

Electronic Supplementary Information

From microscopic insights of H₂ adsorption to uptake estimations in MOFs

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S1. Comparison between experimental, PM6 and UHF results of structural parameters for the IBUs.

Although all the study is based on *ab-initio* calculations, semi-empirical PM6 calculations were also performed in order to check whether this approximations can be of any use to treat this problem. In general, results show that PM6 gives reasonable geometries but far too strong adsorption energies.

The main structural parameters obtained after optimisation of the models employed in the study are presented and compared with the experimental. It should be mentioned that the structural parameters of the small cluster models used in the MP2 calculations were the same than obtained at the UHF level for the IBUs.

UiO-66. (IBU I)

Table S1. Experimental¹ and optimised (with PM6 and UHF/6-31G**;LANL2DZ theoretical models) bond distances (Å) for the IBU(I) of MOF UiO-66.

	Exp.	PM6	UHF
Zr-O _{COO}	2.232	2.282	2.226
Zr-O _{μ3}	2.108	2.249	2.095

The IBU with formula Zr₆O₄(μ₃-OH)₄(CH₃COO)₁₂ (see Figure 1a) was extracted from the crystallographic data reported for the MOF UiO-66¹. In this IBU, the Zr atoms present an oxidation state of 4 (d⁰), without contribution to the total spin, and a coordination number of eight with square anti-prismatic stereochemistry.

The larger deviation in bond distances was obtained for the PM6 results which, as the UHF bond distances, were larger than the experimental. The optimisation of the UHF model gives a difference in bond distances around 0.005 Å, indicating an excellent correspondence with the real structure. Similar results were obtained for the clusters employed in the study of hydrogen adsorption.

MIL-47. (IBU II)

MIL-47, with formula V^{IV}O{O₂C-C₆H₄-CO₂}₂, presents a rod-type secondary building unit in which the vanadium atoms are connected through one oxygen atom and two carboxylate groups forming a chain of octahedral V^{IV} complexes (see Figure 1a).

Table S2. Experimental² and optimised (PM6 and UHF/6-31G**) bond distances (Å) and angles of interest (degrees) for the IBU (II) of the MOF MIL-47.

	Exp.	PM6	UHF
V – O*	1.672	1.720	1.591
V – O†	2.102	2.266	2.137
V – O – V	129.4	131.3	140.8

* shortest bond distance in the chain composed of (V-O)_x atoms.

† longest bond distance in the chain (V-O)_x atoms.

The IBU (Figure 1a) contains a chain of four vanadium atoms connected as mentioned above. For simplicity of the model, the rings of the linker were replaced by methyl groups in the IBU and by H atoms in the small cluster taking into account that any incidence of the rings in the hydrogen adsorption around the metallic centres is expected to be minimal given their orientation in the framework. In the total IBU the three unbonded positions at each extreme of the model were saturated with two (OH)⁻ groups and one water molecule in order to obtain a neutral system and the correct coordination.

The final structure obtained after optimisation with symmetry restrictions at PM6 presented a good correspondence with the experimental values. The V-O distances (in the chain V-O-V) and the V-O-V angles of the optimised IBU at PM6 were 0.1 Å and 2 degrees higher than the experimental (see Table S2). A larger deviation was observed in the V-O-V angle optimised at UHF level where the results indicate a value 11.4 degrees higher than the experimental. The bond distances are close to the experimental where the maximum deviation is 0.081 Å.

In terms of electronic structure, each V^{IV}(d1) atom presents a spin state of ½, however a low magnetic susceptibility has been reported indicating a strong ferromagnetic coupling which cancels the total magnetic moment of the material, The IBU model presents two metallic atoms which generate a total spin coupling and a singlet multiplicity.

MFU-1b. (IBU III)

MFU-1³ presents an isotopological structure to MOF-5. Its IBU is composed of four cobalt(II) atoms bonded through a central oxygen atom in a tetrahedral conformation ([Co₄O]⁺⁶), in a similar fashion to the conformation of the complex [Zn₄O]⁺⁶ in MOF-5. In MFU-1, the cobalt(II) complexes are linked by 1,4-bis[(3,5-dimethyl)-pyrazol-4-yl]benzene leading to a cubic unit cell.

