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ABSTRACT
Metal–organic framework (MOF) glasses have emerged as a new class of melt-quenched glasses; however, so far, all MOF glass production has remained at lab-scale; future applications will require large-scale, commercial production of parent crystalline MOFs. Yet, control of synthetic parameters, such as uniform temperature and mixing, can be challenging, particularly, when scaling-up production of a mixed-linker MOF or a zeolitic imidazolate framework (ZIF). Here, we examine the effect of heterogeneous linker distribution on the thermal properties and melting behavior of ZIF-62. X-ray diffraction (XRD), Raman, and $^1$H nuclear magnetic resonance spectroscopies revealed little discernable structural difference between samples of ZIF-62 synthesized in our lab and by a commercial supplier. Differential scanning calorimetry and variable temperature/isothermal XRD revealed the samples to have significantly different thermal behavior. Formation of ZIF-zni was identified, which contributed to a dramatic rise in the melting point by around 100 K and also led to the alteration of the macroscopic properties of the final glass. Parameters that might lead to the formation of unexpected phases such as an uneven distribution of linkers were identified, and characterization methods for the detection of unwanted phases are provided. Finally, the need for adequate consideration of linker distribution is stressed when characterizing mixed-linker ZIFs.

INTRODUCTION
Metal–organic frameworks (MOFs) are porous, crystalline, and “tunable" materials composed of organic linkers coordinated to inorganic metal centers; component selection results in an almost infinite number of possible framework structures having a wide range of physical and chemical properties. These properties enable implementation in a variety of different applications such as gas storage, gas separation, and catalysis. MOFs are typically synthesized in the form of microcrystalline powders although this is problematic as specialized and/or high-stress applications require MOFs formed in robust, bulk geometries.

To overcome this challenge, melt-quenching of these hybrid framework materials has been proposed, leading to bulk glasses. Accordingly, MOF glasses have emerged as a new class of melt-quenched glasses with unique and potentially advantageous properties stemming from their tunability and structural chemistry, which can be exploited in crystalline and glassy states alike. This ability to form bulk, shapeable materials with enhanced processability and durability, without loss of chemical selectivity, greatly broadens the applicability of MOFs in many fields.

Thus far, only a small number of MOFs have been reported to demonstrate substantial meltability. Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs some of which show melt-quenching behavior; they often have topologies similar to those found in inorganic zeolites (tetrahedral SiO$_4$ and AlO$_4$ species are replaced by isotypic tetrahedral Zn$^{2+}$ or Co$^{2+}$ coordinated by imidazolates, which take the place of the oxygen anion). For
instance, crystal structures of ZIF-4, Zn(Im)$_2$ with cag topology, ZIF-zni, Zn(Im)$_2$ with zni topology, ZIF-62, Zn(Im)$_{1.75}$(bIm)$_{0.25}$ with cag topology, and ZIF-7, Zn(bIm)$_2$ with sod topology are illustrated in Fig. 1.\textsuperscript{12–14} ZIF-62 is one of the most extensively studied MOF glasses because of its relatively low melting temperature and high thermal stability, resulting in a large processing window.\textsuperscript{15} ZIF-62 is a mixed-linker (or heterolinker) ZIF consisting of imidazolate (Im, C$_3$H$_3$N$_2$) and benzimidazolate (bIm, C$_7$H$_5$N$_2$) linkers with the standard stoichiometry of 7:1 Im to bIm or Zn(Im)$_{1.75}$(bIm)$_{0.25}$.

ZIF-62 glass, a$_g$ZIF-62, shows promising results in gas separation applications. For instance, a$_g$ZIF-62 membranes fabricated by Wang \textit{et al.} via melting crystalline ZIF-62 powder on an alumina support showed separation selectivity for different gas mixtures (CO$_2$/CH$_4$, CO$_2$/H$_2$, and CO$_2$/N$_2$). Indeed, the glassy ZIF-62 showed three times higher CO$_2$/N$_2$ selectivity compared to its crystalline counterpart at elevated pressures.\textsuperscript{16} These observations demonstrate the potential of MOF glasses to be implemented in industrial applications.

