Electronic Supplementary Information

Screening of Hypotetical MOFs for Hydrogen storage

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S1. Details and structures of the 'Best-1' materials

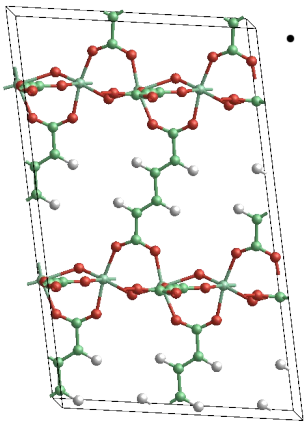
As a result of the different screening conditions (see Table 1) performed over the initial ~138000 structures of the database [7] a total of 10 structures (called 'Best-1') have been obtained that matched the selection criteria. Here we show these structures (Figure S1) and comment some of their properties.

The structures called 'Best-1' do correspond to the Group-1 in Figure 2, and have been further subdivided into three subgroups (Table 3). The first two structures ('1001432', '6000362') belong to Group 1-a (see Table 3) and hold the highest gravimetric and volumetric uptakes values at 1 bar (3 % and 29 g/L, respectively). One important difference with the other 'Best-1' structures is that these MOFs show a rod-type IBU structure (Figure 1) with vanadium as metal centers.

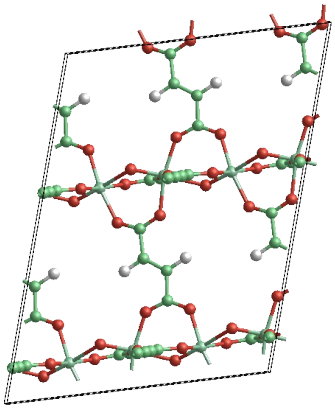
The next two structures ('8702' and '8688') still belong to Group 1-a, but their inorganic building unit is the well known $Zn_4O(RCOO)_6$ of the IRMOF series. They also have high uptake values, but lower than the previous two structures.

The following four structures ('5008565', '5008433', '5008453', and '5005539') present a catenated network with the same IBU ($Zn_4O(RCOO)_6$) but with different ligands in each case. Specifically, MOF '5008565' is the only structure in all 'Best-1' set that contains a NH_2 functional group in one of the ligands.

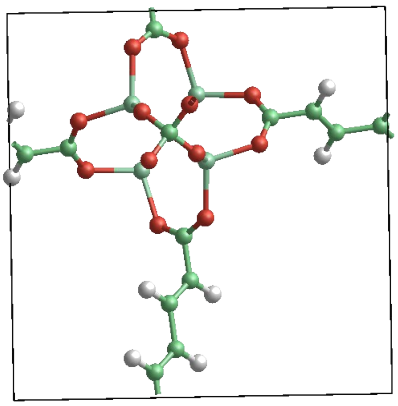
The last two structures ('8627' and '5893') belong to Group 1-c, and they show the lowest gravimetric and volumetric uptake values among all 'Best-1' structures. MOF '8627' is similar to the well known MOF-5, with the only difference of the presence of an oxalate ligand in the [100] direction. The last structure ('5893') has a very similar structure but without the oxalate ligand (C_2O_4), which is replaced by a larger ligand (C_4O_4).



