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Understanding DABCO Nanorotor Dynamics in Isostructural Metal–Organic Frameworks

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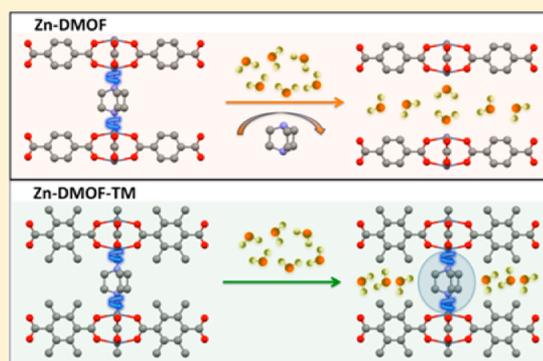
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S Supporting Information

ABSTRACT: Flexible framework dynamics present in the subset of metal–organic frameworks known as soft porous crystals give rise to interesting structural properties that are unique to this class of materials. In this work, we use experiments and molecular simulation to understand the highly dynamic nanorotor behavior of the 1,4-diazabicyclo[2.2.2]octane (DABCO) ligand in the pillared Zn-DMOF and Zn-DMOF-TM (TM = tetramethyl) structures. While DABCO is known to be displaced in the presence of water in the parent Zn-DMOF structure, the Zn-DMOF-TM variation is highly stable even after adsorbing significant amounts of water vapor. The dynamics of DABCO in the presence of water guest molecules is therefore also explored in the Zn-DMOF-TM structure via in situ NMR and IR experiments. This analysis shows that the rotational motion of the DABCO linkers is dependent on water content, but not a likely source of water instability because the dynamics are fast and largely unaffected by the presence of methyl functional groups.



Metal–organic frameworks (MOFs) are crystalline, nanoporous materials that have garnered significant attention due to their fascinating chemistry and array of promising applications arising from their tunable porosity and chemical functionality.^{1,2} A subclass of these materials are termed soft porous crystals and exhibit dynamic flexible properties such as breathing transitions, gate-opening behavior, and local framework dynamics in the presence of external stimuli.³ In turn, this flexible behavior gives rise to unique chemical sensing, gas separation, drug delivery, and catalysis capabilities not possible in rigid porous materials.^{4,5}

Understanding the mechanism of this dynamic behavior in existing structures is critical to the design of next-generation materials with prescribed flexible properties for the application of interest.⁶ For example, ZIF-8 exhibits large structural flexibility due to imidazolate linker reorientations that cause it to adsorb hydrocarbons with kinetic diameters that are much larger than one would expect based on its rigid pore size.^{7,8} Rotation of the phenyl rings in carboxylate-based structures can also lead to significant temperature-dependencies in the effective pore size⁹ and thermal expansion behavior¹⁰ of the structures that should also be accounted for. Experimental techniques such as quasi-elastic neutron scattering,² H NMR, and dielectric relaxation spectroscopy can be used to characterize such librational and rotational behaviors, whereas molecular dynamics simulations accounting for flexible framework behavior can be used to computationally model these

effects.^{9–12} Because metal–ligand coordination bonds represent the most hydrolytically susceptible points in MOFs, understanding the ligand dynamics near these sites may also play a critical role in understanding the chemical stability of structures in the presence of water.¹³

One such flexible material is $Zn_2(BDC)_2(DABCO)$ or Zn-DMOF (BDC = 1,4-benzenedicarboxylate, DABCO = 1,4-diazabicyclo[2.2.2]octane). Zn-DMOF possesses a paddle wheel structure of 2D layers connected by the BDC ligand with DABCO acting as a pillar ligand between these layers to form a 3D framework.¹⁴ It is well-known that the DABCO ligand in this structure is displaced in the presence of moisture, causing its 3D structure to collapse into adjacent 2D layers.^{15,16} These 2D layers containing BDC are then held together by bifurcated water hydrogen bonding interactions involving the oxygen in water interacting with the axial site of the zinc atom of one layer and the hydrogen atom on the same water interacting with the carboxylate oxygen of the adjacent layer.¹⁷

It was shown in past work that the incorporation of methyl groups on all four positions of the BDC ligand in this structure results in an isostructural Zn-DMOF-TM (TM = tetramethyl) variation with significantly improved chemical stability and gas

