# Quantum-chemistry calculations of hydrogen adsorption in MOF–5.

## Electronic Supplementary Information.

## 1. Periodic calculation at PM6 theoretical level.

**Table S1.** Structural parameters (Å) for the MOF-5 unit cell reported experimentally[1] and calculated with PM6.

| Parameters | Experimental | Calculated (PM6) |
|---|---|---|
| Lattice parameter (*a*) | 25.67 | 26.08 |
| Zn-Zn distance | 3.160 | 3.135 |
| C-C (ring) distance | 1.39- 1.46 | 1.39 – 1.40 |
| O-C-O angle | 125º | 126º |
| H-H intramolecular distance | 0.741[a] | 0.763 |

[a] Gas phase distance. Reference 33 in main paper.

**Table S2.** $E(MOF-nH_2)$, $E_{ads}$ y $E_{ads/n}$ (kcal/mol) calculated with PM6 for MOF-5. The number of hydrogen molecules in the system is 16 (cluster and periodic, on a same IBU) and 128 (periodic, 16 per each of the 8 IBUs).

| | n | | |
|---|---|---|---|
| | 16 (cluster) | 16 (periodic)[a] | 128 (periodic) |
| $E_{MOF-nH_2}$ | -1231.9 | -5631.8 | -8656.8 |
| $E_{ads}$ | -20.2 | -21.5 | -164.5 |
| $E_{ads}/n$ | -1.3 | -1.3 | -1.3 |

[a] See Table 4, main manuscript.

The results of periodic calculations with high loadings (n=16×8=128) were compared with the previous calculation (periodic, n=16), and with a calculation without periodic boundary conditions (cluster, n=16), in order to test the dependence of the PM6 results with the model employed (Table S2). From the values reported in Table S2 it can be observed the total similarity between the adsorption energies, coincident at -1.3 kcal/mol on a 'per hydrogen molecule' basis. This indicates that the loading at one IBU can be extrapolated to eight IBUs (full unit cell), and that the IBU-cluster (Figure S1a) is as valid as the periodic model for studying the hydrogen adsorption.

## 2. Adsorption geometries of $H_2$ on the IBU cluster of MOF-5.

Once we found a stable configuration of how 16 hydrogen molecules optimize their physisorbed positions around the IBU, an effort was made in order to check whether alternative conformations

could also lead to an equally stable adsorption energy. We have tried several options of which we report only one possible alternative for a stable configuration. This new configuration is called geometry-2, whilst the previously found conformation is here called geometry-1.

Before getting into numerical details, we outline the main principles that drive the adsorption of hydrogen on an IBU belonging to MOF-5. Zn is the main attractor of hydrogen molecules and, as such, a stable adsorption geometry will be dictated, among other factors, by short $Zn$-$H_2$ distances, and adequate overlap between the respective molecular orbitals. Basically, two stable locations for hydrogen exist, these being called $MO_3$ and $M_3$ in the main text. If one $H_2$ molecule adsorbs at $MO_3$, it locates on top of the Zn atom, but if more than one have to share such location, they have to optimise their proximity (and orbital overlap) with the Zn atom and their intermolecular repulsions. In particular -and this is one of the findings of the present study-, a particularly stable arrangement occurs when three $H_2$ molecules adsorb at a $MO_3$ site, with each locating at the free space between the O-Zn-O atoms.

A different case occurs at the $M_3$ sites, where three Zn atoms are equally accessible, although without a proper orbital overlap with the interacting $H_2$ molecule/s. Our new found conformation, called geometry-2 (see Figure S1c), differs precisely in the way hydrogen interacts with the $M_3$ site. Instead of one hydrogen molecule interacting equally (equidistant) with the three Zn atoms forming a face of the $Zn_4$ tetrahedron (which occurs in geometry-1, Figure S1b), three $H_2$ molecules interact equally, and more weakly, with each of such three Zn atoms. Obviously, this fact leaves less available space for the molecules interacting at the $MO_3$ position, which results in only one hydrogen molecule (instead of the three of geometry-1) interacting with the $MO_3$ site, which then occupies the top of the site.

The values of $E_{ads}$, $E_{ads}/n$ and $E_{ads(i)}$ calculated for each geometry are reported in Table S3. From the results it is observed that the $E_{ads}$ and $E_{ads}/n$ with geometry-1 and geometry-2 are similar. Differences between the two adsorption conformations can be observed on a more detailed analysis of the adsorption energies of each individual hydrogen molecules, which were calculated according to equation 2 in the main text. The relative strength of each value can be interpreted according to the basic features outlined above.