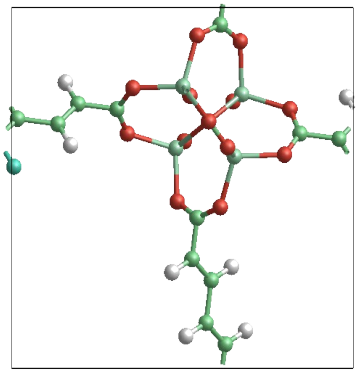
MOF code:1001432



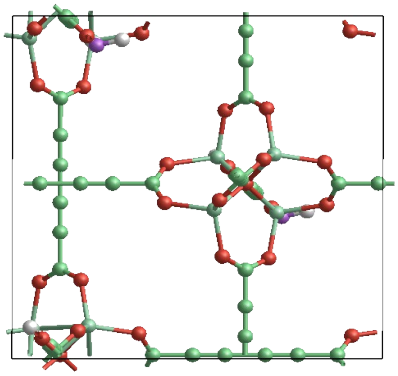
MOF code:6000362



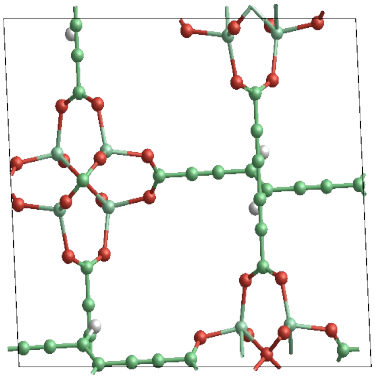
MOF code: 8702



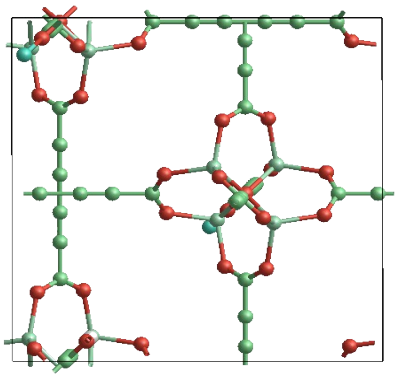
MOF code: 8688



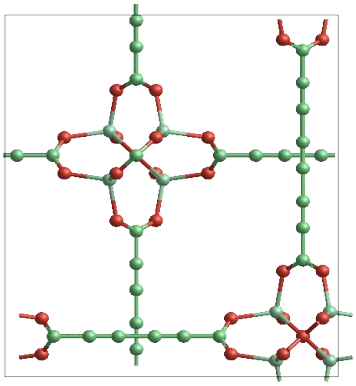
MOF code: 5008565



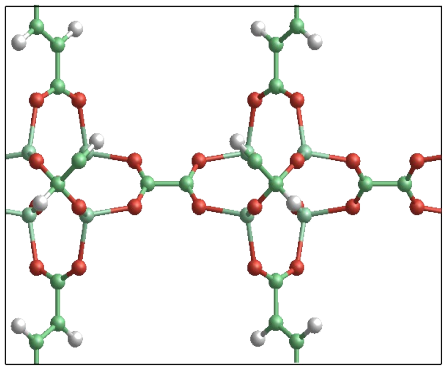
MOF code:5008433



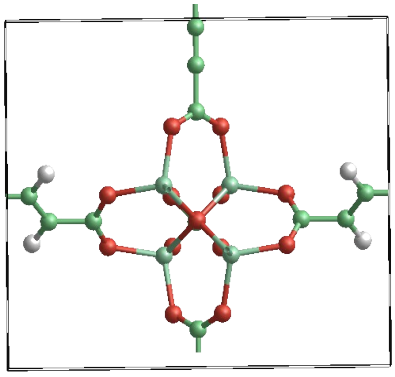
MOF code: 5008453



MOF code: 5005539



MOF code: 8627



MOF code: 5893

Figure S1. Structures of the 'Best-1' group (Table 3). Colour code: dark green, Vanadium; light blue, Zinc; grey, Carbon; red, Oxygen; dark blue, Nitrogen, green, Fluor; white, Hydrogen.

S2. Description of the organic linkers of the ‘Best-1’ materials

Here we describe the different organic linkers that can be found on the ‘Best-1’ structures. In Figure S2, the first row (i-v) shows linkers with 4-6 C atoms. In the second row (vi-ix) the linkers are larger, with a maximum length of 6-8 C atoms. Finally, there is the short oxalate linker (x). Linkers ‘v’ and ‘vii’ have one F atom instead of H, and linker ‘vi’ is the only linker that has a NH_2 group. Table S2 shows the relation between ‘Best-1’ structures and their corresponding ligands (Figure S2).

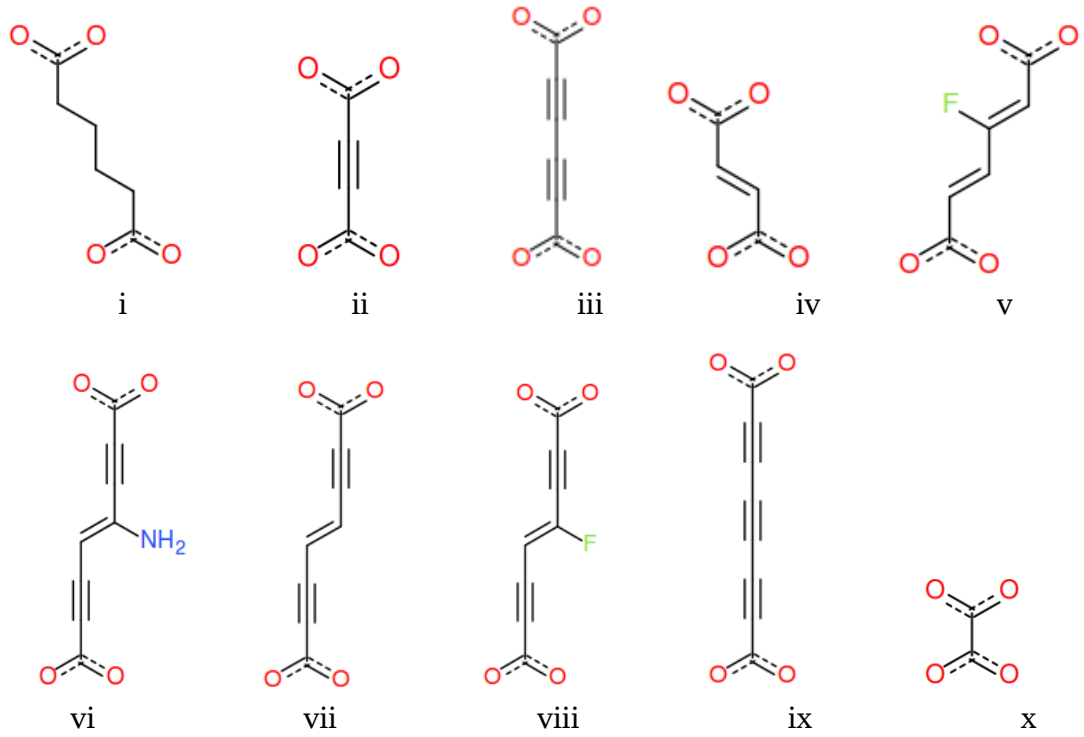


Figure S2. Organic linkers of the MOFs in Table 3 (‘Best-1’), corresponding to the materials showing the largest gravimetric and volumetric hydrogen uptake. Color code: grey, carbon; red, oxygen; blue, nitrogen, turquoise, fluorine; white, hydrogen.

