Chemical structure, network topology, and porosity effects on the mechanical properties of Zeolitic Imidazolate Frameworks

Jin Chong Tan, Thomas D. Bennett, and Anthony K. Cheetham¹

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, CB2 3QZ Cambridge, United Kingdom

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The mechanical properties of seven zeolitic imidazolate frameworks (ZIFs) based on five unique network topologies have been systematically characterized by single-crystal nanoindentation studies. We demonstrate that the elastic properties of ZIF crystal structures are strongly correlated to the framework density and the underlying porosity. For the systems considered here, the elastic modulus was found to range from 3 to 10 GPa, whereas the hardness property lies between 300 MPa and 1.1 GPa. Notably, these properties are superior to those of other metal-organic frameworks (MOFs), such as MOF-5. In substituted imidazolate frameworks, our results show that their mechanical properties are mainly governed by the rigidity and bulkiness of the substituted organic linkages. The framework topology and the intricate pore morphology can also influence the degree of mechanical anisotropy. Our findings present the previously undescribed structuremechanical property relationships pertaining to hybrid open frameworks that are important for the design and application of new MOF materials.

elastic properties | metal-organic frameworks | nanohardness | nanoporosity | zeolitic imidazolate frameworks

eolitic imidazolate frameworks (ZIFs) represent a unique Class of metal-organic frameworks (MOFs) in which the network topology and related properties vary greatly while core chemical connectivity is retained (1, 2). ZIFs currently attract considerable interest by virtue of their exciting potential for hydrogen storage and carbon dioxide capture (3, 4). They adopt porous crystalline structures composed of metal ions and organic linkers, ordered in an analogous fashion to that of silicon and oxygen in zeolites. Specifically, tetrahedral metal centers [typically M = Zn(II) or Co(II)] that are solely coordinated by nitrogen atoms in the 1,3-positions of the imidazolate bridging ligand $(Im = C_3N_2H_3^-)$, subtend an angle of 145° at the M-Im-M center (i.e., analogous to the Si-O-Si angle in silicas and zeolites). Such hybrid architectures can, importantly, give rise to a multitude of extended 3D open frameworks with topologies akin to those found in aluminosilicate zeolites. Over 90 distinct ZIF structures based on 36 of these tetrahedral topologies have been discovered thus far (5). Remarkably, ZIFs combine the classical zeolitic traits of chemical and thermal stability with the rich topological diversity and pore size tunability characteristic of MOFs (6, 7).

By and large, research into MOF materials has been motivated by the prospect of discovering new structures with enhanced functional properties for use not only in gas adsorption and separation fields, but also in heterogeneous catalysis and molecular sensing applications (8–11). Indeed, all the aforementioned applications involve subjecting the porous systems to various modes of mechanical stresses and strains, for which their mechanical properties are critical to reach practical implementations. For instance, the open framework needs to exhibit good stiffness, rigidity, and robustness to retain its structural integrity under high-pressure environments, as encountered in sorption applications. This is especially important for averting excessive structural distortion and framework collapse that can permanently impair their sorption properties. Another example lies in the construction of sensing devices using MOF-type materials (12), whereby a sufficiently high elastic modulus (stiffness) is a prerequisite to induce high responsiveness, in addition to the need for minimizing elastic hysteresis.

It is surprising that, despite their rapid developments toward practical applications, only a handful of reports concerning the mechanical behavior of MOFs and ZIFs exist in the literature. The only elastic modulus (E) and hardness (H) experimental data available on any MOF system is for cubic MOF-5 $[Zn_4O(1,4-benzenedicarboxylate)_3]$, obtained by nanoindentation of single crystals (13). It is noteworthy that the measured *E* value was \simeq 3 GPa, which is an order of magnitude lower than that expected from density functional theory calculations (13, 14); this is thought to be attributed to sample degradation because MOF-5 crystals are particularly moisture sensitive (15). In the case of ZIFs, recent studies have focused on pressure-induced phase transformations under hydrostatic compression in a diamond anvil cell (16-18), from which their bulk moduli (K) have also been approximated. In fact, our knowledge of the mechanical properties of ZIFs is limited to an estimate of the roomtemperature bulk modulus of a phase with the dense zni topology (zni is the three-letter symbol used to designate network topology; see http://rcsr.anu.edu.au/) [$K \simeq 14$ GPa (16)], and another for porous ZIF-8 [$K \simeq 6.5$ GPa (19)]. Their elastic moduli and hardness properties, however, have not been investigated to date.

