Supporting Information for

Atomistic insight in the flexibility and heat transport properties of the stimuli-responsive metal-organic framework MIL-53(Al) for water-adsorption applications using molecular simulations

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S1 Force field

The quantum mechanical potential energy surface (PES) is approximated by a sum of analytical functions of the nuclear coordinates that describe the covalent (cov) and noncovalent (noncov) interactions. The latter are composed of electrostatic and van der Waals interactions.

$$V^{FF} = \underbrace{V_{bond} + V_{bend} + V_{oopd} + V_{torsion} + V_{cross}}_{V_{cov}} + \underbrace{V_{ei} + V_{vdW}}_{V_{noncov}}.$$
(S1.1)

S1.1 Covalent interactions

The covalent interactions – which mimic the chemical bonds between the atoms – are approximated by different terms as a function of the internal coordinates (bonds, bends, out-of-plane distances, and dihedrals). The unknown force field parameters are derived using the QuickFF protocol.¹ We use an extended version² to derive these parameters from a periodic structure and to include anharmonic bond and bend terms.³ The anharmonic bond and bend terms are given by:

$$V_{\text{bond}}^{ij} = \frac{K_{ij}}{2} (r_{ij} - r_{0,ij})^2 \left[1 - \alpha (r_{ij} - r_{0,ij}) + \frac{7}{12} \cdot \alpha^2 \cdot (r_{ij} - r_{0,ij})^2 \right],$$
(S1.2)
$$V_{\text{bend}}^{ijk} = \frac{K_{ijk}}{2} \left(\theta_{ijk} - \theta_{0,ijk} \right)^2 \left[1 - a_1 \left(\theta_{ijk} - \theta_{0,ijk} \right) + a_2 \cdot \left(\theta_{ijk} - \theta_{0,ijk} \right)^2 - a_3 \cdot \left(\theta_{ijk} - \theta_{0,ijk} \right)^3 + a_4 \left(\theta_{ijk} - \theta_{0,ijk} \right)^4 \right],$$
(S1.3)

with $\alpha = 2.55 \text{ Å}^{-1}$, $a_1 = 0.014 \text{ deg}^{-1}$, $a_2 = 5.6 \cdot 10^{-5} \text{ deg}^{-2}$, $a_3 = 7 \cdot 10^{-7} \text{ deg}^{-3}$, and $a_4 = 2.2 \cdot 10^{-8} \text{ deg}^{-4}$. We also add cross terms between the bonds and bends to improve the correspondence with the first-principles data.² The included cross terms are:

- angle stretch-stretch terms (ASS) between neighbouring bonds, *i.e.* part of the same angle
- angle stretch-angle terms (ASA).

The mathematical expression of these terms is given by

$$V_{\rm ASS}^{ijk} = K_{ijk}^{\rm ASS} \left(r_{ij} - r_{0,ij} \right) \left(r_{jk} - r_{0,jk} \right)$$
(S1.4)

$$V_{\text{ASA}}^{ijk} = \left[K_{ijk}^{\text{ASA1}}\left(r_{ij} - r_{0,ij}\right) + K_{ijk}^{\text{ASA2}}\left(r_{jk} - r_{0,jk}\right)\right]\left(\theta_{ijk} - \theta_{0,ijk}\right).$$
(S1.5)

The out-of-plane distances are described using a harmonic potential:

$$V_{oopd}^{ijkl} = \frac{K_{ijkl}}{2} \left(d_{ijkl} - d_{0,ijkl} \right)^2.$$
(S1.6)

This is a four-atom interaction, in which the internal coordinate is the distance between the central atom and the plane determined by its three neighbours. The fourth covalent term is the dihedral energy term. Here, a cosine term is used as a function of the dihedral angle, including the multiplicity m_{ϕ} of the dihedral angle:

$$V_{torsion}^{ijkl} = \frac{K_{ijkl}}{2} \left[1 - \cos(m_{\phi}(\phi_{ijkl} - \phi_{0,ijkl})) \right].$$
(S1.7)

The unknown parameters in all terms (force constants, rest values, and multiplicities) in the covalent energy expression can be estimated directly with QuickFF.

S1.2 Electrostatic interactions

The electrostatic interactions are modeled by a Coulomb interaction between Gaussian charge distributions,⁴ which allows to include all pairwise interactions. The atomic charges q_i are derived with the Minimal Basis Iterative Stockholder (MBIS) partitioning scheme.⁵

$$V_{ei} = \frac{1}{2} \sum_{\substack{i,j=1\\(i\neq j)}} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \operatorname{erf}\left(\frac{r_{ij}}{d_{ij}}\right)$$
(S1.8)

Gaussian charge distributions are used with a total charge q_i and radius d_i , centered on atom *i*. The mixed radius of the Gaussian charges,⁴ d_{ij} , is given by $\sqrt{d_i^2 + d_j^2}$. The interaction depends on the distance r_{ij} between the two atoms.

S1.3 Van der Waals interactions

The van der Waals interactions are described by the MM3-Buckingham model^{6,7} up to a finite cutoff (12 Å) and are supplemented with tail corrections.⁸

$$V_{vdW} = \epsilon_{ij} \left[1.84 \cdot 10^5 \exp\left(-12\frac{r}{\sigma_{ij}}\right) - 2.25 \left(\frac{\sigma_{ij}}{r}\right)^6 \right]$$
(S1.9)

The two parameters σ_{ij} and ϵ_{ij} are the equilibrium distance and the well depth of the potential. These parameters are typically determined with empirical mixing rules for the interaction between atom *i* and atom *j*:

$$\sigma_{ij} = \sigma_i + \sigma_j$$
 and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ (S1.10)

and were taken from the MM3 force field, as tabulated in Ref. 7. In MM3, the 1–2 and 1–3 interactions are discarded to avoid a strong overestimation of the repulsion terms.

