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Emergence of Coupled Rotor Dynamics in Metal–Organic Frameworks via Tuned Steric Interactions

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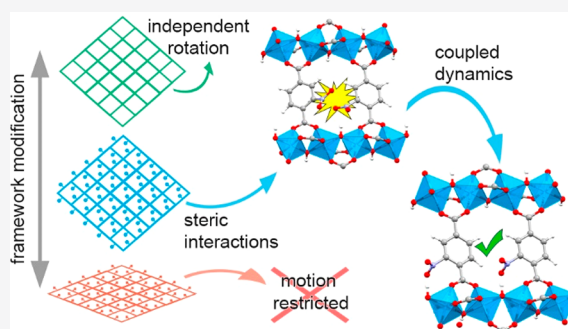


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Supporting Information

ABSTRACT: The organic components in metal–organic frameworks (MOFs) are unique: they are embedded in a crystalline lattice, yet, as they are separated from each other by tunable free space, a large variety of dynamic behavior can emerge. These rotational dynamics of the organic linkers are especially important due to their influence over properties such as gas adsorption and kinetics of guest release. To fully exploit linker rotation, such as in the form of molecular machines, it is necessary to engineer correlated linker dynamics to achieve their cooperative functional motion. Here, we show that for MIL-53, a topology with closely spaced rotors, the phenylene functionalization allows researchers to tune the rotors' steric environment, shifting linker rotation from completely static to rapid motions at frequencies above 100 MHz. For steric interactions that start to inhibit independent rotor motion, we identify for the first time the emergence of coupled rotation modes in linker dynamics. These findings pave the way for function-specific engineering of gear-like cooperative motion in MOFs.



INTRODUCTION

The hybrid nature of metal–organic frameworks (MOFs) goes hand in hand with diverse and often complex behavior. The dynamic traits of these materials are increasingly capturing the curiosity of researchers in the field: MOFs show the potential of displaying intricate dynamics, similar to that observed in other materials built from closely interacting molecules such as crowded movement of proteins in lipid bilayers^{1,2} or concerted molecular motion in liquid crystals.³ The organic components in MOFs are embedded in a crystalline lattice, yet, in contrast to traditional molecular crystals, they are separated from each other by modifiable free space, providing a handle to tune dynamic behavior in an ordered and stable supramolecular arrangement.^{4–7}

A decade ago, Yaghi and Stoddart proposed that “robust dynamics” could be achieved by mechanically interlocking organic components onto the linkers, such that they have the necessary freedom of mobility without compromising the MOF structure.⁸ Since then, it has become evident that stable frameworks that display inherent rotational motion are in fact ubiquitous.^{9–11} However, not all such frameworks are usable in practice, and the performance of a MOF in specific applications is highly dependent on its dynamic properties, a prime example being adsorption behavior in flexible MOFs.^{12–17} Furthermore, MOF-based crystalline molecular machines will require external control of linker motion, making

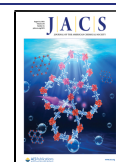
the engineering of correlated dynamics a necessary step to achieve cooperative functional mobility.^{5,6,18,19}

Recent achievements in rotor-MOFs include engineering ultrafast rotation by decreasing the rotation energy barrier via molecular design,^{20–22} reaching rates as high as those in gas or liquid phases. Additionally, the first example of unidirectional rotation in MOF linkers by the Feringa group²³ represents a crucial step toward attaining nanomotors embedded in a crystalline lattice that can produce useful work.²⁴ A recent study on rotor-MOFs presented evidence of steric interactions between rotating phenylene units within a single linker.²⁵ Yet, the understanding, let alone the engineering, of correlated dynamics based on steric interactions between linkers remains extremely limited.

The growing field of rotor-MOFs may benefit from inspiration drawn from the more developed field of crystalline molecular rotors. In many such systems, it has been found that in structures where rotor–rotor distances are small enough, the resulting steric interactions force the rotational dynamics to adopt correlated gear-like mechanisms.^{26–29} Here, we present

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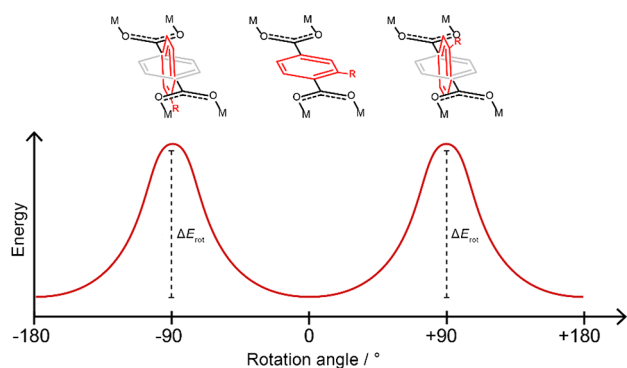


for the first time how correlated motions emerge in linker dynamics as the steric environment of the rotors is gradually modified. We use linker functionalization in the MIL-53 family of materials to tune both the pore dimensions and the rotor–rotor interactions. The MIL-53 topology proves to be an excellent choice due to its functionalization-dependent pore size configurations, that is, the metastability of two phases, large pore (lp), and narrow pore (np). Moreover, terephthalate-based organic linkers are very common among MOFs.

RESULTS AND DISCUSSION

To start, we focus on the intramolecular effects of linker functionalization on rotational motion. In terephthalate linkers, the benzene rings can rotate with respect to the carboxyl groups, which are fixed due to their coordination to the metal nodes. As shown in Chart 1, the maximum energy corresponds

Chart 1. Schematic of the Energy Profile of a Terephthalate Rotor Linker



to a conformation where the benzene rings form a 90° angle with both carboxyl groups,^{30–32} as the overlap between the *p* orbitals in the ring and in the carboxyl groups is minimized.

We modeled with density functional theory (DFT) calculations the intrinsic rotational energy barriers (ΔE_{rot}) of different functionalized terephthalic acids with different functional groups as the relative energy between the transition state and a planar conformer (Table 1 and Chart 1). With respect to the unsubstituted terephthalic acid, most substituent groups decrease the ΔE_{rot} barrier. In these cases, steric

Table 1. Calculated Barriers for 180° Rotation on Terephthalic Acid and Its Derivatives

R	ΔE_{rot} (kJ mol ⁻¹) ^a
H	47.7
hydroxy	81.8
amino	53.7
methoxy	42.1
cyano	34.5
fluoro	35.9
chloro	25.0
bromo	25.1
nitro	17.1

^aMaximum energy state for each molecule (E_{90}) is obtained from constrained geometry optimizations, setting the dihedral angles between carboxylic groups and ring to 90°. Relative values were obtained with respect to a planar conformation energy; see Supporting Information section 3.1 for details.

repulsion between the substituent group and the closest carboxyl oxygen likely destabilizes the planar configuration,^{28,33} decreasing the energy difference between the transition state and the ground state. This effect is particularly significant in the nitro-substituted molecule (Figure S8), where the rotation barrier is the lowest at $\Delta E_{\text{rot}} = 17.1$ kJ mol⁻¹, that is, less than 7 *kT* at room temperature.

Only two substituents, the amino and hydroxy groups, cause an increase in ΔE_{rot} with respect to the unsubstituted molecule. We argue that this is in fact mostly due to stabilization via a hydrogen bond with the adjacent carboxylic acid oxygen (1.93 Å for NH...O and 1.75 Å OH...O, see Figure S9). Indeed, simply breaking the H-bond by rotating the hydroxy group by 180° results in an energy penalty of 31 kJ mol⁻¹. Conversely, the methoxy substituent, which has an electron-donating effect that stabilizes the planar conformation, does not cause a net increase in ΔE_{rot} due to steric effects and lack of H-bond formation.

