Electronic Supplementary Information (ESI)

Exceptionally High H_2 Storage by a Metal Organic Polyhedral Framework

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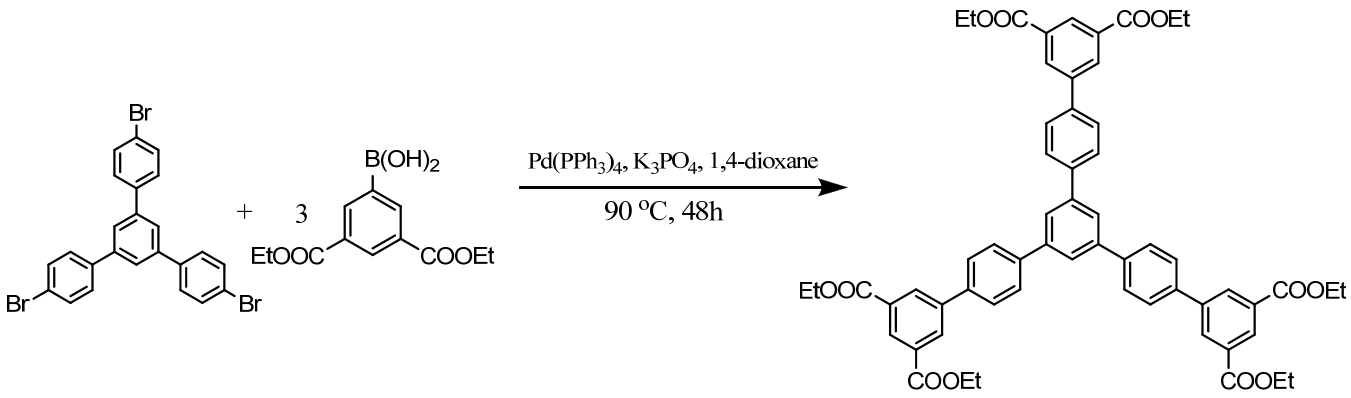
Section I. Synthesis of H_6L and NOTT-112:

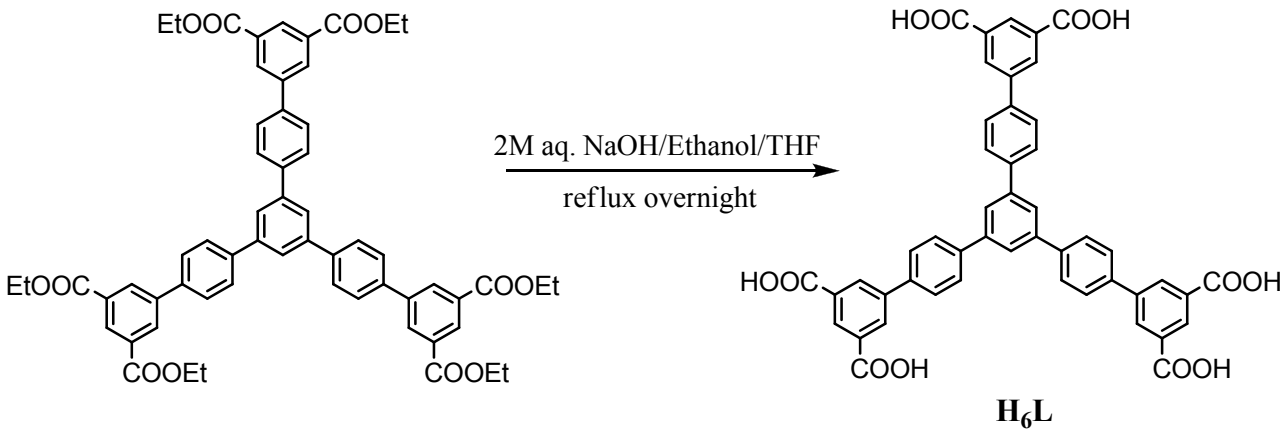
1,3,5-tri(*p*-bromophenyl)benzene was synthesized using the literature method.[1] All other reagents were purchased from Sigma-Aldrich or Acros. All reagents and solvents were used as received.



1,3,5-Tris(3',5'-diethoxycarbonyl[1,1'-biphenyl]-4-yl-)benzene:

1,3,5-Tri(*p*-bromophenyl)benzene (1.5 g, 2.76 mmol), diethylisophthalate-5-boronic acid (2.65 g, 9.9 mmol), and K_3PO_4 (5.2 g, 24.5 mmol) were mixed in 1,4-dioxane (100 mL), and the mixture de-aerated using Ar for 10 mins. $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) was added to the stirred reaction mixture, and the mixture heated at 90°C for 48h under Ar after which 1,4-dioxane was removed under vacuum. The resultant solid was washed with water and then a mixture of ethyl acetate and EtOH (1:1) and dried under vacuum. The pure ester was obtained by column chromatography using ethyl

acetate/petrol ether (3:1) as eluent (2.1 g, 78.6% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.71 (s, 3H), 8.56 (s, 6H), 7.94 (s, 3H), 7.87 (q, 12H), 4.49 (q, 12H), 1.48 (t, 18H) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 165.84, 141.88, 141.27, 140.80, 138.54, 132.12, 131.61, 129.40, 127.99, 127.77, 125.28, 61.53, 14.39 ppm.



