Electronic Supplementary Information for:

Understanding Excess Uptake Maxima for Hydrogen Adsorption Isotherms in Frameworks with *rht* Topology

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S1. Structure Preparation

We started by modifying the asymmetric unit of **NOTT-112**,^{S1} synthesized by Schröder and co-workers. We maintained the same copper paddlewheel cluster, the *Fm3m* group symmetry, and the *rht* network topology. Scheme S1 shows the original **NOTT-112** linker and the different linkers we used to build this series, where some of these materials have been experimentally synthesised: L1 (PCN-61),^{S2} L2 (NU-111),^{S3} L3 (NOTT-112),^{S1} L4 (NOTT-119 / PCN-69),^{S2,S4} L5 (NOTT-116 / PCN-68),^{S2,S5} L6 (PCN-610 / NU-100),^{S2,S6} and L7 (NU-109)^{S7}. After the asymmetric unit was modified, the symmetry operations of the space group allowed the construction of the new structure. Since no modification was done in the unit cell size, the lattice parameters were at this point far away from realistic values. The unit cell was then subject to geometry optimization based on molecular mechanics, modifying the parameters of the unit cell and the atomic coordinates. These calculations were performed with the Forcite module of Materials Studio.^{S8} The bonded and the short range (van der Waals) interactions between the atoms were modelled using the Universal Force Field (UFF).^{S9} A cut-off distance of 18.5 Å was used for the van der Waals interactions during the geometry optimization. Coulombic interactions were modelled by placing partial charges on the framework atoms. The partial charges were

calculated using an extended charge equilibration method developed in our group,^{\$10} and the long-range electrostatic interactions were calculated using the Ewald summation method. Figures \$1 and \$2 show the L1-L8 structures.



Scheme S1. *a*) Hexa-protonated precursor of the linker used to construct the L1-L8 isostructural materials, and *b*) the Lx linker fragments.



Figure S1. Representation of the L1-L4 structures.



Figure S2. Representation of the L5-L8 structures.

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S2. rht Topology

The *rht* topology has been traditionally described as having three different cages. This view arises from drawing straight lines between the copper paddlewheels and fusing the cages such that they form continuous channels. However, there is no unique representation of a MOF in the form of space-filling polyhedra. For some *rht* MOFs, such as NU-111, a fourth cavity can be detected experimentally.⁸³ An alternate choice of space-filling polyhedra, taking the curvature of the ligand into account, gives four types of cages, each corresponding to one of the four experimentally observed cavities. Figure S3 illustrates the representation of the four cavities from the L1 structure, as well as the pore size distribution (PSD), which also shows four main peaks. Since not all of the studied structures regardless of the linker length, with centre at 0, 0.5, 0.5; as well as the largest cavity (purple sphere) at 0.5, 0.5, 0.5; and the cavity at 0.75, 0.75, 0.75 (green sphere), which can be described as a truncated tetrahedron, where the inner surface of the pore is constructed from the R1 portion of the linker (Scheme S1). The sizes of the latter two cavities depend on the linker length. Note that both yellow and blue (centred at 0.5, 0.75, 0.75) cavities have exposed unsaturated metal sites.



Figure S3. (*left*) Space filling model for the **L1** structure with spheres to illustrate cavities and (*right*) PSD for **L1**. All framework atoms are illustrated with a space filling model. C is gray, O is red, Cu is brown, and H is white. The yellow sphere (**III**) represents the cavity that is common across all structures; the purple sphere (**IV**) is the largest cavity. Blue (**I**) and green (**II**) spheres represent the other cavities.



Figure S4. Two representations of the L6 structure with spheres to illustrate cavities. The yellow sphere (III) represents the cavity that is common across all structures; the purple sphere (IV) is the largest cavity; the green sphere (II) can be described as a truncated tetrahedron.

S3. Gas Adsorption Simulations and Computational Structural Characterization

The adsorption of H_2 was investigated using grand canonical Monte Carlo (GCMC) simulations, performed with our in-house multi-purpose code RASPA,^{S11} at 77 K and up to 100 bar.^{S12} Due to quantum diffraction effects, Feynman-Hibbs corrections were used in the simulations. It has been shown that without these corrections, results can be overestimated by 15-20%.^{S13} We used an atomistic model for all MOF structures, in which the framework atoms were kept fixed at their crystallographic positions. H₂ - H₂ and H₂ - framework interactions were calculated using a Lennard-Jones (LJ) + Coulomb potential. LJ parameters for the framework atoms were taken from the Universal Force Field (UFF),⁵⁹ and the H₂ LJ parameters were taken from an empirical model for H_2^{S14} , which places a single LJ sphere at the H_2 centre of mass. Lorentz-Berthelot mixing rules were used for all cross terms, and LJ interactions beyond 12 Å were neglected. Coulomb interactions were calculated using partial charges on the framework atoms (as described in Section S1) and H₂ charges taken from the Darkrim-Levesque^{S15} model, which places a charge of +0.468 on each H atom and a charge of -0.936 on the H_2 centre of mass. The Ewald sum method was used to compute the electrostatic interactions. $6 \cdot 10^4$ Monte Carlo equilibration cycles were performed (i.e. up to $2.5 \cdot 10^8$ steps for up to 4,200 molecules per unit cell in L8) plus $2 \cdot 10^4$ production cycles (i.e. up to $8.3 \cdot 10^7$ steps for up to 4.200 molecules per unit cell in **L8**) to calculate the ensemble averages. In one cycle, an average of N moves were performed, where N is the number of molecules in the system (which fluctuates in GCMC). Monte Carlo moves used with equal probability were translation, rotation, insertion, deletion, and random reinsertion of an existing molecule at a new position. To calculate the gas-phase fugacity, we used the Peng-Robinson (PR) equation of state (EOS).^{S16}