In the current work, we report a systematic study to establish the structure-mechanical property relationships of ZIFs in relation to their chemical structure, network topology, and porosity. Here, we have determined the previously undescribed elastic modulus and hardness properties of representative ZIF structures by means of single-crystal nanoindentation experiments (e.g., refs. 20, 21). Untwinned single crystals were carefully identified from freshly synthesized materials under a microscope equipped with cross-polarizers. Importantly, their crystallinity and structure were confirmed by means of single-crystal X-ray diffraction (see Materials and Methods). We found that ZIFs are indeed ideal candidates for nanoindentation studies by virtue of their well-defined crystal morphologies, chemical stability, and resistance to fracturing. As part of the present study, the mechanical anisotropy associated with framework structures of lower crystal symmetry has been considered. In addition, we have explored the effects of pore-occupancy on the mechanical behavior of a prototypical framework, ZIF-8. Our findings clearly demonstrate that the mechanical properties of ZIFs are strongly corre-

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¹To whom correspondence should be addressed. E-mail: akc30@cam.ac.uk.

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Table 1. Chemical compositions and physical data of ZIF single crystals

| ZIF-n | Composition | Crystal space group | Network topology | Physical density, ρ , g cm ⁻³ | <i>T/V</i> , nm ^{−3} | Porosity, P, % | SAV, % |
|---------|----------------------|----------------------|------------------|---|-------------------------------|----------------|--------|
| ZIF-zni | Zn(Im) ₂ | I4 ₁ cd | zni | 1.56 | 4.66 | 36.9 | 12 |
| ZIF-4 | $Zn(Im)_{2}$ | Pbca | cag | 1.22 | 3.68 | 50.9 | 34.31 |
| ZIF-7 | $Zn(blm)_2$ | RĪ | SOD | 1.24 | 2.49 | 45.6 | 26.57 |
| ZIF-8 | $Zn(mlm)_2$ | lĀ3m | SOD | 0.95 | 2.45 | 58.8 | 50.38 |
| ZIF-9 | $Co(blm)_2$ | RĪ | SOD | 1.23 | 2.51 | 46.6 | 26.78 |
| ZIF-20 | Zn(pur) ₂ | Pm3m | LTA | 1.04 | 2.04 | 57.3 | 47.38 |
| ZIF-68 | Zn(blm)(nlm) | P6 ₃ /mmc | GME | 1.03 | 2.11 | 59 | 48 |

Physical density is based on the theoretical density of the framework with guests removed. Porosity and SAV were calculated using the "VOID" algorithm implemented in the PLATON package (34). *T/V* and topology data adapted from refs. 5 and 35, respectively. Im, Imidazolate; blm, 2-benzimidazolate; mIm, 2-methylimidazolate; pur, purine; nIm, 2-nitroimidazolate; cag, named after CaGa₂O₄ (variscite); SOD, sodalite; LTA, Linde Type A; GME, gmelinite.

lated to the salient features of the framework architecture and distinct from other known classes of materials.

of three times larger than its counterparts. Indeed, the diverse mechanical behavior highlighted above reflects the roles of the underlying framework architectures, dictated by the different combinations of organic and inorganic building blocks.