H_6L

1,3,5-Tris(3',5'-dicarboxy[1,1'-biphenyl]-4-yl-)benzene (H_6L):

1,3,5-Tris(3',5'-diethoxycarbonyl[1,1'-biphenyl]-4-yl-)benzene (1.5 g, 1.6 mmol) was suspended in a mixture of THF (50 mL) and EtOH (50 mL) to which was added 2 M NaOH aqueous solution (50 mL). The mixture was stirred under reflux overnight and the THF and EtOH removed under vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 3. The solid was collected by filtration, washed with water and EtOH, and dried to give H_6L (1.1 g, 90 % yield). ^{1}H NMR ([D_6]DMSO, 300 MHz): δ=8.5 (d, 3H), 8.46 (d, 6H), 8.095 (s, 3H), 8.067 (s, 6H), 7.93 (s, 3H), 7.90 (s, 3H) ppm. MS (ESI) m/z (%) = 797.1656 $[M-1]^-$ (100).

Preparation of NOTT-112:

H_6L (10 mg, 0.012 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (18.2 mg, 0.075 mmol) were dissolved in a mixture of DMSO and DMF (1:1, 2mL), and 0.2 mL H_2O was added to the mixture. The solution was placed in a tightly capped 20 mL vial and heated at 90 ^oC for 24 h. The resulting blue octahedral-shaped single crystals were washed with DMF several times to give $[Cu_3(C_{48}H_{24}O_{12})(H_2O)_3] \cdot 8DMSO \cdot 15DMF \cdot 3H_2O$ NOTT-112 (30 mg, yield: 85%). Elemental analysis (%) calculated: C 46.54, H 6.77, N 7.47; found: C 46.04, H 5.92, N7.88.

Section II. Single Crystal X-ray Structure Determination of NOTT-112:

Intensity data for NOTT-112 were collected at 120(2) K collected on Station 9.8 of the Synchrotron Radiation Source at STFC Daresbury Laboratory. The structure was solved by direct methods and subsequent difference Fourier syntheses, and refined using the SHELXTL software package.[2] The H atoms on the ligand were placed in idealized positions and refined using a riding model. The H atoms of the co-ordinated H_2O molecules could not be located, but are included in the formula. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE[3] to calculate the diffraction contribution of the solvent molecules and, thereby, producing a set of solvent-free diffraction intensities. The final formula was calculated from elemental analyses combined with TGA analysis.

***Table S1*. Crystal data and structure refinement for NOTT-112.**

Empirical formula	$C_{109}H_{189}N_{15}S_8O_{41}Cu_3$
Formula weight	2812.96
Temperature	120 (2)K
Crystal System	Cubic
Space Group	Fm-3m
Unit Cell Dimensions	a = 47.005(3) Å
Volume	103856(11) $Å^3$
Z	32
Density	1.439 gcm^{-3}
Absorption coefficient	0.702 mm^{-1}
F(000)	47712
Crystal Size	0.05 × 0.05 × 0.05 mm^3
Theta range for data collection (2θ)	2.4 to 51.5^o
Reflections collected	159321
Independent reflections	5086 [R(int) = 0.1256]
Absorption correction	multi-scan
Max. and min. transmission	0.9623 and 0.7747
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5075 / 0 /102
GOF on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0755, wR2 = 0.243
R indices (all data)	R1 = 0.0840, wR2 = 0.253
Largest diff. peak and hole	0.73/-0.55 e$Å^3$

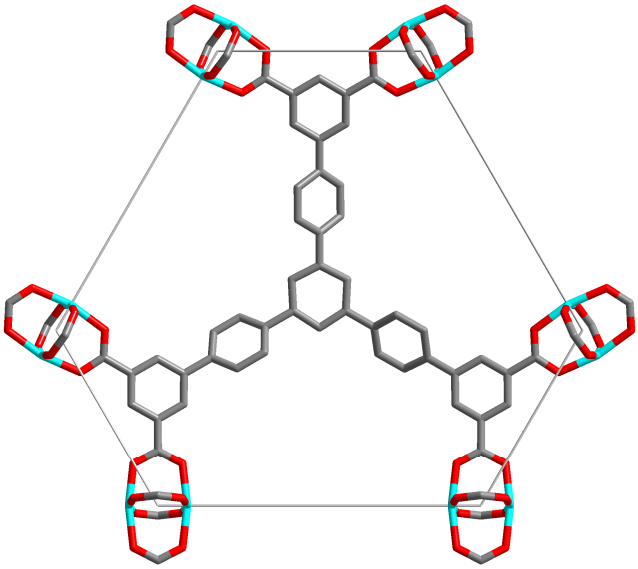


Figure S1: The trigonal L^{6-} linker acting as a hexagonal building block to six binuclear copper paddlewheel units. Copper: blue-green; Carbon: black; Oxygen: red. Water molecules and H atoms are omitted for clarity.

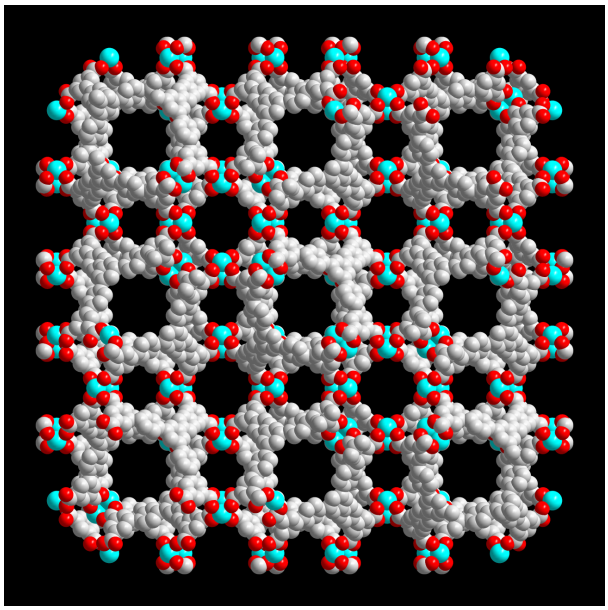


Figure S2: Space filling view of NOTT-112 viewed along the *a* axis.

