Tuning the Electric Field Response of MOFs by Rotatable Dipolar Linkers

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Recently the possibility of using electric fields as a further stimulus to trigger structural changes in metal-organic frameworks (MOFs) has been investigated. In general, rotatable groups or other types of mechanical motion can be driven by electric fields. In this study we demonstrate how the electric response of MOFs can be tuned by adding rotatable dipolar linkers, generating a material that exhibits paralectric behavior in two dimensions and dielectric behavior in one dimension. The suitability of four different methods to compute the relative permittivity $\kappa$ by means of molecular dynamics simulations was validated. The dependency of the permittivity on temperature $T$ and dipole strength $\mu$ was determined. It was found that the herein investigated systems exhibit a high degree of tunability and substantially larger dielectric constants as expected for MOFs in general. The temperature dependency of $\kappa$ obeys the Curie-Weiss law. In addition, the influence of dipolar linkers on the electric field induced breathing behavior was investigated. With increasing dipole moment, lower field strength are required to trigger the contraction. These investigations set the stage for an application of such systems as dielectric sensors, order-disorder ferroelectrics or any scenario where movable dipolar fragments respond to external electric fields.

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Abstract

Recently the possibility of using electric fields as a further stimulus to trigger structural changes in metal-organic frameworks (MOFs) has been investigated. In general, rotatable groups or other types of mechanical motion can be driven by electric fields. In this study we demonstrate how the electric response of MOFs can be tuned by adding rotatable dipolar linkers, generating a material that exhibits paraelectric behavior in two dimensions and dielectric behavior in one dimension. The suitability of four different methods to compute the relative permittivity $\kappa$ by means of molecular dynamics simulations was validated. The dependency of the permittivity on temperature $T$ and dipole strength $\mu$ was determined. It was found that the herein investigated systems exhibit a high degree of tunability and substantially larger dielectric constants as expected for MOFs in general. The temperature dependency of $\kappa$ obeys the Curie-Weiss law. In addition, the influence of dipolar linkers on the electric field induced breathing behavior was investigated. With increasing dipole moment, lower field strength are required to trigger the contraction. These investigations set the stage for an application of such systems as dielectric sensors, order-disorder ferroelectrics or any scenario where movable dipolar fragments respond to external electric fields.
Introduction

Metal-organic frameworks (MOFs) are an emerging class of crystalline, hybrid and porous materials, which are built from oligotopic molecules (linkers) and metal ion nodes.\(^1\text{–}^3\) Potential applications for MOFs are gas separation and storage, water purification, chemical sensing, catalysis, drug delivery and imaging.\(^4\text{–}^8\) Especially, so-called stimuli responsive MOFs, which undergo physical or chemical “changes of large amplitude in response to external stimulation”\(^9\) have gained much attention for the design of new functional materials.\(^10,11\) Well studied external stimuli are temperature, mechanical pressure, guest adsorption or evacuation, and light absorption.

Recently, the possibility to use external electric fields \(E\) as a further stimulus to trigger structural changes in MOFs has been reported. By molecular dynamics simulations, the well known breathing behavior of MIL-53(Cr) could be reproduced, however, only by applying a very high external electric field.\(^12\) One of us proposed a potential mechanism for this transformation, based on field induced dipole-dipole interactions in a winerack type lattice (see Fig. 6).\(^13\) Recently, Kolesnikov and coworkers confirmed this mechanism for a 2D lattice model by statistical mechanics calculations.\(^14\) Furthermore, Knebel \textit{et al.} demonstrated that an electric field can be used to enhance the molecular sieving capability of a ZIF-8 based MOF-polymer membrane by initiating reversible phase transitions.\(^15\)

On the other hand, besides guest adsorption, the regularity and porosity of MOFs makes them an ideal platform to realize molecular machines. The void space allows for the motion of either the MOF building blocks, such as rotating linkers,\(^16\) or molecular guests inside the pores. For example, Loeb and coworkers incorporated a rotaxane moiety in the linker of a MOF.\(^17\) Very recently, the unidirectional rotation of a a light-driven rotor within a MOF was demonstrated.\(^18\) Again, external electric fields are a facile way to trigger motion of movable components in MOFs. For example, Yazaydin and coworkers investigated two interesting systems \textit{in silico}, where the transport of guests is modulated by the help of dipolar groups ordering in an external electric field. In the first case, a large dipolar molecule was
mounted on the open metal coordination sites in Mg-MOF-74, which acts as a molecular gate, controlling the flow of guest molecules along the hexagonal channels. In the second example, the guest diffusion in an IRMOF variant with a dipolar group at the linker was modulated by applying an external field. Due to the ordering of linkers in the field, a non-isotropic self-diffusion was observed.

To gain a deeper understanding of any kind of field induced motion or structural transformation in a system, its dielectric permittivity $\kappa$ needs to be known. However, due to the general interest in MOFs as potential low-$\kappa$ interlayer dielectrics for semiconducting devices, past theoretical investigations were mainly focusing on the electronic polarization of rigid MOFs in the linear response regime. First, Zagorodniy et al. studied the dielectric response of cubic Zn-based frameworks, employing the semi-empirical Clausius-Mossotti model. Later, Warmbier et al. employed density functional perturbation theory to calculate $\kappa$ for similar rigid cubic frameworks. Inspired by these theoretical studies, the dielectric and optical properties of HKUST-1 and ZIF-8 were investigated experimentally, confirming that MOFs are indeed promising candidates for low-$\kappa$ dielectrics. Recent theoretical investigations by Ryder and coworkers, again based on static density functional theory (DFT) calculations, established structure-property relations for the dielectric response of MOFs. They found only a minor dependency of $\kappa$ on the chemical composition of the MOF but an almost linear dependency on the porosity.

The dielectric properties of MOFs with incorporated dipolar rotors have, on the other hand, not been investigated up to now. In contrast to the systems studied by Ryder et al., a strong dependency of $\kappa$ on the chemical composition, and in particular on the dipole strength of the rotor, is expected, since the highly temperature dependent orientation polarization should dominate over the electronic polarization in these systems. As a consequence, molecular dynamics (MD) simulations at finite temperature are needed for the determination of the static dielectric permittivity $\kappa$. In this work we used pillared layer MOFs as reference systems to establish the methodology, and to investigate the influence of increasing dipole...
strength and temperature on the dielectric constant for a given framework structure. In our reference systems, square lattices of 1,4-benzenedicarboxylate (bdc) linked Zinc paddle-wheels are pillared by bispyridine linkers as shown in Fig. 1. The parent system (A) with a central phenyl exhibits no dipolar group. In (B) 1,2-difluorophenyl and in (C) phtalazine replace the phenyl in the backbone with an increasing dipole strength. This setup allows for an easy manipulation of the dielectric response of the material, by keeping its other properties unaffected. Furthermore this system is realistic and could even be deposited as a thin film on a device by layer-by-layer synthesis.  

For the determination of $\kappa$ we followed the work by Zhang and Sprik who proposed four different methods to calculate $\kappa$ from classical MD simulations on the case of liquid water (namely from polarization fluctuations or as finite field derivative with either fixed electric field $E$ or fixed displacement charge field $D$). In contrast to the molecular liquid water, the herein investigated systems are porous crystalline polymers and show a non-isotropic dielectric response, since the dipolar linkers can only rotate around the $z$-axis. Furthermore, the dipole density is much lower and thus also the possible polarization. To determine the numerically most efficient way of predicting $\kappa$ for such systems, the four proposed methods were applied to systems B and C and its performance was validated. In addition, we verified the hypothesis that dipolar groups facilitate the electric field induced breathing which was observed originally for MIL-53. 

**Methods**

**Dielectric constants from MD simulations**

When a material is exposed to an electric field, it gets polarized. The induced polarization $P$ is related to the electric field $E$ by the electric susceptibility $\chi$

$$P = \epsilon_0 \chi E.$$  

(1)
The relative permittivity of a material (i.e. its dielectric constant) $\kappa$ is then given by $\kappa = 1 + \chi$. In general, this relative permittivity is not a constant, but depends on the frequency of the applied field, the temperature $T$, and other parameters. The induced polarization can be divided into three different contributions: electronic $P_{el}$, displacive (ionic) $P_{ion}$, and orientation polarization $P_{orient}$. Consequently, the relative permittivity can be written as $\kappa = 1 + \chi_{el} + \chi_{ion} + \chi_{orient}$. $P_{el}$ corresponds to the response of the electron density to the electric field. At the high frequency limit this contribution is crucial, since the nuclei move too slow to adapt. The ionic polarization is due to the adaptation of the nuclei positions with respect to the electric field. Orientation polarization arises whenever molecules or molecular groups carry a permanent dipole moment $\mu$, which gets partially aligned to the electric field. For polar liquids this third contribution becomes dominating.

In their investigation on liquid water, Zhang and Sprik proposed four different methods to calculate relative permittivities from classical molecular dynamics simulations, based on two different Hamiltonians. In the constant-$E$ method, the electric enthalpy $\mathcal{F}$ of a system
of volume $\Omega$ is written as

$$ F(E,v) = H_{PBC}(v) - \Omega E \cdot P(v), \quad (2) $$

where $H_{PBC}$ is a classical Hamiltonian with $v$ denoting the set of momenta and positions of the atoms, $E$ is the fixed electric field and $P(v)$ is the macroscopic polarization for the microscopic state specified by $v$. Note that the SI unit system is used in this work throughout (conversion formulas to the CGS unit system are given in the SI). Thus, the field-dependent force on atom $i$ is $q_i E$, where $q_i$ is the charge assigned to the atom in the FF model.

