# Supporting Information

London Dispersion Governs the Interaction Mechanism of Small Polar and Non-Polar

# Molecules in Metal-Organic Frameworks

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# 1 Simulation Details

# 1.1 Force Field, LFMM Parameters, Charges and Polarizabilities

Force field, Lennard-Jones and LFMM parameters for the MOF framework are taken from ref [2]. Ligands and pillars are described by using the general amber force field (GAFF).<sup>3</sup> Atomic charges have also been reused from our previous work (given in Table S1, naming in Figure S1).<sup>2</sup>

All guest molecules are modelled by using force field and Lennard-Jones parameters from GAFF to achieve consistency with the description of the MOF framework. Atomic charges of the guest molecules were calculated by employing the ChEIPG formalism<sup>4</sup> implemented in Gaussian09 (RevD.01)<sup>5</sup>. In these calculations the TPSSh functional, a TZVP basis and Radii of 1.2 Å (Hydrogen), 1.77 Å (Carbon), 1.55 Å (Nitrogen), 1.52 Å (Oxygen) and 1.82 Å (Chlorine) were used. Resulting charges are given in Table S1. The naming scheme of the MOF is given in Figure S1. Polarizabilities of methane derivates have been calculated using the same Gaussian09 setup with the keyword "Polar". Resulting isotropic polarizabilities are given in Table S2.

Table S1:Atomic charges in elementary charge units used in MD simulations.

MOF <sup>2</sup>			
c1	0.8500		
са	-0.1290		
cb	-0.1150		
сс	0.0520		
cd	-0.1690		
ce	-0.0850		
cn	-0.1080		
h1	0.1410		
hn	0.1480		
n1	-0.3830		
ni	1.0850		
o1	-0.7300		

	CH₄	
ch	-0.5425	
hc	0.1356	
	CHCl₃	
ch	-0.4802	
cl	0.0479	
hc	0.3365	

	$CH_2CI_2$	
ch	-0.4540	
cl	-0.0434	
hc	0.2704	

CH₃CI			
ch -0.4644			
cl	-0.1380		
hc 0.2008			

CCl <sub>4</sub>		
ch -0.6261		
cl	0.1565	

The Antechamber<sup>6</sup> Software package was used to generate charges and force field parameters from the Gaussian calculation output for the guest molecules. Field and configuration files were set up using our own software.<sup>7</sup>

All parameters and input/output files used are included in the published raw data.<sup>1</sup>



Guest	Dipole [D]	Iso. Pol. [Bohr <sup>3</sup> ]	
$CH_4$	0.00	14.31	
CH₃Cl	2.18	22.15	
	1 98	22.21	
	1.50	52.21	
CHCl₃	1.38	43.25	
CCl <sub>4</sub>	0.00	54.65	

Table S2: Dipole moments of guest molecules from Gaussian ESP calculations. Isotropic polarizabilities of methane derivates. Calculation details are given in section 1.1.

Figure S1: Naming scheme of the force field. Top: dabco pillar omitting hydrogens (hn); bottom: ndc linker. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

The extended DL\_POLY Classic<sup>8</sup> code presented in ref [9] was used to perform molecular dynamics (MD) simulations. The code was altered to allow for execution on multiple processors.

### 1.2.1 Productive MD Runs

We present here the default MD setup used throughout this work. Some calculations use slightly different setups, in all these cases only the changed options are mentioned in the corresponding place. Otherwise the following setup was used:

The N $\sigma$ T ensemble was used by applying a Nosé-Hoover thermostat with a relaxation time of 0.1 ps and a Hoover barostat using a relaxation time of 1.0 ps with a target pressure of 1 atm. The Velocity Verlet Integration Method was used.

Van-der-Waals potentials were cut off at 11.5 Å. For the empty structures a cutoff of 10.5 Å was used because DL\_POLY restricts the cutoff to be smaller than half the perpendicular cell-width, which sometimes occurs during simulations of the empty structures. The error between these two cutoffs was evaluated by comparing obtained energies and was found to be insignificant (less than 1 kcal mol<sup>1</sup> per formula unit MOF). The Verlet neighbor list shell width was set to 0.5 Å. Electrostatics were calculated using the Smoothed Particle Mesh Ewald (SPME) method with a precision parameter of 10<sup>6</sup>. The same cutoff value as for the van der Waals potentials was used for the separation of regions in the Ewald sum. The effect of shifting the Lennart-Jones potential to zero at the cutoff is expected to be negligible.<sup>10</sup>

Using a timestep of 0.5 fs the system was equilibrated during the first 1000 steps (meaning forces were capped at 1000 kT/Å), while the entire simulation consists of  $2*10^6$  steps, resulting in a total simulation time of 1 ns. Every 1000 steps statistics and geometries were printed. A 4x4x4 supercell of conformer B of ref [11] containing a total of 4224 atoms (MOF only) was used for simulations.