Table S2: MOFs of the ‘Best-1’ group with their corresponding organic linkers.

Framework code(*)	Ligands associated	Ligand Size
1001432	i, ii	4.06 / 6.20
6000362	iv, ii	3.73 / 6.20
8702	x, i	1.51 / 6.20
8688	v, x	1.51 / 6.20
5008565	iii, vi	6.91 / 9.17
5008433	iii, vii	6.91 / 9.17
5008453	iii, viii	6.91 / 9.17
5005539	iii, ix	6.91 / 9.64
8627	x, i	1.51 / 5.60
5893	ii, i	4.06 / 5.60

(*): The codes are named after the Snurr-Wilmer database [10].

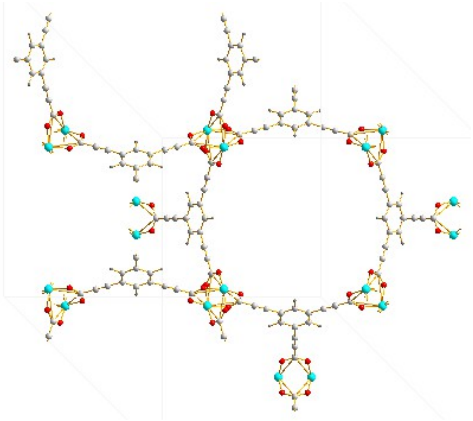
S3. Details and structures of the ‘Best-2’ materials (Paddle-Wheel MOFs).

From the second screening test (see Table 5) performed over the Paddle-wheel MOFs, containing open metal sites, a total of 1411 structures were analyzed. From the screening performed, 8 structures (called ‘Best-2’ materials, Figure 5 and Table 5) matched the selection criteria, which are further analyzed in this section and are shown in Figure S3.

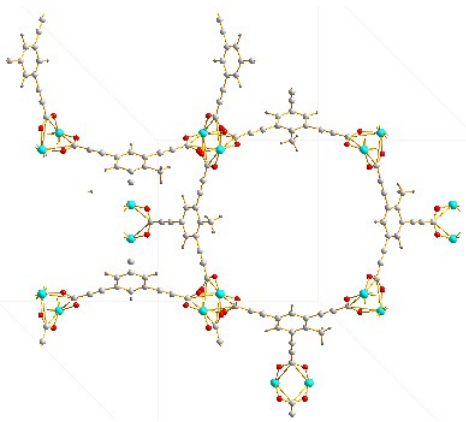
From Figure S3, the structures displayed in the first row (structures ‘2000132’ and ‘2000149’) correspond to materials that reach the gravimetric target at the pressure of 10 bar (Group 2-a, Table 5). Moreover, these are the two structures with the largest pores of all ‘Best-1’ and ‘Best-2’ structures (see Section S4). Both structures are very similar to each other, and they only differ in the presence of a CH_3 group in the aromatic rings of ‘2000149’.

The second, the third row and the first structure of the last row (structures ‘2000066’, ‘2000082’, ‘2000089’, ‘2000108’ and ’2000529’ respectively) belong to Group 2-b. These materials reach the gravimetric target at similar values than the ‘Best-1’ materials (around 20 bar) but at higher pressures in the case of the volumetric target (~40 bar for Group 2-b and ~5 bar for the Group 1-a of the ‘Best-1’ structures). In this group we highlight the structure ‘2000529’ that is the only one which contains Cu instead of Zn atoms as open metal sites.
All these MOFs show a similar behavior on the isotherms (Figure 5) but they have slightly structural differences that can be found on the aromatic rings: structure ‘2000082’ has -CH_3 groups on the benzene rings, structures ‘2000089’ and ‘2000529’ have -C_2H_4, ‘2000108’ has an -OH and ‘2000066’ does not have any substituent.

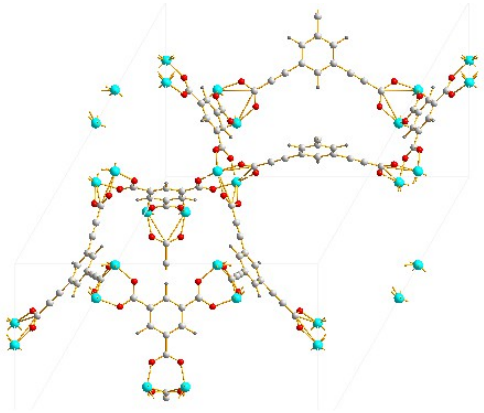
The last structure of the last row (‘2000000’) corresponds to the only structure that does not reach the targets and, as ’2000529’, it has Cu atoms instead of Zn as metal center. It does not have any substitution in the benzene ring.