In the constant-$D$ method, the electric internal energy $U(D,v)$ functional is written as

$$ U(D,v) = H_{PBC}(v) + \frac{\Omega}{2\epsilon_0} [D - P(v)]^2, \quad (3) $$

where $D$ denotes the fixed macroscopic electric displacement field and $\epsilon_0$ the vacuum permittivity.$^{30}$ From this follows that the field dependent force on atom $i$ is $\frac{q_i}{\epsilon_0} (D - P)$. In contrast to MD simulations using the fixed-$E$ approach, here, the instantaneous polarization $P$ has to be known at every time-step, because the force depends explicitly on its value. Since $P$ is a multi-valued property and depends on the choice of the unit-cell,$^{31}$ it has to be assured that all atoms are kept in the same reference frame during the simulation. Furthermore, because MOFs are crystalline periodic materials, it is practically impossible to define a unit cell with a vanishing dipole moment and thus a polarization of zero. Therefore, prerequisite to a simulation with a fixed-$D$ Hamiltonian, a corresponding simulation with $E = 0$ has to be performed in order to sample the polarization at zero field for the unit-cell of choice, which is then used as reference polarization in Eq. 3. In general, as discussed already by Stengel et al., the constant-$E$ Hamiltonian corresponds macroscopically to a capacitor in short circuit, since polarization fluctuations have to be compensated by fluctuating charges on the capacitor plates. In contrast, the constant-$D$ Hamiltonian is related to a capacitor in open-circuit conditions with a fixed value of free charge $Q$ on the plates, with the polarization
fluctuations leading to a fluctuating field $E$.\textsuperscript{29,30}

Relative permittivities $\kappa$ can now be derived either from polarization fluctuations at $E = 0$ (using the fixed-$E$ Hamiltonian from Eq. 2) or $D = 0$ (using the fixed-$D$ Hamiltonian from Eq. 3). With $E = 0$, it can be derived from the fluctuations of the polarization $P$ by

$$\kappa_x = 1 + \frac{\Omega}{\epsilon_0 k_B T} (\langle P_x^2 \rangle_{E=0} - \langle P_x \rangle^2_{E=0}),$$

(4)

where $k_B$ is Boltzmann’s constant and $T$ is the temperature. Note that due to the anisotropy of the investigated systems we do not average over spatial directions. The brackets $\langle \cdot \rangle$ denote here the usual ensemble averages. For $D = 0$, $\kappa$ is calculated from

$$\kappa_x = \frac{1}{1 - \frac{\Omega}{\epsilon_0 k_B T} (\langle P_x^2 \rangle_{D=0} - \langle P_x \rangle^2_{D=0})}.$$  

(5)

Furthermore, relative permittivities can also be estimated from simulations for a finite field by extrapolating then to the limit of zero field. For an electric field $E$, $\kappa$ can be computed by using the relation:

$$\kappa_x = 1 + \frac{\langle P_x \rangle_{E=0}}{\epsilon_0 E},$$

(6)

with $\langle P_x \rangle$ the expectation value of the polarization obtained from a MD run using the constant $E_x = E$ Hamiltonian. The finite $D$ derived value for $\kappa$ follows from the relation:

$$\kappa_x = \frac{1}{1 - \langle P_x \rangle / D},$$

(7)

where the expectation value of the polarization is determined from an average over a trajectory generated by the constant $D_x = D$ Hamiltonian. Note that for both approaches, $\langle P_x \rangle$ is obtained in relation to the average polarization from a trajectory at $E = 0$, with the same choice for the unit-cell.
Computational Details

All molecular dynamics simulations were performed using the MOF-FF force field\textsuperscript{32,33} (parameter sets are provided in the SI), employing our in-house developed \textsc{pydmpoly} code.\textsuperscript{32} The Ewald summation method was used for calculating the electrostatic interactions, and the short range interactions were truncated smoothly at 12 Å. The unit-cells for the materials were chosen as shown in Fig. 6 by a rotation of 45° around the crystallographic $c$-axis of the conventional cell, which results in a unit-cell two times larger than the conventional one. Simulations in the ($N,V,T$) ensemble for the calculations of the dielectric constants were performed in a 2x2x2 super-cell of the rotated unit-cell at temperatures of 150 K, 298 K and 450 K. For every system and applied field strength the material was first equilibrated for 100 ps using a Berendsen thermostat\textsuperscript{34} with a time constant of 200 fs and then further simulated for at least 10 ns using a Nosé-Hoover thermostat\textsuperscript{35} with a time constant of 1 ps. For all simulations a time step of 1 fs was used. The polarization was monitored every 10th timestep. Statistical errors of the polarization $P$ were calculated by performing a reblocking analysis.\textsuperscript{36}

For the investigation of the electric field induced breathing behavior, we always employed a larger 6x2x2 supercell of the rotated unit-cell at 298 K and a pressure of 1 bar. At every field strength the system was first equilibrated for 50 ps in the ($N,V,T$) ensemble using a Berendsen thermostat\textsuperscript{34} with a time constant of 200 fs. Then it was equilibrated in the ($N,\sigma,T$) ensemble for 2 ns by a Berendsen thermostat (time constant of 200 fs) and barostat (time constant of 1 ps) followed by a sampling run of 5 ns using a Nosé-Hoover thermostat (time constant of 1 ps) and barostat (time constant of 1 ps).
Results and discussion

Dielectric Constants

The polarization response $P_x$ for a finite electric field $E_x$, applied in $x$-direction, is shown in Fig. 2 for all three MOF systems (Fig. 1) at temperatures $T$ of 150 K, 298 K, and 450 K. As expected, system A behaves substantially different from systems B and C. Whereas A shows the typical behavior of a dielectric material \textit{i.e.} the polarization $P$ increases as a linear function of the electric field $E$, systems B and C show a nonlinear response, typical for paraelectric materials. The difference is due to the fact that systems B and C carry rotatable dipolar groups. Thus, the first, relatively steep increase of the polarization $P$ with increasing electric field $E$ corresponds to orientation polarization from an alignment of the dipolar groups. The second, flatter part of the curve corresponds to an increasing ionic polarization, as also observed for system A. With increasing dipole moment of the linker groups, the polarization increases substantially for a given field. In addition, in contrast to A, the polarization for B and C becomes highly temperature dependent, since the field alignment is hampered by the entropy of the dipolar rotors. It should be noted, that due to the anisotropy of the systems, the same behavior is observed for a field applied in $y$-direction, whereas for a field applied in $z$-direction, only a dielectric response (as for system A) is observed also for B and C, since the dipolar rotors can only rotate about the $z$-axis.

Note, that this rotation is almost barrier-free. During the force field validation we determined a rotational barrier around the Zn-N bond of only 0.15 kcal mol$^{-1}$ by DFT calculations of non-periodic model systems.

Due to the use of a non-polarizable force-field, only ionic and orientation polarization are taken into account when the relative permittivities $\kappa$ are predicted in the following. However, the additional electronic contribution can be estimated by the structure-property relations developed recently by Ryder \textit{et al.}\

They found an almost linear dependency between porosity and relative permittivity for a variety of MOFs. Using Zeo++ a porosity
of about 50% was calculated for all systems. This corresponds to a $\kappa \approx 1.8$ or $\chi \approx 0.8$, which needs to be added to the here predicted permittivities for a comparison with experimental values. However, since we are mainly interested in relative values, we report in the following on the uncorrected numbers.

In the first step, dielectric constants were calculated based on polarization fluctuations obtained from simulations at $E = 0$ (see Eq. 4) and $D = 0$ (see Eq. 5). Fluctuations were sampled for every system and temperature for 50 ns. The mean of the polarization obtained from the $E = 0$ simulation, was used as reference polarization for the $D = 0$ case. The results are shown in Table 1. $\kappa$ is calculated as average over $\kappa_x$ and $\kappa_y$, since the system is isotropic in $x$ and $y$ direction. This is demonstrated in Fig. 3, where the convergence of the variance $\sigma^2 = \langle P^2 \rangle - \langle P \rangle^2$ over the time of the MD simulation is shown for system B for $E = 0$ and $D = 0$ at 450 K. Both approaches yield the same result in $\kappa$, which proves that our treatment of the multi-valued polarization by making use of the reference polarization in case of constant $D$ simulations is indeed correct. In accordance to the observations by Zhang and Sprik, the polarization fluctuations are lower for $D = 0$ and $\sigma^2$ converges faster in comparison to $E = 0$ simulations (see Fig. 3). Despite that, it has to be taken into account, that prerequisite to a constant $D$ simulation, a constant $E$ simulation needs to be
performed in order to determine the reference polarization. Note that this is not necessary for a molecular dipolar fluid like water, but inevitable for a periodic crystalline polymer like a MOF. As a consequence, the constant $D$ approach is computationally more demanding and also more sensitive to systematic errors due to potentially insufficient sampling of the reference polarization.

![Figure 3](image.png)

Figure 3: Accumulating variance $\sigma^2$ of the total polarization $P$ in $x$ and $y$ directions for system B at 450 K for $E = 0$ (a) and $D = 0$ (b).

Table 1: Dielectric constants $\kappa$ obtained from polarization fluctuations. To give an impression for the sampling error, $\pm 2\sigma$ is given as statistical error.

|          | $T = 150$ K |          | $T = 298$ K |          | $T = 450$ K |
|----------|-------------|----------|-------------|----------|-------------|
|          | $E = 0$     | $D = 0$  | $E = 0$     | $D = 0$  | $E = 0$     | $D = 0$  |
| System B | 2.01(7)     | 2.1(1)   | 1.52(1)     | 1.53(1)  | 1.357(5)    | 1.362(6) |
| System C | 6.8(3)      | 6.8(7)   | 3.65(8)     | 4.0(2)   | 2.65(4)     | 2.85(8)  |

Next, we tested the suitability of the proposed approaches to calculate $\kappa$ as finite field derivative from simulations with an applied $E$ or $D$ field for our case of a MOF with dipolar rotors. Constant $E_x$ simulations were performed at different field strength ranging from 0.005 V Å$^{-1}$ to 0.50 V Å$^{-1}$, sampling the polarization each time for 10 ns. As a consistency check we selected nine values for $E_x$ (see first column of table Table 2) for the case of system C at 150 K and calculated the polarization $P_x$. The relationship $D = \epsilon_0 E + P$ was employed
to obtain the corresponding \( D \) values. These values were then taken as the displacement field in constant \( D_x \) simulations using the Hamiltonian of Eq. 3. The excellent correspondence in the resulting \( P_x \) as obtained by the two different methods underlines again the suitability of our approach of treating the reference polarization in constant \( D \) simulations. Note that the values for \( D_x \) are always larger compared to \( P_x \), due to the dielectric effect. After this consistency check, the \( D \) derivative estimates of the relative permittivity \( \kappa \), were computed by performing constant \( D_x \) simulations for a field strength ranging from \( 0.5 \times 10^4 \text{ eÅ}^{-2} \) to \( 20 \times 10^4 \text{ eÅ}^{-2} \).