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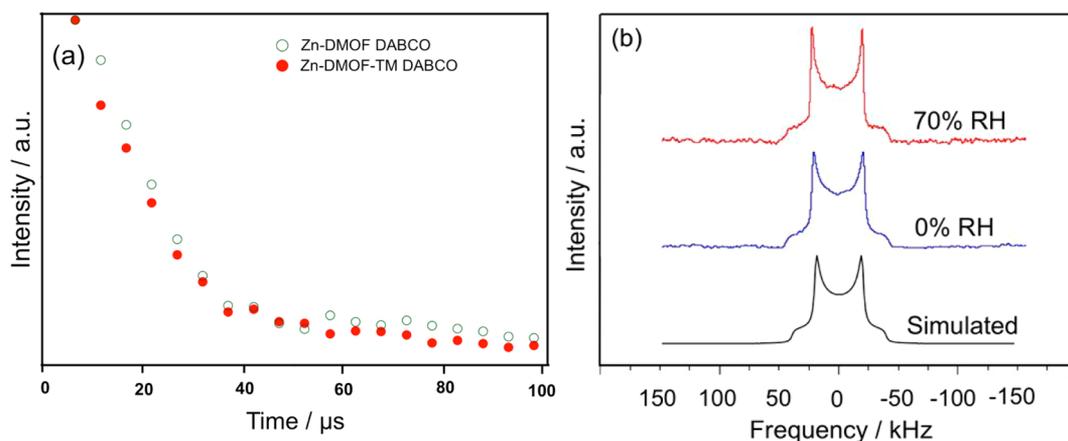


Figure 1. (a) ^1H T_2^* -relaxation of DABCO measured via ^{13}C detection using ^1H – ^{13}C CP-MAS 2D WISE experiments. (b) Comparison of simulated ^2H NMR spectrum with the experimental Zn-DMOF-TM spectrum containing the deuterated DABCO ligand at 297 K in its dry state (0% RH in air) and after adsorbing significant amounts of H_2O (70% RH in air).

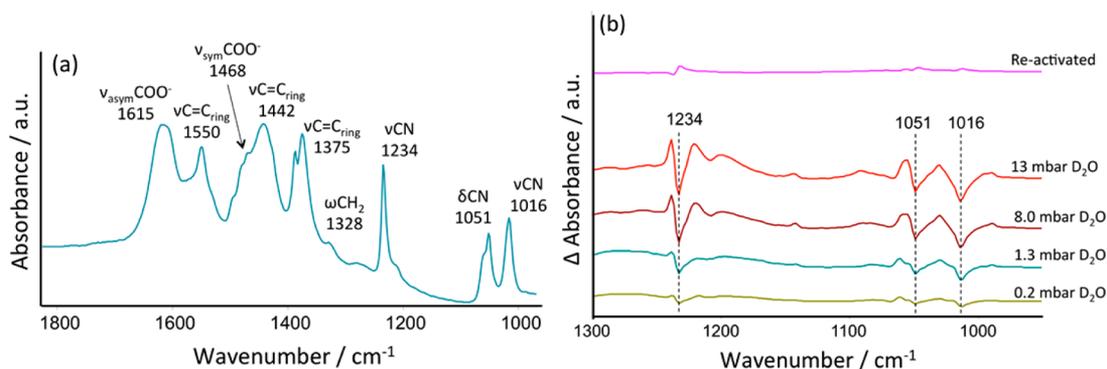


Figure 2. (a) FTIR spectra of Zn-DMOF-TM after first activation. (b) Difference spectra for Zn-DMOF-TM after exposure to various pressures of D_2O vapor followed by sample reactivation.

adsorption properties that are relevant to CO_2 capture from postcombustion flue gas.^{18,19} One interesting similarity between both of these structures is the tertiary diamine DABCO species as the pillaring ligand. DABCO has a symmetric, globular shape that allows it to serve as a highly effective rotator in supramolecular nanorotors by exhibiting fast rotations around its longitudinal N–N axis.^{20,21} Because DABCO is also the labile species in the unstable Zn-DMOF structure, observing the behavior of this ligand can not only provide fundamental insight into the intraframework dynamics in the Zn-DMOF and Zn-DMOF-TM structures but may also shed light on the potential origins of the differences in water stability between these two variations.