For simulations using final states of previous runs, the restart mechanism of DL\_POLY was used. If the simulation temperature was changed, velocities were scaled using the "restart scale" option. Otherwise the option "restart noscale" was used. Both use the atomic positions as well as velocities and forces of the final step of the previous simulation to initialize the new simulation. No other information is transferred between subsequent simulations.

Starting configurations for each loading (same for all temperatures) were obtained using the routine described in the following section.

### 1.2.2 Guest Loading – Stepwise Removal Routine

To obtain suitable starting structures for productive MD runs we employed the following "stepwise removal" routine.

We compared the experimental references to the maximum amount of guest molecules that can be loaded into a sphere of radius 4 Å in the open unit cell (alternating linkers, configuration B of ref [11]) using the PackMol<sup>12</sup> code. The sphere was chosen manually to fit into the unit-cell of the **B(op)** conformer. From these numbers we took the maximum loading to be used in MD simulations. In case the MD simulations resulted in too low cell volumes compared to the fully open DFT optimized structure,<sup>11</sup> the maximum loading was increased. In case the MD simulations destroyed the structure due to too large loadings, the maximum loading was decreased.

Starting structures for lower loadings were generated iteratively using the following procedure:

- 1. NoT simulation at 1 K for 2000 steps (including 100 equilibration steps) with a barostat relaxation time of 5.0 ps. Statistics and geometries were printed every 100 steps.
- 2. The final configuration is stored as starting structure for the long simulation run (atomic positions only).
- Removal of every 64<sup>th</sup> guest molecule, resulting in one guest molecule removed from every MOF-void. If no guest molecules remain, exit.
- 4. Insert new structure with lower loading into step 1.

Some simulations needed special setups to maintain system integrity (exploding structures, bondbreaking etc.). All differences to this general setup are given in Section 1.2.5.

#### 1.2.3 Single Guest Molecule MD Simulations

To estimate the internal energy of the guests at various temperatures we ran MD Simulations using the above settings with the following changes.

The guest molecule was placed inside a cubic cell with edge length a = 500 Å. The NVT ensemble was used by employing a Nose-Hoover thermostat with a relaxation time of 10 ps. A total number of 20,000 timesteps equal to 10 ps simulation time was used. Intermolecular electrostatic interactions were switched off. Statistics were printed at every timestep. The last half of the simulation was analyzed to calculate the average internal energy and its standard deviation. This setup basically disables the thermostat for the duration of the simulation, since the temperature of a single molecule is not properly maintainable in a MD simulation. The respective internal energy is however well represented since the initial velocities are assigned by DL\_POLY to exactly reflect the defined temperature. Tests with varying setups also showed no significant deviation of the resulting energies.

#### 1.2.4 MOF Conformer

DUT8-(Ni) exhibits conformational isomerism due to the nonlinearity of the ndc linker. As presented in ref [11] by us and our colleagues, two of them are of relevance for comparison with experimental data. The isomers can be distinguished by defining the direction in which ndc linkers point (up or down) from a Ni<sub>2</sub> unit. The conformer **A** has two Ni<sub>2</sub> units in the unit cell and all linkers on each metal node point either up or down. Conformer **B** has only one metal node in the unit cell and opposing linkers point either up or down. The naming scheme from ref [11] is used throughout this work.



Figure S2: Graphical representation of DUT8-(Ni) conformer **B** in its open form, viewed along the pillar dimension (left) and along ndc linkers (right). Orange arrows represent the two possible closing vectors. Adapted under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

In conformer **B** another conformational isomerism arises when the structure is closed (**cp**). Since two neighboring linkers on one metal node point in opposite directions (up and down), the closing motion

is not the same following the two diagonals of the pore (viewed along the pillar dimension). See Figure S2 for a graphical representation of conformer **B**. The nomenclature used by Petkov et al.<sup>11</sup> assigns to the closed conformer, where stacked linkers are of alternating orientation, the name **B(cl)**<sup>o</sup> and to the one, where stacked linkers are of the same orientation, **B(cl)**<sup>a</sup>. Due to the higher dispersion interaction between linkers in alternating stacking, the conformer **B(cl)**<sup>o</sup> is the thermodynamically preferred conformer.