Table 2: Simulation conditions at constant \( E_x \) or constant \( D_x \) and the corresponding observed \( \langle P_x \rangle \) for system C at \( T = 150 \text{ K} \). To give an impression for the sampling error, \( \pm 2\sigma \) is given as statistical error.

| \( E_x (\text{VÅ}^{-1}) \) | \( \langle P_x \rangle (10^4 \text{eÅ}^{-2}) \) | \( D_x (10^4 \text{eÅ}^{-2}) \) | \( \langle P_x \rangle (10^4 \text{eÅ}^{-2}) \) |
|-------------------------|-----------------|-----------------|-----------------|
| 0.01                    | 3(1)            | 3.15            | 2.6(6)          |
| 0.02                    | 3.5(4)          | 4.60            | 3.6(4)          |
| 0.03                    | 3.8(2)          | 5.47            | 3.9(1)          |
| 0.04                    | 4.0(1)          | 6.22            | 4.04(9)         |
| 0.05                    | 4.2(1)          | 6.92            | 4.18(8)         |
| 0.10                    | 4.62(6)         | 10.15           | 4.63(5)         |
| 0.19                    | 5.21(3)         | 15.71           | 5.21(3)         |
| 0.28                    | 5.70(3)         | 21.18           | 5.70(2)         |
| 0.50                    | 6.78(1)         | 34.41           | 6.78(1)         |

Fig. 4 shows the comparison of \( \kappa \), obtained as a function of \( E \) and \( D \) for systems B and C at all investigated temperatures. The relative permittivity has to be obtained by an extrapolation to zero field. All in all, this yields results comparable to those from polarization fluctuations listed in Table 1. As already observed by Zhang and Sprik in the case of liquid water, this extrapolation is somewhat more difficult for the constant \( E \) method due to the steeper slope of the curve at the intercept. However, as it can be seen from the error bars, the sampling error is increasing substantially for decreasing field strengths. This is especially pronounced in case of the constant \( D \) simulations due to the disadvantageous dependence of the statistical error on the polarization \( \langle P \rangle \) (see Eq. S6), which makes the extrapolation
equally error prone. Furthermore, for the constant-$D$ approach it has to be taken into account that in case of periodic polymers like a MOF, the reference polarization has to be determined beforehand, which renders this method numerically less efficient. Overall, from our analysis we recommend to compute $\kappa$ from polarization fluctuations at $E = 0$ as long as the saturation for finite field is not of relevance.

Further information on the coupling of the dipolar groups can be gained by analyzing the temperature dependence of systems B and C by a Curie-Weiss plot (Fig. 5). Here, the inverse of the electric susceptibility $\chi = \kappa - 1$ is plotted as a function of temperature. According to the Curie-Weiss law for paraelectric materials (or ferroelectrics beyond the Curie temperature) a linear relationship is expected with

$$\frac{1}{\chi} = \frac{1}{C} T - \frac{\theta}{C},$$

where the Curie constant $C$ is equal to the inverse of the slope. As expected, with $C = 747$ K a substantially larger Curie constant is observed for system C as compared to B with $C = 164$ K, since $C$ should be proportional to the square of the dipole moment $\mu$. Indeed, the ratio of the Curie constants ($\frac{C_C}{C_B} = 4.6$) is roughly equal to the ratio of the squared dipole moments ($\frac{\mu_C^2}{\mu_B^2} = 4.2$). The so-called Weiss constant $\theta$ provides information about the ground state of the material at 0 K. A value of $\theta > 0$ indicates a ferroelectric ground state and for $\theta < 0$ it should be antiferroelectric, whereas for $\theta = 0$ it is paraelectric (no coupling of the dipoles). Our results predict Weiss constants close to zero, indicating only weak interactions between the individual dipoles, which can be rationalized by the porosity of the MOFs and the consequently large spacial separation of the dipoles. For system B, a negative Weiss constant of $\theta_B = -10.9$ K is found, whereas a positive value is predicted for system C ($\theta_C = 24.7$ K). However, for both systems an antiferroelectric ground state is to be expected, since this is clearly indicated by model calculations for simple orthorhombic dipole lattices. The slightly positive Weiss-constant for system C can be explained by the
Figure 4: The static relative permittivity $\kappa_x$ obtained from fixed $E_x$ and fixed $D_x$ simulations for systems B (left column) and C (right column) at temperatures 150 K (top row), 298 K (middle row), and 450 K (bottom row). To give an impression for the sampling error, $\pm 2\sigma$ is plotted as statistical error.
in general weak interactions of the dipoles and the dependency on statistical errors of the predicted dielectric constants.

Figure 5: The inverse of the electric susceptibility $\chi$ for systems B and C, obtained by the two fluctuation methods as a function of temperature $T$. The dashed lines show a linear regression curve to the datasets obtained for both systems.

Field induced Breathing Behavior

As already discussed, Ghoufi and coworkers observed an electric field induced breathing of MIL-53(Cr) in a theoretical simulation at high field strength.\textsuperscript{12} One of us proposed a mechanism for this behavior, by invoking a model of a 2D grid of induced dipoles.\textsuperscript{13} As shown in the upper panel of Fig. 6 the application of an electric field results in a lattice of induced dipoles, oriented along an axis of the unit cell, located mainly at the inorganic building blocks due to the relatively large and alternating charges. The electrostatic interaction between the dipoles depends on the shape of the lattice. By a wine-rack deformation to a rhombic shape the attractive interactions can be increased. Note that the term $\Omega EP$ in the electric enthalpy $\mathcal{F}$ does not depend on the volume of the system (Eq. 2). Thus, the interactions between the induced dipoles are responsible for the transformation, whereas the electric field is just the source for the necessary polarization.

The here investigated systems with dipolar rotors should in principle give rise to the same
The critical field strength $E_c$, which is necessary to trigger the structural transformation, should depend on the strength of the incorporated dipolar organic moieties. Furthermore, since the field strength required to orient the permanent dipoles (lower panel of Fig. 6) is lower than that to induce equally strong dipoles, a lower $E_c$ should be expected in case of a system with rotatable dipolar groups.

![Diagram of induced dipoles and permanent dipoles](image)

Figure 6: Upper panel: 2D lattice of induced (aligned) dipoles. The gray box in the left figure indicates our choice of the unit cell, which is rotated by 90° in respect to the conventional one (size in respect to the conventional is 2x1x1). Lower panel: 2D lattice of permanent dipoles. The dipole—dipole interaction is stabilized undergoing the large pore—small pore phase transition.

To prove this, we performed molecular dynamics simulations in the $N\sigma T$ ensemble, allowing for cell deformations at increasing field strength $E_x$ for systems A, B and C at 298 K. Fig. 7a shows the unit-cell volume $\Omega$ as a function of the electric field. As expected, in all three cases the structure collapses to a closed pore form at sufficiently high field. It should be noted that the force field was parameterized with respect to the sterically relaxed building blocks (see Fig. S1). Thus, the force field becomes less accurate for high deformation.
(see Fig. S2) and potentially underestimates the unit cell volumes of the contracted form. However, the critical field strength $E_c$, at which the contraction sets in, is unaffected by this. The simulations show that dipolar groups favor the transition: whereas system A transforms at $\approx 0.6 \text{ V} \cdot \text{Å}^{-1}$, system B already contracts at $\approx 0.5 \text{ V} \cdot \text{Å}^{-1}$ and C even at only $\approx 0.3 \text{ V} \cdot \text{Å}^{-1}$. In Fig. 7b, the polarization $P_x$ is plotted as a function of the electric field $E_x$. For all three systems a jump in $P_x$ is observed at the critical field strength due to the volume contraction. Interestingly, systems B and C show almost the same value for the critical polarization needed to trigger the contraction ($\approx 5 \cdot 10^4 \text{ e} \cdot \text{Å}^{-2}$). A comparison with Fig. 2 indicates that these values lie above the region of orientation polarization for both materials, which means that additional buildup of displacive polarization is needed to reach the critical level for the collapse. However, the amount of ionic polarization is the smaller, the larger the dipole of the oriented linkers becomes, leading to a lower $E_c$ for system C. Consequently, in order to reach contraction purely by means of orientation polarization, organic moieties carrying even larger dipole moments would have to be incorporated into the framework. Then the field driven breathing would be temperature dependent, since the required field strength needed to reach the critical polarization would also be temperature dependent. As expected, system A needs a higher electric field $E_c$ for the contraction, but to our surprise a smaller critical polarization ($\approx 0.2 \cdot 10^4 \text{ e} \cdot \text{Å}^{-2}$) is necessary. Note that in system A the polarization is mainly induced directly at the inorganic zinc paddle-wheels, which actually serve as hinges during the contraction, potentially lowering the critical polarization.

**Conclusions and Outlook**

In this work, we demonstrated that dipolar rotors used as linkers in MOFs, have a strong impact on the electric permittivity $\kappa$ of the materials and can be used to tune their electric response. The herein investigated systems exhibit substantially larger dielectric constants as expected for MOFs in general and exhibit a strong dependency on the chemical composition of the dipolar linker moiety \textit{i.e.} on its dipole moment. In addition a strong temperature
Figure 7: Simulation of systems A,B and C at 298 K in the $N\sigma T$ ensemble at different electric field strengths $E_x$: (a) unit-cell volume as a function of the applied electric field $E_x$; (b) polarization $E_x$ as a function of the applied electric field $E_x$.

dependence of $\kappa$ was observed, which obeys the Curie-Weiss law for paraelectric materials. The investigated materials exhibit an anisotropic dielectric response. They are paraelectric in $x$ and $y$-direction and dielectric in $z$-direction. This offers new opportunities for the design of specialized dielectric sensors. Future efforts will aim to investigate the effect of adsorbed guest molecules on the dielectric permittivity.

In addition we found that the easiest and most efficient method to calculate $\kappa$ from molecular dynamics simulations is to compute them from polarization fluctuations at zero field, since this makes the need for a reference polarization obsolete. Reference polarizations are needed to tackle the multi-valuedness of the polarization as soon as the computation of the dielectric constant depends somehow on the absolute value of the polarization.

Furthermore, the field induced wine-rack type lattice contraction of the investigated systems was studied with respect to the influence of the dipolar linkers. As observed before by Ghoufi et al. for MIL-53(Cr), a similar breathing behavior was found to be present for the pillared-layer MOFs. However, the dipolar linkers are able to reduce the critical field strength, needed to trigger the contraction, depending on the magnitude of the incorporated dipole moment. With even higher dipole moments and in combination with guest adsorption,
even lower critical field values $E_c$ could be possible, allowing for new routes of potential application of MOFs with rotatable dipolar linkers in sensing or gas separation.

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**Supporting Information Available**

Detailed information about the MOF-FF energy expression, and the parameter sets used within the MD simulations are given in the supporting information. This material is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).