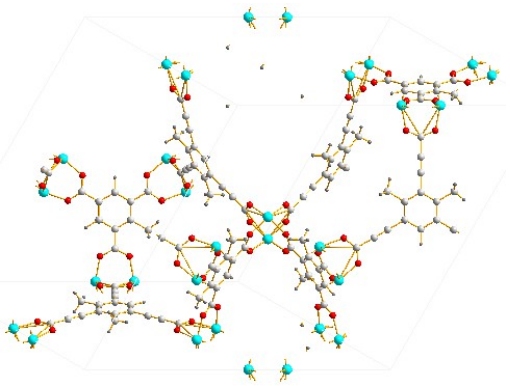
MOF code: 2000132



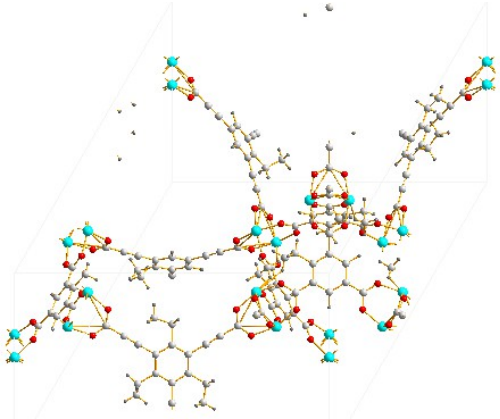
MOF code: 2000149



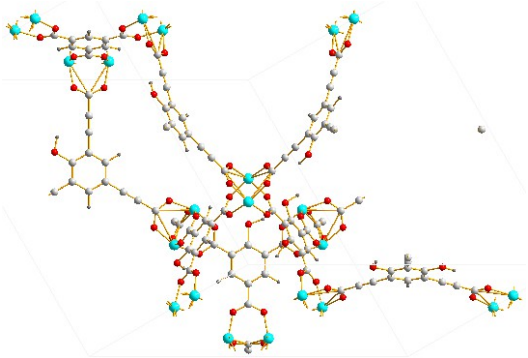
MOF code: 2000066



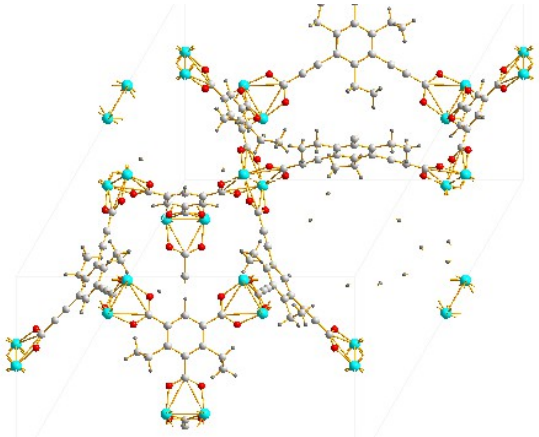
MOF code: 2000082



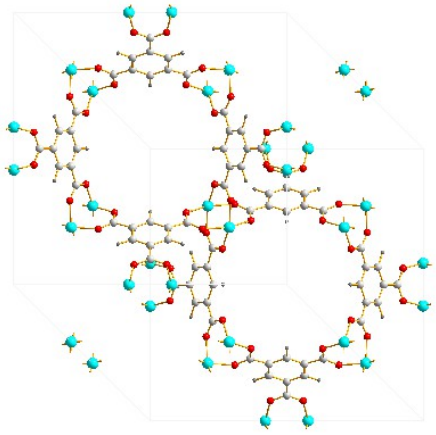
MOF code: 2000089



MOF code: 2000108



MOF code: 2000529 (1)



MOF code: 2000000

Figure S3. Paddle wheel structures forming the ‘Best-2’ group. color code: red, oxygen; gray, carbon; white, hydrogen; turquoise, Zn.
(1) In structure ‘2000529’, the turquoise colour corresponds to Cu.

S4. Pore size distribution of the ‘Best-1’ and 'Best-2' materials.

In this section we analyze the Pore Size Distribution (PSD) of the ‘Best-1’ and 'Best2' materials, that includes the pore diameter and their numbers (frequency). To obtain this data we employed a home-made code that operates on the following manner: 1) Measure distances and locates a pore. 2) Calculates the dimensions of the pore. 3) Calculates the LCD (largest cavity diameter) in the pore. 4) Fills the calculated volume with a sphere. 5) If there are empty spaces left by the previous sphere, put smaller and smaller spheres until there are no empty spaces in the pore. 6) Sums the volumes of the spheres taking into account their frequency. The PSD is then a distribution of sphere sizes with frequencies.

Comments to 'Best-1' and 'Best-2' materials

From all structures among 'Best 1' materials, there is only one structure ('5005539) that has the 100% of its pores in the optimum range, meanwhile the structure '8702' has the lowest percentage (33%). The structures with the largest pore sizes are '8688', '8702' and '8627' with pores of 10.9, 11.4 and 13.0 **Å** respectively.
In IRMOF-62, most pores are located below 5.40, outside of the optimum range; however this also happens in '8688' and '8702' and HKUST-1 (and the isostructural '2000000'). In fact, in the latter case this is more drastic, and only enlarging the lower end of the optimum range it is possible to rationalize the results which otherwise would show 0% of pores in range. Hence, by including the pores of 4.6 **Å** as active for hydrogen adsorption, the value of 50% of pores in range shown in Table 5 was obtained.
Ultimately, this comes from the fact that we stick to the definition of optimum range made in reference 15 and this is not an accurate derivation but rather a rough estimation. As an overall view of HKUST-1, if we assume that HKUST-1 contains significant number (50%) of pores within the optimum range, plus the fact that HKUST-1 contains open metal sites, it is easy to understand the high uptake values, very close to the values of Group 1-a within the 'Best-1' materials. None of the PW MOFs of the database shows a larger uptake than HKUST-1.