Experimental work on MIL-53^{34–36} has established that its *p*-phenylene groups undergo rotation in the form of π -flips, exhibiting similar behavior to several other terephthalate-based MOFs.^{32,37–39} The large-pore (lp) conformation of MIL-53 suggests that the rotating rings should not be subject to significant steric effects. The rotator's closest interactions are between contiguous linkers in the same row (or pore wall): their closest ring-to-ring (–CH...HC–) distance possible is 2.3 Å, which means their van der Waals radii barely overlap. This spacing is limited yet sufficient for unfunctionalized terephthalate rotors to perform full rotations in the form of π -flips, as evidenced experimentally.³⁵

This spacing between the linkers in MIL-53 family is still relatively small, in contrast to other MOFs such as IRMOF and UiO-66. This suggests that ring substituents are likely to influence the dynamics of rotors. On the basis of the DFT calculations of the free linkers, we selected two contrasting groups, nitro and amino, to assess the impact of linker functionalization in the complete framework, a “crowded” environment. Moreover, for MIL-53 materials, functionalization has an important impact on the flexible crystalline conformation: guest-free NO₂-MIL-53(Al) and MIL-53(Al) are usually present in the lp form in a wide temperature range,^{40–42} while guest-free NH₂-MIL-53(Al) remains in the denser narrow-pore (np) form (Figure 1).^{40,43,44} Table 2 presents the characteristic distances between rotors in each form of the framework, showing how the difference in pore opening impacts row-to-row distance but not rotor spacing within a row. The row-to-row distance of the np amino-MOF indicates likely inter-row steric effects prohibiting full rotation of rings. For both functionalized frameworks, steric repulsion between neighboring linkers within the same row is expected.

Each crystallographic unit cell contains four linkers. To explore the energy associated with linker rotation, we forced the rotation steps on one linker starting from the global minimum conformation, followed by partial geometry optimization at each step. The rotational space of a nitroterephthalate linker is defined in Figure 2a and b (for aminoterephthalate see Figure S10). The obtained potential energy curves (or energy profiles as a function of rotation) are shown in Figure 2c. The energy profile of NH₂-MIL-53 shows a very steep increase upon linker rotation, far larger in magnitude than the barrier calculated for the free linker (54 kJ mol⁻¹). This is the result of row-to-row steric hindrance in the tightly packed np phase (see Figure S11), indicating that large

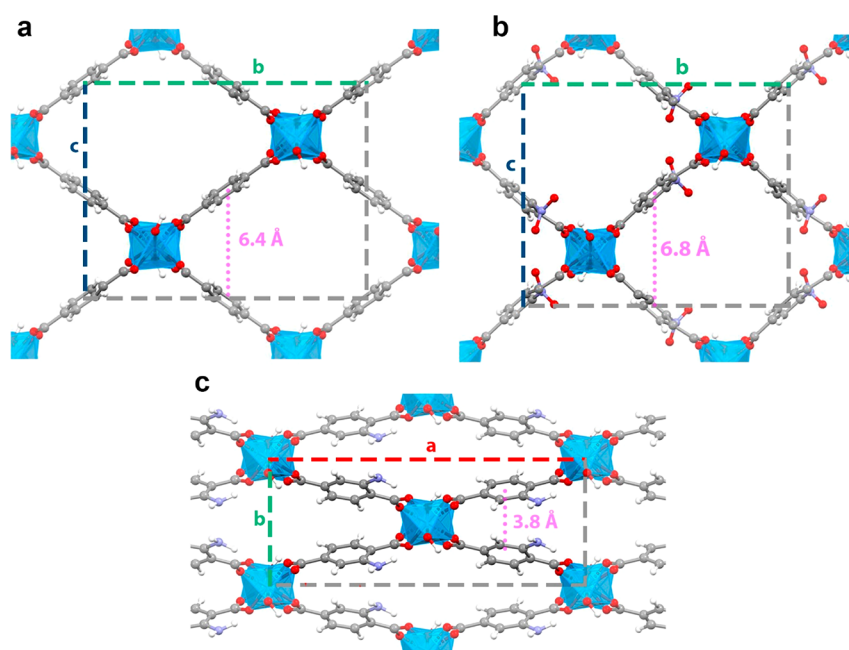


Figure 1. Structure of three members of the MIL-53 family viewed along the pore direction. (a) MIL-53(Al) (lp), (b) NO₂-MIL-53(Al) (lp), and (c) NH₂-MIL-53(Al) (np). This topology is characterized by four distinct rows of linkers per unit cell forming rhombic pores. Closest row distances for each MOF are marked in magenta. For complete unit cell parameters, see Table S2.

Table 2. Unit Cell Geometry Influence on Rotor Spacing

MOF	rotor spacing within row (Å) ^a	pore rhombus angle (deg)	row-to-row distance (Å) ^b
MIL-53(Al) (lp)	6.6	75.0	6.4
NO ₂ -MIL-53(Al) (lp)	6.7	79.5	6.8
NH ₂ -MIL-53(Al) (np)	6.6	43.8	3.8

^aDefined as distance between neighboring C–C rotation axes, see Supporting Information section 3.2. ^bFor definition, see Supporting Information section 3.2.

amplitude rotations are unlikely to occur in this MOF. For NO₂-MIL-53(Al), we find energy minima at $\pm 30^\circ$ and $\pm 150^\circ$, with expected maxima at $\pm 90^\circ$, and local maxima at 0° and 180° due to steric effects experienced by the linker in the planar conformation (intramolecular, *vide supra*, and overlap between nitro and a hydrogen atom of the closest adjacent ring). The potential energy maxima of $\sim 40 \text{ kJ mol}^{-1}$ is in the range of aromatic ring π -flips found in other MOFs,^{34,37,38,45,46} which indicates the feasibility of linker rotation. Nevertheless, these periodic single unit cell calculations force the nitro linkers in a row along [100] to rotate together, as they are periodic images of each other. Such an ordered motion prevents other possible interactions between neighboring linkers in the same row, perhaps most evidently head-to-head interactions between two nitro groups.

To more realistically model these effects in the linker dynamics, $2 \times 1 \times 1$ supercells should be considered. When one linker is rotated in this scenario, the neighbor linker on the same row is not constrained and can move independently. The interaction of a pair of neighboring linkers in such a supercell will depend on the position of the two nitro groups on their respective benzene rings. Single-crystal XRD analysis shows that there is no preferential configuration set during the formation of the crystal (see Figure S12). Therefore, a rotating

linker's nitro group may encounter its neighbor's nitro group in one of the two configurations shown in Figure 2d. Illustrative cases are discussed in the Supporting Information (Figures S13 and S14). The configuration where neighbor linkers have nitro groups located on identical carbon positions has the most impactful steric effects between two rotors due to their closer distance. We find that head-to-head NO₂ interactions lead to a steep energy increase, and that the rotational event can only become energetically feasible when the neighboring linker moves out of the way in a cooperative fashion (Figure S16). For cases where nitro groups are not on equivalent positions, the extent to which the neighboring linker needs to rotate out of the way to make rotational motion of the linker energetically feasible is significantly lower (Figure S17). Hence, as no preference with respect to the two situations in Figure 2d occurs during synthesis, varying degrees of rotational mobility are expected.

Broadband dielectric spectroscopy (BDS) has proven particularly useful for probing the motion of MOF linkers containing polar functional groups.^{47–49} The imaginary part (ϵ'') of the complex dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) contains information about the dynamic relaxation processes of dipolar moieties in the dielectric material.^{50,51} The temperature and frequency dependences of ϵ'' for MIL-53(Al), NH₂-MIL-53(Al), and NO₂-MIL-53(Al) are presented in Figures 3 and S18. Peaks in ϵ'' correspond to dielectric losses due to dipolar motion, with the frequency of the maximum of ϵ'' corresponding to the mean relaxation time of the dipolar motion at that temperature.