The model of the IBU used for the evaluation of the hydrogen adsorption is a modified IBU composed of one [Co₄O]⁺⁶ and six pyrazolate groups (see Figure 1), which was constructed from the structural information reported and the average bond distances Co-N and Co-O. The unit cell parameter (*a*) obtained for the constructed model was 15.452 Å, which is shorter than the experimental value (15.963 Å)³.

On the other hand, the electronic structure of tetrahedral complexes of Co(II) (d7) suggests a low spin state of 3/2. However, given the presence of four Co atoms in the complex and the stability of the wave function calculated for a singlet state (UHF/6-31G), it is possible to think in the presence of an anti-ferromagnetic coupling of the unpaired spins in the total wave function of the model. A good optimisation of the UHF calculation was achieved and the final structure optimised with T_d symmetry.

Table S3. Comparison of distances (Å) and angles (degrees) obtained with PM6 and UHF/6-31G** for the IBUs, original and modified (employed in the study), of MFU-1.

	PM6	UHF	
		Original	Modified
O-Co	1.942	1.868	1.944
Co-N	1.910	2.050	2.025
N-N	1.358	1.375	1.362
N-C	1.396	1.324	1.333
O-Co-N	97.3	101.14	98.7
N-Co-N	119.2	116.36	117.76

MIL-88A(Pd). (IBU IV)

The IBU IV with formula Pd₃(CH₃COO)₆⁴ is composed of three Pd(II) atoms in square planar stereochemistry linked by six carboxylate groups, which come from acetate anions (see Figure 1) forming a

cyclic complex where each palladium atom shares two ligand groups with each other. Unpaired electrons are not expected to be present in this complex given that the eight electrons of the d orbitals ($\text{Pd}^{+2}=[\text{Kr}]5s^06d^8$) are totally coupled in the particular orbital splitting of the square planar stereochemistry leading to a singlet multiplicity. A difference of 0.3 Å in the Pd...Pd distance was the more significant variation of the structural parameters.

As described in the paper, this IBU presents the same topology that the IBU of the MIL-88 family of MOFs. Then, in an attempt to evaluate the gravimetric and volumetric uptakes from the loads calculated for this IBU (no MOF has been found to have this particular IBU), an hypothetical MIL-88A(Pd) with the Pd-IBU is proposed. Given the small differences in the distances between the points of extension (C atom from carboxylate groups) in the IBUs of the original MIL-88A (4.0 and 4.3 Å) and the Pd-IBU (3.8 and 4.6 Å), the changes in the lattice parameters of the hypothetical MIL-88A(Pd) are not expected to be highly influential in the volume of the unit cell. Then, the original parameters of MIL-88A were employed for the estimation of the volumetric uptake.

Table S4. Experimental⁴ and optimised (with PM6 and UHF/6-31G**:LANL2DZ theoretical models) distances (Å) for the IBU IV.

Distances	Exp.	PM6	UHF
Pd...Pd	3.168	3.453	3.531
Pd-O	1.995	2.006	2.043

S2. Adsorption of hydrogen in the IBUs evaluated at PM6 and MP2 level.

Semi-empirical results

As preliminary evaluation, the adsorption of hydrogen on the selected IBUs (no small clusters were used) was evaluated employing the PM6 method. In a previous study⁵ it was found that at this theoretical level the interaction of the H₂ molecules with the metallic centres is overestimated and the H₂...H₂ interactions are underestimated, however qualitatively comparable results were obtained for MOF-5.