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Supporting Information: Tuning the electric field response of MOFs by rotatable dipolar linkers

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1 SI to CGS conversion formulas

The formulas presented in the methods section of the main paper are given sometimes in the literature using the CGS unit system. We decided to show the formulas in the SI unit system, since this is a more natural choice for chemists. Thus, the conversion formulas for the basic quantities electric field $E$, displacement field $D$, polarization $P$, and charge $q$ are given in the following. $\epsilon_0$ is the vacuum permittivity

$$E_{CGS} = \sqrt{4\pi\epsilon_0}E_{SI} \quad (1)$$

$$D_{CGS} = \sqrt{4\pi/\epsilon_0}D_{SI} \quad (2)$$

$$P_{CGS} = P_{SI}/\sqrt{4\pi\epsilon_0} \quad (3)$$

$$q_{CGS} = q_{SI}/\sqrt{4\pi\epsilon_0} \quad (4)$$

2 Propagated uncertainty formulas

To estimate the errors made by the calculation of the dielectric constants as finite field derivatives, we propagated the uncertainties of the polarization $\langle P \rangle$.

For $\kappa$ obtained from finite electric field $E$ simulations, the error $\sigma_{\kappa}$ is defined as

$$\sigma_{\kappa} = \frac{\sigma_{\langle P \rangle_{E=x}}}{|\epsilon_0 E|}, \quad (5)$$

where $\sigma_{\langle P \rangle_{E=x}}$ is the sampling error of the polarization obtained by a reblocking analysis.

For $\kappa$ obtained from finite electric displacement field $D$ simulations, the error $\sigma_{\kappa}$ is defined
as
\[
\sigma_K = \frac{D\sigma_{(P)}_{D=x}}{\langle (P)_{D=x} - D \rangle^2},
\]
where \(\sigma_{(P)}_{D=x}\) is again the sampling error of the polarization obtained from the finite displacement field simulation.

3 Lattice constants

The lattice constants of the rotated unit-cells used for the NVT simulations are given in Table S1. They were obtained from a lattice optimization of the particular system.

Table S1: Lattice constants of the orthorhombic rotated unit-cells used for the NVT simulations.

|        | a [Å] | b [Å] | c [Å] |
|--------|-------|-------|-------|
| System A | 15.61 | 15.61 | 18.49 |
| System B | 15.62 | 15.62 | 18.49 |
| System C | 15.58 | 15.58 | 18.42 |

4 Force field

4.1 MOF-FF Force Field

In the following the potential terms of the MOF-FF energy expression are introduced. This description is based on the supporting information of our recent study extending MOF-FF to ZIF materials.

The MOF-FF energy expression is based on the well known MM3 force field with some modifications as shown in Eq. 7.

\[
E_{MOF-FF} = \sum_b E_b^{stretch} + \sum_a E_a^{bend} + \sum_o E_o^{opb} + \sum_t E_t^{tors} + \sum_n \left( E_n^{vdw} + E_n^{coul} \right)
\]

(7)
The van der Waals interactions (vdW) $E_{vdW}$ are calculated by a dispersion damped Buckingham potential defined as follows:

$$E_{vdW}^{ij} = \epsilon_{ij} \left\{ 1.85 \cdot 10^5 \exp \left( -12 \frac{d_{ij}}{d_{ij}^0} \right) - 2.25 \left( \frac{d_{ij}^0}{d_{ij}} \right)^6 \left[ 1 + 6 \left( \frac{0.25 d_{ij}^0}{d_{ij}} \right)^{14} \right]^{-1} \right\} \tag{8}$$

The parameterization for $\epsilon_{ij}$ and $d_{ij}^0$ are taken directly from the MM3 force field. Note that for the computation of the vdW energy, the 1-2 and 1-3 interactions are excluded.

Electrostatic interactions are calculated by using spherical Gaussian type charge distributions instead of the usually employed point charges. This effectively dampens the electrostatic interactions for high charges at close distances, which enables us to include all atom-atom interactions in the Coulomb sum, and the usual 1-2 and 1-3 exclusions can be skipped. From this follows, that in all bond and angle interactions a certain Coulombic contribution is included. The following Coulombic interaction term is used in MOF-FF:

$$E_{coul}^{ij} = \frac{1}{4\pi \epsilon} q_i q_j \text{erf} \left( \frac{d_{ij}}{\sigma_{ij}} \right) \tag{9}$$

Here $d_{ij}$ is the distance of the two atoms of interaction $n$, $q_i$ and $q_j$ are the atom charges. The Gaussian charge distribution width is $\sigma_{ij}$ is computed by $\sqrt{\sigma_i^2 + \sigma_j^2}$. The values are taken from a fit to Slater functions by Chen and Martinez.

For bond stretches the quartic term from MM3 is also used in MOF-FF,

$$E_{b\, stretch}^{stretch} = \frac{1}{2} k_b (r_b - r_b^0)^2 \cdot [1 - 2.55 (r_b - r_b^0) + \frac{7}{12} (k_{b,2}(r_b - r_b^0))^2] \tag{10}$$

where $r_b$ is the bond distance, $k_b$ the force constant, and $r_b^0$ is the corresponding reference distance. It contains anharmonic contributions in a fixed form, and only the two parameters (force constant and equilibrium angle) need to be determined. In case of coordination bonds
(like Zn-O or Zn-N) a Morse-bond potential is employed

\[ E_{b,morse}^{stretch} = \frac{1}{2\alpha^2} \left( 1 - e^{-\alpha(r_b - r_b^0)} \right)^2, \quad (11) \]

here the additional parameter \( \alpha \) is calculated using the relationship \( E_{diss} = k_b/2\alpha^2 \), where \( E_{diss} \) is the approximate dissociation energy for the corresponding bond.

In the same way, for valence angle bendings the six-order polynomial form of MM3 is used

\[ E_{\text{bend}}^a = \frac{1}{2} k_a (\theta_a - \theta_a^0)^2 \]

\[ \cdot [1 - 0.14(\theta_a - \theta_a^0) + 5.6 \times 10^{-5}(\theta_a - \theta_a^0)^2 \]

\[ - 7.0 \times 10^{-7}(\theta_a - \theta_a^0)^3 + 2.2 \times 10^{-8}(\theta_a - \theta_a^0)^4]. \]

\( \theta_a \) is the bond angle, \( \theta_a^0 \) is the reference bond angle, and \( k_a \) is the force constant.

In addition MOF-FF allows to use a stretch-bend potential for three connected atoms A-B-C to model off-diagonal terms. The angle \( \theta_a \) refers to the angle between the three atoms, the distance \( r_{b,1} \) refers to the distance A-B, and \( r_{b,2} \) refers to the distance B-C. Note that the reference distances and angle \( (r_{b,1}^0, r_{b,2}^0, \theta_a^0) \) are the same as for the corresponding bond and angle type

\[ E_{a}^{\text{str-bend}} = k_{ss}(r_{b,1} - r_{b,1}^0)(r_{b,2} - r_{b,2}^0) \]

\[ + (\theta_a - \theta_a^0) \cdot [k_{sb1}(r_{b,1} - r_{b,1}^0) + k_{sb2}(r_{b,2} - r_{b,2}^0)], \quad (13) \]

where \( k_{ss}, k_{sb1} \) and \( k_{sb2} \) are the corresponding force constants.

For trigonal centers an additional out-of-plane bending term, using the Wilson-Decius definition for \( \theta_o \), is employed. Therefore, a simple harmonic potential with the force constant \( k_o \) is used

\[ E_{o}^{\text{opb}} = \frac{1}{2} k_o \theta_o^2. \]
Torsions are computed in MOF-FF using the usual Fourier series term up to a multiplicity 
$n = 4$

$$E_{t}^{\text{torsion}} = \sum_{n=1}^{n=4} V_{t,n} \left[ 1 + \cos(n\tau_t) \right],$$

(15)

with the height of the barrier $V_t^n$ and the dihedral angle $\tau_t$.

4.2 Reference systems, atomic partial charges and validation

The MOF-FF parameter generation methodology was employed to derive a force field (FF) for the investigated compounds. The molecular systems depicted in Fig. S1 were used as reference systems. The necessary reference information (optimized geometries and Hessians) was obtained at the same level of theory as used for the original MOF-FF using the quantum chemical program package TURBOMOLE. The B3LYP functional was used together with the empirical dispersion correction D3 from Grimme and coworkers. For main group elements the aug-cc-pVDZ basis sets were used and in case of transition metals the corresponding valence basis sets aug-cc-PVDZ-PP together with the appropriate Stuttgart-Dresden effective core potentials were employed.

Figure S1: Depiction of the reference system used to derive the FF, employed in this study.
Atomic partial charges were derived by a fit to the electrostatic potential of the reference systems, according to the method developed by Hu and coworkers, as implemented in the HORTON program package. Reference electrostatic potentials and densities were obtained by the aforementioned TURBOMOLE program package. Constraints due to previously derived charges and atoms with equal atom-types leads to an over-determined set of linear equations, which was solved numerically employing the covariance matrix adaptation evolution strategy (CMA-ES). Table S2 shows a comparison between the dipole moments obtained from DFT and those obtained by the ESP fit.

Table S2: Dipole moments of the in Fig. S1 shown dipolar linker molecules employed for systems B and C, obtained directly from the DFT calculation and from our fit to the electrostatic potential.

|       | DFT | ESP fit |
|-------|-----|---------|
| $\mu_B$ | 2.1 | 2.3     |
| $\mu_C$ | 4.8 | 4.7     |

Fig. S2 shows a comparison between FF and DFT calculations regarding the ability of the FF to describe the winerack motion which is crucially important for the contraction behavior described in the manuscript. For this purpose a distance restraint between the $\alpha$-Carbons marked in orange in Fig. S2b was applied in the FF model and the structure was optimized. The energy of the optimized structure was then calculated also by means of DFT calculations. As expected, the DFT and FF agree well in the harmonic region around the equilibrium angle at 90°, since this structure has been served as reference structure (see Fig. S1) for the parameterization. For larger distortions the FF is too soft, resulting in a too large volume contraction as shown in Fig. 7.

4.3 Parameter sets

The parameters obtained for the in Fig. S1 depicted reference systems are listed in the following. In addition they will be available as downloaded from www.mofplus.org. Furthermore
Figure S2: Validation of the FF in respect to the winerack motion. (a) shows the potential energy evaluated at the DFT and FF level as a function of the distortion angle. The distortion angle (marked in orange) is measured as depicted in (b) between the $\alpha$-Carbons of the two involved phenyls and the center of the two Zinc atoms.

Representative input files will be available online in the data repository at [https://github.com/cmcrub/supporting_data](https://github.com/cmcrub/supporting_data).