NO₂-MIL-53(Al) shows a strong relaxation process with peaks dispersed in terms of both frequency and temperature (Figure 3a,b), a feature typical of dipolar linker relaxations in MOFs.^{48,49,52} In contrast, NH₂-MIL-53(Al) shows no relaxation process (Figure 3c), confirming a strongly hindered environment of the rotors, in correspondence with our DFT results. MIL-53(Al) (Figure 3d) exhibits a very weak dielectric

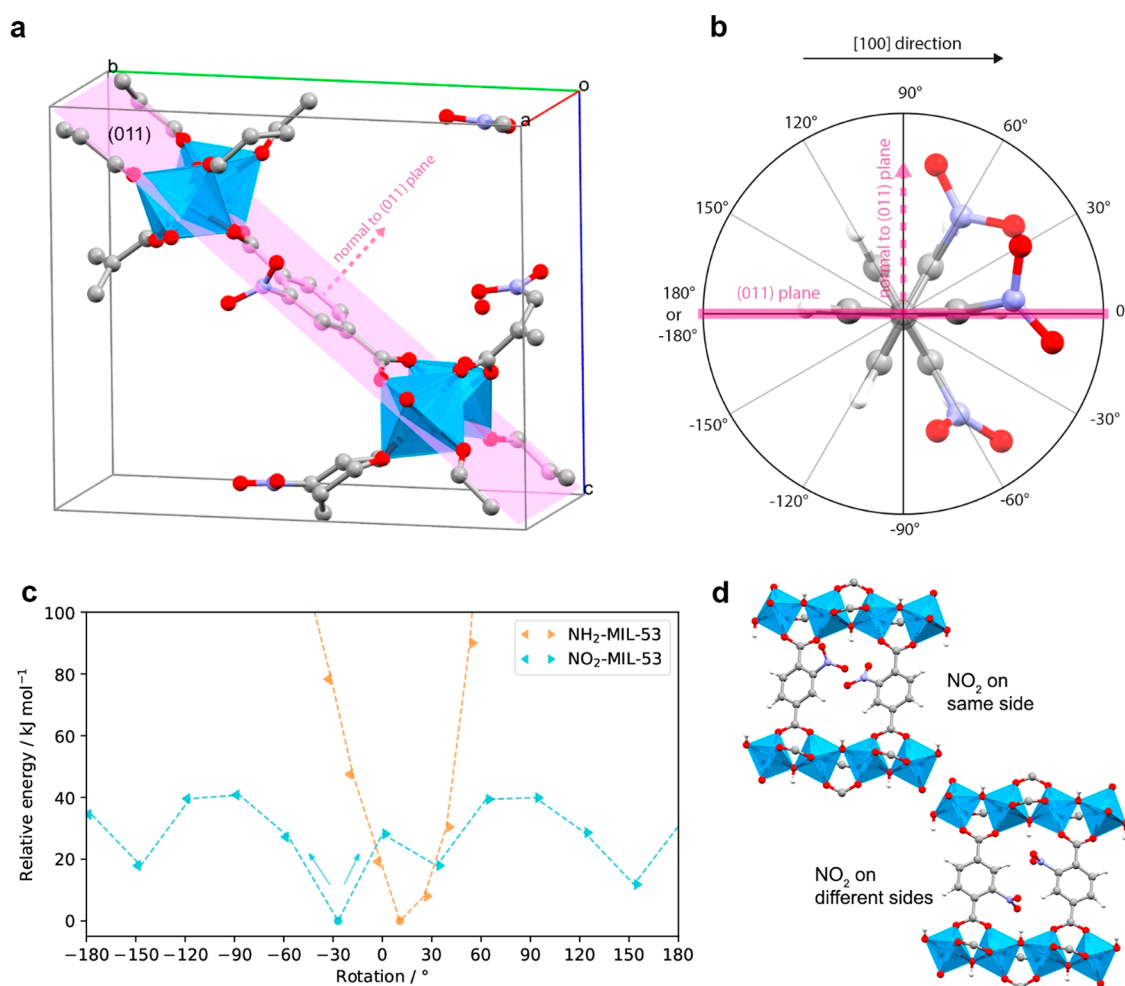


Figure 2. Effect of linker rotation on the potential energy as studied by DFT. (a) Unit cell of NO₂-MIL-53(Al) with central linker in 0° rotation with respect to (011) plane (pink); hydrogens omitted for clarity. (b) Rotation angle is defined as the angle between benzene ring plane and (011) plane, taking 0° as the conformation with the functional group pointing in the positive [100] direction. The sign of the angle is assigned based on the direction normal of the reference plane. (c) Potential energy profiles for the rotation of one linker in a NH₂-MIL-53(Al) and NO₂-MIL-53(Al) unit cell. The direction of rotation is indicated by the direction of the marker. (d) Example of an unfavorable head-to-head nitro group encounters in adjacent linkers when they are located on the same side of the ring (top) and on different sides (bottom).

relaxation, even though the mobile *p*-phenylene units do not have a permanent dipole. This may be due to small deformations of the linkers that lead to spontaneous dipole moments or the presence of polar impurities.⁵¹ We note here that although some MOFs are known to have large proportions of missing linker defects, MIL-53(Al) frameworks are not typically in that category. Thermogravimetric analysis indeed suggests that the linker-to-metal ratio is close to the theoretical value (see Supporting Information sections 1.1 and 1.2).

As expected, the dispersion frequency of the nitro linker relaxation increases with temperature, more specifically, from 2.6 kHz at 180 K to 1 MHz at 250 K. The frequency dependence of ϵ^* at different temperatures was fitted using the Cole–Cole equation (Figure 3b and Figure S18). The best fits indicate a gradual increase of the dispersion broadness parameter (α) as temperature is decreased from 0.3 at 250 K to 0.55 at 180 K (Figure S20). The broadening of the relaxation suggests a larger fraction of interacting dipoles exists when less thermal energy is available. It should be noted, however, that BDS will not detect linkers whose dynamics fall outside the probed frequency range, in particular static linkers, meaning that potential rotation-impeding interactions such as

the one illustrated in the DFT curve may not be covered in the dielectric spectra. Fitting the temperature dependence of the mean relaxation times to the Arrhenius equation delivers an activation energy E_a of 32.3 ± 1.3 kJ mol⁻¹ and a pre-exponential factor τ_0 of 3.4×10^{-14} s (Figure S21). This activation energy is in between the DFT-estimated barriers for a single unit cell of this framework, that is, the smaller barrier at 0° and the larger barrier at ~90°. The obtained τ_0 value, equivalent to 2.9×10^{13} Hz, is larger than the expected attempt frequency based on estimations for *p*-phenylene rotators (usually on the order of 10^{12} Hz; for an overview of activation energies and pre-exponential factors in MOFs, see ref 9).²⁸ This type of result is not uncommon for functionalized *p*-phenylene rotors,^{33,49,53} and it may be interpreted as an indication of a small linear dependence of the rotational barrier with temperature (see Supporting Information section 3.6 for further discussion).⁵⁴ In NO₂-MIL-53(Al), this could hint toward the progressive effect that thermal energy has on the rotor's environment due to increased conformational motions and nitro group rotations.⁵⁵

To obtain specific information about the angular and frequency ranges of the nitro-functionalized linker dynamics,