	σ [Å]	ε/k [K]
С	3.431	52.838
Ν	3.261	34.722
H (MOF)	2.571	22.142
Cu	3.114	2.516
H_2	2.958	36.700

Table S1. Lennard-Jones parameters for framework atoms and the H₂ molecule.

To calculate the exact pressure of the maxima in the excess isotherms, we fit the top range of each individual excess isotherm using an order 3 polynomial equation. We used this equation to calculate the maximum excess uptake and, using the first derivative, the excess maximum pressure.

The pore volume, used to compute excess adsorption from the simulated absolute adsorption, was obtained using a Widom particle insertion method, by probing the structure with a helium molecule at room temperature, recording a large number of random points not overlapping the van der Waals volume of the framework.^{S17,S18} Void fraction was calculated as the quotient between the pore and the unit cell volumes.

The pore size distributions were calculated using the method of Gelb and Gubbins,^{\$19} where the largest sphere that can fit in a random point within a structure without overlapping the van der Waals surface of the framework is recorded for a large number of random points.

The geometric surface areas were calculated by rolling a 3.681 Å-diameter sphere, which corresponds to a nitrogen molecule, across the surface of the material.^{S20}



Figure S5. Evaluation of the Peng-Robinson EOS versus NIST data for the bulk H₂ density at 77 K.



Figure S6. Absolute (diamonds) and excess (triangles and circles) H_2 adsorption isotherms at 77 K. Simulations (red) were performed in L2, and experiments (black) were performed on its analogue, NU-111.^{S3} Red triangles represent the excess isotherm calculated using NIST data, and open red circles, using the PR EOS.



Figure S7. *a*) Absolute and *b*) excess adsorption isotherms of H_2 at 77 K on the L1- L8 materials. *c*) Calculated absolute (black circles) and excess (red circles) adsorption capacity maxima of H_2 isotherms on L1-L8 obtained at 77 K. The H_2 bulk density was obtained from the NIST data. Note the use of gravimetric (*left*) and volumetric (*right*) uptake.

	Geometric Surface Area	Unit Cell Size	Void Fraction	Framework Density	Pore Volume	Pressure Max	Max Excess Uptake	Max Excess Uptake
_	m²/g	Å		g/cm ³	cm ³ /g	bar	mg/g	mg/cm ³
L1	3690	42.99	0.84	0.55	1.51	33.14	63.22	34.98
L2	4698	49.37	0.88	0.40	2.21	40.60	72.52	28.80
L3	4071	47.62	0.87	0.48	1.79	35.00	70.84	34.28
L4	5194	58.32	0.92	0.32	2.82	44.58	83.02	26.94
L5	5033	53.73	0.89	0.36	2.46	41.49	80.22	29.00
L6	5814	59.87	0.91	0.28	3.25	47.29	88.26	24.64
L7	5925	64.44	0.92	0.25	3.61	48.05	90.34	23.02
L8	6838	68.23	0.92	0.20	4.61	51.46	89.36	17.92

Table S2. Adsorption properties for the L1-L8 materials.



Figure S8. Calculated excess adsorption maxima, black circles, of H_2 isotherms on L1-L8 obtained at 77 K versus different structural parameters. Experimental data from **PCN-68**, red triangle, **NOTT-116**, purple diamond, and **NU-111**, green square, are also included. The bulk H_2 density was obtained from the NIST data.

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Figure S9. Comparison of hydrogen adsorption isotherms at 77 K for L5, red symbols, NOTT-116, grey symbols, and **PCN-68**, black symbols. Absolute adsorption is represented by diamonds and excess by triangles. The H_2 density was obtained from the NIST data.