S1.4 q-TIP4P/F

In the q-TIP4P/F force field,⁹ which is used to describe the water molecules in the MIL-53(Al) framework, the O–H stretch is described by a quartic potential:

$$V_{OH} = D_r \left[\alpha_r^2 \left(r - r_{\rm eq} \right)^2 - \alpha_r^3 \left(r - r_{\rm eq} \right)^3 + \frac{7}{12} \alpha_r^4 \left(r - r_{\rm eq} \right)^4 \right],$$
(S1.11)

with $D_r = 116.09 \text{ kcal mol}^{-1}$, $\alpha_r = 2.287 \text{ Å}^{-1}$, and $r_{eq} = 0.9419 \text{ Å}$. The H–O–H bond angle is described by a simple harmonic potential:

$$V_{HOH} = \frac{1}{2} k_{\theta} (\theta - \theta_{eq})^2, \qquad (S1.12)$$

with $k_{\theta} = 87.85$ kcal mol⁻¹ rad⁻² and $\theta_{eq} = 107.4$ deg. The position of the additional interaction site M is determined by the following geometric expression:

$$\mathbf{r}_{M} = \gamma \, \mathbf{r}_{O} + \frac{1-\gamma}{2} \left(\mathbf{r}_{H_{1}} + \mathbf{r}_{H_{2}} \right), \tag{S1.13}$$

with $\gamma = 0.73612$. This interaction site is given a charge of $q_M = -1.1128 e$, whereas the hydrogen atoms possess a positive charge of $|q_M|/2$. The oxygen atoms do not bear a charge, but are subjected to Lennard-Jones interactions:

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \qquad (S1.14)$$

with $\varepsilon = 0.1852$ kcal mol⁻¹ and $\sigma = 3.1589$ Å. Given that the q-TIP4P/F force field only provides a mean-field description of polarization effects, since it lacks an explicit treatment of electronic polarization, one should also ensure its ability to capture the phenomenon of hydrogen bonding by means of this mean-field description. A first indication that this is indeed the case stems from the radial distribution functions (RDFs) in Ref. 9, which show an excellent agreement between the experimental RDFs and those obtained using the q-TIP4P/F force field. Furthermore, we also performed *ab initio* PIMD simulations at a PBE+D3(BJ) level of theory – which do explicitly account for electronic polarization – and compared the hydrogen bond probabilities of the bulk water molecules to those obtained using the q-TIP4P/F force field. The result is shown in Figure S1 for a geometric hydrogen bonding criterion (*i.e.* O–H distance smaller than 2.5 Å and O–H–O angle between 150 and 180 degrees), yielding once more an excellent agreement.



Figure S1: Probability distribution of the different numbers of hydrogen bonds per water molecule for bulk water, as simulated using 16 bead (N, V, T) PIMD simulations with the q-TIP4P/F force field or the PBE-D3(BJ) functional.

S2 Flexibility of MIL-53(Al)

	Classical MD	PIMD
$N_{\rm H_2O} = 0 \; (\rm np)$	816	825
$N_{\rm H_2O} = 0 \ (\rm lp)$	1456	1463
$N_{\mathrm{H_2O}} = 2.5$	1008	1021
$N_{\rm H_{2}O} = 7.5$	1094	1106
$N_{\rm H_{2}O} = 22.5$	1515	1520

Table S1: Equilibrium volume of MIL-53(Al) (in $Å^3$) for the empty and water-loaded framework, as obtained from classical MD simulations and PIMD simulations.



Figure S2: Pressure profile of MIL-53(Al) as a function of its volume, as obtained from $(N, V, \sigma_a = 0, T)$ PIMD simulations at 300 K.



Figure S3: Symmetrised water density in MIL-53(Al) projected onto the *xz*-plane (perpendicular to *b*-axis), the *xy*-plane (perpendicular to *c*-axis), and the *yz*-plane (perpendicular to *a*-axis) for 22.5 water molecules per unit cell at different volumes. In each figure, a $1 \times 2 \times 1$ supercell is shown, containing 45 water molecules. For the *xy*- and *yz*-plane, only the upper half of the simulation cell is shown, as the bottom half is its symmetrical equivalent.



Figure S4: Probability distribution of the different numbers of hydrogen bonds per water molecule for different water loadings of MIL-53(Al) for a volume of 1510 Å³. The full lines represent the probability distribution of hydrogen bonds formed between adsorbed water molecules, which can be compared to the reference of bulk water (grey line). The dashed lines represent the probability distribution of hydrogen bonds formed between atoms of the framework and the hydrogen atoms of the adsorbed water molecules.

S3 Thermal conductivity of MIL-53(Al)



Figure S5: Definition of the thermal conductivity.



Figure S6: (a) Example of a computed normalized heat current autocorrelation function of MIL-53(Al) (HCACF) ($V = 1500 \text{ Å}^3$, *y*-direction). (b) Running integral of the HCACF ($V = 1500 \text{ Å}^3$), which is used to determine the thermal conductivity.



Figure S7: Conventional unit cell volume distribution in supercell MD simulations.



Figure S8: Absolute thermal conductivity of MIL-53(Al) as a function of the volume at room temperature. The volumes in between the lp and the np phase are mechanically unstable.



Figure S9: VDOS spectra of the different atom types in MIL-53(Al) for a unit cell volume of 800 Å³



Figure S10: VDOS spectra of the different atom types in MIL-53(Al) for a unit cell volume of 1500 ${\rm \AA^3}$

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