Results and Discussion

Framework Structure and Topology. We have broadly represented the entire cross-section of ZIFs reported to date (5) by studying the mechanical properties of seven ZIF structures based on five unique network topologies (nets), as summarized in Table 1. Among these materials, the pure imidazolate ZIFs include ZIF-zni and ZIF-4, wherein their bridging units consist solely of Im linkers. Both frameworks exhibit topologies yet to be discovered in zeolites-zni and cag [named after CaGa2O4 (variscite)], respectively. We note that ZIF-zni is the densest of all known ZIF structures and is essentially nonporous; density functional calculations (22) also show that it is the most stable of the ZIF topologies. The other structures considered here have substituted imidazolate-type linkers, such as 2-benzimidazolate (bIm) in ZIF-7 and ZIF-9, 2-methylimidazolate (mIm) in ZIF-8, and purine (pur) in ZIF-20. Moreover, our studies also includes a heterolink ZIF-68 framework, which incorporates both bIm and nIm (2-nitroimidazolate) linkages. Interestingly, these substituted structures possess network topologies that correspond exactly to the zeolite nets—sodalite (SOD) (ZIF-7, -8 and -9), Linde Type A (LTA) (ZIF-20), and gmelinite (GME) (ZIF-68). Substituted ZIF structures of higher crystal symmetry, such as ZIF-8 and ZIF-20 (both cubic symmetry), exhibit relatively low densities and can afford high porosities and large surface areas.

Nanoindentation Studies of ZIFs. For this study, single crystals of ZIFs with well-defined crystal habits were synthesized through solvothermal reactions. Single-crystal X-ray diffraction was employed to confirm the structures and to establish Miller indices of the crystal facets. Their elastic modulus (E) and hardness (H) properties along specific crystallographic orientations were determined by means of nanoindentation experiments (*Materials and Methods*). It is noted that the elastic modulus measures the intrinsic stiffness of the material under an elastic strain, whereas the hardness, in general, indicates its resistance toward plastic deformation.

In Fig. 1*A*, we show the representative load-displacement data collected by probing the seven ZIF structures to a surface penetration depth of 1,000 nm. It can be seen that the maximum load that develops and the extent of elastic strain recovery following complete unloading (indicated by residual depth at zero load) are unique to each structure. It is intriguing that subtle mechanical responses associated with the different ZIF structures can indeed be unambiguously detected via nanoindentation. For instance, the crystal facets of ZIF-zni not only develop higher loads when indented, but also demonstrate substantial elastic recovery upon unloading. In contrast, structures with greater porosities, e.g., ZIF-8, -20 and -68, can sustain relatively low loads (at corresponding indentation depths) and undergo a lesser extent of elastic recovery. We note also that ZIF-20 exhibits more pronounced creep deformation at maximum loading (~ 4 mN), at least a factor Based on the dynamic mode load-displacement data (Fig. 1A), we calculated the elastic moduli (E) of different ZIF structures as



Fig. 1. Nanoindentation data of ZIF single crystals. (*A*) Representative load-displacement (P - h) curves for ZIF-zni {001} and {100}, ZIF-4 {111}, ZIF-7 {101}, ZIF-8 {110}, ZIF-9 {111}, ZIF-20 {111}, and ZIF-68 {001} oriented facets. The inset depicts three rows of residual indents on a ZIF-8 single crystal. (*B*) Elastic moduli as a function of indentation depth, wherein each error bar represents the standard deviation of 20 measurements.

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a function of indentation depth, as shown in Fig. 1*B*. Data obtained in the first 100 nm, however, can be disregarded because the large scatter in this regime is attributed to imperfect indenter tip-to-sample surface contact. More importantly, we found that the *E* values are distinctive to each structure and remain largely constant beyond the initial contact. The latter is a good indication of robust open frameworks, because structure collapse and subsurface cracking can result in deterioration of the mechanical properties. Likewise, similar trends were observed in the hardness (*H*) property, for which the full data are given in Fig. S1. Note that the *E* and *H* properties considered in the subsequent sections are average values over depths of 100–1,000 nm.

Effects of Pore Occupancy. Given that solvothermal synthesis of ZIFs involves the use of structure directing agents such as DMF (N,N-dimethylformamide) (23), it follows that products obtained contain solvent molecules trapped inside the pores (Fig. 2). Apart from ZIF-zni, which has a limited solvent accessible volume (SAV in Table 1), all the ZIFs considered here contain DMF molecules. Because these can be exchanged with another organic solvent or evacuated without causing framework degradation (4), this provided us with an interesting opportunity to study the effects of pore occupancy on the mechanical properties of nanoporous hybrid frameworks.