Nevertheless, the most challenging issue remains unsolved since bringing MOF glasses into real world applications requires scaling-up the synthesis procedures.\textsuperscript{17} In this, several parameters are crucial to the structural integrity and phase purity of the final product, such as reaction time and temperature.\textsuperscript{18,19} The presence of structural defects or tiny amounts of impurities may change the thermal behavior; this can induce a considerable increase in melting temperature or reduce the melting window of the material.\textsuperscript{15}

This is a concern not only for commercial materials but also when analyzing the behavior of newly synthesized materials, where phase purity plays a significant role in dictating thermal behavior. Currently, the MOF glass field tries to identify new meltable MOFs/ZIFs from among a huge number of available crystalline MOFs; thus, small impurities may play a large role by either broadening the melting window or, worse, by falsely identifying melting compositions as non-glass forming.\textsuperscript{20}

In mixed-linker ZIFs, effects of linker ratio on thermal behavior of the corresponding ZIF have been investigated before, and it was shown that increasing the structural disorder, through inclusion of multiple ligands, causing static atomic displacement or distortion in orientation, resulted in lower melting temperature.\textsuperscript{13,21} Statistical models indicate that in mixed-linker ZIFs, different Zn$^{2+}$-linker coordination spheres have corresponding probabilities. These different zinc environments are both kinetically and thermodynamically driven: respective steric hindrances of individual linkers and preferred coordination of each linker to metal sites result in some metal center–linker interactions being more common. For instance, ZIF-62 crystals form with a propensity of Zn to be coordinated by Im over bIm linkers,\textsuperscript{21} possibly promoting regions of
higher-than-average Im coordination. This suggests that homogeneous linker distribution (e.g., through controlling synthesis parameters such as time and temperature) is a crucial factor in tailoring the physical properties of mixed-linker ZIFs/MOFs.

In this study, we investigate the structural and thermal properties of two variants of ZIF-62, one produced in the lab and the other commercially, with different degrees of linker homogeneity. The structures of these samples are studied using x-ray diffraction (XRD), proton nuclear magnetic resonance ($^1$H NMR), and Raman spectroscopy. Differential scanning calorimetry (DSC) and variable temperature/isothermal XRD (VT-XRD) measurements are used to identify the differences in thermal properties, origin of unexpected phases, and changes in the melting behavior of the materials. Important parameters affecting the synthesis processes of a mixed-linker material are addressed, and guidelines to control these issues are discussed.

RESULTS AND DISCUSSION

We compare the structures of the two differently manufactured ZIF-62 samples, obtained via lab synthesis and from a commercial supplier, respectively (denoted as ZIF-62-synthesized and ZIF-62-commercial). Structural characterization was performed using XRD, $^1$H NMR, and Raman spectroscopy, as shown in Figs. 2 and S1. Figure 2(a) compares the XRD patterns of samples of ZIF-62-commercial, ZIF-62-synthesized, and ZIF-62-calculated using crystallographic data from the literature. The XRD patterns of both ZIF-62-synthesized and ZIF-62-commercial display good agreement with the calculated one, with only slight changes in the intensity of some reflections. Figure S2 illustrates the differences in XRD patterns between ZIF-62-synthesized, ZIF-62-commercial, and ZIF-62-calculated. Similarly, the Raman spectra in Fig. S1 are consistent with the previously reported literature and reveal the same features for both samples indicating identical chemical bonding environments.

In mixed-linker ZIFs or MOFs such as ZIF-62, acid-digested $^1$H NMR spectroscopy provides useful information about the integrity of the linkers as well as linker stoichiometry present in the framework. As presented in Fig. 2(b), $^1$H NMR spectra for the ZIF-62-commercial and ZIF-62-synthesized samples are well-matched, confirming that the linkers are intact. Further analysis on the linker composition showed that the linker ratio, defined as bIm/(bIm + Im), deviates slightly from the canonical ZIF-62 linker ratio of 0.125 for both ZIF-62-synthesized (0.156) and ZIF-62-commercial (0.135) samples. Accordingly, linker compositions can be written as $\text{Zn(Im)}_{1.69}(\text{bIm})_{0.31}$ and $\text{Zn(Im)}_{1.73}(\text{bIm})_{0.27}$ for ZIF-62-synthesized and ZIF-62-commercial, respectively, and compared to the canonical composition, $\text{Zn(Im)}_{1.75}(\text{bIm})_{0.25}$. This suggests that both ZIF-62-synthesized and ZIF-62-commercial samples possess similar chemical structures and have slightly more bIm in the structure, as has been reported extensively in the literature.