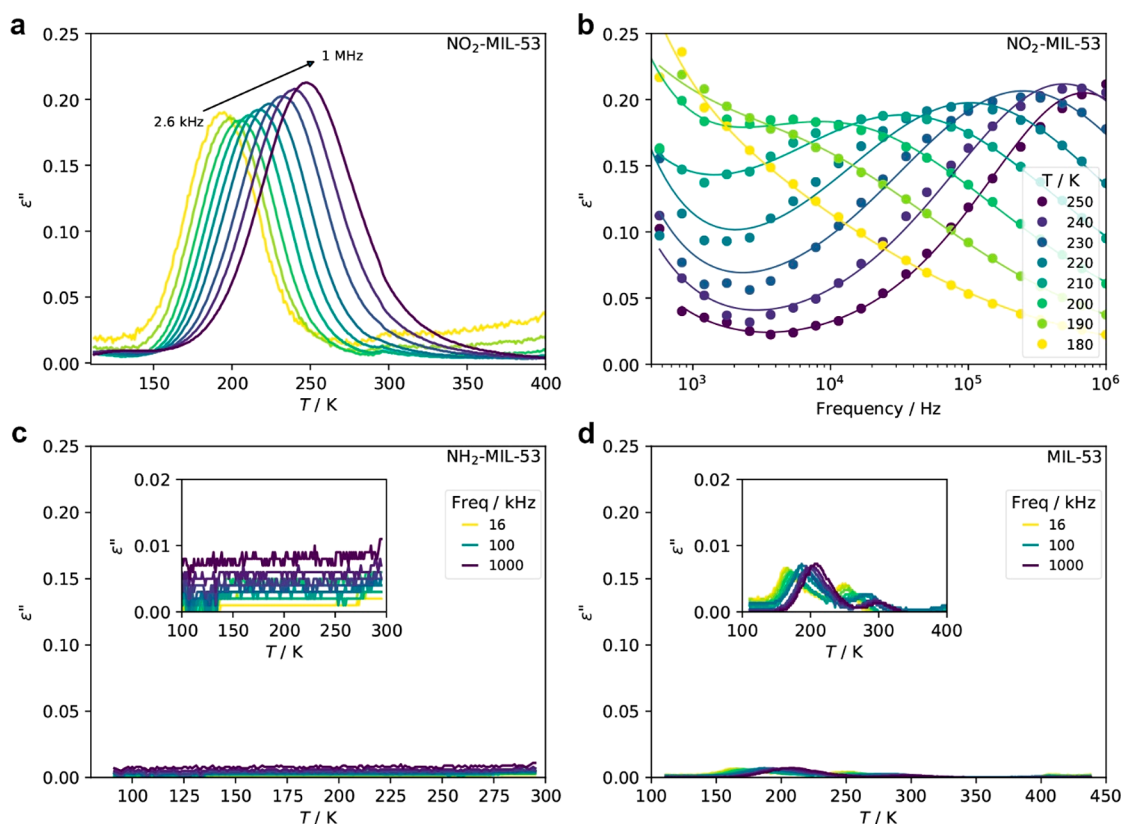


Figure 3. Dielectric spectra of the three systems. (a, b) Imaginary part (ϵ'') of ϵ^* for $\text{NO}_2\text{-MIL-53(Al)}$ with respect to temperature (a) and frequency (b). The latter includes the fitted Cole–Cole model as continuous lines. (c, d) Temperature dependence of ϵ'' for $\text{NH}_2\text{-MIL-53(Al)}$ (c) and MIL-53(Al) (d).

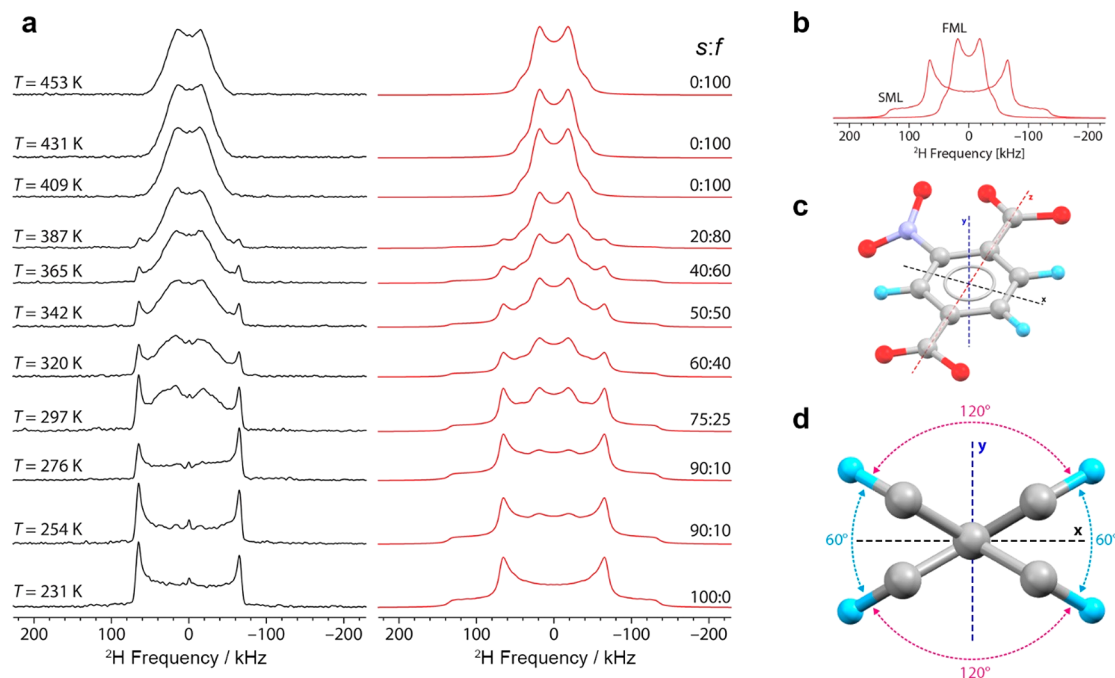


Figure 4. Solid-state ^2H NMR studies of $\text{NO}_2\text{-MIL-53(Al)-d}_3$. (a) Experimental (black) and simulated (red) variable-temperature ^2H SSNMR spectra of $\text{NO}_2\text{-MIL-53(Al)-d}_3$. (b) Spectra are composed of overlapping patterns representing SML ($<10^3$ Hz) and FML ($>10^7$ – 10^8 Hz) motions, with relative integrated intensities indicated to the right of the simulated spectra. (c) Cartesian frame of reference for the rotation model. (d) Representation of ^2H exchange sites and angles used in the model; deuterons are shown in light blue.

we performed variable-temperature solid-state deuterium NMR (^2H SSNMR) spectroscopy. Spatial information about

the deuteron exchange sites can be extracted from the NMR spectra by using relatively simple geometric models.^{56,57} In

addition, this technique is sensitive to all deuterium-labeled rings, and not only to the mobile ones. This enables us to obtain experimental information to complement the BDS data, especially for the nitro-functionalized framework, for which dynamics above 250 K could not be probed due to the high frequency limit. The results for ring-labeled MIL-53(Al)-d₄ (Figure S22) and NH₂-MIL-53(Al)-d₃ (Figure S23) are in line with literature^{46,58,59} as well as our expectations based on the DFT and BDS analyses. The ²H SSNMR data for MIL-53(Al)-d₄ indicate that the phenylene rings undergo an increased rate of 180° reorientations (“ π -flips”) at increased temperatures in the intermediate motion regime (IMR, 1 kHz < k < 100 MHz, where k is the rate constant for the exchange between deuterium sites). For NH₂-MIL-53(Al)-d₃, only static phenylene ring signals are observed in the slow motion limit (SML, k < 1 kHz), evidenced by the Pake doublet (Figure S23), in agreement with the high rotational barrier that prevents rotational dynamics at these temperatures.

The variable-temperature ²H SSNMR spectra for NO₂-MIL-53(Al)-d₃ are remarkably different from the aforementioned situations (Figure 4a). At the lowest temperature, the ²H spectrum indicates a stationary phenylene ring in the SML, whereas the spectra acquired at 409 K and higher indicate dynamics only in the fast motion limit (FML, k > 100 MHz). The spectra in the range of 254 to 387 K display a superposition of the SML and FML powder patterns, with progressive increase in integrated intensity of the FML pattern with respect to the SML pattern with increasing temperature. No pattern corresponding to the IMR was detected in the entire temperature range, differing from earlier ²H SSNMR studies on MOFs with *p*-phenylene rotators;^{34,37,38} this is likely due to diminished intensity of IMR spectra when the rates of motion are on the order of the ²H pattern breadths.^{60–63} Furthermore, the fact that contributions from both SML and FML patterns are observed across the entire temperature range indicates the presence of a distribution of correlation times for the dynamics, which further obscures signals arising from IMR motions.^{39,56,64} Such broad distributions of rotation rates are rarely found in terephthalate MOFs,^{9,33,34,37–39} though they are more often observed for *p*-phenylene moieties in polymeric systems,^{65–67} where structural heterogeneity among the rotors is often cited as the cause of a wide variety of rotation barriers, and consequently, rotation rates. This observation is further supported by the BDS results: there is a very broad distribution of detected frequencies for each temperature in the BDS spectra for NO₂-MIL-53(Al) (Figure 3b). As suggested by the DFT calculations, these broad distributions of rotational rates are a consequence of the varied degree of interlinker steric interactions, which are unique to the nitro-functionalized MOF among the three frameworks.