To explore the DABCO dynamics, samples of Zn-DMOF and Zn-DMOF-TM were synthesized according to past procedures,¹⁸ and the structures were characterized via powder X-ray diffraction (PXRD) and Brunauer–Emmett–Teller (BET) analysis using N_2 adsorption at 77 K (see Supporting Information, SI). ^1H – ^{13}C cross-polarization (CP) magic angle spinning (MAS) NMR experiments were then run, and the presence of all expected ^{13}C peaks were identified in the structures (SI). Semiquantitative information regarding the molecular dynamics of each functional group in the ^{13}C MAS spectrum can be obtained using the wide-line-separation (WISE) experiment, which correlates broad ^1H -lineshapes corresponding to the protons adjacent to each ^{13}C site with the respective ^{13}C chemical shifts.²² Under conditions of slow MAS

(~ 3 – 5 kHz), the ^1H – ^1H dipolar coupling will not be completely averaged so that the measured line widths (or ^1H -decay prior to Fourier transformation in the ^1H dimension) will reflect the amount of molecular motion. As shown in Figure 1a, analysis of the time decay in the ^1H signal dimension associated with the DABCO ^{13}C chemical shifts indicates similar mobility for DABCO in the two structures. Such analysis provides a preliminary survey of the molecular motion within the system, but, because of the nature of the cross-polarization process, it is difficult to extract a truly quantitative evaluation, and ^2H NMR experiments were therefore needed to obtain more detailed insight into the ligand dynamics.

A Zn-DMOF-TM sample containing deuterated DABCO (98.4 atom % ^2H) was then synthesized. ^2H NMR experiments²³ show a typical Pake pattern with a quadrupolar splitting of 38.6 kHz at 297 K (Figure 1b) and variable temperature measurements showed nearly identical spectra throughout the -40 to 90 °C temperature range accessible to the chiller device on the NMR equipment. This quadrupolar coupling value of $\delta = 38.6$ kHz is significantly reduced in comparison to the value ca. 128.0 kHz that is typically observed for rigid ^2H –C bonds. This reduction can be explained by the rotation of DABCO around its N–N axis with frequencies $\gg 100$ kHz throughout the entire -40 to 90 °C range. The ^2H –C bonds in DABCO fall on a cone with an angle of 70° with respect to its rotation axis, and this rotation alone leads to a theoretical Pake spectrum with a 41.5 kHz splitting (which

