virial equation (1). 195K isotherm was excluded as the temperature is too far from the other two.

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

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

are temperature independent empirical parameters

Table S2:	Summary	of the	fitted	Virial	parameters
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A0	-4085.469875
A1	389.1798563
A2	-20.70422446
A3	1.779603265
B0	18.20093392
B1	-0.730874617



Figure S17. Comparison of experimental isotherms to the ones obtained from virial modelling carried out using CO_2 isotherms collected at 0°C and 30°C.



Figure S18. Virial plots carried out using CO₂ isotherms collected at 0°C and 30°C.

IAST fitting parameters:

273K

Gas A =CO₂

Gas $B = N_2$

Gas Mixture			
YA =	0.14		
YB =	0.86		
Gas A		Gas B	
Constants		Constants	
qA1 =	5.576412247	qA1 =	0.02713544
qA2 =	0	qA2 =	0
kA1 =	0.002700762	kA1 =	0.00124629
kA2 =	0	kA2 =	0
na1 =	0.784739867	na1 =	1
na2 =	0	na2 =	0
HA1 =	0.015060563	HB1 =	3.3819E-05
HA2 =	0	HB2 =	0

Gas Mixture			
YA =	0.14		
YB =	0.86		
Gas A			
Constants		Gas B C	Constants
qA1 =	4.730941051	qA1 =	0.02582487
qA2 =	0	qA2 =	0
kA1 =	0.000882289	kA1 =	0.00067469
kA2 =	0	kA2 =	0
na1 =	1	na1 =	1.00026579
na2 =	0	na2 =	0
HA1 =	0.004174056	HB1 =	1.7424E-05
HA2 =	0	HB2 =	0



Figure S19. *IAST* fitting of CO₂ and N₂ isotherms collected at 273K.



Figure S20. *IAST* fitting of CO₂ and N₂ isotherms collected at 303K.

Framework code	Number of independent molecules in the framework	BET surface area(m ² /g)	CO ₂ uptake (cc/g) (temp K)	Reference
HOF-4	1	312	120 (195K)	Chem. Commun., 2014, 50, 1308113084.
SOF-7a	2	900.0	64 (273K)	J. Am. Chem. Soc. 2014, 136, 12828–12831.
HOF-3	1	165.0	24 (296K)	Angew. Chem. Int. Ed. 2015, 54, 574 – 577
HOF-5	1	1101.0	117 (273K)	J. Am. Chem. Soc. 2015, 137, 9963–9970.
HOF-1a	1	359	220 (195K)	J. Am. Chem. Soc. 2011, 133, 14570–14573.
benzo- trisimidazole SOF	1	131	62(195K)	Chem. Commun., 2016, 52, 49914994.
B2	2		15(298K)	Angew. Chem. 2016, 128, 4599 – 4602.
SOF-1a	1	474	125 (195K)	J. Am. Chem. Soc. 2015, 137, 9963–9970.
Тсрв	1	1095	66 (273K)	Chem. Commun., 2015,51, 11642-11645.
HOF-2	1	237.6	80 (195K)	J. Am. Chem. Soc. 2014, 136, 547–549.
IISERP-HOF1	1	500	141(195K) 106 (273K)	This work

Table S3. CO₂ uptakes and surface areas of selected HOFs reported in the literature.

4. Computational details:

All computations were carried out using Material Studio software suite version 6.0 (*Accelrys*). Standard force fields were employed and mostly no constraints were used. The adsorption isotherms were simulated using the Metropolis algorithm of the Grand Canonical Monte Carlo routine. The simulations were carried out independently with and without applying rotational and translation degree of freedom for the CO_2 molecules. However, there was no noticeable difference in the CO_2 positions or orientations. For the final CO_2 positions and geometries a 2 x 1 x 1 cell was constructed and was geometry optimized using Tight Binding- Density functional theory (DFT-TB) methods employing dispersive corrections and smearing. No noticeable difference in geometry of the framework was found even when the framework was not constrained during the DFT-TB calculations, thus indicating that the structure determined from the single crystal x-ray diffraction is quite rigid which can be attributed to the highly directional -COOH...HOOC- hydrogen bonds propagating in three dimensions.



Figure S21. The 1-D channel along a-axis represented with a triangular shape and the CO_2 molecules closer to the apex are vertically aligned with respect to the base of the triangle while the CO_2 molecules closer to the base of the triangle formed by the phenyl rings and planar carboxylate dimers are lying parallel to the base.



Figure S22. A lateral view of the CO_2 in a single channel showing some of the selected $CO_2...CO_2$ distances and the T-shaped orientations between them.