

Amphidynamic Character of Crystalline MOF-5: Rotational Dynamics of Terephthalate Phenylenes in a Free-Volume, Sterically Unhindered Environment

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The design of artificial molecular machinery¹ will require a deep understanding of the relation between order and dynamics in condensed phase media.² Recognizing that internal dynamics with controlled degrees of freedom will require components at the two ends of the dynamics spectrum, we suggested that such *amphidynamic materials*³ will require architectures with (a) free volume compartments, (b) volume-conserving processes (such as the rotation of a cylinder along its principal axis), and/or (c) correlated motions with two or more components undergoing concerted displacements. With that in mind, we have pursued the design, synthesis, and dynamic characterization of molecular structures that emulate the form and function of macroscopic gyroscopes (Figure 1).^{1g,3,4} Structures such as **1** and **2** are built with 1,4-phenylene rotators, bulky trityl^{14a-c} (or triptycyl)^{4d,e} stators, and alkyne linkages to provide a nearly barrierless³ rotational profile. While this approach has been successful, as indicated by crystals with 180° rotational (2-fold flipping) frequencies in the kHz (**1a**, $E_a \approx 13$ kcal/mol),^{4a} MHz (**1b**, $E_a \approx 10.5$ kcal/mol),^{4b} and GHz (**1c**, $E_a \leq 5$ kcal/mol)^{4c} regimes, none of their structures may be considered a free-volume rotor as their relatively close-packed assemblies appear to rely on correlated processes.⁵

We expect the dynamics of externally unhindered rotators to depend only on their intrinsic barrier and on how efficient the coupling between crystal phonons and torsional modes is. An ideal amphidynamic architecture that may be used to explore this concept should be available in evacuated metal-organic frameworks (MOFs). With metal centers providing rigid lattice points to support robust crystal structures, organic spacers should be free to explore their unhindered rotational potential. While many MOFs have been investigated for gas storage,⁶ nonlinear optical properties,⁷ and catalysis,⁸ we decided to investigate the readily available MOF-5 (Figure 1). MOF-5 has a cubic framework composed of Zn₄O clusters (vertices) bridged by 1,4-phenylenedicarboxylates analogous to those of the well-characterized 1,4-phenylene rotators in compounds **1** and **2**.

Experimental estimates on the rotational barriers of 1,4-phenylenedicarboxylates (terephthalates) vary widely. Solid-state NMR measurements with amorphous poly(ethyleneterephthalate) give barriers ranging from 10 to 20 kcal/mol⁹ and as low *ca.* 5.9 kcal/mol for poly(butyleneterephthalate).¹⁰ A state of the art *ab initio* study¹¹ with a model that consists of two Zn clusters, a bridging 1,4-phenylenedicarboxylate, and 10 formate groups [Zn₄O(O₂-CH)₅O₂C-C₆H₄-CO₂(O₂CH)₅Zn₄O] reported barriers of *ca.* 14–16 kcal/mol, depending on the basis set and level of theory. Ground state calculations matched the X-ray structure, with a coplanar arrangement of C₆H₄ and CO₂ groups, and the perpendicularly aligned transition state was shown to be a second-order saddle point with two imaginary frequencies that correspond to the phenylene torsional mode.¹¹

Given the wide range of experimental values,^{9,10} the importance of polymer dynamics on materials properties,^{9,10,12b} and the often

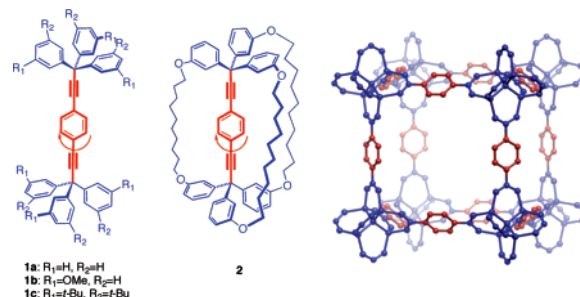


Figure 1. Left and center: Structures that emulate macroscopic toy gyroscopes with open (**1a–1c**) and triply bridged topologies (**2**). Right: a fragment of the structure of MOF-5. The 1,4-dialkynyl phenylene of **1** and **2** are nearly barrierless but sterically hindered. The 1,4-phenylene of MOF-5 has an electronic barrier but no steric hindrance.

debatable accuracy of computational methods on the calculation of barriers involving benzene rings and π -systems,¹² an experimental determination of the barrier of crystalline MOF-5 should be very valuable. Freshly prepared samples of MOF-5 and phenylene deuterated d_4 -MOF-5 were solvent exchanged and transferred to standard 5 mm NMR tubes for activation.^{6a} The solvent was removed, and the sample was evacuated (~ 3 mTorr) at 200 °C for 10 h prior to sealing under vacuum. The ¹³C CPMAS spectrum of a freshly prepared sample consisted of carboxylate and aromatic (ipso- and C–H) carbons and confirmed the complete removal of the solvent and the homogeneity of the sample. The static ¹H NMR (300 MHz) spectrum of evacuated samples showed a broad doublet, consistent with the strong dipolar coupling of adjacent protons. ¹H spin–lattice relaxation measurements (T_1) from 168 to 420 K showed no temperature dependence, as expected for a spin system with dynamic processes that are far from its Larmor frequency.