For example, the adsorption energy at the $MO_3$ site is stronger in geometry-2 than in geometry-1 as only one molecule competes for the Zn site in geometry-2 compared to three molecules in geometry-1, and hence the respective values of -3.4 and -1.8 kcal/mol (Table S3). The stronger adsorption energy at the $M_3$ site in geometry-2 (-0.8 kcal/mol) than in geometry-1 (-0.6 kcal/mol) is due to the different respective orientations, with hydrogen molecules closer to the Zn atom in geometry-2 (3.4 Å) than in geometry-1 (3.6 Å), although other aspects such as orbital overlap may also contribute.
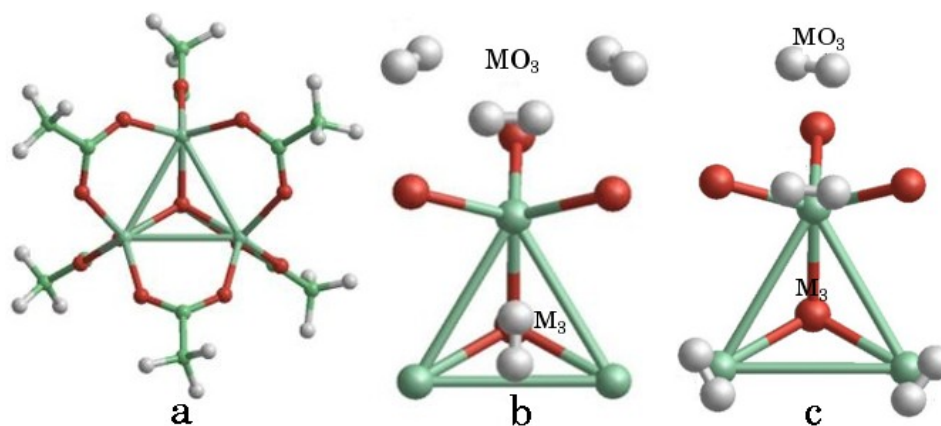
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**Figure S1. a.** Inorganic building unit (IBU) cluster, $Zn_4O(CH_3COO)_6$; **b.** Adsorption geometry-1, with three $H_2$ molecules adsorbed at each $MO_3$ site (only one showed) and one $H_2$ molecule adsorbed at each $M_3$ site (only one showed); and **c.** Adsorption geometry-2, with one $H_2$ molecule adsorbed at each $MO_3$ site (only one showed) and three $H_2$ molecules adsorbed at each $M_3$ site (only one showed). **b. and c.** Only four hydrogen molecules (out of 16 adsorbed at the IBU) are shown.

**Table S3.** Total energies $E_{MOF-nH2}$, $E_{ads}$, $E_{ads}/n$ and $E_{ads(i)}$ (kcal/mol) and shortest H-Zn distance (Å) calculated with PM6 for each geometry conformation. 16 hydrogen molecules are adsorbed at the IBU cluster.

|  | Geometry-1 | Geometry-2 |
|---|---|---|
| $E_{MOF-nH2}$ | -1231.93 | -1232.03 |
| $E_{ads}$ | -20.23 | -20.33 |
| $E_{ads}/n$ | -1.26 | -1.27 |
| $E_{ads}$ ($MO_3$) | -1.75 | -3.38 |
| $E_{ads}$ ($M_3$) | -0.57 | -0.82 |
| H-Zn ($MO_3$) | 3.1 | 2.5 |
| H-Zn ($M_3$) | 3.6 | 3.4 |

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## 2. H$_2$···H$_2$ interactions and H$_2$ binding at PM6 level.

In order to evaluate the performance of PM6 in the simulation of the intermolecular interaction between hydrogen molecules and the H-H bond dissociation, energy profiles were calculated and compared with reported data calculated with electronic methods. Figure S2a shows the energy profiles for the horizontal (--) intermolecular H$_2$···H$_2$ approach calculated with PM6 and HF/MP4[3]. The minimum energy coordinate obtained with PM6 was slightly different in energy and distance (-0.00136 eV, 3.7 Å) than that calculated with MP4 (-0.00095 eV, 3.8 Å). Although the minima obtained with PM6 gives a good correlation with the calculated at MP4 level. The profiles differ in that an unrealistic behaviour at short distances (about 2.7 Å) is found with the PM6 method, where an energy minimum is found (0.00021 eV).