Frentzel-Beyme et al. demonstrated that the melting temperature of ZIF-62 can be tuned ($\sim 70$ °C difference) by varying the Im:bIm ratio in $\text{Zn(Im)}_{2-<x>(\text{bIm})_{x}}$, where $x = 0.02–0.35$. Motivated by this, we investigated the thermal properties of ZIF-62-synthesized and ZIF-62-commercial, starting with the ubiquitous technique of differential scanning calorimetry paired with thermo-gravimetric analysis (DSC-TGA). Figure 3 shows the calorimetric behavior of ZIF-62-commercial and ZIF-62-synthesized samples. According to Fig. 3(a), both ZIF-62-commercial and ZIF-62-synthesized samples show no mass loss upon heating to 600 °C, implying that there is no thermal decomposition prior to this temperature. On the other hand, DSC scans in Fig. 3(b) illustrate significant differences in temperature-driven enthalpic behavior. Although the scan for ZIF-62-synthesized shows the expected thermal response upon heating (an endotherm at $\sim 400$ °C, characteristic of ZIF-62 melting), that of ZIF-62-commercial contained a variety of complex...
features related to various phase transitions, which are different from any kind of thermal behavior that has been reported for ZIF-62 so far.

As noted above, this behavior could be attributed to differences in the linker ratio, originating from higher amounts of bIm in ZIF-62-synthesized compared to ZIF-62-commercial. However, ZIF-62 with higher-than-ideal bIm content has been investigated and showed almost identical enthalpic responses in DSC traces. Considering linker ratio deviation between ZIF-62-synthesized and ZIF-62-commercial, the expected melting temperature difference would be less than 10 °C. To uncover the unusual phase transitions found in our DSC measurements, we performed VT-XRD on both ZIF-62-synthesized and ZIF-62-commercial samples. The results are presented in Figs. 3(c) and 3(d), respectively. We focused on 2-theta values in the range of 8°–25° since most of the crystalline features occur in this range. VT-XRD on ZIF-62-synthesized [Fig. 3(c)] shows the expected loss of crystallinity upon melting starting at ~400 °C, as evidenced by the disappearance of sharp Bragg diffraction peaks and the appearance of broad amorphous scattering, in good agreement with DSC data.

In contrast, ZIF-62-commercial [Fig. 3(d)] first goes through a partial amorphization step around 300 °C (shown as a decrease in diffraction peaks particularly at higher 2-theta values in XRD and an endotherm in DSC), which is followed by the appearance and growth of new crystalline peaks starting at 400 °C (detectable in the DSC trace as an exothermic peak at almost the same temperature) and finally amorphization of the newly emerged crystalline phase (in agreement with the broad endotherm starting at 500 °C in DSC). Rather than full amorphization above 300 °C, the diminishing diffraction peaks (and retention of ZIF-62 peaks) may indicate that another phase which overlaps closely with the ZIF-62 diffraction peaks is amorphizing in this temperature range. We note that small differences between phase transition temperatures as measured by DSC and VT-XRD may arise due to the different atmospheres used: DSC was performed under nitrogen and VT-XRD under argon. To confirm the unexpected DSC scan of ZIF-62-commercial, the experiment was repeated, with consistent results (Fig. S3).

Diffraction patterns and corresponding sample micrographs representative for each selected temperature in the DSC and...
VT-XRD of ZIF-62-commercial are illustrated in Fig. 4(a). As the temperature rises, the crystalline ZIF-62-commercial partially amorphizes and subsequently, a new crystalline phase, matching the XRD pattern of ZIF-zni, emerges. ZIF-zni, a dense zinc imidazolate framework, is a thermodynamically stable ZIF polymorph of ZIF-4, Zn(Im)₂, with zni topology 26 (ZIF-4 has cag topology and crystallizes in the Pbca space group like ZIF-62 16,27). To confirm the formation of ZIF-zni, several isothermal XRD measurements were performed (360 °C for 14 h, 430 °C for 7 h, and 500 °C for 5 h), and the morphologies of the resulting samples were studied using scanning electron microscopy (SEM). We note that different temperatures and times were chosen to allow for the separation and identification of morphological differences between phases as follows: both ZIF-62 and zni phases (360 °C for 14 h), only the zni phase (430 °C for 7 h), and fully amorphous (500 °C for 5 h). In isothermal XRD at 360 °C for 14 h, ZIF-62 and ZIF-zni crystal phases exist in the final XRD pattern, which can also be seen in corresponding SEM images, as small rounded ZIF-62 crystals appear along with the rod-shaped zni phase. 28 When we examined the sample after the isothermal experiment at 430 °C for 7 h, we find that only the crystalline ZIF-zni phase remains, confirmed by the presence of only rod-shaped crystals (along with the substantial amorphous phase) in the SEM images. Finally, ZIF-zni becomes fully amorphous upon the isothermal run at 500 °C for 5 h; no crystals can be detected in its SEM images.