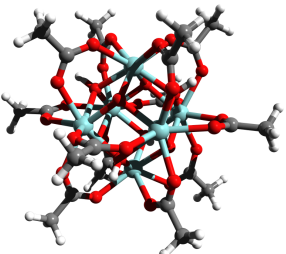
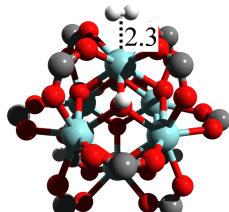
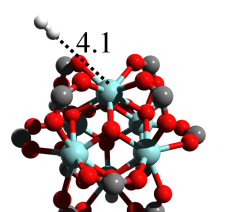
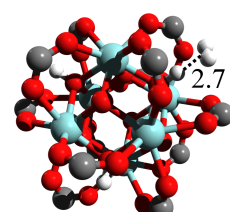
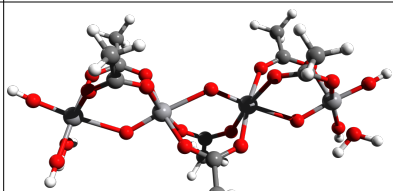
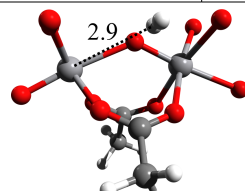
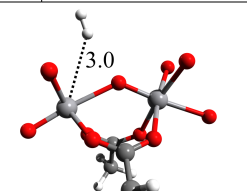
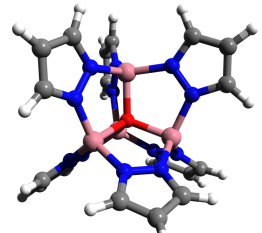
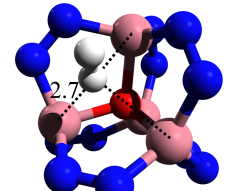
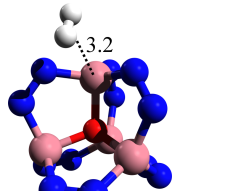
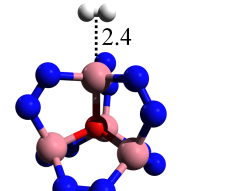
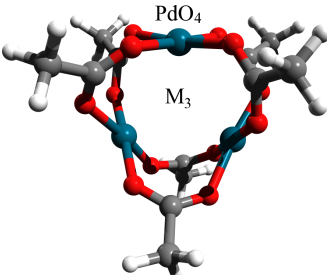
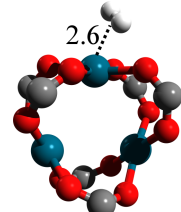
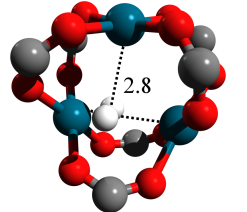
In this study it was found a general overestimation of the adsorption (volumetric and gravimetric uptakes and energies), which can be observed from the values reported in the Table S5 (entries #4 and #5) as compared with the reported in Table 6. The final adsorption positions located from PM6 calculations are presented in Figure S1.

Table S5. Properties of the selected MOF (entry #1). Decomposition of the IBUs in adsorption centres, S_x , (entry #2). Load of H_2 molecules (n_x) per adsorption centre, x (entry #3). PM6 calculated adsorption energies, kJ/mol (entry #4). Gravimetric and volumetric uptakes (entry #5).