Regarding the perpendicular interaction (Figure S2b), larger differences are observed. Equilibrium distances of 3.4 and 2.9 Å are found for MP4 and PM6 respectively, while the energies are -0.00330 and -0.00088 eV respectively. Therefore, the MP4 profile shows a minimum with lower energy and longer H$_2$···H$_2$ distance than that of the PM6 profile. In the context of this work these results can lead to an underestimation of the repulsion between hydrogen molecules when many molecules are adsorbed on the MOF-5 surface and whose interactions are not parallel. This contributes to the overestimation of the physisorption energy observed.

Figure S2c shows the energy profile for the dissociation of the hydrogen molecule. A minimum at 0.76 Å is found, in reasonable agreement with experimental and other theoretical methods (0.74 Å)[2]. In terms of energies, the total energy for the hydrogen molecule (-28.13 eV) and the convergence value at long distance (-22.50 eV) calculated with PM6 are higher than the experimental values (-31.95 eV and -27.21 eV) respectively. However, the behaviour of the potential energy curve obtained with PM6 (UHF) are qualitatively comparable with results obtained with more sophisticated methodologies as CCSD(T). Although the binding energy (BE) calculated with PM6 (UHF) (5.63 eV) was approximately 1 eV higher than that reported from CCSD(T) calculations (4.74 eV), the shape of the curves are similar. At the H-H bond distances involved in weak physisorption, the PM6 results are of sufficient accuracy.
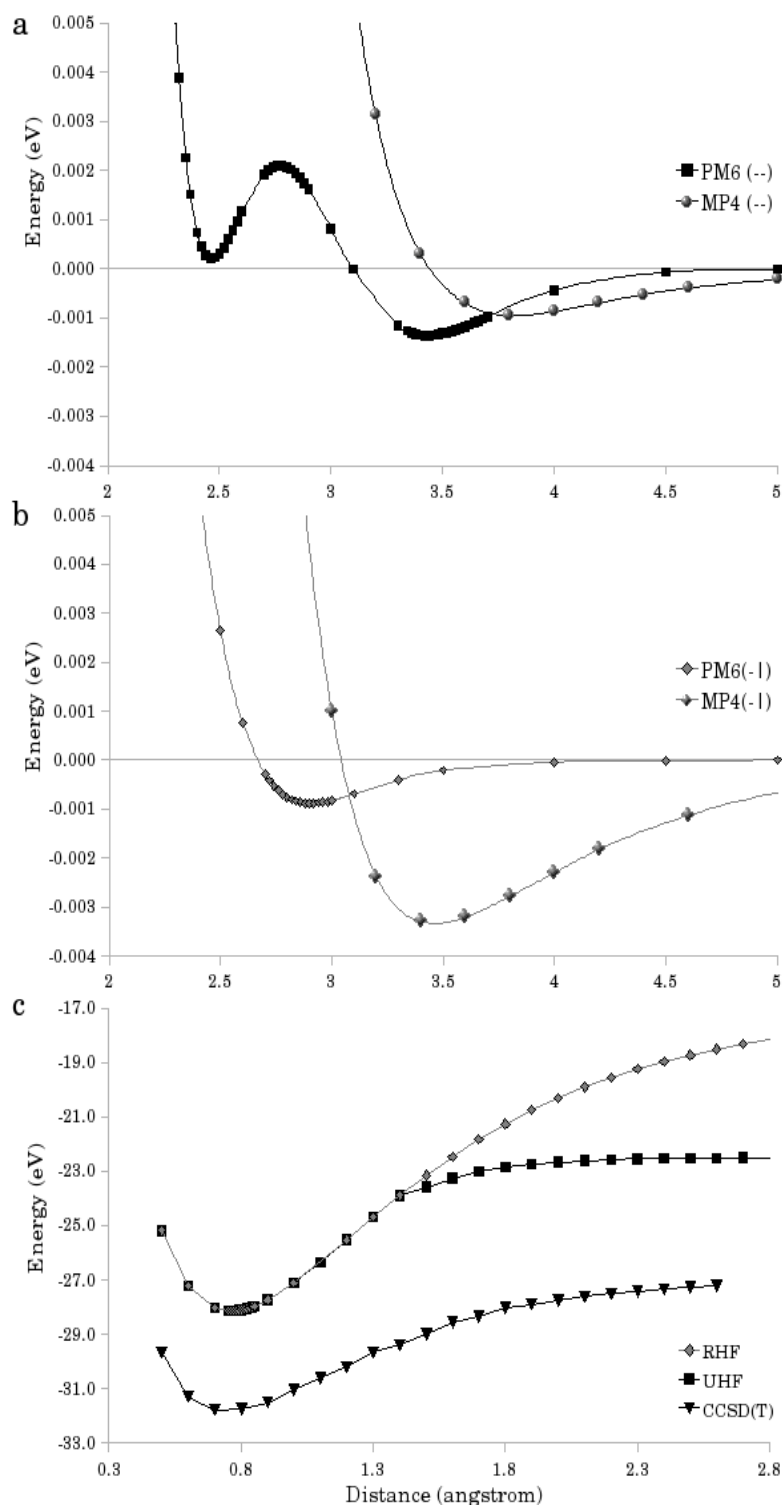
**Figure S2. a**, **b.** Energy profiles calculated with PM6 and compared with values reported with HF/MP4[3] for the interaction between two hydrogen molecules in horizontal (--) and perpendicular(-|) orientations. **c.** Energy profile for the H-H dissociation calculated with PM6 restricted (RHF) and