Previous reports showed that ZIF-zni can be formed via two routes: direct synthesis of ZIF-zni from its chemical precursors and recrystallization from amorphized isomeric Zn(Im)₂ while providing enough thermal energy to the system. 29,30 Comparing the enthalpic behavior of ZIF-62-commercial sample with other ZIF structures, almost identical phase transformations that have been observed for ZIF-1, ZIF-3, and ZIF-4 are detected in the ZIF-62-commercial sample. 29 Crystallization of the zni phase was further examined via analyzing the integrated intensity of the most intense reflection in the temperature range where we observed crystallization in DSC and VT-XRD (2-theta of 15°, ascribed to {400} and {112} reflections of the zni

FIG. 4. Formation of ZIF-zni phase upon heating ZIF-62-commercial. (a) XRD patterns obtained at different temperatures. ZIF-zni XRD was calculated using the crystallographic data from the literature. 14 Isothermal XRD measurements along with SEM images obtained after isothermal XRD runs at: (b) 360 °C for 14 h, (c) 430 °C for 7 h, and (d) 500 °C for 5 h.
crystal structure). Figure S4 illustrates the growth of the \textit{zni} phase with rising temperature (the intensity of the doublet at 2-theta = 15° almost doubles upon an increase of 60 °C). This indicates that there are regions in the sample where sufficiently low amounts of blm are present. Upon heating, these Im-rich pockets recrystallize to the \textit{zni} phase.

Reaction time and temperature can significantly influence the formation of the final crystalline product. For example, starting with zinc nitrate tetrahydrate \text{Zn(NO$_3$)$_2$·4H$_2$O} and imidazolate with slightly different stoichiometric ratios, different isomeric crystals can be synthesized such as ZIF-1 \textit{crb} [Zn(Im)$_2$·(Me$_2$NH)$_2$], ZIF-2 \textit{crb} [Zn(Im)$_2$], ZIF-3 \textit{dif} [Zn(Im)$_2$], ZIF-4 \textit{cag} [Zn(Im)$_2$·(DMF)(H$_2$O)], ZIF-6 \textit{gis} [Zn(Im)$_2$], ZIF-9 \textit{mer} [Zn(Im)$_2$], which have the identical Zn(Im)$_2$ formula but very different crystal structures. We note that N,N-dimethylformamide (DMF) was used as the solvent for the synthesis of isomer crystals except ZIF-3 in which a mixture of DMF and N-methylpyrrolidone (NMP) was used as the solvent. Calculated XRD patterns of these isomer crystals are shown in Fig. S5. It can be seen that the ZIF-4 XRD pattern is the closest to that of ZIF-62, which is explained by the fact that both crystallize in the \textit{Pbca} space group with \textit{cag} topology.

According to our DSC, VT-XRD, and calculated XRD patterns of Zn(Im)$_2$ isomer crystals, the \textit{in situ} formation of ZIF-\textit{zni} during heating can be attributed to the presence of Im-rich, ZIF-4-like regions in the ZIF-62-commercial sample. This is likely due to inhomogeneous coordination processes of the Im and blm linkers to Zn$^{2+}$ during the up-scaled commercial synthesis. To estimate the amount of the ZIF-4-like phase, enthalpy of crystallization for the \textit{zni} phase from the crystallization peak in the DSC scan (Fig. S6) was calculated, obtaining a value of 11.67 J g$^{-1}$. The enthalpy of \textit{zni} formation from pristine ZIF-4 has been reported at 50 J g$^{-1}$.\textsuperscript{31} Based on the corresponding enthalpy of crystallization for \textit{zni} in ZIF-62-commercial, an equivalent of \textasciitilde23.3\% of the ZIF-4-like phase is nominally present in the ZIF-62-commercial sample.

It has been shown previously that extending the synthesis time and increasing the synthesis temperature resulted in \textit{zni} formation during the synthesis of ZIF-4.\textsuperscript{3} To examine this effect in the commercial sample, SEM analysis was performed on as-received ZIF-62-commercial and ZIF-62-synthesized samples, as presented in Fig. 5. As can be seen from Fig. 5(a), there is no \textit{zni} phase (rod-shaped crystals) in the ZIF-62-synthesized sample, whereas in the ZIF-62-commercial case, as seen in Fig. 5(b), a small number of rod-shaped \textit{zni} crystals can be detected, which proves the formation of the \textit{zni} phase during ZIF-62-commercial synthesis. Corresponding melt-quenched glasses of ZIF-62-commercial and ZIF-62-synthesized samples are illustrated in Fig. 5(c).

