Ionic liquid facilitated melting of the metal-organic framework ZIF-8

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Hybrid glasses from melt-quenched metal-organic frameworks (MOFs) have been emerging as a new class of materials, which combine the functional properties of crystalline MOFs with the processability of glasses. However, only a handful of the crystalline MOFs are meltable. Porosity and metal-linker interaction strength have both been identified as crucial parameters in the trade-off between thermal decomposition of the organic linker and, more desirably, melting. For example, the inability of the prototypical zeolitic imidazolate framework (ZIF) ZIF-8 to melt, is ascribed to the instability of the organic linker upon dissociation from the metal center. Here, we demonstrate that the incorporation of an ionic liquid (IL) into the porous interior of ZIF-8 provides a means to reduce its melting temperature to below its thermal decomposition temperature. Our structural studies show that the prevention of decomposition, and successful melting, is due to the IL interactions stabilizing the rapidly dissociating ZIF-8 linkers upon heating. This understanding may act as a general guide for extending the range of meltable MOF materials and, hence, the chemical and structural variety of MOF-derived glasses.
Metal-organic frameworks (MOFs) are porous crystalline three-dimensional networks composed of organic linkers coordinated to inorganic metal centers. They are of great interest owing to their structural tunability and potential applications in gas storage and separation, catalysis, drug delivery, and clean water harvesting. Research on developing new structures has led to the discovery of over 70,000 MOFs, mostly in the form of polycrystalline powders. The use of such powders in certain applications requires handling and processing into bulk and mechanically stable shapes or geometries. For instance, preparation of pellets is a possible route, however, pellet formation and achievement of the required mechanical stability can be challenging. Alternative routes for the fabrication of bulk, shapeable, and robust architectures with enhanced processability are therefore highly desired, thereby broadening the range of potential MOF applications.

Liquid MOFs and melt-quenched MOF glasses from zeolitic imidazolate frameworks (ZIFs) have emerged recently as a new class of materials, offering processable bulk shapes which still retain the advantageous chemical functionality of crystalline MOFs. ZIFs are a subset of MOFs having similar topologies as those which are found in inorganic zeolites (tetrahedral Zn$^{2+}$ are coordinated by imidazolates instead of tetrahedral SiO$_4$$^{4-}$ and AlO$_4$$^{5-}$ species bonded via corner-shared oxygens). However, only a handful of ZIFs have been observed to form melt-quenched glasses. The limited meltability of crystalline MOFs results from the decomposition temperature ($T_d$) being lower than the melting temperature ($T_m$) of the MOF framework. In the majority of cases, the organic linkers decompose prior to metal-ligand coordination bond breakage and reformation (i.e., melting). This prevents the material from reaching the potential liquid state. Post-processing strategies by which $T_m$ could be reduced to below $T_d$ would enable access to a much more diverse array of MOF glasses. This could open a wide variety of physicochemical properties, and significantly broaden the range of potential applications.

The microscopic mechanism of ZIF melting, the breaking and reformation of Zn–N bonds (referred to as defect formation) has been observed for meltable ZIFs such as ZIF-4 [Zn(Im)$_2$, Zn(C$_5$H$_9$N$_2$)$_2$], ZIF-zni [Zn(Im)$_2$, Zn(C$_5$H$_9$N$_2$)$_2$], and ZIF-62 [Zn(Im)$_2$(bIm)$_2$], for $O < x < 0.35$, respectively. This mechanism occurs via rapid dissociation and replacement of an initially coordinated linker with a neighboring linker. Melting requires that the vibrational displacement of atoms in the crystal structure reaches a characteristic level (instability), which is achieved by heating. In the more open networks such as ZIF-8 [Zn(mim)$_2$, Zn(C$_3$H$_7$N$_2$)$_2$], the (calculated) temperature at which Lindemann’s ratio reaches the threshold for melting by far exceeds those of ZIF-4 (1200–1500 K) and ZIF-zni (1500–1750 K): the higher energy barrier for linker mobility in ZIF-8 precludes framework melting.