Our simulations concentrate on conformer **B**, due to its higher stability and the accessible breathing motion. The cell vectors *A* and *B* are defined along the ndc linkers, such that  $\gamma$  angles larger than 90° correspond to the **B(cl)**° conformer and  $\gamma$  angles smaller than 90° correspond to the **B(cl)**° conformer. Our *C* axis follows the nickel atoms between layers, such that it follows the bonding via the dabco pillars.

### 1.2.5 Differing Setups

In the following we collected all deviations of our simulations from the above setup. They were motivated by simulations resulting in decomposition or linker detachment. For clarity we used bullet points for each simulation temperature and sub-points for loadings.

Restarts without further explanation were performed from the final state of the previous calculation (atomic positions and velocities) by scaling velocities using the "restart scale" option of DL\_POLY.

Intermediate temperature simulations (steps of 50 K) were used to slowly heat up the system and avoid rapid expansion, causing the MOF to break. They used only 200,000 steps (a tenth of the full simulation time). Entries reading *"restarted from X K, intermediate X+50 K"* therefore mean that the simulation *X* K was restarted by scaling velocities to *X*+50 K for 200,000 steps and then restarted by scaling velocities to the final temperature.

Preceding NVT simulations used 100.000 steps.

### 1.2.5.1 CH<sub>4</sub>

- 300 K:
  - 3 Molecules: Restarted from 200 K, intermediate 250 K simulation. Restarted using no scaling of velocities and relaxation times of 1.0 ps and 5.0 ps for thermostat and barostat.
- 400 K:
  - 2 Molecules: Restarted from 200 K.
  - o 4 Molecules: Restarted from 300 K, intermediate 350 K simulation.

### 1.2.5.2 CH<sub>3</sub>Cl

- 200 K:
  - 2 Molecules: Preceding 100 K simulation for 200.000 steps.
- 300 K:
  - 2 Molecules: Restarted from 200 K.
- 400 K:
  - 1 Molecule: Restarted from 300 K.
  - $\circ$  2 Molecules: restarted from 300 K, intermediate 350 K simulation.

### 1.2.5.3 CH<sub>2</sub>Cl<sub>2</sub>

- 300 K:
  - 1 and 11 Molecules: Restarted from 200 K.
  - 2 Molecules: Restarted from 200 K with relaxation times of 1.0 ps and 5.0 ps for thermostat and barostat.
- 400 K:
  - 1 and 2 Molecules: Restarted from 300 K, intermediate 350 K simulation. Restarted using no scaling of velocities and relaxation times of 1.0 ps and 5.0 ps for thermostat and barostat.
  - o 11 Molecules: Restarted from 200 K.

### 1.2.5.4 CHCl<sub>3</sub>

Stepwise removal procedure employed 5000 timesteps per iteration.

- 300 K:
  - $\circ$  1 Molecule: Restarted from 200 K with intermediate 250 K simulation.
- 400 K:
  - $\circ$  1 Molecule: Restarted from 300 K with intermediate 350 K simulation.

### 1.2.5.5 CCl<sub>4</sub>

Simulations with 7 molecules added after initial simulations. Stepwise removal procedure therefore starts using 6 molecules.

- 200 K:
  - $\circ$   $\,$  1 Molecule: Preceding 100 K simulation for 200,000 steps.
- 300 K:
  - 1 Molecule: Restarted from 200 K.
  - 2 Molecules: Restarted from 400 K.

- 400 K:
  - $\circ$  1 Molecule: Restarted from 300 K with intermediate 350 K simulation.
  - o from ref [2] 200 K using 10.000 equilibration steps.
  - o 8 Molecules: Restarted from ref [2] 300 K. Intermediate 350 K simulation.

### 1.2.6 MD Analysis

The last 100 frames (equal to 50 ps) of the 1 ns productive MD simulations (see Section 1.2.1) were used for all analysis purposes. A self-written Python library was used for retrieving DL\_POLY outputs.<sup>13</sup> Plots were produced using the matplotlib library.<sup>14</sup> The Jupyter framework<sup>15</sup> and numpy (version 1.16.1) were used extensively. All scripts, notebooks and codes are available in the published raw data.<sup>1</sup>