Table 55. Simulated absolute ausorption isotherms of Π_2 on L1-L6 at $1/\Lambda$

Р	L1	L2	L3	L4	L5	L6	L7	L8
bar	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g
1.00E-02	0.44	0.33	0.46	0.38	0.34	0.37	0.27	0.21
1.58E-02	0.66	0.57	0.73	0.60	0.49	0.58	0.45	0.35
2.51E-02	1.03	0.79	1.15	0.86	0.81	0.86	0.69	0.48
3.98E-02	1.50	1.20	1.60	1.33	1.19	1.22	1.02	0.72
6.31E-02	2.14	1.71	2.40	1.99	1.76	1.79	1.49	1.15
1.00E-01	3.06	2.53	3.48	2.96	2.52	2.57	2.25	1.73
1.58E-01	4.34	3.62	5.04	4.26	3.69	3.61	3.39	2.56
2.51E-01	6.17	5.29	7.33	6.23	5.36	5.10	4.87	3.71
3.98E-01	8.79	7.29	10.38	9.00	7.65	7.32	7.10	5.51
6.31E-01	12.38	10.23	14.41	12.67	10.83	10.52	10.26	7.96
1.00	16.98	14.23	19.90	17.76	15.36	14.88	14.73	11.76
2.00	26.76	21.26	29.89	26.52	23.44	22.42	22.32	17.46
3.00	33.62	28.25	37.71	34.90	31.24	30.28	30.92	25.24
4.00	39.09	34.24	44.14	41.77	37.64	37.31	38.01	32.03
5.00	43.75	39.22	48.99	47.84	43.56	43.49	44.58	38.55
6.00	47.60	43.73	53.51	53.21	48.90	49.05	50.40	44.55
7.00	50.70	47.80	57.01	57.69	53.23	53.97	55.81	49.97
8.00	53.42	51.61	60.04	62.24	57.37	58.69	60.68	55.21
9.00	55.75	54.97	62.78	66.24	61.11	62.90	65.26	60.38
10.0	57.72	58.59	65.48	70.08	65.36	67.55	70.27	66.03
20.0	70.50	80.48	79.99	93.16	88.22	97.37	101.11	103.69
30.0	77.51	93.00	88.51	108.27	102.73	116.02	121.30	127.96
40.0	83.09	101.49	93.69	119.74	112.30	130.07	136.82	148.24
50.0	87.22	107.88	96.87	128.79	119.77	141.18	149.11	164.47
60.0	90.52	112.76	99.80	135.46	125.53	149.59	159.06	178.11
70.0	93.29	117.00	102.30	140.75	130.19	155.96	166.85	189.87
80.0	95.19	120.45	104.37	145.60	133.64	162.09	173.49	200.35
90.0	96.21	123.25	106.02	149.19	136.64	167.08	179.95	210.45
100.0	96.35	126.09	107.64	152.43	139.34	171.90	186.03	219.50

Table S4. Simulated excess adsor	ption isotherms of H_{2}	, using NIST data,	on L1-L8 at 77 K.

Р	L1	L2	L3	L4	L5	L6	L7	L8
bar	mg/g							
1.00E-02	0.66	0.66	0.73	0.80	0.70	0.85	0.81	0.89
1.58E-02	0.88	0.89	1.00	1.01	0.85	1.06	0.98	1.03
2.51E-02	1.25	1.11	1.40	1.27	1.16	1.32	1.21	1.14
3.98E-02	1.71	1.51	1.85	1.72	1.53	1.67	1.52	1.36
6.31E-02	2.33	2.00	2.64	2.36	2.08	2.21	1.96	1.75
1.00E-01	3.24	2.79	3.69	3.29	2.81	2.95	2.67	2.28
1.58E-01	4.49	3.83	5.21	4.53	3.93	3.93	3.74	3.01
2.51E-01	6.27	5.44	7.45	6.41	5.52	5.31	5.10	4.01
3.98E-01	8.81	7.32	10.40	9.04	7.68	7.37	7.15	5.58
6.31E-01	12.29	10.09	14.29	12.49	10.67	10.30	10.02	7.66
1.00	16.69	13.81	19.55	17.22	14.89	14.26	14.04	10.88
2.00	25.95	20.08	28.93	25.01	22.12	20.68	20.38	14.99
3.00	32.29	26.30	36.14	32.42	29.08	27.42	27.75	21.19
4.00	37.24	31.54	41.95	38.32	34.63	33.34	33.61	26.40
5.00	41.39	35.76	46.18	43.43	39.72	38.42	38.94	31.34
6.00	44.73	39.52	50.09	47.84	44.22	42.86	43.53	35.77
7.00	47.31	42.83	52.98	51.36	47.71	46.67	47.71	39.63
8.00	49.52	45.89	55.41	54.95	51.01	50.30	51.35	43.29
9.00	51.34	48.50	57.54	57.99	53.92	53.40	54.71	46.91
10.0	52.79	51.37	59.62	60.88	57.34	56.95	58.50	50.99
20.0	60.51	65.84	68.12	74.50	71.96	75.87	77.23	73.19
30.0	62.54	71.07	70.73	80.32	78.36	83.83	85.53	82.27
40.0	63.24	72.41	70.10	82.67	79.99	87.37	89.37	87.65
50.0	62.58	71.77	67.59	82.77	79.65	88.17	90.21	89.24
60.0	61.17	69.77	64.93	80.66	77.76	86.47	88.92	88.53
70.0	59.34	67.25	61.95	77.33	74.92	82.92	85.69	86.21
80.0	56.72	64.07	58.65	73.74	71.00	79.33	81.52	82.89
90.0	53.30	60.39	55.04	69.05	66.80	74.79	77.40	79.47
100.0	49.10	56.87	51.51	64.19	62.43	70.29	73.11	75.28

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