Looking at the pore size distributions (see below) of the firsts two MOF structures of 'Best-2' (‘2000132’ and ‘2000149’) one can see the large pores of 21.0 Å that no other structure shows. The other structures have lower pore diameters and a consequent decrease in the gravimetric uptakes at high pressure. All ‘Best-2’ structures have something in common, all of them having few number of pores that are in the range of the optimum pore size. This fact strengthens the argument in this study about the large pore size of the two firsts compounds. They show the lowest number of pores in the optimum range.

Pore size distribution of 'Best-1' materials

Structure: 1001432

Pore diameter (Å)	Frequency
9.10	1
8.70	1
6.10	1
5.70	1
4.80	1
4.60	2
4.20	1

Structure: 6000362

Pore diameter (Å)	Frequency
9.70	2
6.60	1
6.40	1
6.00	1
4.40	1
4.00	1

Structure: 8702

Pore diameter (Å)	Frequency
11.40	1
7.80	1
7.10	1
4.90	1
4.80	1
4.70	2
4.40	1
4.20	1

Structure: 8688

Pore diameter (Å)	Frequency
10.9	1
7.90	1
6.60	1
5.70	1
5.40	1
5.30	1
4.60	2
4.00	2

Structure: 5008565

Pore diameter (Å)	Frequency
8.90	1
8.80	1
7.80	2
5.50	2
5.40	2
5.30	1
4.00	1

Structure: 5008433

Pore diameter (Å)	Frequency
9.30	1
9.20	1
7.40	2
6.30	1
5.50	1
5.40	1
5.30	1
4.60	1

Structure: 5008453

Pore diameter (Å)	Frequency
8.90	1
8.80	1
7.80	2
5.70	1
5.50	1
5.40	3
4.00	1

Structure: 5005539

Pore diameter (Å)	Frequency
9.00	1
8.80	1
7.90	1

7.80	1
6.20	2
5.70	1
5.60	1

Structure: 8627

Pore diameter (Å)	Frequency
13.00	1
8.00	1
6.40	1
5.10	1
4.60	1

Structure: 5893

Pore diameter (Å)	Frequency
9.90	1
4.10	1

Structure: IRMOF-62

Pore diameter (Å)	Frequency
11.0	**1**
10.10	**1**
10.0	**1**
9.90	**1**
9.20	**1**
9.0	**2**
8.70	**1**
8.20	**1**
8.10	**1**
8.0	**1**
7.90	**1**
7.50	**1**
7.30	**1**
7.10	**1**
6.50	**2**
6.20	**1**
6.0	**2**
5.90	**2**
5.80	**1**
5.70	**1**
5.60	**2**
5.50	**1**
5.40	**1**
5.20	**1**
5.10	**2**
5.0	**4**
4.90	**4**
4.80	**3**
4.70	**1**
4.60	**4**
4.50	**4**
4.40	**2**
4.30	**4**
4.20	**3**
4.10	**4**
4.00	**5**

Pore size distribution of 'Best-2' materials

Structure: 2000132

Pore diameter (Å)	Frequency
21.0	1
16.5	1
14.7	1
10.9	1
9.1	1
8.9	1
6.5	1
5.8	1
5.7	1
5.3	1
5.1	3
4.8	1
4.6	3
4.5	1
4.4	2
4.3	1
4.2	2

Structure 2000149

Pore diameter (Å)	Frequency
21.0	1
16.5	1
14.7	1
10.9	1
9.1	1
8.9	1
6.5	1
5.8	1
5.7	1
5.3	1
5.1	2
5.0	1
4.8	1
4.6	3
4.4	2
4.3	1
4.2	2
4.1	2
4.0	4

Structure: 2000066

Pore diameter (Å)	Frequency
14.1	1
12.2	1
11.8	1
10.5	1
9.0	2
7.6	1
4.5	2
4.4	2
4.1	1

Structure: 2000082

Pore diameter (Å)	Frequency
16.9	1
13.1	1
11.8	1
10.7	1
9.0	1
8.1	1
7.4	1
4.9	1
4.3	1
4.1	2

Structure: 2000089

Pore diameter (Å)	Frequency
15.2	1
11.9	1
11.2	1
11.3	1
8.3	1
6.7	1
5.7	1
5.5	1
5.0	1
4.8	1
4.7	1
4.4	2
4.3	1

4.2	3
4.1	1

Structure: 2000108

Pore diameter (Å)	Frequency
17.1	1
12.5	1
11.8	1
10.0	1
9.3	1
6.0	1
5.5	1
5.2	1
4.8	1
4.4	2
4.2	1
4.0	3