Fig. 2. Pore morphologies and accessible volumes (indicated by yellow surfaces) of (*A*) ZIF-zni, (*B*) ZIF-4, (*C*) ZIF-7, (*D*) ZIF-8, (*E*) ZIF-20, and (*F*) ZIF-68. Although hydrogen atoms are omitted here for clarity, they were considered in the calculation of the accessible volumes. Pink, zinc; gray, carbon; blue, nitrogen.

Table 2. Mechanical properties of the $\{110\}$ -oriented facets of ZIF-8 single crystals with different pore occupancy. Note that data for (b) and (c) were obtained from the same single crystal (ZIF-8'). The standard deviations were calculated from 20 indentation experiments

| Crystal condition | Pore occupancy | Elastic modulus, <i>E</i> , GPa | Hardness, <i>H</i> , GPa |
|----------------------|---------------------------------|---------------------------------------|-----------------------------|
| ZIF-8 | (a) DMF solvent | 3.199 ± 0.092 | 0.531 ± 0.028 |
| ZIF-8′ | (b) Desolvated | 2.973 ± 0.063 | 0.501 ± 0.023 |
| (evacuated) | (c) Reexposed to DMF solvent | 3.145 ± 0.169 | 0.515 ± 0.024 |

Motivated by the relatively large solvent accessible volume of ZIF-8 (~50%), we decided to probe the elastic modulus and hardness of the {110}-oriented facets under three distinct conditions (Table 2): (i) as-prepared single crystal with DMF and water molecules trapped in the pores, (ii) a desolvated crystal without DMF in the pores, and *(iii)* an evacuated crystal but with DMF subsequently reintroduced into the pores (see Materials and Methods). The results are summarized in Table 2, wherein the desolvated crystals were found to exhibit marginally lower modulus and hardness values (reduction of $6 \sim 7\%$). Here, it is important to demonstrate that such an outcome is indeed attributed to the absence of guest molecules and is not simply associated with framework degradation inflicted by the evacuation process. Interestingly, we found that the desolvated crystal (i.e., crystal ZIF-8' in Table 2) can indeed recover up to 98% of its original stiffness and hardness properties upon subsequent exposure to DMF. Our results here confirm the permanent porosity characteristic of ZIFs (6) and further establish the reversible nature pertaining to solvent uptake-removal exhibited by robust MOF-type materials (24). Our study on the prototypical ZIF-8 indicates that pore occupancy can have some contribution toward the overall mechanical properties of the framework (albeit small, this could be adequate for sensing applications). For the purpose of this study, however, because the overall effects tend to be relatively small under ambient conditions, all properties reported hereafter correspond only to as-prepared crystals.

Effects of Framework Density and Network Topology. This section will demonstrate how the mechanical properties of ZIFs can be rationalized in terms of their framework densities and topologies, starting first with the effects of density. Fig. 3A shows the elastic moduli (E) of ZIFs as a function of physical density (ρ) of the frameworks. Interestingly, despite the diverse chemical structures being considered here, we found that an excellent correlation can indeed be established across their densities. In particular, the moduli scale nonlinearly with respect to the density, whereby the stiffness increases considerably as the framework structure turns denser. It can be seen that the higher stiffness values correspond to that of ZIF-zni ($E \simeq 8-9$ GPa), which is indeed the densest structure (1.56 g cm^{-3}) across the entire family of ZIFs. Moreover, the tetragonal symmetry of the zni topology also gives rise to elastic anisotropy, as indicated by the distinctive moduli measured in the {001}- and {100}-oriented facets (i.e., $E_{\{001\}}/E_{\{100\}} \simeq 1.1$). It is noteworthy that the mechanical behavior of ZIF-zni resembles those reported in dense hybrid systems whose stiffnesses are of the order of 10 GPa (20, 21). In contrast, our findings show that low-density open frameworks, such as ZIF-8, -20 and -68, can exhibit relatively low stiffnesses with their E values in the range of 3–4 GPa. Given its low density of 0.95 g cm⁻³, ZIF-8 was identified as the most compliant structure in this study.