ZIF-8, a commercially available ZIF with sodalite topology, has been investigated extensively in the literature for a wide range of applications such as microelectronics, catalysis, drug delivery, and gas separation. Theoretical studies on ZIF-8 melting revealed that the bond cleavage activation enthalpy and entropy of ZIF-8 exhibit a significant difference (43% for enthalpy and 60% for entropy) between Zn–N and Zn–Im coordination. However, for other ZIFs such as ZIF-4 and ZIF-zni variations of activation enthalpy and entropy in Zn–N and Zn–Im are less than 3%. This observation showed that Zn–N bonding strength is not the only parameter determining meltability. The specific behavior of ZIF-8 was further confirmed in simulation studies which found Zn to retain fourfold coordination up to 1250 K (in silico). The extent of interionic interactions, i.e., interactions between metal cations and organic anions, is, therefore, a crucial factor for melting; weaker interionic interactions facilitate melting.

The energy of defect formation was found to be similar for ZIF-8, ZIF-4, and ZIF-zni, i.e., 71, 56, and 67 kJ mol$^{-1}$, respectively. The striking difference between these three ZIFs is in their surface area (or porosity); ZIF-8 has a dramatically higher porosity as compared to the other two ZIFs (~1200 vs. 400 and 4 m$^2$ g$^{-1}$). This difference is even more evident (see Fig. 1a) when comparing the pore diameter $d_p$ of ZIF-8 (11.6 Å) with those of ZIF-4 (2.1 Å) and ZIF-62 (1.3 Å). Fig. 1a suggests that porosity is a key factor determining meltability.

There is thus a major constraint which prevents the melting of ZIF-8. Specifically, the relatively high porosity of the framework, which is linked to the absence of charge stabilization of the newly dissociated linker. Hence, melting should occur where the high free energy (stemming from the highly porous nature of ZIF-8) and interionic interactions between the metal cation and organic anion are both diminished. Following this hypothesis, we incorporated an ionic liquid (IL), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [EMIM][TFSI] into ZIF-8 pores aiming to decrease the $T_m$ of ZIF-8 to below its $T_d$, and reaching

**Fig. 1** Crystal structure of ZIF-8 and ZIF-62 and molecular structure of [EMIM][TFSI] used in IL@ZIF-8 composite. (a) Crystal structures and pore diameters of ZIF-8 and ZIF-62. The orange spheres in the crystal structures are drawn to mark the free space inside the cages. Crystallographic data of ZIF-8 and ZIF-62 are taken from literature. (b) Molecular structure of [EMIM][TFSI]. Color codes: Zn – purple tetrahedra, N – blue, C – gray, S – yellow, O – red, F – olive, H – omitted for clarity.
the liquid state as a result of interactions between the IL and ZIF-8 at elevated temperatures.

Interactions between different ILs and MOFs have been extensively investigated experimentally and computationally at low temperatures. It has previously been shown that the interactions between IL molecules and the MOF structure are crucial in creating new functional sites favorable for adsorption, catalysis, and ion conduction\(^{27}\). For example, a simulation study investigated IRMOF-1 supported IL membranes for CO\(_2\) capture. Four different ILs with fixed cation and different anions were used to demonstrate that the anion of the IL plays an important role in the extent of interactions between IL and MOF\(^{28}\).

Combined density functional theory (DFT) calculations and experimental vibrational spectroscopy have also been used to probe the molecular interactions between a Cu-based MOF, copper benzene-1,3,5-tricarboxylate (CuBTC), and an IL, 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO\(_4\)]). Here, the results showed that interactions between the IL anion and Cu\(^{2+}\) ions caused the transfer and redistribution of electron density over the metal sites. A corresponding red-shift was observed in the experimental vibrational spectra in IR bands associated with Cu–O bonding. It was concluded that intermolecular interactions between the linker molecules and Cu weaken upon simultaneous interaction with IL ions\(^{29}\). Weakening metal-linker bonding was further shown via incorporating seven different imidazolium-based ILs into CuBTC pores. It was shown that when the interionic interaction within the IL was higher, the IL was interacting strongly with the structure and Cu–O bonding became weaker, resulting in lower thermal stability of the IL@MOF composites\(^{30}\).