Quantification of the \textit{zni} phase in ZIF-62-commercial using Rietveld refinement is presented in Fig. 6. Results revealed 1.8\% of the \textit{zni} phase in the ZIF-62-commercial sample (see the section titled “Materials and methods” for further details).

Accordingly, our results demonstrate that ZIF-\textit{zni} and ZIF-4-like pockets were formed during ZIF-62-commercial synthesis. Moreover, as ZIF-62-commercial was heated, additional ZIF-\textit{zni} is formed via recrystallization of amorphized ZIF-4-like pockets. In many cases, the presence of a small impurity, unwanted chemicals/phases, or phase separation can significantly influence the macroscopic properties of glasses. As illustrated in Fig. 5(c), melt-quenched glasses formed from ZIF-62-synthesized and ZIF-62-commercial are different, while the glass of the ZIF-62-synthesized sample is transparent (consistent with the literature), the glass of ZIF-62-commercial is completely opaque because of the presence of \textit{zni} crystals. These macroscopic differences in these two

![FIG. 5. Morphology of ZIF-62-synthesized and ZIF-62-commercial samples: (a) ZIF-62-synthesized and (b) ZIF-62-commercial, yellow arrows highlight rod-shaped \textit{zni} crystals. (c) Melt-quenched glasses obtained from ZIF-62-synthesized and ZIF-62-commercial upon heating the powder samples to 450 °C with a ramp rate of 5 °C min$^{-1}$ and subsequent cooling to room temperature.](image-url)
glasses would clearly hamper the use of such glasses in optical applications.

We hypothesize that, based on the evidence presented, the ZIF-62-commercial sample undergoes incongruent melting. This may be a result of inhomogeneous linker distribution during synthesis which manifests in dispersed ZIF-4-like regions in ZIF-62. In collapsible framework structures such as ZIF-62, allowing the synthesis reaction to reach its maximum entropy (complete mixing of Im and bIm linkers) is of great importance. However, providing too much energy helps the reaction to find the enthalpic minimum and form the thermodynamically stable state (ZIF-zni). To show the complex behavior of ZIF-62-commercial, a pseudo-phase diagram is illustrated in Fig. 7(a). Although many ZIFs, including those in this study, are metastable, precluding a proper equilibrium phase diagram, due to their deep energy well, we believe that such a pseudo-phase diagram is still a useful tool for understanding the melting behavior of these complex systems.

According to the pseudo-phase diagram in Fig. 7(a), we can hypothesize possible linker ratios that result in incongruent melting. Even though enthalpic behavior of the system can be controlled, inhomogeneities might occur because the reaction is also affected by kinetics. At any linker ratio of Im and bIm, Im-rich regions and bIm-rich regions can form, and incongruent melting may occur. Without reaching complete mixing, it is possible for the material to be composed of two or more compositional points on the pseudo-phase diagram (at constant T). The melting behavior of ZIF-62-synthesized shows that, it is clearly possible to avoid the pink “liquid + ZIF-zni” region entirely as was investigated by Frentzel-Beyme et al. Their experimental data points are included in the phase diagram. However, this is not achieved only by satisfying the proper linker ratio ([Im/bIm]): From NMR of ZIF-62-commercial, we expect that the material would not go through incongruent melting (X = 0.27). Instead, linker heterogeneity creates at least two different local Zn^{2+}-linker environments and constrains ZIF-62-commercial to go through two different paths upon heating, as illustrated by the two white composition points in the phase diagram. Figure 7(b) illustrates the behavior of ZIF-62-commercial linker distribution during synthesis, showing the early clustering of Im linkers. In Fig. 7(c), continued synthesis produces both canonical and Im-rich ZIF-62 phases, along with small amounts of ZIF-zni crystals. When such kind of ZIF-62 polycrystals are heated, more zni crystals form from the Im-rich pockets, and the final product is a melted, amorphous ZIF-62 phase with zni crystals, as shown in Fig. 7(d).