Although ²H NMR signals corresponding to motions in the IMR are not observed due to their low intensities and broad frequency distributions, it is possible to model motions in the FML and obtain simulations that agree well with experimental data.⁶⁸ Single rotational angle models (e.g., 60°, 120°, or 180°) do not adequately fit the line shape (Figure S24), suggesting a more complex mechanism. A four-site model based on energy minima separated by two distinct jumps of 60° and 120° (as predicted by DFT calculations, Figure 4c,d) was successful. The simulated ²H FML shape was found to be sensitive to small deviations in these angles (Figure S25). The complete simulated spectra are shown in Figure 4a. For the overlapped spectra at 254–387 K, the appropriate ratios of weighted

integrated signal intensities for static and mobile components were selected (i.e., $s:f$, corresponding to the SML and FML patterns, Figure 4b) and are included in Figure 4a. It should be noted that similar four-site rotations have been observed in *p*-phenylene rotators within branched linkers that cause intralinker steric interactions.^{25,69}

To summarize the NO₂-MIL-53(Al) experimental results, our BDS and ²H SSNMR experiments detect dynamics corresponding to complementary portions of the frequency spectrum. BDS only includes the mobile fraction of linkers up to 1 MHz, which is the mean frequency of motion at ~250 K. ²H SSNMR detects all linkers undergoing slow dynamics below 1 kHz as well as all with fast dynamics above ~100 MHz, which go largely unobserved in BDS due to its lower and upper frequency limits. Effectively, the only overlap between the two spectroscopic analyses (i.e., where both methods detect signals) is at 230–250 K. At 250 K, the ²H SSNMR model indicates that a large majority of the linkers are static, which means the BDS peak at 1 MHz omits information on a significant population of linkers. For this reason, the estimated activation energy should be taken as valid only for this fraction of rotors. In the high-temperature region of the ²H SSNMR spectra, we observe no signal from the SML, and that all rotational motion likely exists within the FML. Both sets of data provide clear evidence that the rotational motions in NO₂-MIL-53(Al) are spread along a very broad frequency range, which is a rare phenomenon that we can attribute to the addition of the bulky nitro substituent.

To understand the observed frequency broadening and the effect of temperature on how neighboring linkers influence rotational motion in NO₂-MIL-53(Al), we performed *ab initio* molecular dynamics (MD) simulations at 300, 450, 700, and 1200 K. To probe the emergence of coupled dynamics, we focused on the situation where –NO₂ groups are positioned on equivalent C atoms (NO₂ same side in Figure 2d), the situation with highest steric hindrance. The higher temperatures are not directly relevant to the physical situation (NO₂-MIL-53(Al) combusts at ~700 K), yet they allow for more rotation events to be observed during shorter simulation times.^{70,71} In periodic MD simulations involving a single unit cell (Figure S25), clear preferential conformations are observed, consistent with the potential energy minima observed in zero-Kelvin calculations. At lower temperatures (e.g., 300 K), the linkers undergo discrete 60° rotations between 30° and –30°, whose frequency increases with temperature. At higher temperatures, we also see the occurrence of 120° jumps between $\pm 30^\circ$ and $\pm 150^\circ$. Both motions are consistent with the ²H SSNMR data and the DFT-predicted energy barriers.

A similar trend in angular mobility ranges is observed for 2 × 1 × 1 supercell simulations. At 300 K, only small angle librations ~20° are observed (Figure S26). In the midtemperature range (450–700 K), two sets of rotational jumps appear, in addition to librations (Figures S27 and S28). At the highest temperature simulated (1200 K), the linkers' motion becomes so fast and extensive that even rotation beyond 180° occurs (Figure S29).

Interestingly, barring the 1200 K simulations, the time traces of rotation angles feature repeated occurrences of apparent correlated fluctuations in both librations and jumps of adjacent linker pairs. This is less evident in the 300 K simulations, where rings did not undergo any large-angle jumps. To analyze the relation between this apparent correlated motion and the

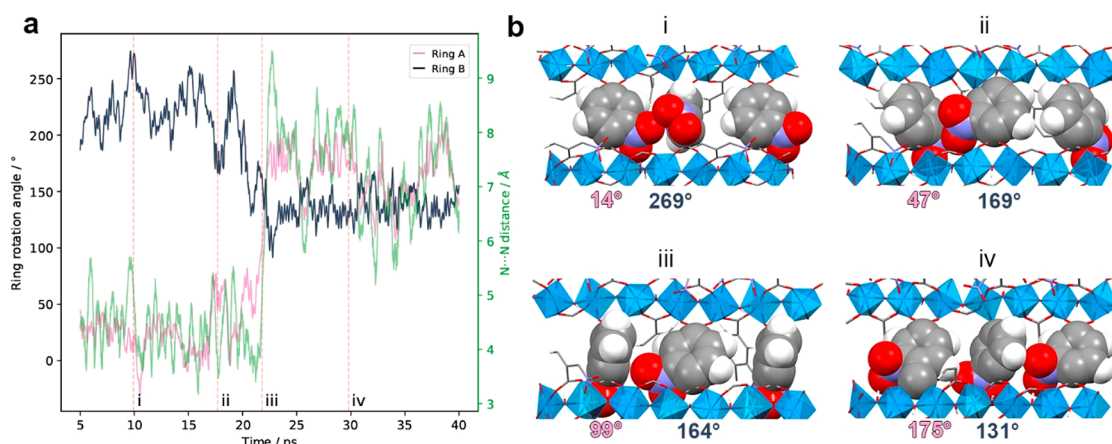


Figure 5. Cooperative rotation in NO_2 -MIL-53(Al). (a) Rotation angle traces of two neighboring rings in a $2 \times 1 \times 1$ cell MD simulation at 700 K. Correlated motion is observed, with simultaneous angle changes in opposite directions (i, ii, iii), when nitro groups are in proximity ($\text{N}\cdots\text{N}$ distance ca. 4 Å). (b) Selected snapshots (i–iv) of linker pair conformation during a coupled rotation. As ring A rotates in the positive direction, ring B reaches the space originally occupied by ring A.

steric effect of linkers within a row, we compare the distance between nitro groups of each pair of neighboring linkers (defined as the distance between the two nitrogen atoms, see Supporting Information section 3.9) with the angle traces at 450 and 700 K. Figure 5a shows representative linker dynamics. The rotational angle traces for all linker pairs at 450 and 700 K can be found in Figures S31–S34. It can be observed that the phenylene rings at these temperatures perform mirrored small angle fluctuations ($\sim 50^\circ$) when the distance between their nitro groups is small (Figure 5b). In the portions of the simulations where the nitro distances are large enough as to not cause steric effects, the mirrored correlated motion is not present, and faster, shorter fluctuations are observed.

Although large-angle jumps are relatively rare in the supercell simulations, Figures 5, S32, and S34 show at 700 K examples of correlated large-angle motions that occur when nitro groups are in proximity. A closer analysis of the molecular conformations during a simulation provides a clear example of these coupled dynamics, presented in Figure 5 and the Supplementary Video. The snapshot sequence presented in Figure 5b illustrates how the limited space of the rotors requires cooperative motion to allow the change in angles from i to iv. In this case, ring A could be seen as rotating cooperatively in the positive direction (most noticeable in snapshots ii to iii) allowing ring B to rotate in the negative direction (i–iv), resulting in the pair performing a gear-like rotation. This correlated motion is facilitated by the neighbors' close arrangement, which implies that to achieve certain conformations, cooperative rotation between neighbors is required.

Because of the high computational cost of these calculations, we were not able to reach long simulation times, which prevented the reliable determination of the free energy profile and further numerical analysis. To overcome these limitations, free energy techniques such as metadynamics simulations or Blue Moon sampling could be adequate options for future work. Nevertheless, the MD simulation data provide qualitative insight into the effect of interlinker interactions. We propose that this type of complex dynamics is in fact what causes NO_2 -MIL-53(Al) to display the intriguing behavior determined by BDS and ^2H SSNMR analysis. The vast array of possible

dynamics observed in this MOF, evidenced by the coexistence of both static and rapidly rotating rings at most temperatures, is a result of functionalizing the phenylene rotators with a substituent that (i) drastically decreases the intrinsic rotation barrier and (ii) facilitates intrarow steric interactions. The computational results support the hypothesis that intrarow steric effects lead to coupled motion for fraction of the neighboring linkers, while the static rings are the inevitable result of energetically disfavored noncooperative rotation.