Structure: 2000529

Pore diameter (Å)	Frequency
15.7	1
12.3	1
11.7	1
10.7	1
9.7	1
8.9	2
4.3	1
4.1	2
4.0	1

Structure: HKUST-1

Pore diameter (Å)	Frequency
13.1	4
11.1	4
4.6	8

Structure: 2000000

Pore diameter (Å)	Frequency
13.1	4
11.1	4
4.6	8

Structure: MOF-5

Pore diameter (Å)	Frequency
24.9	1
12.2	1
9.9	1
8.4	1
6.6	1
6.2	1
5.9	2
5.6	1
5.1	1
5.0	1
4.8	1
4.6	1
4.5	2
4.1	1

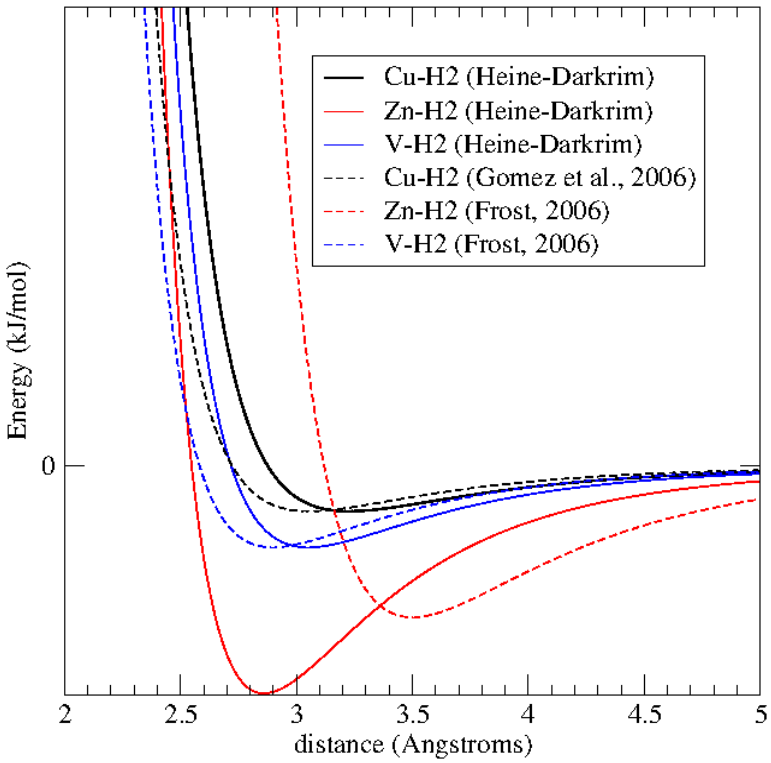
S5. Lennard-Jones parameters for Metal-H_2 interaction.

Set of parameters (σ and ε) for Lennard-Jones potentials used in this work.

	σ (Å)	ε (K)	ε (kcal×mol^{-1})
H_2[a]	2.958	36.7	0.0729
Cu[b]	3.495	2.516	0.0049
Zn[b]	2.763	62.375	0.1239
V[b]	3.144	8.052	0.0160
Cu-H_2	3.227	9.610	0.0191
Zn-H_2	2.860	47.855	0.0951
V-H_2	3.051	17.190	0.0341

[a] From Darkrim-Levesque (**40**). [b] From Heine et al. (**39**).

The parameters for Hydrogen are taken from the work of Darkrim-Levesque [40] , meanwhile the parameters for the metals (Copper, Zinc and Vanadium) are taken from the work of Heine et. al. [39] Following the Lorentz-Berhelot mixing rules, we combined the parameters for the metals with the parameters for the hydrogen in order to get the parameters to describe the H_2-Metal interaction. The rest of parameters (interaction of H_2 with the non metallic atoms of the MOF) were taken from the DREIDING forcefield as in previous work [15, 42].



Comparison between different set of potentials for Metal-H_2 interaction. Solid lines correspond to the combination of Heine and Darkrim-Levesque. Dashed lines belong to the potentials taken from Frost et al. except for the Cu-H_2 parameters that are taken from Gomez et. al. [15].

S6. Details of the GCMC simulations

Here we describe usefull information we used in our GCMC simulations for the obtention of the adsorption isotherms. First, details of the reference materials are listed. Then, for the 'Best-1' materials and finally, for the 'Best-2'**.**

The software used was MUSIC [42], ”Multipurpose Simulation Code”. It is a molecular simulation code developed by Northwestern University. His code is able to run multiple types of simulations, such as GCMC, NVT-MC, NPT-MC, Hybrid Monte Carlo, MD and NEMD. It also includes forcefield van der Waals interactions as 12-6 Lennard-Jones and Buckigham forms. Coulombic interactions are handled with Ewald summations and also smooth cutoff schemes are introduced.

We used MUSIC to predict macroscopic adsorption properties such as the uptake of a gas on metal-organic frameworks, zeolites and mesoporous oxides.

For all the structures calculated, the number of iterations was 8000000 and the temperature was 77 K. 23 pressure values were taken between 0 and 100 atm in regular intervals, and the size of the unit cell was made sufficiently large (if necessary by constructing supercells) so as to allow a cutoff distance in the nonbonding potential term to satisfy the default criteria for energy convergence.