Entry		IBU I	IBU II	IBU III	IBU IV
	MOF	UiO-66 ¹	MIL-47 ²	MFU-1b ⁶	MIL-88A ⁷ (Pd)
1	U.C. Composition	Zr ₂₄ O ₁₂₀ C ₁₉₂ H ₉₆	V ₄ O ₂₀ C ₃₂ H ₁₆	Co ₃₂ N ₉₆ C ₂₈₈ H ₁₉₂	Pd ₆ C ₂₄ O ₂₄ H ₁₂
	U.C. Volume (Å ³)	8870.3	1534.2	32541.2	1580.6
	U.C. mass (a.m.u.)	6656.2	924.2	7011.1	1322.86
	ρ_{MOF} (g/cm ³)	1.24	1.00	0.36	1.39
	m (M. atoms/Å ³) ^{a,i}	0.0027	0.0026	0.0010	0.0040
2	IBU Composition	Zr ₆ O ₄ (OH) ₄ (CH ₃ COO) ₁₂	V ₄ O ₃ (OH) ₆ (CH ₃ COO) ₆	Co ₄ O(pyrazol) ₆	Pd ₃ (CH ₃ COO) ₆
	IBU _{U.C.} ^b	4	Rod type IBU	8	2
	S_x ^c (see Fig. 1)	<i>a</i> ZrO ₄ ($S_a=6$) <i>b</i> μ 3-OH ($S_b=4$)	VO ₄ -O-VO ₄ ($S_a=1$)	Co ₃ ($S_a=4$) CoN ₃ ($S_b=4$)	PdO ₄ ($S_a=3$) C ₃ ($S_b=2$)
3	Ads. Uptake ^d	n_a 5 n_b 1 n_{max} 34	5 - 5	4 1 20	4 1 14
	n (N ^o H ₂ /M-atom) ^{e,i}	5.7	2.5	5.0	4.7
	$E_{ads}^{n_a}$ (kJ/mol)	-21.30	-41.88	-98.03	-68.28
	$E_{ads}^{n_b}$ (kJ/mol)	-5.86	-	-35.56	-16.69
4	$E_{ads}^{n_{max}}$ (kJ/mol)	-150.29	-41.88	-403.50	-240.00
	$E_{ads}^{n_{max}}/n_{max}$ (kJ/mol) ^f	-4.42	-8.37	-20.18	-17.14
5	x (wt%) ^{g,i}	4.0	4.2	4.4	4.1
	ρ_{H_2} (g/L) ^h	51.3	43.6	16.5	53.3

^a number of metal atoms per cubic angstroms; ^b number of IBUs per unit cell; ^c Label and number (S_x) of adsorption centres; ^d H_2 molecules adsorbed per adsorption centre; ^e H_2 molecules adsorbed per metal atom; ^f average adsorption energy for the IBU at saturation; ^g gravimetric uptake; ^h volumetric uptake; ⁱ See equation 4 for the relation between x , m and n .

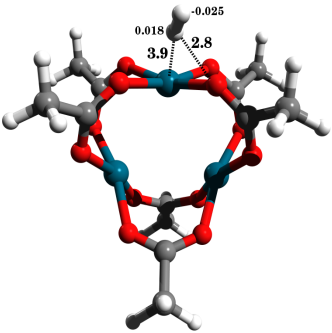
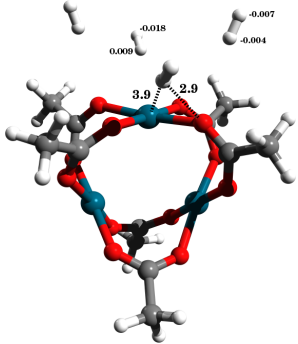
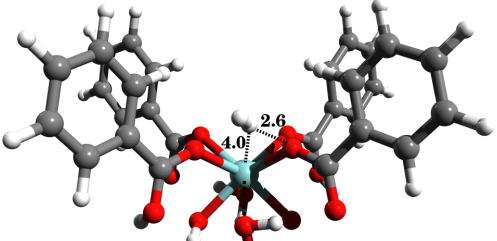
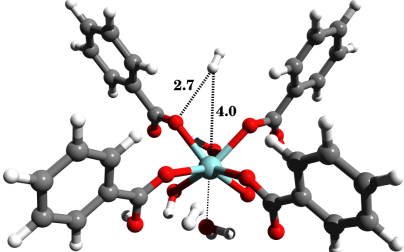
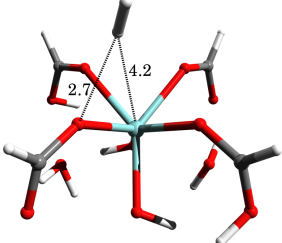
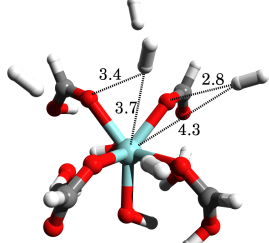
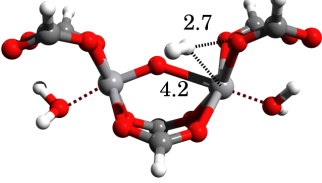
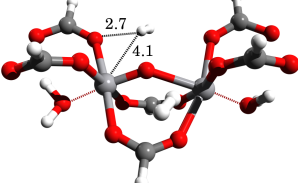
Figure S1. PM6 results of adsorption positions per adsorption centre “x”, adsorption energies (E_{ads}^x) and interaction distances ($M \cdots H_2$ Å) obtained for each IBU.