unrestricted (UHF) (BE=5.6 eV, 0.76 Å) and comparison with CCSD(T) (BE=4.47 eV, 0.74 Å) calculations[2].

## 3. Hartree-Fock (HF) and MP2 results with and without counterpoise.

**Table S4.** Calculated energies for the system $H_2$-MOF-5, where the IBU cluster (Figure 3a) and 16 hydrogen molecules have been considered. [sp] stands for single point, [cpoise] stands for counterpoise (used to calculate the basis set superposition error). $E$(MP2-sp) is calculated as the difference between the full system and the sum of the parts at the MP2 level. $E$(HF-sp) is the same as before but for HF level of theory. $E$(MP2-cpoise) is the basis set superposition error corrected energy difference, calculated as explained in the text.

| System | Theory Level/Basis | Energy (a.u.) |
|---|---|---|
| (16) $H_2$/MOF-5 sp | HF/6-31G | -8566.2770 |
| | MP2/6-31G | -8570.1300 |
| | HF/6-31G(d,p) | -8566.9400 |
| | MP2/6-31G(d,p) | -8572.4400 |
| | HF/6-31G++(d,p) | -8567.0400 |
| | MP2/6-31G++(d,p) | -8572.7297 |
| (16) $H_2$ sp | HF/6-31G | -18.0280 |
| | MP2/6-31G | -18.3060 |
| (16) $H_2$ cpoise | HF/6-31G | -18.0296 |
| | MP2/6-31G | -18.3087 |
| | HF/6-31G(d,p) | -18.1021 |
| | MP2/6-31G(d,p) | -18.5200 |
| | HF/6-31G++(d,p) | -18.1053 |
| | MP2/6-31G++(d,p) | -18.5352 |
| MOF-5 sp | HF/6-31G | -8548.2440 |
| | MP2/6-31G | -8551.8050 |
| MOF-5 cpoise | HF/6-31G | -8548.2450 |
| | MP2/6-31G | -8551.8180 |
| | HF/6-31G(d,p) | -8548.8400 |
| | MP2/6-31G(d,p) | -8553.9091 |
| | HF/6-31G++(d,p) | -8548.9397 |
| | MP2/6-31G++(d,p) | -8554.1798 |
| E (MP2-sp) | -11.537 (kcal/mol) | |
| E (HF/6-31G-sp) | -3.198 (kcal/mol) | |
| E (HF/6-31G-cpoise) | -1.506 (kcal/mol) | |
| E (MP2/6-31G-cpoise) | -2.204 (kcal/mol) | |
| E (MP2/6-31G(d,p)-cpoise) | -5.273 (kcal/mol) | |
| E (MP2/6-31G++(d,p)-cpoise) | -9.158 (kcal/mol) | |

# References

1   H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, Nature, 1999, **402**, 276-279.
2   A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, J. Phys. Chem. A, 2005, **109**, 11006-11014.
3   S. Tsuzuki, T. Uchimaru, and K. Tanabe, J. Mol. Struct. (Teochem), 1993, **280**, 273-281.