Moreover, in order for MOFs/ZIFs to perform as expected in gas storage, gas separation, and catalysis applications, the parent material must be sufficiently phase-pure to guarantee optimal performance. Specifically, in a glass derived from ZIF-62, the presence of a small amount of ZIF-zni can significantly influence the gas separation and catalytic performance since adsorption and diffusion of certain molecules will no longer be possible in dense zni regions, while it would be possible in the absence of such unfavorable phases. We note that both ZIF-62 and ZIF-zni crystal habits have been described previously in detail, and the morphological differences between them enabled us to detect the presence of zni in ZIF-62. Similarly, amorphization of ZIF-62 upon heating allowed clear discernment of ZIF-zni peaks in the XRD patterns at higher temperatures, corroborating the formation of ZIF-zni during commercial synthesis. However, in other systems, there may be different crystal phases with the same crystal habits, hindering easy phase identification, while contributing to unexpected behavior and performance in applications.
Furthermore, when identifying new meltable MOFs/ZIFs, the inhomogeneity of linker distribution and/or the presence of impurities or other crystalline phases can change the thermal properties substantially, impeding the accurate evaluation of thermal stability and melting windows. Given that thermal behavior is a deciding factor in application-driven MOF research and is arguably the most important factor in the discovery and characterization of novel amorphous MOFs, we believe that more effort should be spent on characterizing the linker distribution in mixed-linker ZIFs. Without proper consideration of linker heterogeneity, thermal characterization is only applicable to that singularly synthesized MOF and should not be generalized for all MOFs of that composition and topology. Although linker distribution analysis adds an extra step to investigations, it also brings attention to the fact that we now have an additional method to tune the physical MOF properties.

We can tentatively summarize the important characterization steps to confirm the homogeneity of a mixed-linker MOF/ZIF material after synthesis in terms of subsequent transformation into a glassy state. Typical structural characterization must be combined with in-depth thermal analysis. XRD, SEM, Raman/FTIR, and NMR spectroscopy can provide useful information about overall structural and linker integrity; at the first glance, this information may confirm that the material has the intended structure. However, the most important step is the evaluation of the thermal behavior: it probes the dynamics of the system revealing differently behaved inhomogeneities and phases. Only by combining DSC with VT-XRD (and SEM) were the different phase changes of the inhomogeneous regions apparent. The information presented in this work provides a roadmap to identify synthesis differences, which may occur in mixed-linker MOFs/ZIFs.

**CONCLUSION**

In summary, we investigated the structural heterogeneity and thermal properties of meltable variants of ZIF-62. Our results showed that in such mixed-linker MOFs/ZIFs, uneven distribution of linkers might cause formation of polymorphs, which can result in significant changes in thermal properties. This can cause a dramatic increase in melting temperature and/or change the macroscopic properties, which is of importance for accurate characterization and in further processing of materials such as glasses. Thermal characterization methods such as DSC and VT-XRD are of great importance in testing the integrity and characteristics of a mixed-linker MOF/ZIF product. From a practical standpoint, results presented here can provide a guideline for characterizing the success of...
scaling-up or large-scale production of ZIFs/MOFs. Yet, the striking differences in thermal behavior also stress the necessity of determining linker distribution in mixed-linker ZIFs and highlight that linker heterogeneity is an additional route to tune MOF physical properties.

**MATERIALS AND METHODS**

**Materials**

ZIF-62-synthesized was prepared using the same procedure reported previously and compared to a commercial ZIF-62 material as-received from ACSYNAM. Both materials were heated at 170 °C under vacuum overnight prior to use.

**X-ray diffraction**

VT-XRD and isothermal XRD experiments were conducted using a Rigaku Smartlab diffractometer (Cu Kα x-ray source with a wavelength of 1.54059 Å) with a Hypix-3000 (horizontal configuration) in 1D scanning mode. The voltage and current of the x-ray tube were set to 40 kV and 50 mA, respectively. For both experiments, the general Bragg–Brentano geometry was used with a 10 mm length-limiting slit as the incident section, a 2.5° Soller slit with a Kβ filter, and an anti-scattering slit in the receiving part. A powder sample (~40 mg) was placed in a corundum holder and installed on a HTK1200N (Anton Paar) heating stage. The vacuum stage was connected to the heating stage, and all the connections were sealed. The sample compartment was flushed two times using argon gas in the chamber and pulling vacuum afterward. A turbo-molecular pump (TMP) was used to evacuate the sample compartment. After the final evacuation step, a continuous argon flow of 50 ml min⁻¹ was used during the whole experiment. For VT-XRD, a temperature control loop was set using “constant up down measurement” mode. Target temperature and ramp rate were set to 600 °C and 5 °C min⁻¹, respectively. Diffraction patterns were collected in the 2θ range of 5°–40° with a step size of 0.03° and at a rate of 10° min⁻¹. The set ramp rate provided diffraction patterns every 6 min. XRD data presented in Fig. 2(a) were collected using a Rigaku MiniFlex diffractometer in the 2θ range of 5°–40° with a step size of 0.01°. Rietveld refinement was performed using GSAS-II software. Instrumental parameters were extracted using LaBW as the reference.