Nº	Simulated IBU (MOF)	Adsorption Positions per sub-IBU (Adsorption Energy kJ/mol)		
I	 (UiO-66)	 $n_a=1$ $S_a=ZrO_4$ ($E_{ads}^a = -15.9$ kcal/mol)	 $n_a=1$ $S_a=ZrO_4$ ($E_{ads}^a = -1.7$ kcal/mol)	 $n_b=1$ $S_b=\mu_3-OH$ ($E_{ads}^b = -7.1$ kcal/mol)
II	 (MIL-47)	 $n_a=1$ $S_a=VO_4-O-VO_4$ ($E_{ads}^a = -10.9$ kcal/mol)	 $n_a=1$ $S_a=VO_4-O-VO_4$ ($E_{ads}^a = -9.2$ kcal/mol)	
III	 (MFU-1b)	 $n_a=1$ $S_a=Co_3$ ($E_{ads}^a = -35.6$ kcal/mol)	 $n_a=1$ $S_a=Co_3$ ($E_{ads}^a = -15.5$ kcal/mol)	 $n_b=1$ $S_b=CoN_3$ ($E_{ads}^b = -46.4$ kcal/mol)
IV	 PdO ₄ M ₃	 $n_a=1$ $S_a=PdO_4$ ($E_{ads}^a = -23.0$ kcal/mol)	 $n_b=1$ $S_b=Pd_3$ ($E_{ads}^b = -18.4$ kcal/mol)	

Ab initio results

As explained in the main text, the evaluation of the H₂ adsorption at the MP2 or RI-MP2 theoretical levels was done employing small clusters (optimised at UHF level) with further optimisation of the coordinates of the H₂ molecules. The final positions and orientations of the adsorbed molecules are presented in Figure S2.

Figure S2. Adsorption positions per adsorption centre, adsorption energies ($E_{ads+BSSE}^x$, kJ/mol) and interaction distances (Å) obtained on each sub-IBU at RI-MP2/def2-TZVP + SD(28,MWB) ECP for Zr and Pd atoms (entry I and II) and MP2/6-31++G(d,p)//MP2/6-31G + LanL2DZ for Zr atoms (entry IIa, III and IV) theoretical levels.

N ^o	H ₂ molecules adsorbed per sub-IBU "x" and Adsorption Energies, $E_{ads+BSSE}^x$ (kJ·mol ⁻¹)	
I	 <p data-bbox="391 682 623 741">$S_a=3$, PdO₄ $n_a=1$, $E_{ads+BSSE}^a=-2.36$</p>	 <p data-bbox="1094 703 1256 762">$S_a=3$, PdO₄ $n_a=4$, $E_{ads+BSSE}^a=-8.60$</p>
II	 <p data-bbox="391 1039 623 1098">$S_a=6$, ZnO₄ $n_a=1$, $E_{ads+BSSE}^a=-1.75$</p>	 <p data-bbox="1094 1039 1256 1098">$S_a=6$, ZnO₄ $n_a=1$, $E_{ads+BSSE}^a=-4.00$</p>
IIa	 <p data-bbox="391 1354 623 1413">$S_a=6$, ZnO₄ $n_a=1$, $E_{ads+BSSE}^a=-2.38$</p>	 <p data-bbox="1094 1354 1256 1413">$S_a=6$, ZnO₄ $n_a=5$, $E_{ads+BSSE}^a=-11.01$</p>
III	 <p data-bbox="391 1627 623 1686">$S_a=$ rod type, VO₄-O-VO₄ $n_a=1$, $E_{ads+BSSE}^a=-2.80$</p>	 <p data-bbox="1094 1627 1256 1686">$S_a=$ rod type, VO₄-O-VO₄ $n_a=2$, $E_{ads+BSSE}^a=-2.18$</p>