S7. Excess Uptake Isotherms of the 'Best 1' and 'Best 2' materials.

Here we present the isotherms of the excess uptake (both gravimetric and volumetric) for the 'Best-1' and 'Best-2' materials.
Excess uptake represents the corrected absolute uptake due to the amount of gas that would be absorbed in the free volume of the pores of the material in the same conditions of pressure and temperature.

The excess uptake can be calculated from the following formula:

$$N_{exc} = N_{abs} - \rho * V_p$$

Where N_{exc} is the excess adsorption, N_{abs} the absolute amount of gas adsorbed, ρ the density of the bulk gas and V_p the volume of all the accessible pores of the absorbent.

Also, the final term can be calculated using the definition of porosity (volume of the accessible pores divided by unit cell volume) and we obtain:

$$N_{exc} = N_{abs} - \rho * \text{porosity} * V_{u.c.}$$

With this applied to the isotherms, and to the values in Tables 2 and 5 (Table 2 for 'Best1' and Table 5 for 'Best2' materials) we have obtained the isotherms of the excess uptake, shown below.

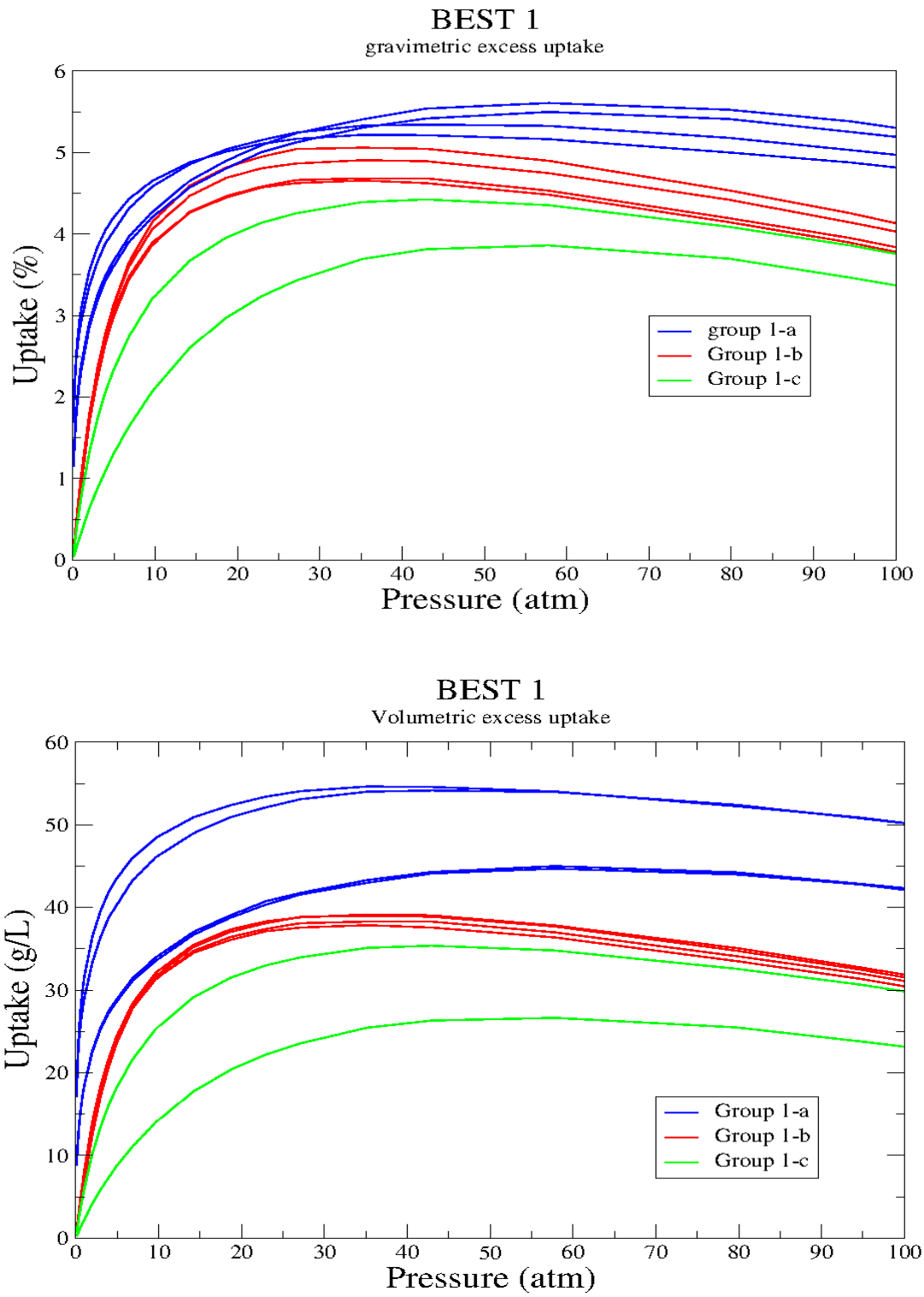


Figure S7.1. Excess uptake isotherms for the 'Best 1' materials. Top) gravimetric uptake. Bottom) volumetric uptake.