**Differential scanning calorimetry coupled with thermo-gravimetric analysis (DSC-TGA)**

DSC-TGA analyses were performed using a Netzsch STA 449 F1 instrument. Approximately, 15 mg of each sample was placed in a platinum crucible and gently pressed by hand to ensure a good contact between the crucible and the powder sample. All the measurements were performed under 20 ml min⁻¹ nitrogen flow. First, the sample was heated to 120 °C with a ramp of 20 °C min⁻¹ and equilibrated for 4 h to remove any volatiles. Subsequently, it was heated to 600 °C with a ramp rate of 10 °C min⁻¹.

**Scanning electron microscopy (SEM)**

The morphology of samples after isothermal XRD runs and as-synthesized and as-received commercial samples were analyzed using a JSM-7001 F electron microscope (Jeol Ltd., Japan). Approximately, 10 mg of each sample was placed on the carbon tape pasted on an aluminum cell. Samples were coated with a thin layer of carbon prior to measurement. Working distance and voltage were set to 15 mm and 15 kV, respectively.

**Raman spectroscopy**

Raman spectra for powder samples were collected using Renishaw inVia Raman microscope at 20× magnification with an excitation wavelength of 785 nm. Samples were placed on a glass slide and flattened. Spectra were collected in the wavenumber range of 500 cm⁻¹–1600 cm⁻¹ with 50% laser power, acquisition time of 10 s, and one accumulation.

**Nuclear magnetic resonance spectroscopy**

¹H NMR spectra were measured on a Bruker 300 MHz spectrometer. Approximately, 6 mg of each sample was digested in a mixture of DCl (20%)/D₂O (0.1 ml) and DMSO-d₆ (0.6 ml). Data analysis was performed in TopSpin software.

**Glass samples**

Approximately, 100 mg of ZIF-62-commercial and ZIF-62-synthesized were pressed into pellets (1 cm diameter) with 0.7 tons for 1 min. Prepared pellets were transferred into a tube furnace (Carbolite), and the furnace was flushed with nitrogen gas for half an hour before heating to 450 °C at 5 °C min⁻¹ and holding for 10 min. After heating, the pellets were left to cool down to room temperature at the natural rate of cooling of the tube furnace. Both heating and cooling steps were done under a constant nitrogen flow.

**SUPPLEMENTARY MATERIAL**

See the supplementary material for further structural and thermal characterizations.