Here, we use the synergistic concepts of (i) an adjustment of metal-linker bond strength and (ii) a greater extent of energetic stabilization of a newly dissociated linker, to investigate the IL mediated melting of a prototypical porous framework, ZIF-8.

### Results

[EMIM][TFSI] was chosen since it is a hydrophobic IL, enabling incorporation into the hydrophobic pores of ZIF-8\(^{31}\). It has a very high \(T_d\) (\(-440 °C\)) compared to other imidazolium-based ILs\(^{31,32}\), 35 wt% of [EMIM][TFSI] were loaded into ZIF-8 using a wet impregnation technique (see Methods section for further details). The resultant composite is herein referred to as IL@ZIF-8 (Fig. 1). The IL loading was adjusted in such a way as to obtain a powder sample without the presence of excess liquid.

The IL@ZIF-8 composite was characterized using X-ray diffraction (XRD) (Fig. 2a), scanning electron microscopy (SEM) (Supplementary Fig. 1), and Fourier transform infrared spectroscopy (FTIR) (Fig. 2b). XRD and SEM results confirmed that IL incorporation did not damage the crystal structure and morphology of ZIF-8. FTIR measurements were carried out in order to examine the incorporation of IL into ZIF-8; they show that all IL IR features are present in the composite sample. These results are in agreement with previous studies on crystalline IL@MOF composites\(^{33–36}\).

To study the bonding interactions between the IL and ZIF-8 at high temperature, thermogravimetric analyses (TGA) coupled with differential scanning calorimetry (DSC), TGA-DSC, were done on ZIF-8, the IL, and the IL@ZIF-8 composite (Fig. 2c and Supplementary Fig. 2). No phase transitions were observed in pristine ZIF-8 and the bulk IL before the start of decomposition at around 550 and 440 °C, respectively. A small endothermic peak at 381 °C was noted in the IL@ZIF-8 composite, very close to the decomposition temperature (\(-412 °C\)). To properly assign this feature to melting, IL@ZIF-8 was heated at 387 and 390 °C under nitrogen (slightly above \(T_m\), defined as the offset temperature of the melting peak) for 30 and 40 min, defined as LT (low temperature) and HT (high temperature) conditions, respectively. After heating, samples were cooled down to room temperature at a rate of 50 °C·min\(^{-1}\). The obtained samples are henceforth referred to as \(a_g(\text{IL@ZIF-8-LT})\) and \(a_g(\text{IL@ZIF-8-HT})\).