From the DL\_POLY output, system enthalpies ( $H_{Svs}$ ) and system energies ( $E_{Svs}$ ) can be obtained. For analysis of the individual components we decompose the energy into two parts: The MOF energy  $(E_{MOF})$  and the guest energy ( $E_{Guest}$ ). Both are obtained by calculating single-point energies for the respective parts of the last 100 snapshots. We thereby obtain the MOF-guest interaction ( $E_{\text{Interaction}}$ ) via  $E_{Sys} = E_{MOF} + E_{Guest} + E_{Interaction}$ . Throughout this work we use the relative value  $\Delta E_{Sys}$  by substituting  $E_{\text{MOF}}$  by the relative value with respect to the empty closed MOF ( $\Delta E_{\text{MOF}}(n)$  =  $E_{\text{MOF}}(n) - E_{\text{MOF}}(n = 0)$ , with *n* beeing the number of guest molecules per formula unit MOF). We approximated the adsorption energy by further treatment of  $E_{\text{Guest}}$ . For each guest and relevant temperature, we ran MD simulations using the NVT ensemble with a cubic cell (a = 500 Å, one guest molecule per cell) and no electrostatics for 10 ps. From these simulations we obtained the internal energy of each guest at every relevant temperature ( $U_{\text{Single-Guest}}$ ). Using  $E_{\text{Guest}}(n) = U_{\text{Single-Guest}} *$  $n + E_{Guest-Guest}(n)$ , we derived an approximative guest-guest interaction energy  $E_{Guest-Guest}$ . Combining all the above we approximate the adsorption energy as  $E_{Ads} = E_{Interaction} + E_{Guest-Guest}$ . The interaction and adsorption energy can also be interpreted stepwise by calculating  $\Delta E(n) =$ E(n) - E(n-1). Note that all terms discussed here are functions of the number of guest molecules n and temperature T. Yet we suppressed these here and in the following, to improve the readability. In order to evaluate the contributions of London dispersion and electrostatic interactions we performed further single point calculations. DL\_POLY, separates the intermolecular forces into electrostatic and van-der-Waals (vdW) contributions. The van-der-Waals terms used in this work therefore model mostly the short-ranged London dispersion force (a non-polarizable force field is used). The van-der-Waals potential is modelled using a Lennard-Jones functional form. By disabling the vdW/electrostatics and analyzing the differences to the values of  $E_{Svs}$ ,  $E_{Guest}$  and  $E_{MOF}$  we can therefore, using the equations above, extract the vdW/electrostatic ( $E_{vdW}$  and  $E_{Elstat}$ ) contributions

to  $E_{\text{Guest-Guest}}$  and  $E_{\text{Interaction}}$ . We use the unit of energy "kJ·mol<sub>f.u.</sub>-1". This should be read as "kJ·per mol of Ni<sub>2</sub>(ndc)<sub>2</sub>(dabco)· $\pi$ ", where n is the number of guest molecules as in the equations above. The "mol" therefore references the MOF and not the adsorbed guest. DL\_POLY prints energies in units of kcal mol<sup>-1</sup>. We therefore used a conversion factor of 4.184. By dividing  $E_{\text{Ads}}$  by n we obtained the molar adsorption energy of the guest that can be compared to experimentally obtained values. For the comparison of different guests, we used the relative loading from zero to one as  $n_{\text{rel}} = n/n_{\text{max}}$ . In all plots, error-bars visualize the standard deviation of the corresponding value.

Autocorrelation functions were calculated using the Python library tidynamics.<sup>16</sup> From each guest molecule one bond vector (C-Cl bond if available, otherwise C-H bond) was extracted and converted to fractional coordinates for all analyzed frames (the last 50 ps of each simulation). All autocorrelation functions of one system (n \* 64 in total, because of the 4x4x4 supercell) were then averaged by calculating their mean and standard deviation using numpy.

Temperatures of the entire systems, the MOF and the Guest were calculated a posteriori using the velocities from the DL\_POLY restart file (corresponding to the last frame). The instantaneous temperature was approximated using the formula

$$T = \sum_{i=0}^{N} \frac{m_i * \left(v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2\right)}{k_{\rm B} * (3N - 3)},\tag{1}$$

where N is the number of atoms, m is the mass of the respective atom, v the velocity component in x, y or z direction and  $k_{\rm B}$  is the Boltzmann constant.

### 1.3 MP2 Calculations

MP2 Calculations were performed using Gaussian09 (RevD.01).<sup>5</sup> For preliminary geometry optimizations a TZVP basis set was employed. Subsequent single point calculations employed a Def2QZVPP basis with a counterpoise correction using the two molecules as individual fragments. The resulting interaction energies were compared to the result of a geometry optimization of the MP2 clusters in DL\_POLY.