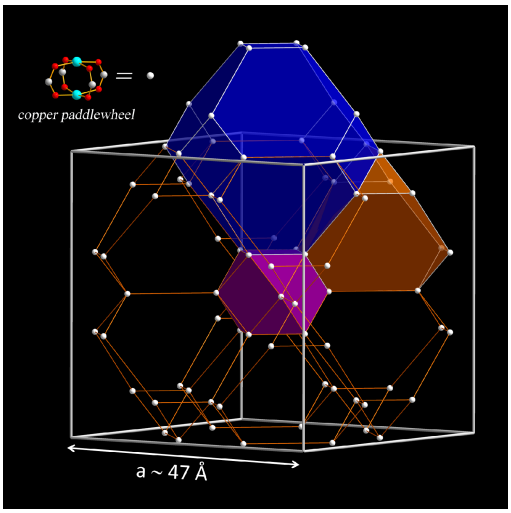


Figure S3: The polyhedral network of NOTT-112 shown as a natural tiling within the unit cell of the crystal structure.

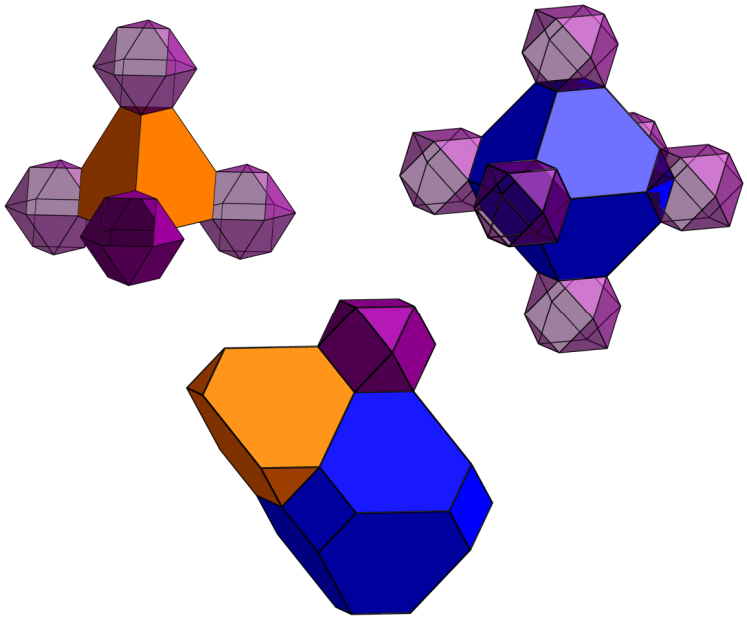


Figure S4: The packing modes of the three types of polyhedron in the crystal structure of NOTT-112.

Each truncated tetrahedron is connected to four cuboctahedrons by sharing of triangular windows, and each truncated octahedron is connected to eight cuboctahedrons by sharing the truncated vertices which are the square windows formed by the $\{Cu_2\}$ paddlewheels. Cage B and Cage C stack together by sharing faces which are the hexagonal building blocks generated from molecules of L^{6-}.

Section III. Thermogravimetric Analysis (TGA) of NOTT-112:

Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (60 ml/min) with a heating rate of 2 °C/min using a TA SDT-600 thermogravimetric analyzer.

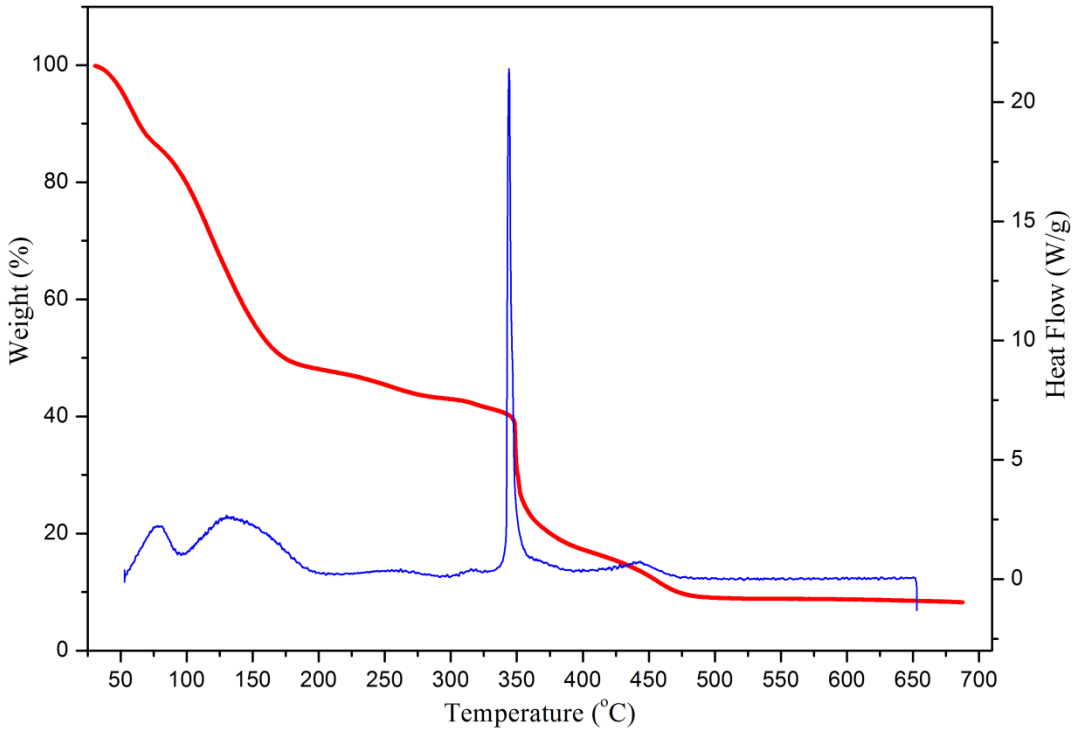


Figure S5: TGA-DSC of as-synthesized sample of NOTT-112.