CONCLUSIONS

To conclude, the MIL-53 topology, where the distance between the rotational axes of phenylene rings along the pore direction is only ~ 6.6 Å, has proven to be an excellent scaffold in which to tune rotational mobility in different dynamic regimes. By selecting two different ring substituents, nitro and amino, distinct pore geometries, and rotor–rotor interactions were achieved. At the two extremes, there are (i) unfunctionalized phenylene units that can rotate independently, with specific temperature-dependent rates, and (ii) amino-functionalized phenylene units that cannot rotate at all, due to intralinker hydrogen bonding and increased steric hindrance from the narrow-pore configuration. Between these extremes, for nitrophenylene linkers, we observe complex rotational dynamics that evolve with temperature, spanning a broad frequency range. Among these, we identify for the first time the emergence of coupled rotational dynamics between neighboring linkers in MOFs. In fact, such coupled dynamics should be expected in other framework systems, provided that the appropriate degree of rotational mobility and interlinker steric interactions are encountered. This discovery paves the way to engineering gear-like functional motion in MOFs if linker dynamics can also be controlled externally, for example, by electric fields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c03630>.

Experimental section, synthesis and characterization, computational details, supporting figures and discussion, rotation angle measurement pseudocode (PDF)

MD simulation of supercell NO₂-MIL-53(Al) at 700 K (MPG)

Structure factors file of single-crystal XRD data of NO₂-MIL-53(Al) (TXT)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) van Meer, G.; Voelker, D. R.; Feigenson, G. W. Membrane Lipids: Where They Are and How They Behave. *Nat. Rev. Mol. Cell Biol.* **2008**, *9* (2), 112–124.
- (2) Duncan, A. L.; Reddy, T.; Koldsø, H.; Hélie, J.; Fowler, P. W.; Chavent, M.; Sansom, M. S. P. Protein Crowding and Lipid Complexity Influence the Nanoscale Dynamic Organization of Ion Channels in Cell Membranes. *Sci. Rep.* **2017**, *7* (1), 16647.
- (3) van der Kooij, H. M.; Semerdzhiev, S. A.; Buijs, J.; Broer, D. J.; Liu, D.; Sprakel, J. Morphing of Liquid Crystal Surfaces by Emergent Collectivity. *Nat. Commun.* **2019**, *10* (1), 1–9.
- (4) Catalano, L.; Naumov, P. Exploiting Rotational Motion in Molecular Crystals. *CrystEngComm* **2018**, *20* (39), 5872–5883.
- (5) Vogelsberg, C. S.; Garcia-Garibay, M. A. Crystalline Molecular Machines: Function, Phase Order, Dimensionality, and Composition. *Chem. Soc. Rev.* **2012**, *41* (5), 1892–1910.
- (6) Khuong, T.-A. A. V.; Nunez, J. E.; Godinez, C. E.; Garcia-Garibay, M. A. Crystalline Molecular Machines: A Quest toward Solid-State Dynamics and Function. *Acc. Chem. Res.* **2006**, *39* (6), 413–422.
- (7) Comotti, A.; Bracco, S.; Sozzani, P. Molecular Rotors Built in Porous Materials. *Acc. Chem. Res.* **2016**, *49* (9), 1701–1710.
- (8) Deng, H.; Olson, M. A.; Stoddart, J. F.; Yaghi, O. M. Robust Dynamics. *Nat. Chem.* **2010**, *2* (6), 439–443.
- (9) Gonzalez-Nelson, A.; Coudert, F.-X.; van der Veen, M. Rotational Dynamics of Linkers in Metal–Organic Frameworks. *Nanomaterials* **2019**, *9* (3), 330.
- (10) Martinez-Bulit, P.; Stirk, A. J.; Loeb, S. J. Rotors, Motors, and Machines Inside Metal–Organic Frameworks. *Trends in Chemistry. Cell Press September* **2019**, *1*, 588–600.
- (11) Dong, J.; Wee, V.; Peh, S. B.; Zhao, D. Molecular-Rotor-Driven Advanced Porous Materials. *Angew. Chem., Int. Ed.* **2021**, *60*, 2–16.
- (12) Gee, J. A.; Sholl, D. S. Effect of Framework Flexibility on C 8 Aromatic Adsorption at High Loadings in Metal–Organic Frameworks. *J. Phys. Chem. C* **2016**, *120* (1), 370–376.
- (13) Park, J.; Agrawal, M.; Sava Gallis, D. F.; Harvey, J. A.; Greathouse, J. A.; Sholl, D. S. Impact of Intrinsic Framework Flexibility for Selective Adsorption of Sarin in Non-Aqueous Solvents Using Metal–Organic Frameworks. *Phys. Chem. Chem. Phys.* **2020**, *22* (11), 6441–6448.
- (14) Agrawal, M.; Bhattacharyya, S.; Huang, Y.; Jayachandrababu, K. C.; Murdock, C. R.; Bentley, J. A.; Rivas-Cardona, A.; Mertens, M. M.; Walton, K. S.; Sholl, D. S.; Nair, S. Liquid-Phase Multicomponent Adsorption and Separation of Xylene Mixtures by Flexible MIL-53 Adsorbents. *J. Phys. Chem. C* **2018**, *122* (1), 386–397.