### 1.4 Dimer DFT-Force Field Comparison

To validate the force field parameters and our setup in terms of van-der-Waals and electrostatic interactions we performed a DFT-FF comparison. For all methane derivates we optimized the respective dimer using DFT in the ADF2019 software.<sup>17</sup> We used the PBE functional with Grimme's D3 dispersion correction<sup>18</sup> and a TZP basis set. Input files are available in the published raw data.<sup>1</sup> We ran geometry optimizations on the dimers so that we obtain dimers with a maximized total dipole moment

(aligned dipole moments of the two molecules). In case of methane and CCl<sub>4</sub> we used the staggered alignment. Using the fragmentation approach of ADF2019 we then decomposed the energy contributions to obtain the dimer formation energy and the dispersion contribution therein. The difference between the two we approximate to be the electrostatic contribution.

We then performed single point calculations on the DFT optimized dimers using our force field setup described above. From the DLPOLY output we directly obtain van-der-Waals and electrostatic energies.

# 2 Experimental References

Experimental results for the maximum amount of guest molecules are available in the cases of  $CH_xCl_{4-x}$ ( $x \in \{0; 1; 2; 3\}$ ).<sup>19,20</sup> See Table S3 for an overview of the experimental maximum loadings. Note that the maximum experimental loadings given in Table S3 are different from the loadings in the adsorption experiments performed for the heats of adsorption. See the main text for details.

Table S3: Experimental references for maximum uptakes of guests in DUT-8(Ni) and values used in this work. Maximum loadings given are in guest molecules per formula unit MOF.

Guest	Max. Loading	References	Used
CH4	16	[20]	20
CH₃Cl	11	[20]	15
$CH_2CI_2$	9	[19]	11
CHCl₃	7	[19]	9
CCl <sub>4</sub>	6	[19]	7

Table S4: Kinetic Diameters of guests.

Guest	Kin. Diam. [Å]	Ref
CH4	3.8	[20]
CH₃CI	4.05	[20]
$CH_2CI_2$	4.7	[19]
CHCl₃	5.47	[19]
CCl <sub>4</sub>	5.83	[20]

Table S5:Melting points (MP) and Boiling points (BP) of methane and its chlorinated derivatives in degree Celsius. Retrieved from PubChem<sup>21</sup> and rounded to integers.

	MP [°C]	BP [°C]
CH <sub>4</sub>	-183	-162
CH₃CI	-98	-24
$CH_2CI_2$	-95	40
CHCl₃	-64	61
CCl <sub>4</sub>	-23	77



Figure S3: Melting (blue) and boiling (red) points of all guests in degree Celsius. Retrieved from PubChem<sup>19</sup> and rounded to integers. Top: Magnitude of the dipole moments; Bottom: Isotropic Polarizability from DFT calculations. See section 1.1. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

### 3 Results

We present necessary simulation results here, to complete argumentations from the main text. For all further plots and the simulation outputs themselves, we refer the interested reader to the published raw data.<sup>1</sup>

A color code is used to distinguish simulation temperatures and symbols. Line shapes distinguish different variables.

### 3.1 Structural

Not all MD simulations resulted in interpretable results. The most common problem occurring is structural decomposition of the MOF framework due to rapidly expanding guest clusters. The expansion of the adsorbed species leads to the dissociation of the oxygen nickel bonds and in turn to the total decomposition of the MOF. In most cases this could be circumvented by applying preliminary MD steps and scaling temperature stepwise. All deviations from the general setup are given in Section 1.2.5. By applying the stepwise removal procedure (see Section 1.2.2 for details), most simulations maintained the intended B(cl)<sup>o</sup> configuration. Especially in the regions of large volume expansion of the MOF, rapid expansion regularly causes "flips" into the **B(cl)**<sup>a</sup> conformer. This flipping is accompanied by a change of the y angle from above 90 degree to below 90 degree (see e.g. Figure S25). As shown in our previous work,<sup>11</sup> the **B(cl)**<sup>a</sup> conformer is characterized by less strain but also less dispersion interactions, resulting in a thermodynamically less stable phase. Since the switching from B(cl)° to B(cl)<sup>a</sup> happens at intermediate loadings, the energetic difference between these two conformers is less profound. Dispersion interactions between linkers are highly distance dependent and therefore the energetic preference of B(cl)<sup>o</sup> diminishes fast when opening the structure. Since the obtained plots of  $\Delta E_{MOF}$  are smooth for all occurrences of this flipping, we decided not to remove those datapoints since our aim here was not to investigate the subtle differences between the two conformers but between different guests. The observed defects occurring during simulations do not differ from those presented in our previous work: Linker detachment, layer-slipping and domain forming.<sup>2</sup> It should be noted, that domain formation here refers to the formation of two partially (or completely) closed conformers. The recently investigated domain forming<sup>22,23</sup> during the process of opening and closing (domains of **op** and **cp** in one crystal) is in the case of DUT-8(Ni) complicated by the possible presence of two distinct closed phases and a resulting total of three coexisting phases. How this might affect the energetics of domain interfaces is beyond the scope of the present paper and will be studied in future work.