The density of ZIFs, in accordance with the traditional zeolite convention, is commonly expressed in terms of the number of



Fig. 3. Elastic modulus of ZIF single crystals. (A) Plot of *E* as a function of the physical density and *T/V* (*Inset*). The modulus-density correlation can be approximated by a quadratic relationship of the form $E = A + B\rho + C\rho^2$ (red dotted curve) where A = 0.0392, $B = -1.6167 \times 10^{-4}$, and $C = 3.5323 \times 10^{-6}$. (*B*) The sodalite cage for ZIF-7, -8, and -9, wherein the node is Zn(II) or Co(II) while the linkers are substituted imidazolates. (C) Representations of the Zn-mlm-Zn and Zn-blm-Zn linkages found in ZIF-8 and ZIF-(7, 9) respectively.

tetrahedral (metal) sites per unit volume, or T/V (5, 6). Upon further examination of this relationship, we were unable to establish any clear correlation between them (see Fig. 3A, Inset). In fact, this is not surprising because the value of T/V is primarily governed by the type of framework topology. To illustrate, we consider ZIF-7, -8 and -9, which possess the SOD network topology but incorporate two different functionalized groups (Fig. 3 B and C). It is striking to see that, although their densities can be represented by essentially the same magnitude of T/V of 2.45-2.51 nm⁻³, the elastic moduli of ZIF-7 and ZIF-9 are both about a factor of two greater than that of ZIF-8 (Fig. 3A). Two important observations can be made here. Firstly, the fact that analogous ZIF-7 and ZIF-9 structures exhibit similar stiffnesses regardless of the type of metal centers, indicates that their mechanical properties are determined by the rigid imidazolate building blocks, whereas the metal-centered tetrahedral sites $(ZnN_4 \text{ or } CoN_4)$ provide flexible coordination environments (nodes) for connecting adjacent linkages. This characteristic is consistent with recently reported experimental (23) and theoretical (25) studies on rigid organic linkers. Secondly, our results suggest that sterically bulky substituted imidazolate ligands can confer higher stiffnesses as a result of ligand-ligand interactions. Specifically, the 2-benzimidazolate linkages found in ZIF-7 and ZIF-9 are indeed sterically bulkier compared to 2-methylimidazolate of ZIF-8 (see Fig. 3C).

Effects of Porosity and Pore Architecture. We now focus our discussion on the internal cavity of ZIFs to establish relationships between the porosity and mechanical behavior of hybrid open

frameworks. The porosity (P in percent) of ZIFs summarized in Table 1, was determined on the basis of the volume fraction of the unit cell that is unoccupied by the van der Waals volumes. Although the total porosity was found to range from $P \simeq 37\%$ (ZIF-zni) to $\sim 60\%$ (e.g., ZIF-8 and -68), due to the complex pore configurations shown in Fig. 2, certain sites are in fact not accessible, even to the smallest of guest species. Consequently, we quantify the accessible pore volume that corresponds to the sum of all void space large enough to accommodate a hydrogen atom (1.2 Å radius) as the solvent accessible void or SAV (see Table 1). As anticipated, it can be seen that the SAV values are consistently lower than their corresponding total porosity P. Specifically, the difference between them was found to lie between 8 and 25% for all structures considered here, dictated mainly by factors such as crystal symmetry, network topology, and pore morphology. In particular, because of the presence of tortuous channels oriented along the tetragonal c axis (Fig. 2A), we note that the SAV of ZIF-zni is significantly reduced (up to ~25%). In comparison, the cubic ZIF structures clearly indicate considerably larger SAV, of near total porosity levels, especially in the case of ZIF-8 and -20, which we attribute to their somewhat spherical pore morphologies (Fig. 2 D and E).

In Fig. 4*A*, we demonstrate that the elastic modulus of ZIFs exhibit strong inverse correlation to the internal accessible void space, wherein all highly porous frameworks such as ZIF-8, -20 and -68 have consistently low stiffnesses. In terms of the hardness (*H*) properties, however, the correlation appears to be less obvious, particularly at high SAV values (Fig. 4*B*). We believe this is due to the fact that hardness measurement depends on both elastic and plastic deformation mechanisms that are active under the indenter. The plastic response of a nanoporous structure



Fig. 4. Elastic modulus (A) and hardness (B) properties of ZIFs as a function of pore solvent accessible volume.