Section IV. Powder X-Ray Diffraction.

Powder X-ray diffraction (PXRD) data were collected over the 2θ range 4 ~ 40° on a Philips X'pert diffractometer using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40mA. The intensities of the PXRD patterns are relative intensities. The correct positions of the diffraction peaks reveal that the

framework structure is the same in bulk as in the single crystal structure. The collected diffraction data are, however, of low resolution which can not be refined with a better goodness-of-fit indicator. The as-synthesized sample contained solvents inside the pores, and the relative intensities of the diffraction peaks depend upon the morphology (dimension, orientation and sizes) of the sample. The activated sample was generated by degassing the sample under high vacuum at 115 ^{o}C for 16 h and transferred into a glove box. The sample was mounted on a sealed sample holder under an Ar atmosphere and PXRD data collected.

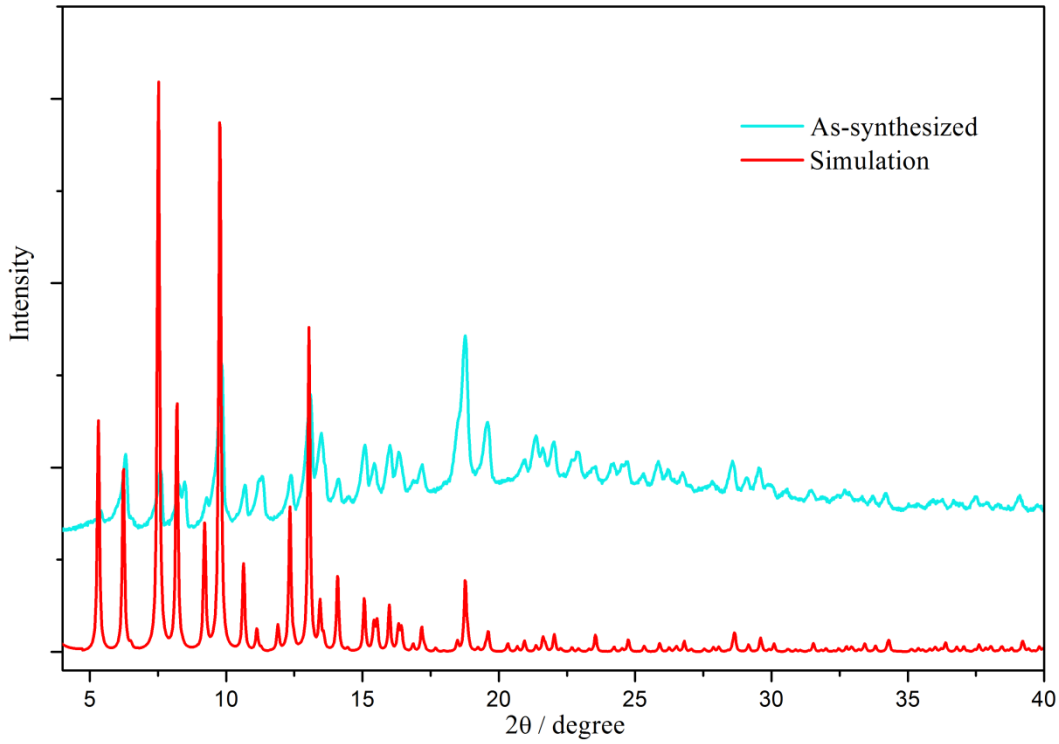


Figure S6: PXRD patterns of as-synthesized NOTT-112 and the simulation from single crystal structure.

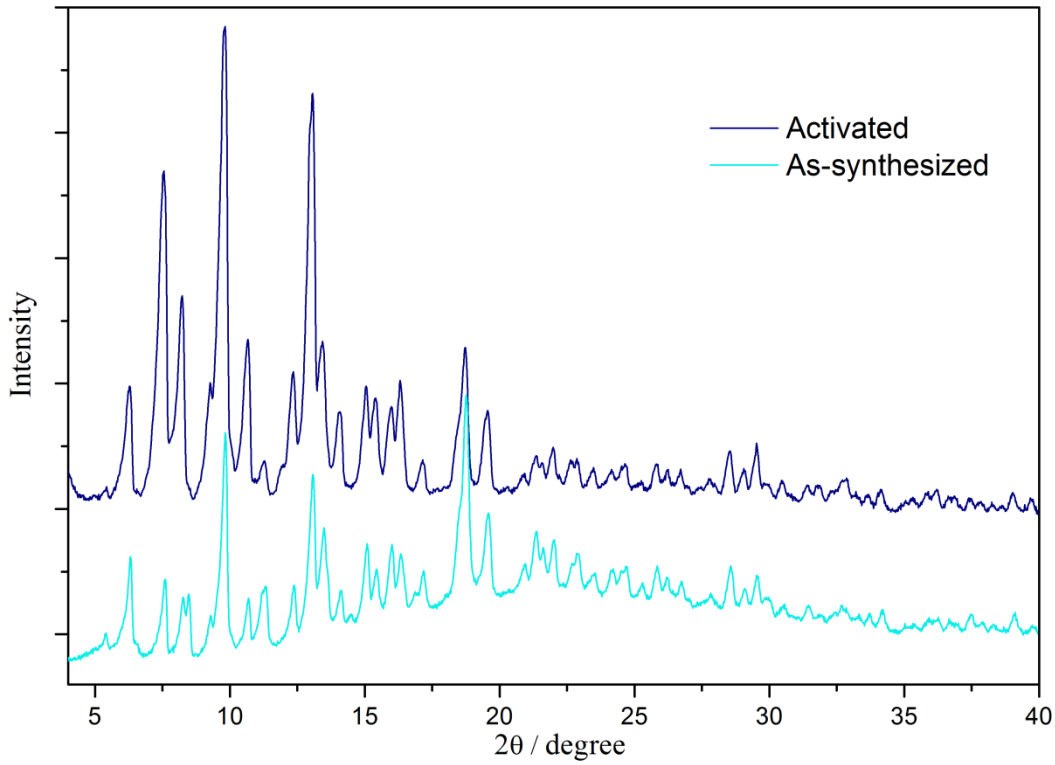


Figure S7: PXRD patterns of NOTT-112. The activated sample was archived by degassing the sample in vacuum at 115 ^{o}C for 16h.