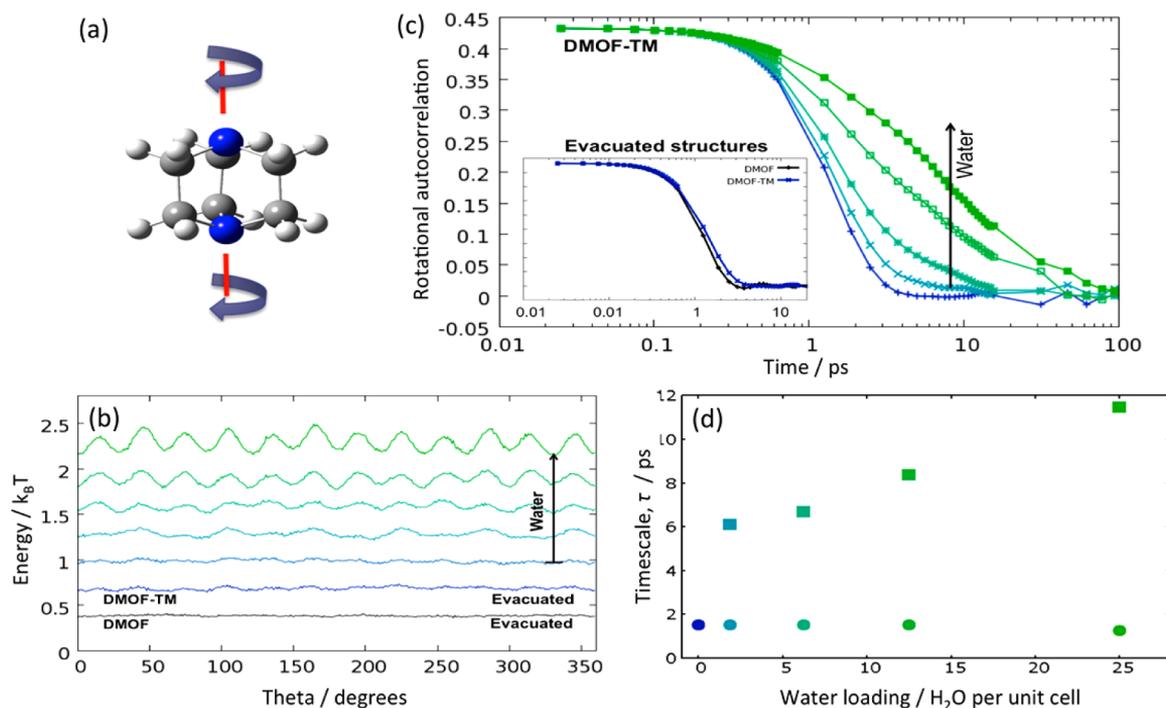


Figure 3. Molecular simulation results. (a) Schematic of DABCO rotation around its N–N axis, (b) free energy profiles for DABCO rotation in the evacuated structures and the Zn-DMOF-TM structure as a function of water loading, (c) rotational autocorrelation functions for DABCO in the evacuated structures (inset) and the Zn-DMOF-TM structure as a function of water loading, and (d) plot of τ_1 (circle) and τ_2 (square) values from exponential fittings of the Zn-DMOF-TM DABCO rotational autocorrelation function. All results were obtained from canonical (NVT) ensemble molecular dynamics simulations at 298 K.

can be readily simulated using the online NMR WEBLAB tool²⁴). Small fluctuations of the cone angle can occur through conformational changes within the DABCO molecules²⁵ and, by assuming a Gaussian fluctuation of the cone-angle with a width of 18.5° , one obtains a simulated splitting in agreement with the experimental value of 38.6 kHz. The influence of adsorbed water on the DABCO dynamics was also explored by introducing H_2O directly into the NMR apparatus using a previously described experimental set up²⁶ and collecting in situ 2H NMR measurements. After exposure to 70% relative humidity (RH) in air, conditions where the Zn-DMOF-TM structure adsorbs significant amounts of water,¹⁸ no discernible change in the 2H NMR spectra for the structure was observed, indicating that the fast DABCO rotation still persists. It was not possible to obtain the quantity of deuterated DABCO needed to perform similar experiments on the Zn-DMOF sample, but as evidenced from the molecular simulation analysis that follows, one would expect it to exhibit a 2H spectrum that is nearly identical to the Zn-DMOF-TM sample in its evacuated state.

In situ Fourier transform infrared (FTIR) measurements were next performed to observe any perturbations to the DABCO environment in the Zn-DMOF-TM structure in the presence of water. Figure 2 shows the FTIR spectra for the activated, nondeuterated Zn-DMOF-TM sample as well as the difference spectra for the structure after being exposed to increasing partial pressures of D_2O . D_2O was used instead of H_2O to minimize potential interference between the adsorbate and framework infrared bands, and reactivating the sample after water exposure returns the spectra back to its original state. This further supports the exceptional stability of this structure relative to the more unstable parent Zn-DMOF variation.

Assignment of the IR modes for the parent Zn-DMOF structure was performed by Tan et al.;¹⁶ here, we extend this analysis to the Zn-DMOF-TM structure and note the presence of three peaks near 1234, 1051, and 1016 cm^{-1} in the difference spectra after exposure to 13 mbar D_2O (Figure 2b). These bands indicate perturbations in the C–N vibrational modes of DABCO that can be attributed to interactions between D_2O and DABCO. The complete FTIR spectra over the 600–1800 cm^{-1} range can be found in the SI.

To better understand the nature of the DABCO dynamics in the two structures at the molecular level, flexible framework force field models for the two structures^{19,27} were utilized. These flexible models, originally developed to reproduce the unit cell parameters and breathing behavior of the parent Zn-DMOF structure in the presence of different adsorbates, were first analyzed to ensure consistency between characteristics of the classical and ab initio energy profile for the rotation of DABCO inside the structures at 0 K. Analysis of these profiles indicates the energy barrier for DABCO rotation is not governed by the methyl groups in Zn-DMOF-TM and is instead governed by short-range repulsive van der Waals forces between DABCO and the carboxylate oxygen atoms attached to zinc in both structures (SI).