Atoms are discriminated based on two descriptors which define the chemical environment of an atom. The first one is the atom-type which describes the local bonding situation of an atom and is comprised of three different parts: (i) chemical element, (ii) coordination number and (iii) the elements of the connected atoms and its number of occurrence. For example the sp2 Carbon atom in benzene gets the atom-type c3_c2h1, as shown in Fig. S3. The second one is the fragment-type, it defines a coarser representation of the chemical environment. By combining atom-type and fragment-type, atoms with the same local chemical environment can be distinguished, as shown in Fig. S3.
Figure S3: Depiction of fragments and atom-types inside the Zinc paddle-wheel reference system.
4.3.1 Phenyl

Table S3: Force Field Parameters of the reference system Phenyl

(a) Charge parameters of the reference system Phenyl

| type                  | potential     | q[e] | σ[˚Å] |
|-----------------------|---------------|------|-------|
| c3,c2h1@ph           | gaussian      | −0.134 | 1.163 |
| h1,c1@ph             | gaussian      | 0.134  | 0.724 |

(b) Van der Waals parameters of the reference system Phenyl

| type                  | potential     | r_{ij}[^Å] | ε_{ij} [kcal/mol/˚Å] |
|-----------------------|---------------|-------------|---------------------|
| h1,c1@ph             | buck6d        | 1.50        | 0.020               |
| c3,c2h1@ph           | buck6d        | 1.96        | 0.056               |

(c) Bond stretching parameters of the reference system Phenyl

| types                  | potential     | k_b [kcal/mol/˚Å^2] | r_0_b [˚Å] |
|------------------------|---------------|---------------------|------------|
| c3,c2h1@ph-c3,c2h1@ph | mm3           | 982.334              | 1.395      |
| c3,c2h1@ph-h1,c1@ph   | mm3           | 781.038              | 1.094      |

(d) Angle bending parameters of the reference system Phenyl

| types                  | potential     | k_a [kcal/mol/˚Å^2 rad^-2] | φ_0 [°] |
|------------------------|---------------|-----------------------------|--------|
| c3,c2h1@ph-c3,c2h1@ph-c3,c2h1@ph | mm3           | 154.186                     | 119.638 |
| c3,c2h1@ph-c3,c2h1@ph-h1,c1@ph  | mm3           | 93.394                      | 114.685 |

(e) Out-of-plane bending parameters of the reference system Phenyl

| types                  | potential     | k_o [kcal/mol/˚Å^2 rad^-2] | γ_0 [°] |
|------------------------|---------------|-----------------------------|--------|
| c3,c2h1@ph-c3,c2h1@ph-c3,c2h1@ph-ph-h1,c1@ph | harm         | 6.299                       | 0.000  |

(f) Dihedral angle parameters of the reference system Phenyl

| types                  | potential     | V_1 [kcal/mol] | V_2 [kcal/mol] | V_3 [kcal/mol] |
|------------------------|---------------|----------------|----------------|----------------|
| h1,c1@ph-c3,c2h1@ph-c3,c2h1@ph-h1,c1@ph | cos3         | 0.000          | 3.998          | 0.000          |
| c3,c2h1@ph-c3,c2h1@ph-c3,c2h1@ph-ph-h1,c1@ph | cos3         | 0.000          | 6.739          | 0.000          |
| c3,c2h1@ph-c3,c2h1@ph-c3,c2h1@ph-ph-c3,c2h1@ph | cos3         | 0.000          | 7.121          | 0.000          |
### 4.3.2 Pyridine

Table S4: Force Field Parameters of the reference system Pyridine

(a) Charge parameters of the reference system Pyridine

| type             | potential    | q[e]  | σ[˚A] |
|------------------|--------------|-------|-------|
| n2,c2@pyr       | gaussian     | −0.423| 1.125 |
| h1,c1@pyr       | gaussian     | 0.112 | 0.724 |
| c3,c2h1@pyr     | gaussian     | −0.097| 1.163 |
| c3,c1h1n1@pyr   | gaussian     | 0.078 | 1.163 |

(b) Van der Waals parameters of the reference system Pyridine

| type             | potential    | r̃[ij][˚A] | ε[ij] |
|------------------|--------------|------------|-------|
| n2,c2@pyr       | buck6d      | 1.93       | 0.043 |
| h1,c1@pyr       | buck6d      | 1.50       | 0.020 |
| c3,c1h1n1@pyr   | buck6d      | 1.96       | 0.056 |
| c3,c2h1@pyr     | buck6d      | 1.96       | 0.056 |

(c) Bond stretching parameters of the reference system Pyridine

| type             | potential    | k[b kcal mol⁻¹ Å²] | r̃₀[b Å] |
|------------------|--------------|--------------------|---------|
| c3,c2h1@pyr-h1,c1@pyr | mm3         | 793.218            | 1.092   |
| c3,c1h1n1@pyr-c3,c2h1@pyr | mm3         | 959.387            | 1.394   |
| c3,c1h1n1@pyr-n2,c2@pyr | mm3         | 1058.140           | 1.336   |
| c3,c2h1@pyr-c3,c2h1@pyr | mm3         | 983.727            | 1.395   |
| c3,c1h1n1@pyr-c3,c1h1n1@pyr | mm3         | 774.959            | 1.095   |

(d) Angle bending parameters of the reference system Pyridine

| type             | potential    | k[a kcal mol⁻¹ rad⁻²] | φ₀[a °] |
|------------------|--------------|-----------------------|--------|
| c3,c1h1n1@pyr-c3,c2h1@pyr-h1,c1@pyr | mm3         | 73.364                | 119.553|
| c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | mm3         | 74.046                | 120.689|
| h1,c1@pyr-c3,c1h1n1@pyr-n2,c2@pyr | mm3         | 99.604                | 117.409|
| c3,c2h1@pyr-c3,c1h1n1@pyr-n2,c2@pyr | mm3         | 190.764               | 124.693|
| c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr | mm3         | 131.343               | 123.029|
| c3,c1h1n1@pyr-c3,c2h1@pyr-c3,c2h1@pyr | mm3         | 138.067               | 121.932|
| c3,c2h1@pyr-c3,c1h1n1@pyr-h1,c1@pyr | mm3         | 65.240                | 120.304|
| c3,c1h1n1@pyr-n2,c2@pyr-c3,c1h1n1@pyr | mm3         | 119.314               | 116.931|

(e) Out-of-plane bending parameters of the reference system Pyridine

| type             | potential    | k[α kcal mol⁻¹ rad⁻²] | γ[α °] |
|------------------|--------------|-----------------------|-------|
| c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | harm       | 3.202                 | 0.000 |
| c3,c1h1n1@pyr-c3,c2h1@pyr-h1,c1@pyr-n2,c2@pyr | harm       | 9.953                 | 0.000 |
| c3,c2h1@pyr-c3,c2h1@pyr-c3,c1h1n1@pyr-h1,c1@pyr | harm       | 4.316                 | 0.000 |

(f) Dihedral angle parameters of the reference system Pyridine

| type             | potential    | V₁[kcal mol⁻¹] | V₂[kcal mol⁻¹] | V₃[kcal mol⁻¹] |
|------------------|--------------|----------------|----------------|----------------|
| h1,c1@pyr-c3,c1h1n1@pyr-n2,c2@pyr-c3,c1h1n1@pyr | cos3      | 0.000          | 9.545          | 0.000          |
| c3,c2h1@pyr-c3,c1h1n1@pyr-n2,c2@pyr-c3,c1h1n1@pyr | cos3      | 0.000          | 9.093          | 0.000          |
| c3,c1h1n1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 9.157          | 0.000          |
| c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 5.992          | 0.000          |
| n2,c2@pyr-c3,c1h1n1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 2.737          | 0.000          |
| n2,c2@pyr-c3,c1h1n1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 6.043          | 0.000          |
| h1,c1@pyr-c3,c1h1n1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 4.225          | 0.000          |
| h1,c1@pyr-c3,c1h1n1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 4.176          | 0.000          |
| h1,c1@pyr-c3,c2h1@pyr-c3,c1h1n1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 6.883          | 0.000          |
| c3,c1h1n1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-c3,c2h1@pyr-h1,c1@pyr | cos3      | 0.000          | 3.320          | 0.000          |
4.3.3 Pyridine-Phenyl-Pyridine

Table S5: Force Field Parameters of the reference system Pyridine-Phenyl-Pyridine

(a) Charge parameters of the reference system Pyridine-Phenyl-Pyridine

| type          | potential   | q [e] | σ [Å] |
|---------------|-------------|-------|-------|
| c₃c₃@pyr     | gaussian    | −0.015| 1.163 |
| c₃c₃@ph     | gaussian    | 0.029 | 1.163 |

(b) Van-der-Waals parameters of the reference system Pyridine-Phenyl-Pyridine

| type          | potential   | rᵢⱼ [Å] | εᵢⱼ |
|---------------|-------------|---------|------|
| c₃c₃@ph      | buck6d      | 1.96    | 0.056|
| c₃c₃@pyr     | buck6d      | 1.96    | 0.056|

(c) Bond stretching parameters of the reference system Pyridine-Phenyl-Pyridine

| type          | potential   | kᵦ [kcal/mol/Å²] | rᵦ₀ [Å] |
|---------------|-------------|-----------------|--------|
| c₃c₂h₁@pyr-c₃c₃@pyr | mm3        | 987.642 | 1.397 |
| c₃c₃@ph-c₃c₂h₁@pyr | mm3        | 956.517 | 1.400 |
| c₃c₂h₁@pyr-c₃c₃@pyr | mm3        | 769.619 | 1.472 |

(d) Angle bending parameters of the reference system Pyridine-Phenyl-Pyridine

| type          | potential   | kᵦ [kcal mol⁻¹ rad⁻²] | φ₀ [°] |
|---------------|-------------|-----------------------|-------|
| c₃c₂h₁@pyr-c₃c₃@pyr-c₃c₂h₁@pyr | mm3        | 155.385 | 119.186 |
| c₃c₂h₁@pyr-c₃c₂h₁@ph-c₃c₂h₁@pyr | mm3        | 47.699 | 119.390 |
| c₃c₃@ph-c₃c₂h₁@pyr-c₃c₂h₁@pyr | mm3        | 155.385 | 117.002 |
| c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr | mm3        | 150.666 | 119.518 |
| c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr | mm3        | 92.702 | 115.805 |
| c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr | mm3        | 141.665 | 118.177 |
| c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr | mm3        | 126.261 | 117.636 |