Throughout these experiments, the heating temperature and time were selected in such a way that fully and partially amorphous samples could be acquired for HT and LT conditions respectively, as demonstrated by XRD analysis (see Fig. 2a). The XRD pattern of \(a_g(\text{IL@ZIF-8-HT})\) contains the broad diffuse scattering characteristic of glass (with a small unidentified Bragg peak at 11.6°). A pure sample of ZIF-8 subjected to the same (HT) treatment retained its crystallinity. However, \(a_g(\text{IL@ZIF-8-LT})\) contained weak diffuse scattering, alongside Bragg peaks reminiscent of the starting crystalline phase. This suggests that treatment temperature and time are important parameters in the formation of IL@ZIF-8 glasses and crystal-glass composite samples, as indicated in Supplementary Fig. 3 for a range of tested synthesis conditions. A DSC upscan (Fig. 2c) performed on \(a_g(\text{IL@ZIF-8-HT})\) revealed a glass transition temperature (\(T_g\)) of 322 °C (595 °F), confirming the glassy nature of this sample. With the melting temperature (temperature of \(\sim 381 °C\) (654 °F)), this results in a nominal value of \(T_g/T_m\) of \(-0.91\), which even surpasses the ultrahigh glass-forming ability of 0.84 which was reported for melts of ZIF-62\(^{37}\). To more clearly observe the glass transition, referenced DSC runs were conducted in order to extract the isobaric heat capacity \(C_p\) (denoted \(C_p\) scans). Cyclical \(C_p\) scans were performed on \(a_g(\text{IL@ZIF-8-HT})\) samples at various heating and cooling rates (see Methods section for further details). Figure 2d shows a cyclic \(C_p\) scan for \(a_g(\text{IL@ZIF-8-HT})\) using 20 °C·min\(^{-1}\) as heating and cooling rate. A pronounced glass–liquid transition is detected at \(-328 °C\), with a configurational heat capacity \(\Delta C_p\) of \(-0.11 \text{J·g}^{-1}·\text{K}^{-1}\) (Fig. 2d). The magnitude of the jump in \(C_p\) is comparable to the values observed for other ZIF glasses such as ZIF-4, 0.11 and 0.16 J·g\(^{-1}\)·K\(^{-1}\) for LDA and HDA phases, and 0.19 J·g\(^{-1}\)·K\(^{-1}\) for ZIF-62\(^{37,38}\). The minor up-shift in the glass transition as compared to the DSC scan (Fig. 2c) is attributed to the higher scanning rate (20 °C·min\(^{-1}\) vs. 5 °C·min\(^{-1}\)). Although the second upscan exhibits a similar \(\Delta C_p\) to the first, a slight delay is found in the glass transition. We attribute this observation to the continuing interaction between the glass phase and residual IL, simultaneously overlapping with ongoing IL decomposition during extended exposure of the glass to high temperatures in the first upscan and subsequent down scan (which is why we limited the scanning range to the upper limit of 360 °C). Additional cycle \(C_p\) scans with different cooling/heating rates are provided in Supplementary Fig. 4. For \(a_g(\text{IL@ZIF-8-LT})\), shown in Supplementary Fig. 5, the glass–liquid transition is not as clearly visible as in the HT sample, which is because crystalline ZIF-8 (together with residual IL) remains the primary phase in this case, and neither ZIF-8 nor the IL exhibit a DSC feature in this temperature range (Fig. 2c). However, in the second upscan, a weak glass transition is detected also for the LT sample, which is in line with our interpretation of progressive reactions during DSC scanning.

Confocal microscopy images displayed in Fig. 3 show clear evidence of macroscopic flow as a result of melting, as well as direct light transmittance and smooth glass-like surfaces. Macroscopic flow and melting of the IL@ZIF-8 heated from room temperature to 390 °C were observed in situ using a laser scanning microscope (LSM), whereas no morphological changes were seen when heating the parent ZIF-8 to the same temperature (observations are provided as Supplementary Movies 1 and 2 for ZIF-8 and IL@ZIF-8, respectively. All these observations show that ZIF-8, a non-meltalbe MOF, transforms into a meltable, glass-forming composite through the incorporation of an IL into its pores.

To uncover the microscopic mechanism which facilitates the melting of the IL@ZIF-8 composite, FTIR, TGA,
**Fig. 2** Structural characterization, enthalpic responses, and cyclic $C_p$ scan. 

**a** XRD patterns of ZIF-8, IL@ZIF-8 crystalline composite, $a_g$(IL@ZIF-8-LT), and $a_g$(IL@ZIF-8-HT) samples. Crystallographic data were taken from literature. 