Canonical (NVT) ensemble molecular dynamics simulations at 298 K were then performed using the RASPA software²⁸ in both structures to further understand the DABCO dynamics observed from experiment. In agreement with the variable temperature 2H spectra measurements, free energy profiles for rotation of the N–C bond in DABCO around its N–N axis show an energy barrier of $E_a \ll 1 k_B T$ in each of the evacuated structures, indicating that entropic effects allow a near barrier-free rotation at room temperature (Figure 3b). Visual inspection of the trajectory movies from the molecular

dynamics simulations (SI) also support this, showing full rotations of DABCO around its N–N axis over the picoseconds time scale of the simulation. Upon introduction of water until a loading of ~ 6 H₂O per DABCO ligand (or 25 molecules per unit cell) in Zn-DMOF-TM, a water loading well-above what corresponds to breakdown in the parent Zn-DMOF structure,¹⁸ a relatively low energy barrier of $<0.5 k_B T$ is still observed.

To observe the time-dependent dynamical behavior of the system, the rotational autocorrelation function for DABCO was also analyzed (Figure 3c). In the evacuated structures, the autocorrelation function can be well-described by a single compressed exponential function of the form

$$C_1(t) = \exp(-(t/\tau)^\beta) \quad (1)$$

with $\tau = 1.4$ and 1.5 ps and $\beta = 1.9$ and 1.7 ps in the Zn-DMOF and Zn-DMOF-TM structures, respectively. A compressed exponential with $1 < \beta < 2$ indicates a strong ballistic component to the rotational motion that is consistent with the free DABCO rotation exhibited in these structures, and after ~ 10 ps there is a complete decay in their autocorrelation functions. These findings are in excellent agreement with the ²H NMR results, which also indicate DABCO rotations at frequencies $\gg 100$ kHz. Upon introduction of water into the Zn-DMOF-TM structure, the autocorrelation function can no longer be described by a single exponential and instead requires a double exponential of the form

$$C_2(t) = \exp(-(t/\tau_1)^{\beta_1}) + \exp(-(t/\tau_2)^{\beta_2}) \quad (2)$$

A plot of the τ_1 and τ_2 values as a function of water loading is shown in Figure 3d. In this case, the time scale τ_1 characteristic of free DABCO rotation remains near constant, but a second characteristic time scale τ_2 also emerges as a function of water loading. This fitting captures the DABCO–water interactions evidenced by experimental IR measurements by indicating there are two characteristic time scales governing the system: τ_1 that is characteristic of the ballistic rotational behavior inherent to the DABCO ligand, and τ_2 that is a result of perturbations to this behavior due to water-induced intermolecular interactions. However, both $1/\tau_1$ and $1/\tau_2$ are fast on the time-scale of the ²H NMR experiment and are therefore not reflected in the spectroscopic line shapes.

In summary, this work provides fundamental insight into the highly dynamic nanorotor behavior of DABCO in the isostructural MOFs via in situ experiments combined with molecular simulation. NMR and simulation results both support the presence of free DABCO rotation in the structures, which is largely unaffected by the presence of the methyl functional groups on the BDC ligand in the Zn-DMOF-TM structure. Furthermore, this free rotation persists after the introduction of water into the highly stable Zn-DMOF-TM structure but results in DABCO–water interactions that slightly perturb the rotational dynamics. The presence of DABCO as the labile ligand in the Zn-DMOF structure also allows one to rule out a steric locking mechanism as the governing stability mechanism in Zn-DMOF-TM, a finding supported by the persistent free rotation of the DABCO ligand in this structure even under water loadings that correspond to structural breakdown in the Zn-DMOF structure.¹⁸ This indicates that further insight into the intraframework interactions introduced by the BDC-TM ligand, a focus of ongoing work, must be obtained to fully understand the stability differences between these two structures. Overall, this work provides the ground-

work for the design for next-generation flexible materials with functionality not present in rigid porous solids and also addresses the important topic of water stability in MOFs, a critical challenge for the use of these materials under real world conditions.

■ ASSOCIATED CONTENT

📄 Supporting Information

PXRD patterns, N₂ adsorption isotherms, NMR and FTIR spectra, further simulation details, and a 500 ps excerpt of the trajectory movies from molecular dynamics simulations can be found in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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