Section V. Gas Adsorption Measurements on NOTT-112

Ultra-high purity N_2 (99.999%), H_2 (99.9995%) were purchased from British Gas and used as received. N_2, H_2 and sorption isotherms were measured using a Hiden Isochema Intelligent Gravimetric Analyser (IGA-003), which is an ultra-high-vacuum, clean instrument with a diaphragm and turbo pumping system. Before the sorption measurement, H_2 was further purified by using calcium aluminosilicate and activated carbon adsorbents to remove trace amounts of H_2O and other impurities. The measurement protocols used were validated by the complete desorption of H_2 and the comparison of results from porous carbon samples on two different instruments. Gravimetric H_2 sorption isotherms were recorded from 0 – 1 bar at 78 K and 88K, respectively. All data were rigorously corrected for the buoyancy of the system, samples and adsorbates.

1. PSD analysis from the nitrogen isotherms

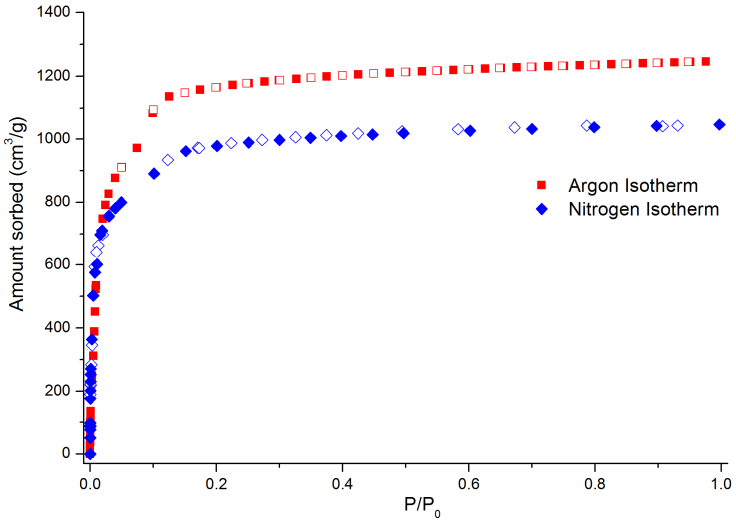


Figure S8: N_2 and Ar sorption isotherms of NOTT-112 recorded at 78 and 87K, respectively, in the pressure range 1.5 x 10^{-6} < P/P_0 < 1.

Pore size distribution (PSD) data for NOTT-112 were obtained by applying Dubinin-Astakhov analysis to the N_2 sorption isotherm. The analyses were carried out with IGASwin V1.03.140, and the constants for N_2 are: Sorbate Phase Density = 0.808 g/cc; Surface Tension = 8.85mN/m; DA Interaction Constant = 2.96KJnm^3/mol.

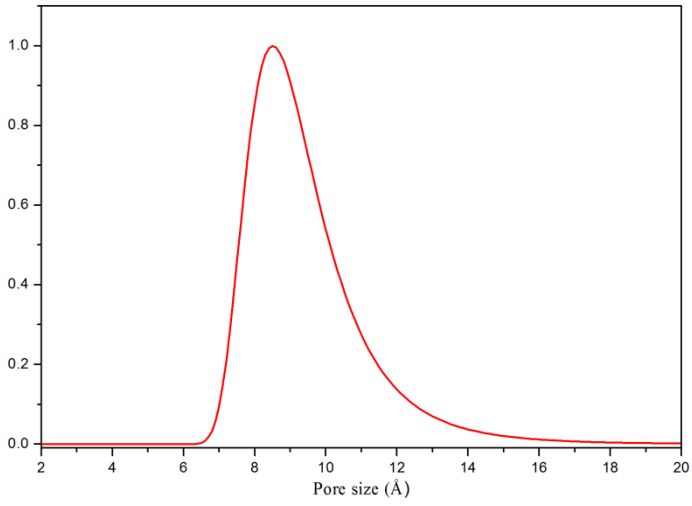


Figure S9: Pore size distribution for NOTT-112.

Pore size distribution (PSD) data for NOTT-112 was also determined by analyzing the Ar isotherm at 87 K using a non-local density functional theory implementing a hybrid kernel based on a zeolite/silica model containing cylindrical pores as implemented in the Autosorb1 software package.