toward a high-strain gradient (induced by a sharp indenter tip) is indeed not well understood and warrants further investigations. In any case, our current data confirm that ZIF-zni is the stiffest and the hardest structure amongst ZIFs, partly given its extremely low SAV of just 12%. Interestingly, despite their SOD topology, both ZIF-7 and ZIF-9 contain noticeably smaller accessible void volume (~20% less than total porosity). This is because the sterically bulky aromatic rings of benzimidazolate linkers project into the pore regions, hence inducing a higher degree of pore space filling. We found that such an architecture can confer moderate mechanical properties among the ZIF-type materials ($E \simeq 6$ GPa and $H \simeq 650$ MPa).

In addition, there is also evidence that intricate pore morphology within the ZIF structures can give rise to anisotropic mechanical behavior, as exemplified in the case of ZIF-68. Specifically, the unique pore morphology associated with the GME topology is clearly anisotropic (Fig. 2F and Fig. S2), and yet ZIF-68 can afford large channels along the *c* axis combined with wide apertures (26). We found that the elastic moduli determined parallel and perpendicular to the channels were $E_{\{100\}} \simeq 4$ GPa and $E_{\{001\}} \simeq 3.5$ GPa, respectively. It follows that a substantial hardness anisotropy was also detected (Fig. 4B), wherein $H_{\{100\}}/$ $H_{\{001\}} \simeq 1.5$.

Comparison with the Mechanical Properties of other Classes of Mate-

rials. Our results can be represented as an elastic modulus versus hardness materials selection map, as shown in Fig. 5, where they are plotted alongside the three major categories of conventional materials, i.e., metals, ceramics, and polymers. In addition, we have included the mechanical properties of recently reported dense hybrid systems (20, 21) and nanoporous MOF-5 (13) for comparison. It is striking to see that the domain corresponding to ZIFs, to some extent, straddles the border between polymeric (purely organic), ceramic (purely inorganic), and metallic materials. Here it is certain that ZIF-zni defines the upper bound of the ZIF domain. The lower bound, however, is yet to be identified, but it is most likely to be associated with ZIFs of even higher porosities than the ones being investigated here [e.g., ZIF-95 and ZIF-100 (27)], and especially in view of the many promising structures awaiting discovery (5).



Fig. 5. Elastic modulus versus hardness materials property map for dense and nanoporous hybrid framework materials shown alongside purely organic and inorganic materials.

It can be seen that the elastic modulus and hardness properties of dense hybrid frameworks [e.g., copper phosphonoacetates (21) and cerium oxalate-formate (20)] are approximately an order of magnitude higher than the ZIF-type materials, but still not comparable with classical ceramic materials such as alumina, zirconia, and tungsten carbide (Fig. 5). On the whole, we note that ZIFs are relatively compliant and soft materials (i.e., low *E* and *H* values), which can be attributed to their flexible M-Im-M linkages (23) and large void spaces (Fig. 2). Furthermore, it is important to recognize that the hardnesses of ZIFs are at least an order of magnitude higher than that of MOF-5 [$H \simeq 40$ MPa (13)]. It appears that the mechanical properties of ZIFs are superior to those of other MOFs due to their zeolite-like architectures.

Concluding Remarks

This work represents a comprehensive study of the elastic modulus and hardness of ZIFs. We have successfully established their structure-mechanical property relationships over a wide range of structures, topologies, and porosities. We also discovered that sterically bulky imidazolate-type linkages are rigid building blocks that have a marked influence on the overall stiffness and hardness properties. It will obviously be of interest to gain insights into the behavior of ZIFs at the atomic level under elastic and plastic deformations. In our future work, we propose to address this issue both experimentally using micro-Raman spectroscopy (see, e.g., ref. 28), and computationally using density functional theory (DFT) and molecular dynamics (MD) simulations. Specifically, the elastic constants of different ZIF structures can be revealed by DFT, which will be important for understanding the origin of elastic anisotropy. Detailed structural information (changes in bond distances and angles) relating to the stiff versus compliant basic building blocks can be gained from such theoretical work. Beyond the elastic limit, MD studies (see, e.g., ref. 29) can reveal the underlying plastic deformation mechanisms and advance our understanding of the onset of plasticity and dislocation motions.