(e) Out-of-plane bending parameters of the reference system Pyridine-Phenyl-Pyridine

| type          | potential   | kᵦ [kcal mol⁻¹ rad⁻²] | φ₀ [°] |
|---------------|-------------|-----------------------|-------|
| c₃c₃@pyr-c₃c₂h₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph | harm       | 16.145 | 0.000 |
| c₃c₃@ph-c₃c₂h₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph | harm       | 46.070 | 0.000 |
| c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@ph-c₃c₂h₁@ph | harm       | 5.044  | 0.000 |

(f) Dihedral angle parameters of the reference system Pyridine-Phenyl-Pyridine

| type          | potential   | V₁ [kcal mol⁻¹] | V₂ [kcal mol⁻¹] | V₃ [kcal mol⁻¹] |
|---------------|-------------|----------------|----------------|----------------|
| c₃c₃@ph-c₃c₂h₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph | cos³       | 0.000 | 2.346 | 0.000 |
| h₁c₁@pyr-c₃c₂h₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph | cos³       | 0.000 | 1.048 | 0.000 |
| c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr-c₃c₂h₁@pyr | cos³       | 0.000 | 3.387 | 0.000 |
| h₁c₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr | cos³       | 0.000 | 1.628 | 0.000 |
| c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr-c₃c₂h₁@pyr | cos³       | 0.000 | 1.365 | 0.000 |
| h₁c₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr | cos³       | 0.000 | 1.838 | 0.000 |
| c₃c₃@ph-c₃c₂h₁@pyr-c₃c₂h₁@ph-h₁c₁@ph | cos³       | 0.000 | 3.934 | 0.000 |
| c₃c₂h₁@pyr-c₃c₂h₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph | cos³       | 0.000 | 0.673 | 0.000 |
| c₃c₂h₁@pyr-c₃c₂h₁@pyr-c₃c₃@ph-c₃c₂h₁@pyr | cos³       | 0.000 | 1.408 | 0.000 |
### 4.3.4 Pyridine-Phthalazine-Pyridine

Table S6: Force Field Parameters of the reference system Pyridine-Phthalazine-Pyridine

(a) Charge parameters of the reference system Pyridine-Phthalazine-Pyridine

| type | potential | $q[e]$ | $\sigma[Å]$ |
|------|-----------|--------|-------------|
| $c_3c_3@pyr$ | gaussian | 0.166 | 1.163 |
| $c_3c_2h1@phthalaz$ | gaussian | 0.073 | 1.163 |
| $h_1c_1@phthalaz$ | gaussian | 0.072 | 0.724 |
| $c_3c_1h1n1@phthalaz$ | gaussian | 0.134 | 1.163 |
| $c_3c_3R2@phthalaz$ | gaussian | 0.281 | 1.163 |
| $n_2c_1n1@phthalaz$ | gaussian | $-0.310$ | 1.125 |
| $c_3c_3@phthalaz$ | gaussian | $-0.475$ | 1.163 |

(b) Van der Waals parameters of the reference system Pyridine-Phthalazine-Pyridine

| type | potential | $r_0^h[Å]$ | $\epsilon_{ij}$ |
|------|-----------|------------|----------------|
| $n_2c_1n1@phthalaz$ | buck6d | 1.93 | 0.043 |
| $h_1c_1@phthalaz$ | buck6d | 1.50 | 0.020 |
| $c_3c_3@pyr$ | buck6d | 1.96 | 0.056 |
| $c_3c_2h1@phthalaz$ | buck6d | 1.96 | 0.056 |
| $c_3c_3@phthalaz$ | buck6d | 1.96 | 0.056 |
| $c_3c_1h1n1@phthalaz$ | buck6d | 1.96 | 0.056 |

(c) Bond stretching parameters of the reference system Pyridine-Phthalazine-Pyridine

| type | potential | $k_b[kcal/mol/Å^2]$ | $r_0^b[Å]$ |
|------|-----------|----------------------|------------|
| $c_3c_1h1n1@phthalaz-c_2c_1n1@phthalaz$ | mm3 | 1083.916 | 1.320 |
| $c_3c_2h1@phthalaz-c_3c_3@pyr$ | mm3 | 954.014 | 1.402 |
| $c_3c_3@phthalaz-c_3c_3@pyr$ | mm3 | 716.614 | 1.361 |
| $c_3c_3@phthalaz-c_3c_3@pyr$ | mm3 | 739.020 | 1.476 |
| $c_3c_3@phthalaz-c_3c_3@phthalaz$ | mm3 | 1023.464 | 1.382 |
| $c_3c_3@phthalaz-c_3c_3@phthalaz-c_3c_3@phthalaz$ | mm3 | 851.913 | 1.421 |
| $c_3c_3@phthalaz-c_3c_3@phthalaz-c_3c_3@phthalaz$ | mm3 | 800.281 | 1.090 |
| $c_3c_3@phthalaz-c_3c_3@phthalaz-c_3c_3@phthalaz$ | mm3 | 903.113 | 1.406 |
| $c_3c_1h1n1@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 797.199 | 1.091 |
| $c_3c_3@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 829.052 | 1.424 |
| $c_3c_3R2@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 919.371 | 1.407 |

(d) Angle bending parameters of the reference system Pyridine-Phthalazine-Pyridine

| type | potential | $k_\phi[kcal mol^{-1} rad^{-2}]$ | $\phi_0^\phi[°]$ |
|------|-----------|-------------------------------|----------------|
| $c_3c_2h1@phthalaz-c_3c_3@pyr-c_3c_3@phthalaz$ | mm3 | 11.129 | 117.997 |
| $c_3c_2h1@phthalaz-c_3c_3@phthalaz-c_3c_3@phthalaz$ | mm3 | 129.993 | 122.539 |
| $c_3c_3@pyr-c_3c_2h1@phthalaz-c_3c_3@pyr$ | mm3 | 74.761 | 119.698 |
| $c_3c_3@phthalaz-c_3c_3@phthalaz-c_3c_3@phthalaz-c_3c_3@phthalaz$ | mm3 | 136.104 | 118.890 |
| $h_1c_1@phthalaz-c_3c_1h1n1@phthalaz-n_2c_1n1@phthalaz$ | mm3 | 96.884 | 115.966 |
| $c_3c_2h1@phthalaz-c_3c_2h1@phthalaz-h_1c_1@phthalaz$ | mm3 | 43.916 | 127.086 |
| $c_3c_3R2@phthalaz-c_3c_1h1n1@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 141.911 | 122.912 |
| $c_3c_3@phthalaz-c_3c_3R2@phthalaz-c_3c_3R2@phthalaz-c_3c_3@phthalaz$ | mm3 | 121.222 | 118.759 |
| $c_3c_3R2@phthalaz-c_3c_1h1n1@phthalaz-n_2c_1n1@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 200.188 | 125.014 |
| $c_3c_3@phthalaz-c_3c_3R2@phthalaz-c_3c_3R2@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 130.844 | 121.431 |
| $c_3c_3@phthalaz-c_3c_3R2@phthalaz-n_2c_1n1@phthalaz-n_2c_1n1@phthalaz$ | mm3 | 185.168 | 118.984 |
| $c_3c_3@phthalaz-c_3c_3@phthalaz-c_3c_3R2@phthalaz-c_3c_3@phthalaz$ | mm3 | 89.686 | 121.693 |
| $c_3c_3R2@phthalaz-c_3c_3R2@phthalaz-c_3c_3R2@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 86.135 | 123.932 |
| $c_3c_3R2@phthalaz-c_3c_1h1n1@phthalaz-h_1c_1@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 64.597 | 117.648 |
| $c_3c_3@phthalaz-c_3c_3R2@phthalaz-c_3c_3R2@phthalaz-c_3c_3R2@phthalaz$ | mm3 | 150.815 | 110.622 |
| $c_3c_3@phthalaz-c_3c_2h1@phthalaz-h_1c_1@phthalaz-c_3c_3@phthalaz$ | mm3 | 74.835 | 122.811 |
| $c_3c_1h1n1@phthalaz-c_3c_3R2@phthalaz-c_3c_3@phthalaz-c_3c_3@phthalaz$ | mm3 | 134.879 | 121.734 |
(e) Out-of-plane bending parameters of the reference system Pyridine-Phthalazine-Pyridine

| type | potential $k_o$ [kcal mol$^{-1}$ rad$^{-2}$] | $\gamma_0$ [$^\circ$] |
|------|---------------------------------------------|------------------|
| c3_c3@pyr-c3_c2h1@pyr-c3_c2h1@pyr-c3_c3@phthalaz | harm | 1.039 | 0.000 |
| c3_c1h1n1@phthalaz-c3_c3R2@phthalaz-h1_c1@phthalaz-n2_c1n1@phthalaz | harm | 18.380 | 0.000 |
| c3_c2h1@phthalaz-c3_c2h1@phthalaz-c3_c3@phthalaz-h1_c1@phthalaz | harm | 2.645 | 0.000 |
| c3_c3R2@phthalaz-c3_c1h1n1@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | harm | 1.045 | 0.000 |
| c3_c3@phthalaz-c3_c2h1@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | harm | 42.300 | 0.000 |