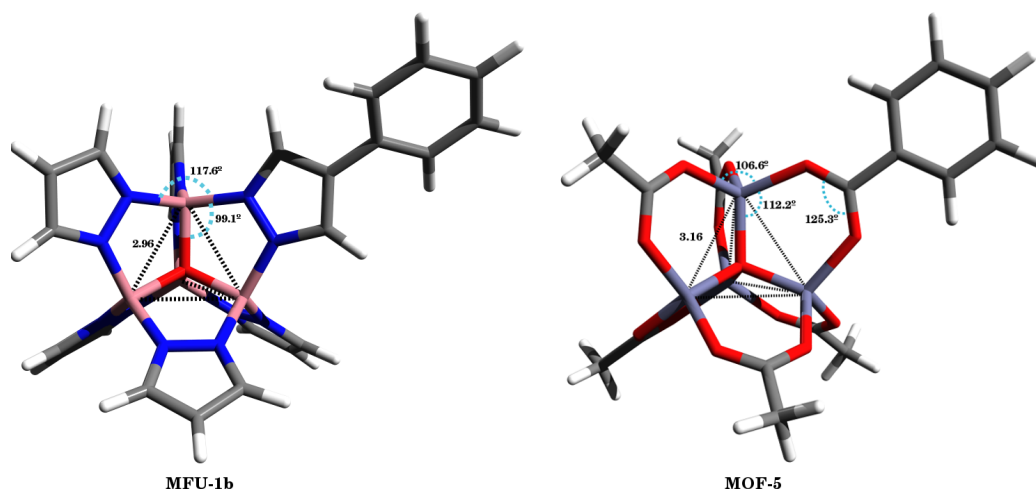
To our knowledge there is not experimental studies focused on the evaluation of the selectivity of adsorption in the selected MOFs. However, some insights regarding to the effect of the presence of solvent molecules can be extracted from the experimental reports related with their stabilities. In general words the set of MOFs selected are characterized for a high stability at different conditions of temperature and solvent presence.

UiO-66 is one of the most stable structures synthesized so far. No effects on the crystalline structure were observed after evaluation of stability with different solvents such as water, DMF, benzene and acetone¹. For MIL-47 the experimental information indicates that after solvent evacuation at 573 K the structure keep the crystallinity and does not reabsorb atmospheric water².

Similar results were reported for the MFU-1 whose stability was evaluated at different ratios of ethanol:water and for long-time exposure at ambient conditions³. The IBU evaluated in the study corresponds to a modification of the original IBU which could lead to instabilities of the framework, however the geometry optimization done does not indicate critical problems to achieve an stable structure.

S3. Comparison between isotopologic IBUs of MFU-1 and MOF-5.

Figure S3. Isotopologic IBUs corresponding to MFU-1b and MOF-5.



S4. Total energies as a sum of adsorption per centres

Equation (2) in the manuscript indicates that the adsorption energies can be obtained by summation of the adsorption at the small clusters. This assumes that the small clusters are representative of the IBU and, eventually, the unit cell, and such assumption has been carefully checked. We show here two cases (UiO-66 and MIL-88) in which we make no assumptions and compare with the approximated value following equation (2). For this task, instead of using the demanding methodology used in the manuscript, we use a HF/6-31G methodology.

UiO-66. (IBU I)

Table S5. Adsorption energies (kJ/mol) obtained at HF/6-31G level at $n_a=5$ and $n_{max}=30$ for the small cluster and the IBU of UiO-66.