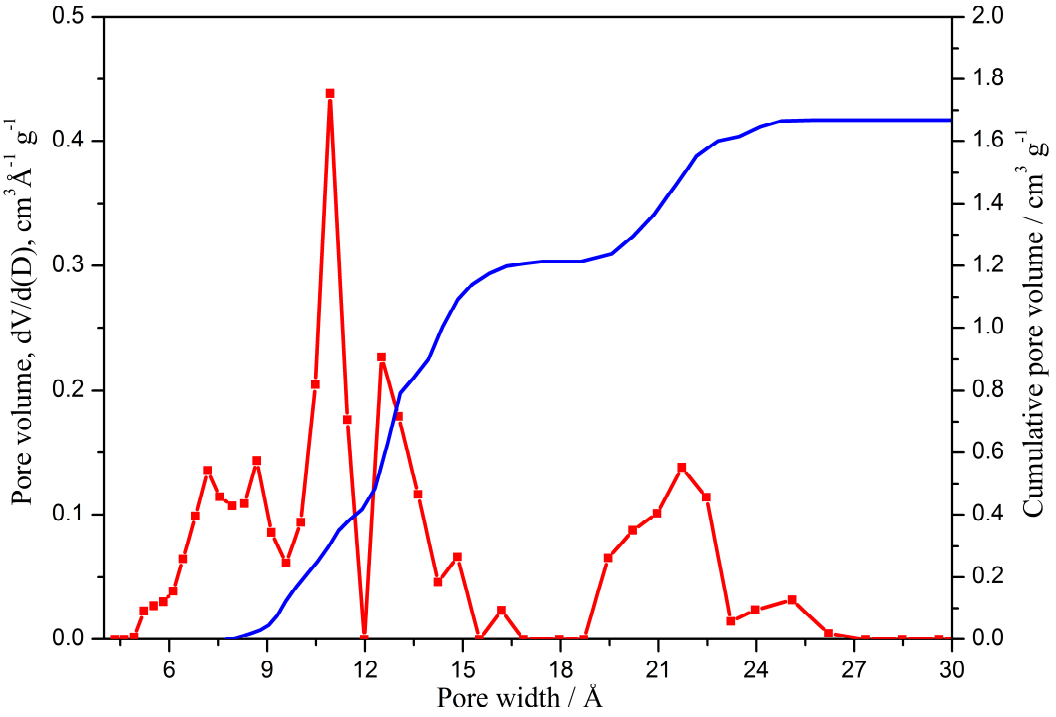


Figure S10: Pore size distribution (left axis) and cumulative pore volume (right axis, blue curve) for NOTT-112, calculated from a NLDFT fit to the Ar adsorption data for NOTT-112.

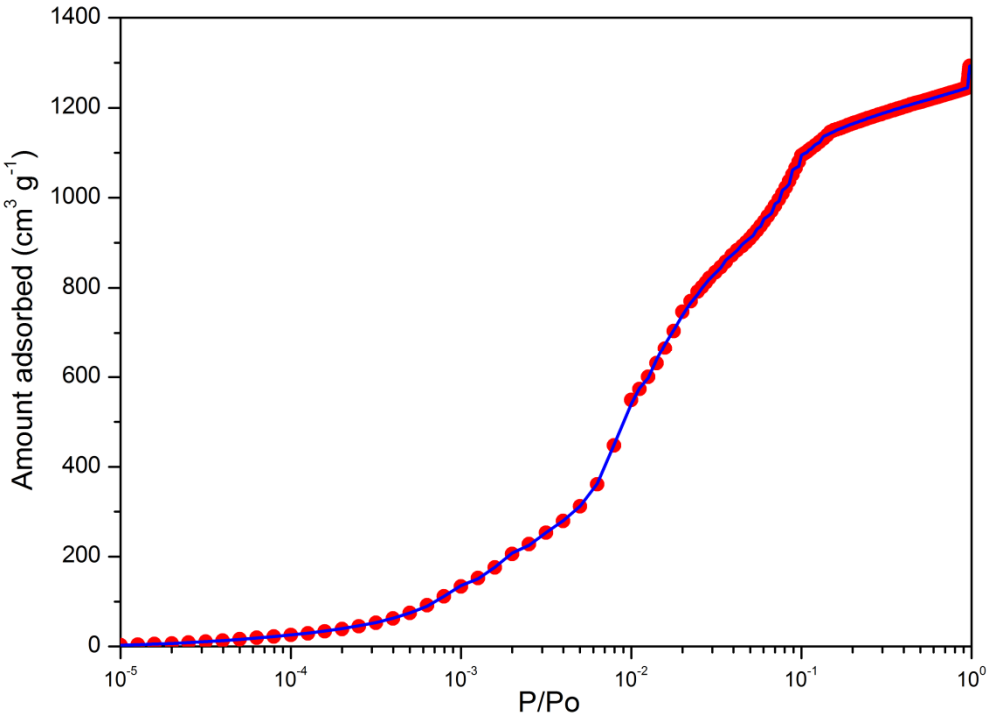


Figure S11: Ar sorption isotherm at 87 K for NOT-112: comparison between experimental (red circles) and NLDFT isotherm (blue curve).

2. H_2 sorption using gravimetric method:

Table S2. Total H_2 uptake on desolvated NOTT-112 at 78K and 88K.

78K		88K	
Pressure / mbar	Hydrogen uptake wt%	Pressure / mbar	Hydrogen uptake wt%
13.564	0.15178	16.172	0.08436
23.721	0.21477	22.897	0.10073
33.877	0.27703	34.426	0.12689
44.309	0.34157	43.622	0.1499
53.367	0.38955	53.367	0.175
64.073	0.44611	62.975	0.19884
72.857	0.48971	73.818	0.22502
83.426	0.53878	83.563	0.24802
93.171	0.58039	93.171	0.26979
104.288	0.62703	104.014	0.29567
113.484	0.66465	114.17	0.31834
122.68	0.70018	124.053	0.3406
133.248	0.7398	133.523	0.36159
144.091	0.77773	144.503	0.38452
153.562	0.81027	153.974	0.40499
173.738	0.87608	175.111	0.44701
192.679	0.93386	194.463	0.48442
214.502	0.9966	215.188	0.523
243.051	1.07427	246.619	0.57886
272.148	1.14704	274.756	0.62738