- (15) Verploegh, R. J.; Kulkarni, A.; Boulfefel, S. E.; Haydak, J. C.; Tang, D.; Sholl, D. S. Screening Diffusion of Small Molecules in Flexible Zeolitic Imidazolate Frameworks Using a DFT-Parameterized Force Field. *J. Phys. Chem. C* **2019**, *123* (14), 9153–9167.
- (16) Witman, M.; Ling, S.; Jawahery, S.; Boyd, P. G.; Haranczyk, M.; Slater, B.; Smit, B. The Influence of Intrinsic Framework Flexibility on Adsorption in Nanoporous Materials. *J. Am. Chem. Soc.* **2017**, *139* (15), 5547–5557.
- (17) Lennox, M. J.; Düren, T. Understanding the Kinetic and Thermodynamic Origins of Xylene Separation in UiO-66(Zr) via Molecular Simulation. *J. Phys. Chem. C* **2016**, *120* (33), 18651–18658.
- (18) Evans, J. D.; Krause, S.; Feringa, B. L. Cooperative and Synchronized Rotation in Motorized Porous Frameworks: Impact on Local and Global Transport Properties of Confined Fluids. *Faraday Discuss.* **2021**, *225*, 286–300.
- (19) Aprahamian, I. The Future of Molecular Machines. *ACS Cent. Sci.* **2020**, *6* (3), 347–358.
- (20) Vogelsberg, C. S.; Uribe-Romo, F. J.; Lipton, A. S.; Yang, S.; Houk, K. N.; Brown, S.; Garcia-Garibay, M. A. Ultrafast Rotation in an Amphidynamic Crystalline Metal Organic Framework. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (52), 13613–13618.
- (21) Bracco, S.; Castiglioni, F.; Comotti, A.; Galli, S.; Negroni, M.; Maspero, A.; Sozzani, P. Ultrafast Molecular Rotors and Their CO₂ Tuning in MOFs with Rod-Like Ligands. *Chem. - Eur. J.* **2017**, *23* (47), 11210–11215.
- (22) Perego, J.; Bracco, S.; Negroni, M.; Bezuidenhout, C. X.; Prando, G.; Carretta, P.; Comotti, A.; Sozzani, P. Fast Motion of Molecular Rotors in Metal–Organic Framework Struts at Very Low Temperatures. *Nat. Chem.* **2020**, *12* (9), 845–851.
- (23) Danowski, W.; van Leeuwen, T.; Abdolazadeh, S.; Roke, D.; Browne, W. R.; Wezenberg, S. J.; Feringa, B. L. Unidirectional Rotary Motion in a Metal–Organic Framework. *Nat. Nanotechnol.* **2019**, *14* (5), 488–494.
- (24) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. Artificial Molecular Rotors. *Chem. Rev.* **2005**, *105* (4), 1281–1376.
- (25) Yan, Y.; Kolokolov, D. I.; da Silva, I.; Stepanov, A. G.; Blake, A. J.; Dailly, A.; Manuel, P.; Tang, C. C.; Yang, S.; Schröder, M. Porous Metal–Organic Polyhedral Frameworks with Optimal Molecular Dynamics and Pore Geometry for Methane Storage. *J. Am. Chem. Soc.* **2017**, *139* (38), 13349–13360.
- (26) Sokolov, A. N.; Swenson, D. C.; MacGillivray, L. R. Conformational Polymorphism in a Heteromolecular Single Crystal Leads to Concerted Movement Akin to Collective Rack-and-Pinion Gears at the Molecular Level. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105* (6), 1794–1797.
- (27) Jarowski, P. D.; Houk, K. N.; Garcia-Garibay, M. A. Importance of Correlated Motions on the Low Barrier Rotational Potentials of Crystalline Molecular Gyroscopes. *J. Am. Chem. Soc.* **2007**, *129* (11), 3110–3117.
- (28) Howe, M. E.; Garcia-Garibay, M. A. The Roles of Intrinsic Barriers and Crystal Fluidity in Determining the Dynamics of Crystalline Molecular Rotors and Molecular Machines. *J. Org. Chem.* **2019**, *84* (16), 9835–9849.
- (29) Lemouchi, C.; Iliopoulos, K.; Zorina, L.; Simonov, S.; Wzietek, P.; Cauchy, T.; Rodríguez-Forteza, A.; Canadell, E.; Kaleta, J.; Michl, J.; Gindre, D.; Chryso, M.; Batail, P. Crystalline Arrays of Pairs of Molecular Rotors: Correlated Motion, Rotational Barriers, and Space-Inversion Symmetry Breaking Due to Conformational Mutations. *J. Am. Chem. Soc.* **2013**, *135* (25), 9366–9376.
- (30) Damron, J. T.; Ma, J.; Kurz, R.; Saalwächter, K.; Matzger, A. J.; Ramamoorthy, A. The Influence of Chemical Modification on Linker Rotational Dynamics in Metal–Organic Frameworks. *Angew. Chem., Int. Ed.* **2018**, *57* (28), 8678–8681.
- (31) Zhou, W.; Yildirim, T. Lattice Dynamics of Metal–Organic Frameworks: Neutron Inelastic Scattering and First-Principles Calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *74* (18), 180301.
- (32) Ryder, M. R.; Van De Voorde, B.; Civalleri, B.; Bennett, T. D.; Mukhopadhyay, S.; Cinque, G.; Fernandez-Alonso, F.; De Vos, D.; Rudić, S.; Tan, J. C. Detecting Molecular Rotational Dynamics Complementing the Low-Frequency Terahertz Vibrations in a Zirconium-Based Metal–Organic Framework. *Phys. Rev. Lett.* **2017**, *118* (25), 1–6.
- (33) Liepuoniute, I.; Huynh, C. M.; Perez-Estrada, S.; Wang, Y.; Khan, S.; Houk, K. N.; Garcia-Garibay, M. A. Enhanced Rotation by Ground State Destabilization in Amphidynamic Crystals of a Dipolar 2,3-Difluorophenylene Rotator as Established by Solid State ²H NMR and Dielectric Spectroscopy. *J. Phys. Chem. C* **2020**, *124* (28), 15391–15398.
- (34) Kolokolov, D. I.; Jobic, H.; Stepanov, A. G.; Guillerme, V.; Devic, T.; Serre, C.; Férey, G. Dynamics of Benzene Rings in MIL-53(Cr) and MIL-47(V) Frameworks Studied By ²H NMR Spectroscopy. *Angew. Chem., Int. Ed.* **2010**, *49* (28), 4791–4794.
- (35) Kolokolov, D. I.; Stepanov, A. G.; Jobic, H. Guest Controlled Rotational Dynamics of Terephthalate Phenylenes in Metal–Organic Framework MIL-53(Al): Effect of Different Xylene Loadings. *J. Phys. Chem. C* **2014**, *118* (29), 15978–15984.
- (36) Khudozhitkov, A. E.; Jobic, H.; Freude, D.; Haase, J.; Kolokolov, D. I.; Stepanov, A. G. Ultraslow Dynamics of a Framework Linker in MIL-53 (Al) as a Sensor for Different Isomers of Xylene. *J. Phys. Chem. C* **2016**, *120* (38), 21704–21709.
- (37) Khudozhitkov, A. E.; Kolokolov, D. I.; Stepanov, A. G.; Bolotov, V. A.; Dybtsev, D. N. Metal-Cation-Independent Dynamics of Phenylene Ring in Microporous MOFs: A ²H Solid-State NMR Study. *J. Phys. Chem. C* **2015**, *119* (50), 28038–28045.
- (38) Gould, S. L.; Tranchemontagne, D.; Yaghi, O. M.; Garcia-Garibay, M. A. Amphidynamic Character of Crystalline MOF-5: Rotational Dynamics of Terephthalate Phenylenes in a Free-Volume, Sterically Unhindered Environment. *J. Am. Chem. Soc.* **2008**, *130* (11), 3246–3247.
- (39) Kolokolov, D. I.; Stepanov, A. G.; Guillerme, V.; Serre, C.; Frick, B.; Jobic, H. Probing the Dynamics of the Porous Zr Terephthalate UiO-66 Framework Using ²H NMR and Neutron Scattering. *J. Phys. Chem. C* **2012**, *116* (22), 12131–12136.
- (40) Biswas, S.; Ahnfeldt, T.; Stock, N. New Functionalized Flexible Al-MIL-53-X (X = -Cl, -Br, -CH₃, -NO₂, -(OH)₂) Solids: Syntheses, Characterization, Sorption, and Breathing Behavior. *Inorg. Chem.* **2011**, *50* (19), 9518–9526.
- (41) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) upon Hydration. *Chem. - Eur. J.* **2004**, *10* (6), 1373–1382.
- (42) Liu, Y.; Her, J. H.; Dailly, A.; Ramirez-Cuesta, A. J.; Neumann, D. A.; Brown, C. M. Reversible Structural Transition in MIL-53 with Large Temperature Hysteresis. *J. Am. Chem. Soc.* **2008**, *130* (35), 11813–11818.
- (43) Munn, A. S.; Pillai, R. S.; Biswas, S.; Stock, N.; Maurin, G.; Walton, R. I. The Flexibility of Modified-Linker MIL-53 Materials. *Dalt. Trans.* **2016**, *45* (10), 4162–4168.
- (44) Stavitski, E.; Pidko, E. A.; Couck, S.; Remy, T.; Hensen, E. J. M.; Weckhuysen, B. M.; Denayer, J.; Gascon, J.; Kapteijn, F. Complexity behind CO₂ Capture on NH₂-MIL-53(Al). *Langmuir* **2011**, *27* (7), 3970–3976.
- (45) Shustova, N. B.; Ong, T.-C.; Cozzolino, A. F.; Michaelis, V. K.; Griffin, R. G.; Dinca, M. Phenyl Ring Dynamics in a Tetraphenylethylene-Bridged Metal–Organic Framework: Implications for the Mechanism of Aggregation-Induced Emission. *J. Am. Chem. Soc.* **2012**, *134* (36), 15061–15070.
- (46) Kolokolov, D. I.; Stepanov, A. G.; Jobic, H. SI: Guest Controlled Rotational Dynamics of Terephthalate Phenylenes in Metal–Organic Framework MIL-53(Al): Effect of Different Xylene Loadings. *J. Phys. Chem. C* **2014**, *118* (29), 15978–15984.
- (47) Balčiūnas, S.; Simenas, M.; Pavlovaite, D.; Kinka, M.; Shieh, F.-K.; Wu, K. C.-W.; Banys, J.; Grigalaitis, R. Low-Frequency Dipolar Dynamics and Atmospheric Effects in ZIF-90 Metal–Organic Framework. *J. Phys. Chem. C* **2019**, *123* (1), 631–636.