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The authors declare that they have no competing financial interests, or other interests that might be perceived to influence the results and discussion reported in this paper.
DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1. H. Furukawa, K. E. Cordova, M. O’Keeffe, and O. M. Yaghi, Science 341, 1230444 (2013).
2. H.-C. Zhou, J. R. Long, and O. M. Yaghi, Chem. Rev. 112, 673 (2012).
3. J.-R. Li, R. J. Kuppler, and H.-C. Zhou, Chem. Soc. Rev. 38, 1477 (2009).
4. J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, and J. T. Hupp, Chem. Soc. Rev. 38, 1450 (2009).
5. A. Ahmed, M. Forster, R. Cloowes, P. Myers, and H. Zhang, Chem. Commun. 50, 14314 (2014).
6. S. Wei, Y. Liu, J. Zheng, S. Huang, G. Chen, F. Zhu, J. Zheng, J. Xu, and G. Ouyang, Chem. Commun. 55, 7223 (2019).
7. T. D. Bennett and S. Horike, Nat. Rev. Mater. 3, 431 (2018).
8. J. M. Tuffnell, C. W. Ashling, J. Hou, S. Li, L. Longley, M. L. Rios Gómez, and T. D. Bennett, Chem. Commun. 55, 8705 (2019).
9. K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe, and O. M. Yaghi, Proc. Natl. Acad. Sci. U. S. A. 103, 10186 (2006).
10. Y.-Q. Tian, Y.-M. Zhao, Z.-X. Chen, G.-N. Zhang, L.-H. Weng, and D.-Y. Zhao, Chem. -Eur. J. 13, 4146 (2007).
11. Y.-Q. Tian, C.-X. Cai, X.-M. Ren, C.-Y. Duan, Y. Xu, S. Gao, and X.-Z. You, Chem. -Eur. J. 9, 5673 (2003).
12. D. W. Lewis, A. R. Ruiz-Salvador, A. Gómez, L. M. Rodriguez-Albelo, F.-X. Coutert, B. Slater, A. K. Cheetham, and C. Mellot-Draznieks, CrystEngComm 11, 2272 (2009).
13. I. Frenzel-Beyme, M. Klooß, P. Kolodziejski, R. Pallach, and S. Henke, J. Am. Chem. Soc. 141, 12362 (2009).
14. K. E. Spencer, R. J. Angel, N. L. Ross, B. E. Hanson, and J. A. K. Howard, J. Am. Chem. Soc. 131, 4022 (2009).
15. A. Qiao, T. D. Bennett, H. Tao, A. Krajnc, C. M. Doherty, A. W. Thornton, J. C. Mauro, G. N. Greaves, and Y. Yue, Sci. Adv. 4, eaao6827 (2018).
16. H. F. Rahul Banerjee, A. Phan, R. Wang, C. Knobler, and O. M. Y. Michael O’Keeffe, Science 319, 939 (2008).
17. Y. Wang, H. Jin, Q. Ma, K. Mo, H. Mao, A. Feldhoff, and X. Cao, Angew. Chem., Int. Ed. 59, 4365 (2020).
18. M. Stepniewska, M. B. Østergaard, C. Zhou, and Y. Yue, J. Non-Cryst. Solids 530, 119806 (2020).
19. M. F. Thorne, M. L. R. Gómez, A. M. Rumstead, S. Li, and T. D. Bennett, Green Chem. 22, 2505 (2020).
20. A. M. Rumstead, M. L. Rios Gómez, M. F. Thorne, A. F. Sapnak, I. Longley, J. M. Tuffnell, D. S. Keeble, D. A. Keen, and T. D. Bennett, CrystEngComm 22, 3627 (2020).
21. M. L. Rios Gómez, G. I. Lampronti, Y. Yang, J. C. Mauro, and T. D. Bennett, Dalton Trans. 49, 850 (2020).
22. I. Longley, S. M. Collins, C. Zhou, G. I. Smales, S. E. Norman, N. J. Brownhill, C. W. Ashling, P. A. Chater, R. Tovey, C. Schönlieb, T. F. Headen, N. J. Terrill, Y. Yue, A. J. Smith, F. Blanc, D. A. Keen, P. A. Midgley, and T. D. Bennett, Nat. Commun. 9, 2135 (2018).
23. A. M. Rumstead, M. F. Thorne, and T. D. Bennett, “Identifying the liquid and glassy states of coordination polymers and metal–organic frameworks,” Faraday Discuss. (published online).
24. T. D. Bennett, Y. Yue, P. Li, A. Qiao, H. Tao, N. G. Greaves, T. Richards, G. I. Lampronti, S. A. T. Redfern, F. Blanc, O. K. Farha, J. T. Hupp, A. K. Cheetham, and D. A. Keen, J. Am. Chem. Soc. 138, 3484 (2016).
25. R. S. K. Madsen, A. Qiao, J. Sen, I. Hung, K. Chen, Z. Gan, S. Sen, and Y. Yue, Science 367, 1473 (2020).
26. A. K. Cheetham, E. R. Barney, E. G. Bithell, M. T. Dove, A. K. Soper, J.-C. Tan, T. D. Bennett, D. A. Keen, A. L. Goodwin, and M. G. Tucker, Phys. Rev. Lett. 104, 115503 (2010).
27. T. D. Bennett, P. Simoncic, S. A. Moggach, F. Gozzo, P. MacChi, D. A. Keen, J.-C. Tan, and A. K. Cheetham, Chem. Commun. 47, 7983 (2011).
28. J. Zhang, A. Qiao, H. Tao, and Y. Yue, J. Non-Cryst. Solids 525, 119665 (2019).
29. T. D. Bennett, D. A. Keen, J.-C. Tan, E. R. Barney, A. L. Goodwin, and A. K. Cheetham, Angew. Chem. 123, 3123 (2011).
30. C. Zhou, M. Stepniewska, J. M. Sorensen, L. Scarpa, G. Magnacca, V. Boffa, T. D. Bennett, and Y. Yue, Microporous Mesoporous Mater. 265, 57 (2018).
31. J. Zhang, L. Longley, H. Liu, C. W. Ashling, P. A. Chater, A. K. Beyer, K. W. Chapman, H. Tao, D. A. Keen, T. D. Bennett, and Y. Yue, Chem. Commun. 55, 2521 (2019).
32. M. Zeeshan, V. Nozari, M. B. Yagci, T. Isik, U. Unal, V. Ortalan, S. Keskin, and A. Uzun, J. Am. Chem. Soc. 140, 10113 (2018).
33. M. Hovestadt, S. Friebe, L. Helmich, M. Lange, J. Möllmer, R. Gläser, A. Mundstock, and M. Hartmann, Molecules 23, 889 (2018).
34. B. H. Toby and R. B. Von Dreele, J. Appl. Crystallogr. 46, 544 (2013).