### 3.2 Energetics

We omit the discussion of the guest energetics of the 200 K simulations, since the guest molecules are trapped in a quenched state defined by the initial random orientation. Only starting during the 300 K simulations do the guest molecules move significantly enough to interpret their interactions. See Figure S21 for the instantaneous temperature of all components.



Figure S4:  $\Delta E_{MOF}(\mathbf{op-cp})$  (color) and corresponding cell volumes of the op phase (grey) at 300 K (blue, diamonds) and 400 K (red, circles). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

The **cp**-**op** energy differences (see Figure S4) coincide with the already published energy differences. Closing the MOF from the **op** to the **cp** form ( $\Delta E_{MOF} = E_{MOF}(cp) - E_{MOF}(op)$ ) results in an energy gain. DFT calculations predict an energy gain of -86 kJ mol<sup>-1</sup><sup>11</sup> and the previous LFMM study of CO<sub>2</sub> in DUT-8(Ni) -110 kJ mol<sup>-1</sup>.<sup>2</sup> Our systems lead to energy gains of -95 to -122 kJ mol<sup>-1</sup> (colored points in Figure S4). This spread is due to the choice of maximum loading as can be seen from the correlation with the cell volume. We attribute the overall higher energy gain of the LFMM model in comparison with DFT results mainly to one difference: The larger available conformational space of the LFMM supercell model allows for further relaxation. This is especially visible in the linker-bending. In the single unit cell picture of DFT, the linkers extend over the unit cell boundary and therefore an "S" shape is imposed, that is chemically unintuitive compared to a trampoline<sup>24–27</sup> or "C" shape that our LFMM simulations predict. Of course all other differences arising from the classical treatment using a force-field also contribute to the difference, but these are not expected to singularly favor the **cp** phase over the **op** phase. The relevant measure, if a guest can open the MOF from a thermodynamics perspective is not the adsorption energy per guest molecule, but the total adsorption energy of all molecules adsorbed in the open state in comparison to the energy required to open the MOF. The lowest energy gain (least negative  $E_{Ads}$  value) upon adsorption is predicted for methane (see colored values in Figure S5) as expected. The difference between  $E_{Ads}$  and  $\Delta E_{MOF}$  (cp-op) in Figure S5 (distance between colored and grey values) is equal to the total energy gain of the adsorption process to the maximum filling and opening of the flexible MOF.



Figure S5: Total adsorption energy at full loading (color) and  $\Delta E_{MOF}(cp-op)$  (grey). 300 K (blue, diamonds) and 400 K (red, circles). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

The individual adsorption sites inside the MOF are diverse since the MOF changes its local structure upon each additional adsorbed guest molecule. It is therefore of interest to follow the average adsorption energy to elaborate how the adsorption energy of each added guest molecule changes. In general, we observe a similar trend of the average adsorption energies for all guest molecules. As expected, the highest adsorption energy gain (most negative value) is observed for the first few molecules inserted into the structure. The average adsorption energy then fluctuates and rises at intermediate loadings to converge towards a final value (see Figure S13). This is an important result, since a thermodynamic barrier for the adsorption of the first few guest molecules could lead to the structure staying closed, even though a full loading would exhibit an overall negative adsorption energy. Especially for larger guests that exhibit weak interactions with the MOF, this might occur. For the guests studied here however, no such barrier is observed in our calculations.



Figure S6: Cell volume per formula unit MOF with respect to the relative loading at 300K (top) and 400K (bottom). Volumes of empty DFT optimized MOF structures of  $B(cl)^{\circ}$  and B(op) are given as dashed lines.<sup>11</sup> Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S7: MOF-guest interaction energy (top) and MOF-guest interaction energy per guest molecule (bottom) at full loading. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S8: MOF-guest interaction energy with respect to the relative loading at 300K (top) and 400K (bottom). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

### 3.5 Guest-Guest Interaction



Figure S9: Guest-guest interaction energy (top) and guest-guest interaction energy per guest molecule (bottom) at full loading. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S10: Guest-guest interaction energy with respect to the relative loading at 300K (top) and 400K (bottom). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

### 3.6 Adsorption Energies

An important difference of adsorption inside a flexible material compared to a rigid one, is the temperature dependence of the adsorption energy ( $\Delta_T E = E(T_2) - E(T_1)$ ). It has been shown that already in almost rigid zeolites the heats of adsorption are temperature dependent due to changes between different adsorption sites.<sup>28</sup> In flexible MOFs not only multiple adsorption sites can coexist, but also the individual adsorption site is highly dependent on the changing local structure of the framework. Therefore, the adsorption should not be evaluated independently from those factors that influence the frameworks configuration, e.g. loading, temperature and pressure.