- (48) Winston, E. B.; Lowell, P. J.; Vacek, J.; Chocholoušová, J.; Michl, J.; Price, J. C. Dipolar Molecular Rotors in the Metal–Organic Framework Crystal IRMOF-2. *Phys. Chem. Chem. Phys.* **2008**, *10* (34), 5188.
- (49) Devautour-Vinot, S.; Maurin, G.; Serre, C.; Horcajada, P.; Paula Da Cunha, D.; Guillerm, V.; De Souza Costa, E.; Taulelle, F.; Martineau, C. Structure and Dynamics of the Functionalized MOF Type UiO-66(Zr): NMR and Dielectric Relaxation Spectroscopies Coupled with DFT Calculations. *Chem. Mater.* **2012**, *24* (11), 2168–2177.
- (50) Kremer, A.; Schönhals, F. Theory of Dielectric Relaxation. In *Broadband Dielectric Spectroscopy*; Springer-Verlag: Berlin Heidelberg, 2003; pp 1–33. DOI: 10.1007/978-3-642-56120-7_1.
- (51) Frunza, S.; Schönhals, A.; Frunza, L.; Ganea, P.; Kosslick, H.; Harloff, J.; Schulz, A. Molecular Relaxation Processes in a MOF-5 Structure Revealed by Broadband Dielectric Spectroscopy: Signature of Phenylene Ring Fluctuations. *J. Phys. Chem. B* **2010**, *114* (40), 12840–12846.
- (52) Knebel, A.; Geppert, B.; Volgmann, K.; Kolokolov, D. I.; Stepanov, A. G.; Twiefel, J.; Heitjans, P.; Volkmer, D.; Caro, J. Defibrillation of Soft Porous Metal–Organic Frameworks with Electric Fields. *Science* **2017**, *358* (6361), 347–351.
- (53) Horansky, R. D.; Clarke, L. I.; Price, J. C.; Khuong, T. A. V.; Jarowski, P. D.; Garcia-Garibay, M. A. Dielectric Response of a Dipolar Molecular Rotor Crystal. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72* (1), 1–5.
- (54) Horansky, R. D.; Clarke, L. I.; Winston, E. B.; Price, J. C.; Karlen, S. D.; Jarowski, P. D.; Santillan, R.; Garcia-Garibay, M. A. Dipolar Rotor–Rotor Interactions in a Difluorobenzene Molecular Rotor Crystal. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *74* (5), 1–12.
- (55) Jiang, X.; O'Brien, Z. J.; Yang, S.; Lai, L. H.; Buenaflor, J.; Tan, C.; Khan, S.; Houk, K. N.; Garcia-Garibay, M. A. Crystal Fluidity Reflected by Fast Rotational Motion at the Core, Branches, and Peripheral Aromatic Groups of a Dendrimeric Molecular Rotor. *J. Am. Chem. Soc.* **2016**, *138* (13), 4650–4656.
- (56) Hansen, M. R.; Graf, R.; Spiess, H. W. Solid-State NMR in Macromolecular Systems: Insights on How Molecular Entities Move. *Acc. Chem. Res.* **2013**, *46* (9), 1996–2007.
- (57) Spiess, H. W. Molecular Dynamics of Solid Polymers as Revealed by Deuteron NMR. *Colloid Polym. Sci.* **1983**, *261*, 193–209.
- (58) Khudozhnikov, A. E.; Jovic, H.; Freude, D.; Haase, J.; Kolokolov, D. I.; Stepanov, A. G. Ultraslow Dynamics of a Framework Linker in MIL-53 (Al) as a Sensor for Different Isomers of Xylene. *J. Phys. Chem. C* **2016**, *120* (38), 21704–21709.
- (59) Serra-Crespo, P.; Van Der Veen, M. A.; Gobechiya, E.; Houthoofd, K.; Filinchuk, Y.; Kirschhock, C. E. A.; Martens, J. A.; Sels, B. F.; De Vos, D. E.; Kapteijn, F.; Gascon, J. NH₂-MIL-53(Al): A High-Contrast Reversible Solid-State Nonlinear Optical Switch. *J. Am. Chem. Soc.* **2012**, *134* (20), 8314–8317.
- (60) Spiess, H. W. Deuteron NMR — a New Tool for Studying Chain Mobility and Orientation in Polymers. In *Characterization of Polymers in the Solid State I: Part A: NMR and Other Spectroscopic Methods Part B: Mechanical Methods*; Kaush, H. H., Zachman, H. G., Eds.; Springer: Berlin, Heidelberg, 1985; pp 23–58. DOI: 10.1007/3-540-13779-3_16.
- (61) Gedat, E.; Schreiber, A.; Albrecht, J.; Emmler, T.; Shenderovich, I.; Findenegg, G. H.; Limbach, H. H.; Buntkowsky, G. 2H-Solid-State NMR Study of Benzene-D₆ Confined in Mesoporous Silica SBA-15. *J. Phys. Chem. B* **2002**, *106* (8), 1977–1984.
- (62) Larsen, F. H. Simulation of Molecular Motion of Quadrupolar Nuclei in Solid-State NMR Spectra. In *Annu. Rep. NMR Spectrosc.*; Elsevier Ltd, 2010; Vol. 71, pp 103–137. DOI: 10.1016/B978-0-08-089054-8.00004-6.
- (63) Aliev, A. E.; Mann, S. E.; Rahman, A. S.; McMillan, P. F.; Cora, F.; Iuga, D.; Hughes, C. E.; Harris, K. D. M. High-Resolution Solid-State H-2 NMR Spectroscopy of Polymorphs of Glycine. *J. Phys. Chem. A* **2011**, *115* (44), 12201–12211.
- (64) Schadt, R. J.; Cain, E. J.; English, A. D. Simulation of One-Dimensional Deuteron NMR Line Shapes. *J. Phys. Chem.* **1993**, *97* (32), 8387–8392.
- (65) Leisen, J.; Ohlemacher, A.; Boeffel, C.; Spiess, H. W. Molecular Dynamics in Side-Group Polymers with and without Liquid Crystalline Phases from 2H NMR. *Berichte der Bunsengesellschaft für Phys. Chemie* **1993**, *97* (10), 1306–1311.
- (66) Pschorn, U.; Spiess, H. W.; Hisgen, B.; Ringsdorf, H. Deuteron NMR Study of Molecular Order and Motion of the Mesogenic Side Groups in Liquid-crystalline Polymers. *Makromol. Chem.* **1986**, *187* (11), 2711–2723.
- (67) Wehrle, M.; Hellmann, G. P.; Spiess, H. W. Phenylene Motion in Polycarbonate and Polycarbonate/Additive Mixtures. *Colloid Polym. Sci.* **1987**, *265* (9), 815–822.
- (68) O'Dell, L. A.; Ratcliffe, C. I. Quadrupolar NMR to Investigate Dynamics in Solid Materials. In *Encyclopedia of Magnetic Resonance*; Harris, R. K., Wasylishen, R. E., Ed.; John Wiley & Sons, Ltd: Chichester, UK, 2012; pp 3814–3829. DOI: 10.1002/9780470034590.emrstm1209.
- (69) Moreau, F.; Kolokolov, D. I.; Stepanov, A. G.; Easun, T. L.; Dailly, A.; Lewis, W.; Blake, A. J.; Nowell, H.; Lennox, M. J.; Besley, E.; Yang, S.; Schröder, M. Tailoring Porosity and Rotational Dynamics in a Series of Octacarboxylate Metal–Organic Frameworks. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (12), 3056–3061.
- (70) Haigis, V.; Coudert, F.-X.; Vuilleumier, R.; Boutin, A.; Fuchs, A. H. Hydrothermal Breakdown of Flexible Metal–Organic Frameworks: A Study by First-Principles Molecular Dynamics. *J. Phys. Chem. Lett.* **2015**, *6* (21), 4365–4370.
- (71) Gaillac, R.; Pullumbi, P.; Beyer, K. A.; Chapman, K.; Keen, D. A.; Bennett, T. D.; Coudert, F.-X. Liquid Metal–Organic Frameworks. *Nat. Mater.* **2017**, *16* (11), 1149–1155.