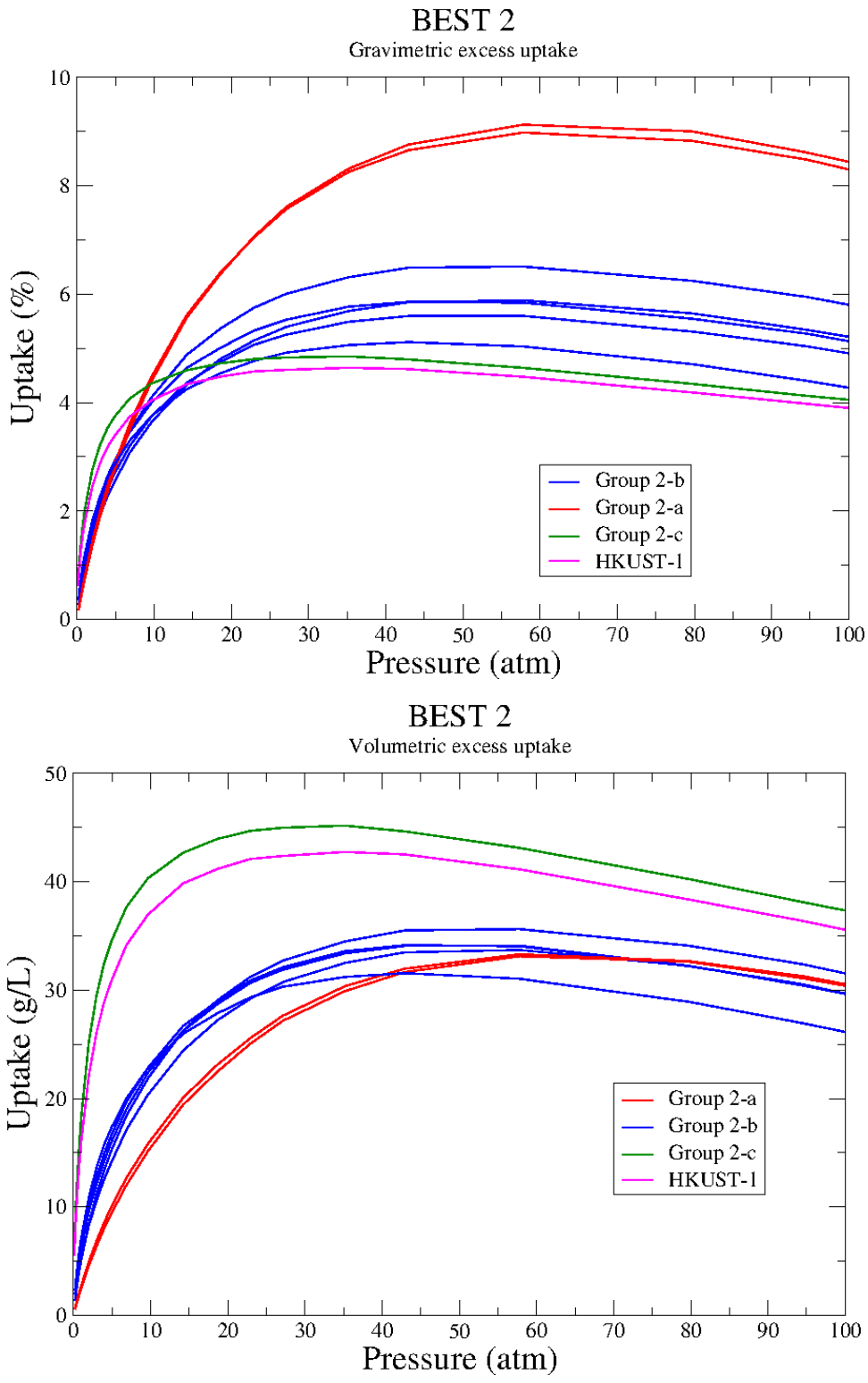


Figure S7.2. Excess uptake isotherms for the 'Best 2' materials. Top) gravimetric uptake. Bottom) volumetric uptake.

Table S7. Absolute and excess uptake (gravimetric and volumetric) for all 'Best' materials at the pressure of 100 atm.

Uptake (100 atm)				
	Absolute		Excess	
Framework code	%	g/L	%	g/L
Best-1				
1001432	6.47	68.7	4.78	50.0
6000362	6.74	69.1	4.95	49.9
8702	7.93	64.9	5.27	41.9
8688	7.74	64.6	5.15	42.1
5008565	6.34	52.4	3.77	30.5
5008433	6.66	54.2	4.00	31.8
5008453	6.42	53.4	3.83	31.0
5005539	6.91	54.2	4.11	31.4
8627	6.44	52.7	3.73	29.7
5893	6.63	47.2	3.35	23.1
Best-2				
2000132	14.79	57.2	8.39	30.3
2000149	14.44	56.8	8.25	30.4
2000066	9.78	56.1	5.77	31.4
2000082	8.83	53.4	5.13	29.5
2000089	8.43	52.7	4.90	29.5
2000108	9.11	53.7	5.19	29.4
2000592	7.84	49.8	4.25	25.9
2000000	5.91	55.8	3.14	28.6
HKUST-1	5.78	53.7	3.91	35.5