*Figure S11: Temperature dependence of adsorption energies. Values are in reference to the corresponding adsorption energy at 300 K. Reproduced under the terms of the Creative Commons Attribution 4.0 License.*<sup>1</sup>

The temperature dependence of our calculated adsorption energies of the fully loaded structures  $(\Delta_T E_{Ads}(n_{max})/n_{max})$  are shown in Figure S11. Since the shape of the individual adsorption sites in the fully loaded simulations should not strongly depend on the temperature, the deviations are remarkably large. In Figure S12 the difference of  $\Delta_T E_{Ads}(n)/n$  between 300 K and 400 K shows two important features: First, the temperature dependence of the adsorption energies of the first few guest molecules are well within the error margin. This means, that the occupied adsorption sites are not temperature dependent or all adsorption sites, that are occupied in this temperature range, exhibit similarly strong interactions. Second, a maximum of the temperature dependence is visible at intermediate loadings where the opening of the MOF is observed. This leads to the conclusion that the temperature only affects the overall adsorption energetics slightly, but during the opening of the framework the energetic differences are significant and could lead to different behavior.



Figure S12: Temperature dependence of the adsorption energy per guest molecule at 400 K relative to 300 K with respect to the relative loading. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S13: Adsorption energy per guest molecule with respect to the relative loading at 300K (top) and 400K (bottom). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S14: Stepwise adsorption energy per guest molecule with respect to the relative loading at 300K (top) and 400K (bottom). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

### 3.7 Energy Decomposition at 400 K



Figure S15: Van-der-Waals interaction energies of guest-guest and MOF-guest interaction energies per guest molecule at 400 K and full loading. Calculated isotropic polarizabilities are given on the right y-axis. Note that the polarizability axis is inverted to visualize the correct dependence of the interaction energies. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S16: Electrostatic energy contribution to the guest-guest (blue) and MOF-guest (red) interaction energies per guest molecule at 400 K and full loading. Dipole moments of the guest from DFT (grey crosses). Note that the dipole is given on an inverted y axis on the right side of the plot to visualize the dependence of the electrostatic interaction on the dipole magnitude. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

# 3.8 Autocorrelation of Guests



Figure S17: Average autocorrelation of guests at 400 K and loading corresponding to the opening of the framework. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S18: Average Autocorrelation of guest orientations at 300K (top) and 400K (bottom) and full loading. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

# 3.9 Chlorinated Methanes

# 3.9.1 MP2 Calculations



Figure S19: Dimers of CCl<sub>4</sub> and CHCl<sub>3</sub>. Chlorines colored ochre, hydrogens white and carbons black. CHCl<sub>3</sub> in two configurations: Aligned dipole moments (a) and opposing dipole moments (b). CCl<sub>4</sub> (c) in the same configuration as b). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

The MP2 calculations yield interaction energies for the dimers of - 11.9 kJ mol<sup>-1</sup> for CCl<sub>4</sub> and - 14.4/-9.9 kJ mol<sup>-1</sup> for CHCl<sub>3</sub> (configuration a/b respectively, see Figure S19). The optimizations using the GAFF parameters exhibit interaction energies of - 11.2 kJ mol<sup>-1</sup> and - 17.1/-9.1 kJ mol<sup>-1</sup> respectively.

### 3.9.2 Dimer DFT-FF Comparison

The procedure described in Section 1.4 resulted in the energy contributions given in Table S6.

		Dispersion/vdW		Electrostatic	
		DFT	LFMM	DFT	LFMM
	$CH_4$	-3.27	-1.97	-0.34	+0.21
	CH₃Cl	-2.64	-1.92	-3.05	-3.10
	$CH_2CI_2$	-6.65	-5.44	-4.79	-4.02
	CHCl₃	-8.44	-8.41	-4.36	-4.31
	CCl <sub>4</sub>	-9.15	-10.88	+0.37	+0.54

Table S6: Dimer DFT-FF comparison of dispersion/vdW and electrostatic contributions. Values given in kJ mol<sup>-1</sup>.