(f) Dihedral angle parameters of the reference system Pyridine-Phthalazine-Pyridine

| type | potential $V_1$ [kcal mol$^{-1}$] | $V_2$ [kcal mol$^{-1}$] | $V_3$ [kcal mol$^{-1}$] |
|------|----------------------------------|-------------------|------------------|
| c3_c3@pyr-c3_c3@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 3.214 | 0.000 |
| n2_c1n1@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 6.101 | 0.000 |
| c3_c1h1n1@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz-c3_c3@phthalaz | cos3 | 0.000 | 4.681 | 0.000 |
| c3_c1h1n1@phthalaz-n2_c1n1@phthalaz-c3_c1h1n1@phthalaz | cos3 | 0.000 | 1.281 | 0.000 |
| h1_c1@phthalaz-c3_c3R2@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 5.135 | 0.000 |
| c3_c3@phthalaz-c3_c2h1@phthalaz-c3_c2h1@phthalaz-h1_c1@phthalaz | cos3 | 0.000 | 3.556 | 0.000 |
| h1_c1@phthalaz-c3_c2h1@phthalaz-c3_c2h1@phthalaz-c3_c3@phthalaz | cos3 | 0.000 | 2.671 | 0.000 |
| n2_c1n1@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz-c3_c3@phthalaz | cos3 | 0.000 | 3.412 | 0.000 |
| c3_c2h1@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 5.213 | 0.000 |
| c3_c2h1@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz-c3_c1h1n1@phthalaz | cos3 | 0.000 | 0.600 | 0.000 |
| c3_c2h1@phthalaz-c3_c3R2@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 4.301 | 0.000 |
| c3_c2h1@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 1.360 | 0.000 |
| c3_c1h1n1@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 1.988 | 0.000 |
| c3_c2h1@phthalaz-c3_c3R2@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 0.682 | 0.000 |
| h1_c1@phthalaz-c3_c2h1@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 1.922 | 0.000 |
| c3_c3@phthalaz-c3_c2h1@phthalaz-c3_c2h1@phthalaz-c3_c3@phthalaz | cos3 | 0.000 | 2.438 | 0.000 |
| h1_c1@phthalaz-c3_c2h1@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 0.125 | 0.000 |
| c3_c3@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 1.475 | 0.000 |
| c3_c3@pyr-c3_c3@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 6.446 | 0.000 |
| h1_c1@phthalaz-c3_c1h1n1@phthalaz-c3_c3R2@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 2.435 | 0.000 |
| c3_c3R2@phthalaz-c3_c1h1n1@phthalaz-n2_c1n1@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 0.425 | 0.000 |
| c3_c1h1n1@phthalaz-c3_c3R2@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 2.676 | 0.000 |
| c3_c3R2@phthalaz-c3_c3@phthalaz-c3_c3@phthalaz-c3_c3R2@phthalaz | cos3 | 0.000 | 2.464 | 0.000 |
| h1_c1@phthalaz-c3_c1h1n1@phthalaz-n2_c1n1@phthalaz-n2_c1n1@phthalaz | cos3 | 0.000 | 2.077 | 0.000 |
| h1_c1@phthalaz-c3_c1h1n1@phthalaz-n2_c1n1@phthalaz-n2_c1n1@phthalaz | cos3 | 0.000 | 2.362 | 0.000 |
4.3.5 Pyridine-Difluorophenyl-Pyridine

Table S7: Force Field Parameters of the reference system Pyridine-Difluorophenyl-Pyridine

(a) Charge parameters of the reference system Pyridine-Difluorophenyl-Pyridine

| type               | potential | \( q[e] \) | \( \sigma [\text{Å}] \) |
|--------------------|-----------|------------|--------------------------|
| c3,c2f1@ph        | gaussian  | 0.268      | 1.163                    |
| c1,c1@ph          | gaussian  | 0.133      | 0.724                    |
| c3,c3@pyr         | gaussian  | 0.100      | 1.163                    |
| c3,c2h1@ph        | gaussian  | −0.138     | 1.163                    |
| c3,c3@ph          | gaussian  | −0.161     | 1.163                    |
| f1,c1@f           | gaussian  | −0.187     | 1.110                    |

(b) Van der Waals parameters of the reference system Pyridine-Difluorophenyl-Pyridine

| type               | potential | \( r_0^ij [\text{Å}] \) | \( \epsilon_{ij} \) |
|--------------------|-----------|--------------------------|----------------------|
| c3,c2f1@ph        | buck6d    | 1.96                     | 0.056                |
| c3,c2h1@ph        | buck6d    | 1.96                     | 0.056                |
| c3,c3@pyr         | buck6d    | 1.96                     | 0.056                |
| h1,c1@ph          | buck6d    | 1.50                     | 0.020                |
| f1,c1@f           | buck6d    | 1.71                     | 0.075                |
| c3,c3@ph          | buck6d    | 1.96                     | 0.056                |

(c) Bond stretching parameters of the reference system Pyridine-Difluorophenyl-Pyridine

| type               | potential | \( k_b [\text{kcal/mol/Å}^2] \) | \( r_0^b [\text{Å}] \) |
|--------------------|-----------|---------------------------------|--------------------------|
| c3,c2h1@pyr-c3,c3@pyr | mm3       | 1005.149                        | 1.393                    |
| c3,c2f1@ph-c3,c3@ph | mm3       | 972.031                         | 1.391                    |
| c3,c2h1@ph-c3,c3@ph | mm3       | 942.442                         | 1.401                    |
| c3,c2h1@ph-h1,c1@ph | mm3       | 794.111                         | 1.091                    |
| c3,c2h1@ph-c3,c2h1@ph | mm3      | 1004.601                        | 1.387                    |
| c3,c2f1@ph-c3,c2f1@ph | mm3      | 999.519                         | 1.389                    |
| c3,c2f1@ph-f1,c1@f  | mm3       | 878.626                         | 1.352                    |
| c3,c3@ph-c3,c3@pyr | mm3       | 771.025                         | 1.470                    |

(d) Angle bending parameters of the reference system Pyridine-Difluorophenyl-Pyridine

| type               | potential | \( k_a [\text{kcal mol}^{-1} \text{ rad}^{-2}] \) | \( \phi_0 [^\circ] \) |
|--------------------|-----------|---------------------------------|--------------------------|
| c3,c3@ph-c3,c2h1@ph-h1,c1@ph | mm3       | 74.954                          | 118.316                  |
| c3,c2h1@pyr-c3,c3@pyr-c3,c3@ph | mm3       | 91.430                          | 122.611                  |
| c3,c2f1@ph-c3,c3@ph-c3,c3@ph | mm3       | 126.295                         | 121.885                  |
| c3,c2h1@ph-c3,c3@ph-pyr-c3,c2h1@ph | mm3      | 149.215                         | 117.306                  |
| c3,c2h1@ph-c3,c3@ph-c3,c3@pyr | mm3       | 87.322                          | 122.938                  |
| c3,c2f1@ph-c3,c3@ph-c3,c3@pyr | mm3       | 91.866                          | 121.191                  |
| c3,c2f1@ph-c3,c3@ph-c3,c2h1@ph | mm3       | 142.393                         | 121.483                  |
| c3,c2f1@ph-c3,c3@ph-c3,c2h1@ph | mm3       | 133.870                         | 118.987                  |
| c3,c1h1@pyr-c3,c3@ph-pyr-c3,c3@pyr | mm3      | 157.898                         | 117.560                  |
| c3,c3@pyr-c3,c2h1@pyr-h1,c1@pyr | mm3       | 77.854                          | 118.777                  |
| c3,c2h1@ph-c3,c3@ph-h1,c1@ph | mm3       | 71.981                          | 120.057                  |
| c3,c3@ph-c3,c2f1@ph-f1,c1@f  | mm3       | 140.074                         | 118.690                  |
| c3,c2f1@ph-c3,c2f1@ph-f1,c1@f | mm3       | 134.904                         | 116.673                  |

(e) Out-of-plane bending parameters of the reference system Pyridine-Difluorophenyl-Pyridine

| type               | potential | \( k_o [\text{kcal mol}^{-1} \text{ rad}^{-2}] \) | \( \gamma^0 [^\circ] \) |
|--------------------|-----------|---------------------------------|--------------------------|
| c3,c2h1@ph-c3,c3@ph-h1,c1@ph | harm      | 10.755                          | 0.000                    |
| c3,c3@pyr-c3,c2h1@ph-pyr-c3,c3@ph | harm    | 0.001                           | 0.000                    |
| c3,c3@ph-c3,c2f1@ph-c3,c2h1@ph-c3,c3@pyr | harm | 41.516                          | 0.000                    |
| c3,c2h1@ph-c3,c2f1@ph-c3,c3@ph-f1,c1@f | harm  | 7.180                           | 0.000                    |
(f) Dihedral angle parameters of the reference system Pyridine-Difluorophenyl-Pyridine

| type | potential | \( V_1 \) [kcal mol\(^{-1}\)] | \( V_2 \) [kcal mol\(^{-1}\)] | \( V_3 \) [kcal mol\(^{-1}\)] |
|------|-----------|-------------------------------|-------------------------------|-------------------------------|
| h1_c1@ph-c3_c2h1@ph-c3_c3@ph-c3_c3@pyr | cos 3 | 0.000 | 0.945 | 0.000 |
| f1_c1@f-c3_c2f1@ph-c3_c3@f-c3_c1@f | cos 3 | 0.000 | 1.439 | 0.000 |
| h1_c1@pyr-c3_c2h1@pyr-c3_c3@pyr-c3_c3@ph | cos 3 | 0.000 | 3.330 | 0.000 |
| c3_c3@ph-c3_c2h1@ph-c3_c2h1@ph-c3_c3@ph | cos 3 | 0.000 | 2.223 | 0.000 |
| c3_c2f1@ph-c3_c2f1@ph-c3_c3@ph-c3_c2h1@ph | cos 3 | 0.000 | 0.012 | 0.000 |
| c3_c3@ph-c3_c2f1@ph-c3_c2f1@ph-c3_c3@ph | cos 3 | 0.000 | 2.312 | 0.000 |
| c3_c2h1@ph-c3_c2h1@ph-c3_c3@ph-c3_c2f1@ph | cos 3 | 0.000 | 0.584 | 0.000 |
| c3_c2f1@ph-c3_c2f1@ph-c3_c3@ph-c3_c3@pyr | cos 3 | 0.000 | 1.448 | 0.000 |
| c3_c2f1@ph-c3_c3@ph-c3_c3@pyr-c3_c2h1@pyr | cos 3 | 0.000 | 1.357 | 0.000 |
| f1_c1@f-c3_c2f1@ph-c3_c3@ph-c3_c3@pyr | cos 3 | 0.000 | 8.575 | 0.000 |
| c3_c3@ph-c3_c2h1@ph-c3_c2h1@ph-c1_h1@ph | cos 3 | 0.000 | 0.435 | 0.000 |
| c3_c1h1n1@pyr-c3_c2h1@pyr-c3_c3@pyr-c3_c3@ph | cos 3 | 0.000 | 0.182 | 0.000 |
| h1_c1@ph-c3_c2h1@ph-c3_c2h1@ph-c1_h1@ph | cos 3 | 0.000 | 2.764 | 0.000 |
| h1_c1@ph-c3_c2h1@ph-c3_c3@ph-c3_c2f1@ph | cos 3 | 0.000 | 0.218 | 0.000 |
| c3_c2h1@ph-c3_c2h1@ph-c3_c3@ph-c3_c3@pyr | cos 3 | 0.000 | 3.911 | 0.000 |
| c3_c3@ph-c3_c2f1@ph-c3_c2f1@ph-c3_c3@pyr-f1_c1@f | cos 3 | 0.000 | 2.952 | 0.000 |
| c3_c2h1@ph-c3_c3@ph-c3_c3@pyr-c3_c2h1@pyr | cos 3 | 0.000 | 1.468 | 0.000 |
| f1_c1@f-c3_c2f1@ph-c3_c3@ph-c3_c2h1@ph | cos 3 | 0.000 | 0.613 | 0.000 |
4.3.6 Zinc Paddlewheel