	Small cluster	Total IBU		
	$n_a=1$	$n_a=1$	$n_a=5$	$n_{max}=30$
E_{ads}	-2.31	-1.84	-4.92	-29.24
$E_{ads + BSSE}$	-0.75	-0.80	-1.83	-11.07
E_{ads}/n	-	-	-0.37	-0.37

The adsorption energies, BSSE corrected, reported in Table S5 for the saturation of the adsorption centre ZrO_4 , $n_a=5$, is -1.83 kJ/mol. Given that the IBU has six similar centres, well defined and oriented toward different directions, the adsorption energy should reach a value of six times (-10.98 kJ/mol) the energy obtained for one centre. The calculated value presented in Table S5, -11.07 kJ/mol, confirms the low effect of repulsion between molecules adsorbed on different adsorption centres. Moreover, the value of adsorption energy per molecule, $E_{ads}/n = -0.37$ kJ/mol is conserved in both loadings ($n_a=5$, $n_{max}=30$).

MIL-88A(Pd). (IBU IV)

Table S6. Adsorption energies (kJ/mol) obtained at HF/6-31G level at $n_a=4$ and $n_{max}=12$ for IBU of MIL-88.

	$n_a=4$	$N_{max}=12$
E_{ads}	-6.43	-19.07
$E_{ads + BSSE}$	-1.98	-5.82
E_{ads}/n	-0.50	-0.49

In a similar way, the IBU of MIL-88A(Pd) presents values of adsorption energy per centre, $n_a=4$, of -1.98 kJ/mol and at saturation, $n_{max}=12$, of -5.98 kJ/mol (Table S6). The latter presents a slight deviation (0.12 kJ/mol) from the expected value of the multiplication by three (number of adsorption centres “a”, -5.94 kJ/mol) of the former. The small difference of this values and the conservation of the adsorption energy per molecule adsorbed (-0.49 kJ/mol) indicates, as the case above, a low effect of the simultaneous adsorption over different adsorption centres.

S5. Calculation of volumetric and gravimetric hydrogen uptakes.

Derivation of equations 3 and 4.

Equation 3:

From the definitions of gravimetric and volumetric storage:

$$x\% = \frac{m_{H_2}}{m_{H_2} + M(MOF)_{uc}} \cdot 100 \quad (S1)$$

and

$$\rho_{H_2} = \frac{m_{H_2}}{V_{uc}} \quad (S2)$$

it is possible to express each equation as a function of the mass of hydrogen adsorbed per unit cell, m_{H_2} , $M(MOF)_{uc}$ as the mass of the MOF unit cell, and V_{uc} as the MOF unit cell volume, with this volume also being the volume of the compressed hydrogen. Doing so and equalling the resulting expressions we can obtain:

$$\rho_{H_2} \cdot V_{uc} = \frac{M(MOF)_{uc} \cdot x\%}{100 - x\%} \quad (S3)$$

After regrouping terms, it is possible to obtain an expression which relates the MOF properties (unit cell mass and volume, ρ_{MOF}) with the gravimetric uptake ($x\%$) and the volumetric density (ρ_{H_2}):

$$\rho_{H_2} = \frac{M(MOF)_{uc}}{V_{uc}} \cdot \left(\frac{x\%}{100 - x\%} \right) \quad (S4)$$

Which expressed in the appropriate units gives:

$$\rho_{H_2} (g/L) = \rho_{MOF} \left(\frac{g}{cm^3} \right) \cdot \left(\frac{x\%}{100 - x\%} \right) \cdot 1000 \quad (S5)$$

Equation 4:

The previous equation (S1) for the gravimetric uptake can be divided (numerator and denominator) by the unit cell volume and we obtain:

$$x\% = \frac{\frac{m_{H_2}}{V_{uc}}}{\frac{m_{H_2}}{V_{uc}} + \frac{M(MOF)_{uc}}{V_{uc}}} \cdot 100 \quad (S6)$$

As discussed in the paper, from the microscopic point of view it is useful to express the storage capacity as a function of “n”, the number of H₂ molecules adsorbed per metal atom, which, when multiplied by the metal atoms density, “m”, gives the amount of hydrogen adsorbed per volume unit, and hence we obtain:

$$x\% = \frac{m \cdot n \cdot M(H_2)}{m \cdot n \cdot M(H_2) + \rho_{MOF}} \cdot 100 \quad (S7)$$