302.344	1.21989	305.638	0.67784
333.089	1.28977	335.559	0.72524
362.873	1.35373	366.853	0.7719
392.519	1.41388	397.46	0.81668
422.44	1.47286	427.244	0.85914
453.734	1.53151	457.852	0.90067
482.008	1.58293	486.4	0.93768
501.635	1.61683	504.792	0.96221
533.203	1.6702	539.38	1.00522
567.654	1.72777	573.281	1.04616
601.144	1.78121	605.673	1.08494
634.084	1.83172	639.437	1.12366
668.398	1.88308	673.75	1.16233
701.75	1.93129	706.005	1.1976
733.867	1.97608	741.553	1.23589
767.357	2.0232	772.984	1.26851
801.67	2.06757	805.65	1.30196
834.199	2.10918	840.787	1.33709
866.728	2.15078	871.257	1.36715
902.276	2.19487	905.159	1.39944
952.511	2.25514	960.334	1.45087
1001.922	2.31257	1006.863	1.4928

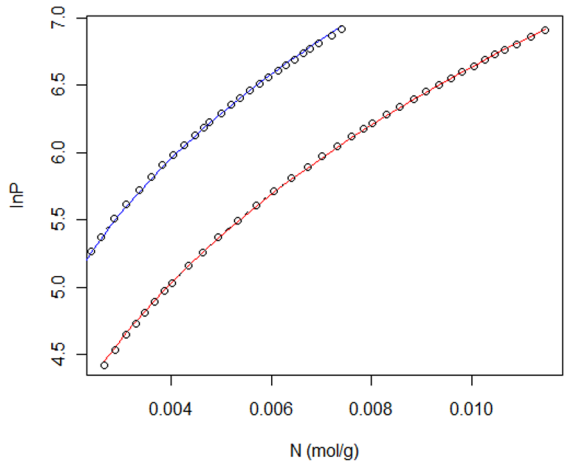
Section VI. Estimation of H_2 adsorption enthalpies

The two H_2 adsorption isotherms at 78 K and 88 K were fitted to the virial expression (1). P is the pressure expressed in bar, N is the amount adsorbed in mol/g, T is the temperature in K, a_i and b_j are

virial coefficients, and *m*, *n* represent the number of coefficients. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using equation (2). Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

$$\ln(P) = \ln(N) + (1/T)\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j \quad (1)$$

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \quad (2)$$



a_o= -6.781e+02

a_1= 1.174e+04

a_2= -2.004e+05

b_0= 1.869e+01

Residual standard error: 0.01086 p-value: < 2.2e-16

Figure S12: Virial expression fits of H_2 adsorption data for NOTT-112 at 78 K (red) and 88 K (blue).

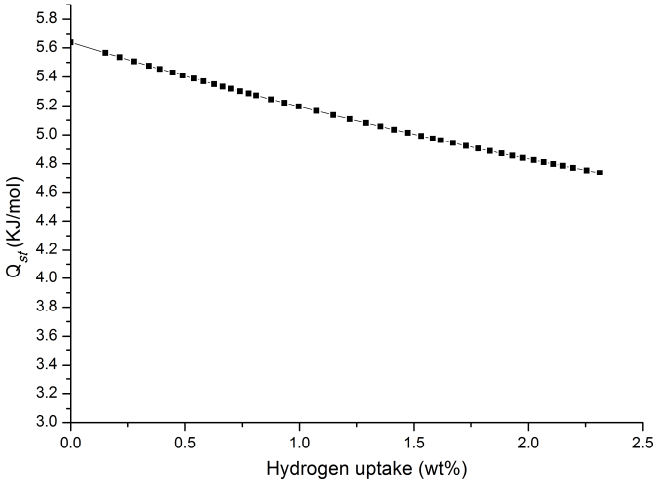


Figure S13: Adsorption enthalpies of NOTT-112.

Section VII. High-Pressure Hydrogen Sorption Measurements.

Volumetric H_2 sorption measurements were performed at General Motors over a pressure range 0-80 bar using an automatically controlled Sievert's apparatus (PCT-Pro 2000 from Hy-Energy LLC). Sample tubes of a known weight were loaded with approximately 300 mg of sample under an argon atmosphere. Samples were degassed at 105 °C for 72 h. All measurements were made with ultra high purity grade (99.999%) H_2 and He. Measurements were carried out at 77 K by submerging the sample holder in a liquid nitrogen bath, the level of which was maintained constant throughout each experiment. Our volumetric analysis can be viewed as a precise application of the real gas law taking into account deviation from non-ideal behaviour found at high pressures and/or low temperatures. The non-ideal gas behaviour is taken into account by determining the H_2 compressibility factor, Z, from National Institute of Standards and Technology (NIST) data.[5] The volume of the sample holder was determined using helium at 298 K and H_2 at 298 K and 77 K. H_2 was used to determine the dead space volume correction for a non-porous inert insert of a known geometrical volume (typically steel or aluminum); this correction accounts for the change in effective sample volume observed when cooling the sample holder from room temperature to 77 K. Also, helium was used to determine the volume occupied by a sample in the sample holder at 298 K because of its negligibly small adsorption on solid surfaces.

Total Adsorption and Volumetric Capacity at High Pressure.

Excess adsorption is the amount of gas adsorbed by a material above that which would have been adsorbed in the pores at the same temperature and pressure if the energy of interaction between the adsorbent and the pore walls was zero. The total adsorption of a material is the amount of gas adsorbed in the volume occupied the bulk material, which includes the gas taken up due to compression in the void pore space. Since excess adsorption is what is obtained from the measurements described above, total adsorption can be calculated from the equation:

$$Q_{tol} = Q_{exc} + \frac{100 \times d_g \times V_{pore}}{1 + d_g \times V_{pore}} \quad (3)$$

where Q_{tot} = total adsorption (wt. % H_2)

Q_{exc} = excess adsorption (wt. % H_2)

d_g = density of the compressed gas (H_2) as a function of temperature and pressure (g/cm^3)

V_{pore} = pore volume (cm^3/g)

The density of the compressed H_2, d_g, was obtained from the NIST website.[5] The pore volume was determined from the nitrogen isotherm.