Table S8: Force Field Parameters of the reference system Zinc Paddlewheel

(a) Charge parameters of the reference system Zinc Paddlewheel

| type              | potential   | q[e]   | σ[Å]  |
|-------------------|-------------|--------|-------|
| zn6_n1o4zn1@zn2p | gaussian    | 1.179  | 2.073 |
| o2_c1zn1@co2     | gaussian    | -0.790 | 1.118 |
| c3_c3@ph         | gaussian    | -0.123 | 1.163 |
| n3_c2zn1@pyr     | gaussian    | -0.186 | 1.125 |
| c3_c1o2@co2      | gaussian    | 0.994  | 1.163 |

(b) Van-der-Waals parameters of the reference system Zinc Paddlewheel

| type              | potential     | r^0_ij[Å] | ε_ij   |
|-------------------|---------------|-----------|--------|
| o2_c1zn1@co2     | buck6d       | 1.82      | 0.059  |
| c3_c1o2@co2      | buck6d       | 1.96      | 0.056  |
| c3_c3@ph         | buck6d       | 1.96      | 0.056  |
| n3_c2zn1@pyr     | buck6d       | 1.93      | 0.043  |
| zn6_n1o4zn1@zn2p | buck6d       | 2.29      | 0.760  |

(c) Bond stretching parameters of the reference system Zinc Paddlewheel

| type              | potential     | k_b[kcal/mol/Å^2] | r^0_b[Å] | E_diss[kcal mol^-1] |
|-------------------|---------------|-------------------|---------|-------------------|
| c3_c1o2@co2,c3_c3@ph | mm3          | 679.642           | 1.498   |                    |
| c3_c1h1n1@pyr-n3_c2zn1@pyr | mm3 | 1084.866         | 1.336   |                    |
| c3_c1o2@co2,c3_c1zn1@co2 | mm3 | 1135.020         | 1.281   |                    |
| c3_c2h1@ph-c3_c3@ph | mm3          | 985.655           | 1.394   |                    |
| zn6_n1o4zn1@zn2p-zn6_n1o4zn1@zn2p | mm3 | 216.546          | 2.819   | 50.000            |
| o2_c1zn1@co2,zn6_n1o4zn1@zn2p | mm3 | 138.454          | 2.019   |                    |
| n3_c2zn1@pyr,zn6_n1o4zn1@zn2p | mm3 | 175.037          | 2.035   | 25.000            |

(d) Angle bending parameters of the reference system Zinc Paddlewheel

| type              | potential     | k_ab1[kcal mol^-1 rad^-2] | k_ab2[kcal mol^-1 rad^-2] | k_ss[kcal/mol/Å^2] | r^0_ab[Å] | r^0_ss[Å] | φ^0[°] |
|-------------------|---------------|---------------------------|---------------------------|-------------------|---------|---------|--------|
| o2_c1zn1@co2-c3_c1o2@co2-c3_c1zn1@co2 | mm3          | 0.000                     | 0.000                     |                   |         |         |        |
| c3_c3@ph-c3_c1o2@co2-c3_c1zn1@co2 | mm3          | 204.939                  | 109.605                  |                   |         |         |        |
| c3_c1o2@co2,c3_c1zn1@co2-c3_c2h1@ph | mm3          | 146.953                  | 113.195                  |                   |         |         |        |
| o2_c1zn1@co2,c3_c1o2@co2-c3_c1zn1@co2 | mm3          | 295.131                  | 120.063                  |                   |         |         |        |
| c3_c3@ph-c3_c2h1@ph-h1_c1@ph | mm3          | 89.347                   | 111.111                  |                   |         |         |        |
| c3_c2h1@ph-c3_c3@ph-c3_c2h1@ph | mm3          | 166.005                  | 115.736                  |                   |         |         |        |
| c3_c2h1@ph-c3_c3@ph-c3_c2h1@ph | mm3          | 168.716                  | 118.076                  |                   |         |         |        |
| c3_c1o2@co2-c3_c1zn1@co2-c3_c2h1@ph-c3_c3@ph | mm3 | 10.172                   | 119.299                  |                   |         |         |        |
| c3_c1h1n1@pyr-n3_c2zn1@pyr-c3_c1h1n1@pyr | mm3 | 135.041                  | 119.951                  |                   |         |         |        |
| c3_c2h1@pyr-c3_c1h1n1@pyr-n3_c2zn1@pyr | mm3 | 193.469                  | 122.284                  |                   |         |         |        |
| h1_c1@pyr-c3_c1h1n1@pyr-n3_c2zn1@pyr | mm3 | 104.031                  | 113.417                  |                   |         |         |        |
| o2_c1zn1@co2-c3_c1o2@co2,c3_c1zn1@co2 | mm3          | 133.206                  | 72.677                   |                   |         |         |        |
| n3_c2zn1@pyr-zn6_n1o4zn1@zn2p-zn6_n1o4zn1@zn2p | mm3 | 20.523                   | 100.646                  |                   |         |         |        |
| c3_c1h1n1@pyr-n3_c2zn1@pyr-zn6_n1o4zn1@zn2p | mm3 | 2.487                    | 116.139                  |                   |         |         |        |
| n3_c2zn1@pyr-zn6_n1o4zn1@zn2p-zn6_n1o4zn1@zn2p | mm3 | 0.000                    | 0.000                    |                   |         |         |        |

(e) Stretch-bend coupling parameters of the reference system Zinc Paddlewheel

| type              | potential     | k_1[kcal mol^-1 rad^-2] | k_2[kcal mol^-1 rad^-2] | k_3[kcal/mol/Å^2] | r^0_1[Å] | r^0_2[Å] | φ^0[°] |
|-------------------|---------------|-------------------------|-------------------------|-------------------|---------|---------|--------|
| o2_c1zn1@co2-c3_c1o2@co2-c3_c1zn1@co2 | strbnd       | 24.246                  | 24.246                  | -44.027 28       | 1.281  | 1.281  | 120.063 |
(f) Out-of-plane bending parameters of the reference system Zinc Paddlewheel type | potential $k_{ij} [\text{kcal mol}^{-1} \text{ rad}^{-2}]$ | $\gamma^0 [\degree]$  
--- | --- | ---  
c_3c_1c_2c_0c_2c_3c_2p-h-c_3c_1h_1c_0c_2-o_2c_1c_2n_1c_0c_2 | harm | 38.242 | 0.000  
c_3c_3p-h-c_3c_1c_2c_0c_2c_3h_1c_0p-h-c_3c_2h_1c_0p | harm | 9.198 | 0.000  
n_3c_2z_n_1p_y_r-c_3c_1h_1n_1p_y_r-c_3c_1h_1n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p | harm | 0.078 | 0.000  
c_3c_1h_1n_1p_y_r-c_3c_2h_1c_0p-h_1c_1p_y_r-n_3c_3c_2z_n_1p_y_r | harm | 10.427 | 0.000  
c_3c_2h_1c_0p-h-c_3c_2h_1c_0p-c_3c_3p-h-c_3c_2h_1c_0p | harm | 6.320 | 0.000  

(g) Dihedral angle parameters of the reference system Zinc Paddlewheel type | potential $V_i [\text{kcal mol}^{-1}]$ | $V_2 [\text{kcal mol}^{-1}]$ | $V_3 [\text{kcal mol}^{-1}]$ | $V_4 [\text{kcal mol}^{-1}]$  
--- | --- | --- | --- | ---  
c_3c_2h_1c_0p-h-c_3c_2h_1c_0p-c_3c_3p-h-c_3c_1c_2c_0c_2 | cos3 | 0.000 | 5.809 | 0.000  
c_3c_1c_1h_1n_1p_y_r-n_3c_2z_n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p | cos3 | 0.000 | 0.000 | 0.000 | 0.000  
h_1c_1p_h-c_3c_2h_1c_0p-c_3c_3p-h-c_3c_1c_2c_0c_2 | cos3 | 0.000 | 6.772 | 0.000  
c_3c_1c_2c_0c_2-c_4c_2c_1c_2c_0c_2-c_3c_3p-h-c_3c_2h_1c_0p | cos3 | 0.000 | 0.000 | 0.000 | 0.000  
c_3c_3p-h-c_3c_1c_2c_0c_2-c_4c_2c_1c_2c_0c_2-c_3c_3p-h-c_3c_2h_1c_0p | cos3 | 0.000 | 1.472 | 0.000  
c_3c_3p-h-c_3c_1c_2c_0c_2-c_4c_2c_1c_2c_0c_2-c_3c_3p-h-c_3c_2h_1c_0p | cos3 | 0.000 | 0.000 | 0.000 | 0.000  
oc_3c_1c_2c_0c_2-o_2c_1c_2c_0c_2-o_2c_1c_22c_0c_2-c_3c_3p-h-c_3c_2h_1c_0p | cos3 | 0.000 | 0.000 | 0.000 | 0.000  
n_3c_2z_n_1p_y_r-n_3c_1c_2n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p-o_2c_1c_2n_1c_0c_2 | cos3 | 0.000 | 0.000 | 0.000 | 0.000  
h_1c_1p_y_r-n_3c_2z_n_1p_y_r-n_3c_1c_2n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p | cos3 | 0.000 | 1.898 | 0.000  
c_3c_1c_2c_0c_2-o_2c_1c_2c_0c_2-o_2c_1c_22c_0c_2-c_3c_3p-h-c_3c_2h_1c_0p | cos3 | 0.000 | 0.000 | 0.000 | 0.000  
oc_3c_1c_2c_0c_2-o_2c_1c_2c_0c_2-o_2c_1c_22c_0c_2-c_3c_3p-h-c_3c_2h_1c_0p | cos3 | 0.000 | 5.099 | 0.000  
n_3c_2z_n_1p_y_r-n_3c_1c_2n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p-o_2c_1c_2n_1c_0c_2 | cos3 | 0.000 | 0.000 | 0.000 | 0.000  
c_3c_1c_1h_1n_1p_y_r-n_3c_2c_2n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p | cos3 | 0.000 | 4.017 | 0.000  
c_3c_2h_1p_y_r-n_3c_1c_2n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p-o_2c_1c_2n_1c_0c_2 | cos4 | 0.000 | 0.000 | 0.000 | 0.000  
oc_3c_1c_2n_1p_y_r-n_3c_2c_2n_1p_y_r-z_n_6n_1o_4z_n_1o_2z_n_2p-o_2c_1c_2n_1c_0c_2 | cos4 | 0.000 | 0.000 | 0.000 | 2.552
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