We set out to determine the dynamics of MOF-5 with d_4 -phenylene labeled samples using variable temperature ²H NMR. The orientation-dependence of ²H NMR quadrupolar coupling with respect to the magnetic field reports on exchange rates in the range of 10⁴ and 10⁸ s⁻¹,¹³ as shown qualitatively by Gonzalez et al.¹⁴ Spectra of d_4 -MOF-5 obtained at 300 K are characteristic of deuterons in the slow exchange regime (Figure 2). Spectra recorded between 363 and 435 K displayed changes in line shapes characteristic of the intermediate regime. To estimate the exchange rate as a function of temperature, the spectra were simulated¹⁵ with a two-fold flipping model (180° rotation) and an adjustable frequency. A reduction of the quadrupolar coupling constant from 180 to 160 kHz from the static spectra to the intermediate exchange is consistent with fast libration along the 1,4-axis,¹⁶ indicating population of higher quantum states of torsional modes previously calculated at 43 and 87 cm⁻¹.¹¹

Arrhenius analysis of the exchange rate data resulted in $E_a = 11.3 \pm 2.0$ kcal/mol and a pre-exponential factor $A = 1.6 \times 10^{12}$ s⁻¹ (Figure 3). The uncertainty in the experimental barrier was determined from the range of simulated rate values that gave a

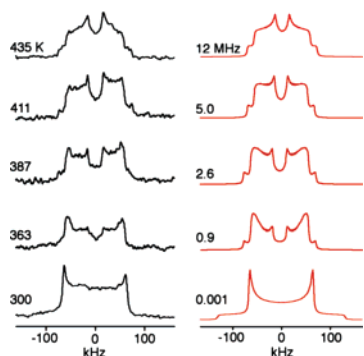


Figure 2. Selected experimental (left) and calculated (right) quadrupolar echo solid state ^2H NMR of d_4 -MOF-5 sample sealed at 3 mTorr.

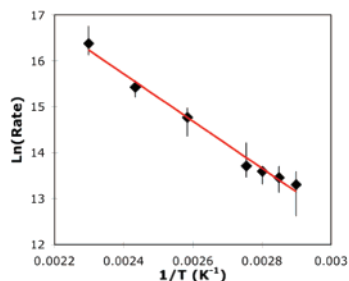


Figure 3. Arrhenius plot of the 2-fold exchange (180° rotation) rate in d_4 -MOF-5.

reasonable match. The pre-exponential factor agrees well with the frequency derived from the moment of inertia of a phenylene free rotor ($2.4 \times 10^{12} \text{ s}^{-1}$).¹⁷ The experimental activation energy is lower than the theoretical value of $ca. 14 \pm 1 \text{ kcal mol}^{-1}$,^{11,18} with differences that could be assigned to the truncated model, to dynamic effects^{20,22} not considered in the calculation, or to the limitations of *ab initio* theory.¹² The discrepancy with amorphous poly(terephthalate)s is puzzling as one may expect that the barrier for rotation should be lowest when there is no steric hindrance. While some disagreement should arise from the different electronics of ester and carboxylate groups,¹⁹ we propose that amorphous polymers and MOF-5 represent very different portions of the energy surface. Rotation in MOF-5 takes place in a well-defined frame of reference where the CO_2 groups remain static, using a trajectory that goes over a second-order saddle point.¹¹ Rotations in polymers involve trajectories that start from a broad population of high-energy conformers with a range of $\text{O}_2\text{C}-\text{Ph}-\text{CO}_2$ dihedral angles,²⁰ which may take advantage of local fluidity that allows for concerted two bond rotations.

In conclusion, the experimental results confirm our expectations for rotational motion in a sterically unhindered environment and reveal a difference with theory that is similar to that previously reported for analogous systems.¹² A comparison of MOF-5 with polymeric terephthalates highlights the potential benefits of ground state destabilization and alternative trajectories. Current efforts in our group involve the synthesis of MOFs with *ortho*-substituents that remove the coplanarity of the terephthalate ground state, with diethynylarylene carboxylates, and with volume-conserving spacers with high rotational symmetry.²¹ Rotation in those cases is expected to approach the THz regime and to have interesting effects on the physical properties of these materials. Dynamic effects on the properties of MOF-5 have been highlighted by molecular dynamics simulations²² and may be expected to play a central role in the design of functional molecular machinery.

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Supporting Information Available: ^{13}C CPMAS NMR, static ^1H NMR spectra, ^1H T_1 inversion recovery data, and XRPD of d_4 -MOF-5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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