The volumetric capacity of the sample was then calculated using:

$$C_{vol} = Q_{ads} \times d_{bulk} \quad (4)$$

where C_{vol} = volumetric adsorption (g H_2/L)

Q_{ads} = quantity of H_2 adsorbed (if excess adsorption is used then excess volumetric capacity is obtained. If total adsorption is used, then total volumetric capacity is obtained.)

Table S3. High pressure H_2 uptake on desolvated NOTT-112 at 77K.

Pressure (bar)	Gravimetric Excess H_2 uptake (wt%)	Gravimetric Total H_2 uptake (wt%)	Volumetric Excess H_2 uptake (g/L)	Volumetric Total H_2 uptake (g/L)
0.25951	1.12251	1.13575	5.64622	5.71284
0.70865	2.09011	2.12629	10.51325	10.69524
1.33114	2.87709	2.9451	14.47176	14.81383
2.21822	3.62855	3.74199	18.25161	18.8222
3.22201	4.22949	4.39444	21.27434	22.10405
4.50524	4.78648	5.01745	24.07599	25.23775
5.91681	5.22565	5.52944	26.28504	27.81307
7.62185	5.63028	6.02229	28.32031	30.29212

9.38828	5.94326	6.42697	29.89461	32.32764
11.17685	6.1763	6.75313	31.06679	33.96826
13.02617	6.36233	7.03574	32.00252	35.38978
14.9068	6.5086	7.28047	32.73824	36.62076
16.80245	6.62413	7.49547	33.31936	37.70219
19.15544	6.78543	7.7805	34.13072	39.13591
21.54965	6.86816	7.98934	34.54686	40.1864
23.93047	6.93425	8.18097	34.87928	41.15029
26.32659	6.99505	8.36814	35.18508	42.09177
28.69981	7.03464	8.53286	35.38426	42.92028
30.93971	7.05283	8.66898	35.47573	43.60499
33.3624	7.06188	8.80539	35.52126	44.29113
35.76837	7.07113	8.9407	35.56779	44.97171
38.13581	7.06533	9.05846	35.5386	45.56405
40.50872	7.05907	9.17569	35.5071	46.15374
42.75005	7.0312	9.26368	35.36695	46.5963
45.60561	7.03114	9.41041	35.36661	47.33438
48.44157	6.99156	9.51556	35.16754	47.86329
51.26732	6.92165	9.58834	34.81591	48.22936
54.11354	6.85068	9.65972	34.45893	48.58838
56.93409	6.79532	9.74392	34.18045	49.01192
59.48851	6.75279	9.82621	33.96653	49.42585
62.35631	6.6562	9.86806	33.48068	49.63635
65.22855	6.57781	9.92631	33.08636	49.92936
68.05688	6.48137	9.96252	32.60129	50.11149
70.88974	6.36841	9.98034	32.03309	50.20111

73.74792	6.28753	10.02933	31.6263	50.44754
76.61913	6.15831	10.02825	30.9763	50.44208
77.03621	6.12353	10.01195	30.80137	50.36012
72.67514	6.32035	10.01367	31.79138	50.36875
68.35016	6.46365	9.95852	32.51216	50.09137
64.06127	6.62078	9.91406	33.30254	49.86771
59.84131	6.73579	9.8263	33.88105	49.42631
55.73947	6.85167	9.7413	34.46389	48.99871
51.57528	6.95129	9.63345	34.96497	48.45627
47.49641	7.00761	9.48355	35.2483	47.70224
43.42411	7.03365	9.30097	35.37927	46.7839
39.38134	7.05446	9.11247	35.48392	45.83574
35.40091	7.05786	8.90822	35.50104	44.80835
31.42705	7.05577	8.69762	35.49051	43.74902
27.23661	7.00417	8.42525	35.23099	42.37902
23.42354	6.91138	8.13136	34.76424	40.90073
19.63673	6.77068	7.7911	34.05653	39.18921
15.93851	6.54854	7.37453	32.93916	37.09387
12.32233	6.27229	6.90891	31.54961	34.75181
9.4576	5.96818	6.45549	30.01994	32.47111
7.31152	5.50617	5.8821	27.69604	29.58699
5.78564	5.17209	5.4691	26.01561	27.50955
4.63056	4.77433	5.01176	24.0149	25.20914
3.76097	4.40426	4.59691	22.15342	23.12246
3.09483	4.04917	4.20759	20.36731	21.16417
2.57636	3.71981	3.85161	18.71063	19.3736

2.16946	3.41697	3.52791	17.18737	17.74538
1.84459	3.13872	3.23301	15.78776	16.26204
1.58207	2.88588	2.96672	14.51595	14.92261
1.36878	2.65736	2.72729	13.3665	13.71826
1.19814	2.44931	2.51051	12.32002	12.62786
1.05048	2.25504	2.30869	11.34287	11.61273
0.93234	2.08493	2.13254	10.4872	10.72669
0.83062	1.92431	1.96672	9.67927	9.8926
0.74202	1.77921	1.81709	8.94942	9.13998
0.66654	1.64933	1.68336	8.29615	8.46731
0.61076	1.53057	1.56175	7.69877	7.8556
0.55497	1.41174	1.44007	7.10103	7.24354

The density of the host material was taken as the crystallographic density for the desolvated framework, 0.503 g cm^{-3}.

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[5] The data of H_2 density at different pressures (from 0 – 80 bar) at 77 K was obtained from the website of National Institute of Standards and Technology (NIST) of the USA: http://webbook.nist.gov/chemistry/fluid.