Using the units of: number of metal atoms per Å³ for 'm'; number of hydrogen molecules adsorbed per metal atom for 'n'; and atomic mass units for the mass of a hydrogen molecule (2.014 a.m.u); and with the following conversion factor:

$$\frac{a.m.u.}{\text{\AA}^3} = \frac{a.m.u.}{\text{\AA}^3} \cdot \frac{1.66 \times 10^{-24} \text{ g}}{1 a.m.u.} \cdot \frac{1 \text{\AA}^3}{1.0 \times 10^{-24} \text{ cm}^3} = 1.66 \cdot \frac{\text{g}}{\text{cm}^3}; \quad \rho\left(\frac{a.m.u.}{\text{\AA}^3}\right) = \frac{1}{1.66} \cdot \rho\left(\frac{\text{g}}{\text{cm}^3}\right) \quad (\text{S8})$$

We obtain equation 4:

$$x\% = \frac{m \cdot n}{m \cdot n + \frac{\rho_{MOF}(\text{g/cm}^3)}{1.66 \cdot 2.014}} \cdot 100 \quad (\text{S9})$$

In a compact form the equation 4 presents the factor 3.343.

S6. Useful MOF densities for hydrogen storage.

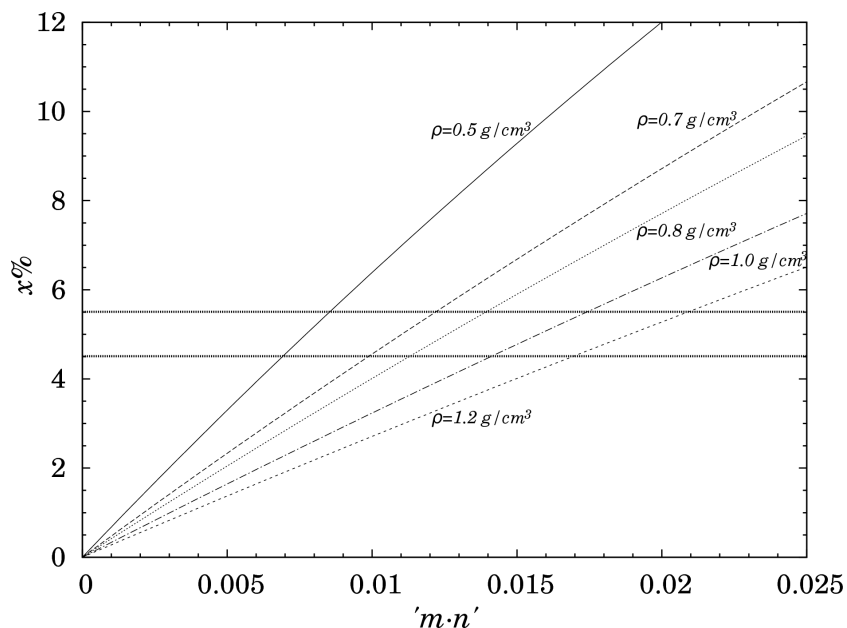


Figure S3. Gravimetric uptake ($x\%$) as a function of ' $m \cdot n$ ' according to equation 4 for different values of MOF densities (g/cm^3). Horizontal lines indicate the gravimetric targets for 2010 (4.5 %) and 2015 (5.5%).

From equation 4, plotted in Figure S3, in which the gravimetric uptake is represented as a function of the product ' $m \cdot n$ ', it is possible to estimate the effect of the MOF density on the gravimetric uptakes. Values of ' $m \cdot n$ ' up to 0.012 seem plausible within currently synthesised MOFs, but we depict the above graph up to values of 0.025 that might be attainable in future materials. Figure S3 shows that materials with low density are preferred. If, together with this result, we recall that Figure 2 indicates the negative impact of low densities in volumetric uptakes, then we can envisage that the “optimum” MOF density should take into account these two opposite trends.

It is not the purpose of this study to make an accurate estimation of the optimum density that a MOF should attain for hydrogen storage, but, if we use our estimation that MOFs reaching values of ' $m \cdot n$ ' around 0.025 can be synthesised in the future, then MOFs with densities between 0.7-1.0 g/cm^3 should be able to reach the commercial targets.

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