### 3.9.3 Dimer Calculations of Parallel and Antiparallel CH<sub>3</sub>Cl

We performed single point calculations using DLPOLY and GAFF (same setup as for the MD simulations) on a CH<sub>3</sub>Cl dimer in an antiparallel and parallel orientation of the dipole vectors. The dimers were optimized using DFT (PBE-D3, DZ in ADF) with restricted Cl-C-C-Cl dihedrals and Cl-C-C angles. The restrictions were necessary to keep the dipoles in their respective orientation.

The resulting vdW and electrostatic energy contributions are given in Table S7.

Table S7:VdW and electrostatic contributions to the  $CH_3Cl$  dimer in parallel and antiparallel orientation of the dipole vector. Values given in kJ mol<sup>-1</sup>.

	vdW	Elstat.
Parallel	-3.32	3.95
Antiparallel	-1.18	-5.82



Figure S20: Normalized radial distribution function (RDF) of carbons (top) and chlorines (bottom) in the guest molecules at 400 K for 6 molecules of  $CCl_4$  and 9 molecules of  $CHCl_3$ . The resolution step size is 0.1 Å, the RDF was averaged over the last 100 frames. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

### 3.10 Temperature of Subsystems

To assert that the guests are not artificially cold and therefore frozen inside the MOF, we calculated the temperatures of the entire system, the MOF and the guests for the last frame using equation (1). The resulting temperatures at maximum loadings are given in Figure S21.



Figure S21: Instantaneous temperature calculated from atom velocities for the entire system (triangles), the MOF (stars) and the guest only (crosses) for the 200 K (black), 300 K (blue) and 400 K (red) simulations. Values shown for the respective maximum loading simulation. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

## 3.11 Overviews per guest

For each guest we provide an overview of the simulations excluded from analysis and the reason therefore. We further give plots of cell vector lengths/angles as well as an overview of  $\Delta E_{\text{MOF}}$ ,  $E_{\text{Guest}}$  and  $E_{\text{Interaction}}$ . For a description of the simulation cell see Section 1.2.4.

### $3.11.1 \ CH_4$

- 300 K, 3 Molecules: MOF breaks, lots of linker detachment, excluding.
- 400 K, 4 Molecules: MOF breaks, lots of linker detachment, excluding.
- Contracted *C* axis due to significant linker turning disorder.



Figure S22: Overview of energy contributions with respect to the number of guest molecules per formula unit MOF (symbols). Volume of the simulation cell per formula unit MOF (dashed lines). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S23: Cell vector angles (top) and lengths (bottom) with respect to the number of guest molecules per formula unit MOF. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

### 3.11.2 CH<sub>3</sub>Cl

- 400 K, 2 Molecules: MOF explodes, excluding.
- Contracted C axis at 2 molecules loading due to layer-slip defect.
- Bond stretching starting at 12 molecules loading.



Figure S24: Overview of energy contributions with respect to the number of guest molecules per formula unit MOF (symbols). Volume of the simulation cell per formula unit MOF (dashed lines). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S25: Cell vector angles (top) and lengths (bottom) with respect to the number of guest molecules per formula unit MOF. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

 $3.11.3 \ CH_2Cl_2$ 

- 400 K, 1+2 Molecules: Lots of linker detachment, excluding.
- Low loading swings to **B(cl)**<sup>a</sup> conformer (1 and 2 molecules are restarted from 200 K).
- Contracted *C* axis due to layer-slip defect.



Figure S26: Overview of energy contributions with respect to the number of guest molecules per formula unit MOF (symbols). Volume of the simulation cell per formula unit MOF (dashed lines). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S27: Cell vector angles (top) and lengths (bottom) with respect to the number of guest molecules per formula unit MOF. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

### 3.11.4 CHCl<sub>3</sub>

• Intermediate loadings swing into **B(cl)**<sup>a</sup> conformer.



Figure S28: Overview of energy contributions with respect to the number of guest molecules per formula unit MOF (symbols). Volume of the simulation cell per formula unit MOF (dashed lines). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S29: Cell vector angles (top) and lengths (bottom) with respect to the number of guest molecules per formula unit MOF. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

3.11.5 CCl<sub>4</sub>

- 200 K, 2 Molecules: Cell length deviation due to intra-layer disorder, correlates with amount of turned linkers.
- 400 K, 1 Molecule: Lots of linkers detach, excluding.



Figure S30: Overview of energy contributions with respect to the number of guest molecules per formula unit MOF (symbols). Volume of the simulation cell per formula unit MOF (dashed lines). Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>



Figure S31: Cell vector angles (top) and lengths (bottom) with respect to the number of guest molecules per formula unit MOF. Reproduced under the terms of the Creative Commons Attribution 4.0 License.<sup>1</sup>

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