From the practical standpoint, given that ZIFs are expected to operate under mechanical stresses and substantial pressures, the basic understanding of their mechanical properties is clearly important. Our current results will complement the extensive research already been done on their synthesis, structures, and functional properties. Furthermore, the characterization techniques developed here can be easily extended to study the mechanical behavior of other metal-organic framework materials, e.g., the soft porous crystals recently highlighted in ref. 30. We believe that the conclusions drawn in this study can be used to more accurately design candidate MOF materials for various emerging applications, ultimately leading to better performing systems.

Materials and Methods

ZIF Synthesis. ZIF-4, -7, -8, and -9 were synthesized as reported in ref. 6. The syntheses of ZIF-68 and -20 followed the procedures described in refs. 4 and 31, respectively. We have prepared ZIF-zni $[Zn(Im)_2]$ as follows: an aqueous solution (2 mL) of zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ (0.20 M, 4×10^{-3} mol) was combined with sodium boroimidazolate NaB(Im)₄ (0.12 g, 4×10^{-3} mol) and DMF (5 mL). The resultant solution was placed in a 23 mL Teflon-lined autoclave and heated to 180 °C for 72 h in a programmable oven, before cooling to room temperature at a rate of 5° Ch⁻¹. Rod-shaped single crystals were isolated from the mother liquor by filtration, washed with dichloromethane (5 mL twice) and air dried. The crystal structures and crystallinity of the synthesized compounds were verified by X-ray diffraction. We found that the materials maintained high crystallinity at ambient conditions, showing no sign of amorphization.

Readsorption Studies. Single crystals of prototypical ZIF-8 were optimally evacuated by following the protocol set out in ref. 6. The reintroduction of DMF into the crystal was achieved by soaking the evacuated species for 48 h, followed by filtering and air drying. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q-500 series thermal gravimetric analyzer, with samples (~10 mg) held on a platinum pan under a continuous flow of dry N₂ gas, and at a heating rate of 10°C min⁻¹. The

curve for ZIF-zni shows a plateau up to 450 °C, whereupon thermal decomposition sets in. Here, the plateau evidences the lack of solvent in the dense framework. In comparison, the TGA curves of ZIF-8 with different pore occupancy are presented in Fig. S3. The as-prepared ZIF-8 shows an initial weight loss step of 30.48%. The evacuated framework shows negligible weight loss up to ~500°C, whereupon thermal decomposition occurs. It is noted that weight loss from the framework with reintroduced DMF is initially lower than that of the as-synthesized species, but this is to be expected, given that the only solvent present in the former is DMF, as opposed to a mixture of DMF and water present in the as-prepared structure. This observation also explains the more rapid weight loss of the former as the thermal decomposition temperature of 500 °C is approached. Powder X-ray diffraction patterns of ZIF-8 with different pore occupancy are presented in Fig. S4.

Nanoindentation Studies. Nanoindentation experiments were performed using an MTS Nanoindenter XP, located in an isolation cabinet to shield against thermal fluctuations and acoustic interference. The crystal surface to be probed was first cold-mounted using an epoxy resin and then carefully polished using increasingly fine diamond suspensions to achieve an rms sur-

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face roughness of less than 10 nm (confirmed by Atomic Force Microscope examinations). Good surface preparation is critical to ensure accurate contact area determination and to minimize experimental scatter. Indentations were conducted under the dynamic displacement-controlled "continuous stiffness measurement" mode, so that the *E* and *H* mechanical properties can be determined as a function of the surface penetration depth. A 2-nm sinusoidal displacement at 45 Hz was superimposed onto the system's primary loading signal, and the loading and unloading strain rates were set at $5 \times 10^{-2} \text{ s}^{-1}$. All tests were performed to a maximum indentation depth of 1,000 nm using a Berkovich (i.e., three-sided pyramidal) diamond tip of radius ~100 nm. In each case, the indenter axes were aligned normal to the crystal facets. The raw data (load-displacement curves) obtained were analyzed using the Oliver and Pharr method, described in refs. 32 and 33.

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