**b** FTIR spectra obtained for ZIF-8, IL, crystalline IL@ZIF-8 composite, $a_g$(IL@ZIF-8-LT), and $a_g$(IL@ZIF-8-HT). 

**c** DSC scans of ZIF-8, IL, IL@ZIF-8, and $a_g$(IL@ZIF-8-HT) samples with a heating rate of 5 °C·min$^{-1}$. $T_m$ and $T_d$ are indicated as offset temperatures of the melting peak and onset temperature of decomposition of IL@ZIF-8, respectively. $T_g$ is defined as the onset temperature of the glass transition feature of $a_g$(IL@ZIF-8-HT). 

**d** Cyclic $C_p$ scan of $a_g$(IL@ZIF-8-HT) with heating and cooling rates of 20 °C·min$^{-1}$. 

**Fig. 3** Confocal microscopy images showing evidence of melting and glass formation. 

**a–c** $a_g$(IL@ZIF-8-LT). 

**d–f** $a_g$(IL@ZIF-8-HT). Scale bars are 100 µm.
thermogravimetric analysis coupled with mass spectrometry (TG–MS), 1H NMR, 13C NMR, and total scattering measurements were performed on ZIF-8, IL, IL@ZIF-8, a_4(IL@ZIF-8-LT), and a_4(IL@ZIF-8-HT) samples. As expected, IR bands in the glassy composites are broader compared to crystalline ZIF-8 and the IL@ZIF-8 composite (see Fig. 2b). Further analysis of deconvoluted spectra in Supplementary Figs. 6 and 7, corresponding to 600–800 cm⁻¹ (out of plane bending of imidazole ring) and 800–1700 cm⁻¹ (in-plane bending and entire ring stretching of imidazole ring) regions, revealed that the IR bands belonging to ZIF-8 are shifted in IL@ZIF-8, a_4(IL@ZIF-8-LT), and a_4(IL@ZIF-8-HT) samples. The shifts are summarized in Supplementary Tables 1 and 2. They reflect a clear difference in the interactions between ZIF-8 and IL in crystalline IL@ZIF-8, the melt-quenched glass, a_4(IL@ZIF-8-HT), and the crystal-glass composite a_4(IL@ZIF-8-LT). The shifts are significantly larger in a_4(IL@ZIF-8-LT) and a_4(IL@ZIF-8-HT) compared to crystalline IL@ZIF-8, representing stronger electrostatic interactions between the metal center and organic linker of ZIF-8 and the IL and cation of the IL component in these samples, respectively. The shifts show that most of the IR bands of ZIF-8 are shifted to lower frequencies (redshifted), indicating that intramolecular bonding within the 2-methylimidazolate ring of ZIF-8 becomes weaker as a result of intense interaction with IL ions, which only occurs at higher temperatures. The resulting interaction becomes stronger when temperature and heating time increase, as evidenced by larger redshifts in IR features of a_4(IL@ZIF-8-HT) compared to a_4(IL@ZIF-8-LT). The thermal stability of the bulk IL, pristine ZIF-8, and IL@ZIF-8 composites was examined with the same thermal treatment used to melt the a_4(IL@ZIF-8-LT) and a_4(IL@ZIF-8-HT) samples. TGA measurements are presented in Supplementary Fig. 8, demonstrating the differences between IL vs. IL@ZIF-8 weight losses. Corresponding quantitative data are provided in Supplementary Table 3. Consistent with the XRD result obtained for ZIF-8-HT, pristine ZIF-8 shows almost no mass loss (1.0 and 0.9% for LT and HT conditions, respectively), while the bulk IL loses 17.5 and 50.0% of its initial mass when heated to LT and HT conditions, respectively, attributed to the decomposition of IL that happens mostly in the isothermal heating step (see Supplementary Fig. 8). The thermal stability of ILs has been studied in dynamic and isothermal TGA experiments previously. ILs mostly decompose at lower temperatures when heated isothermally as compared to the onset decomposition temperature in dynamic heating conditions and in Supplementary Fig. 24. In the present case, the IL@ZIF-8 composite showed 20.7 and 34.4% weight loss for LT and HT heating conditions, respectively.

To understand whether the decomposed species are IL or ZIF-8 in IL@ZIF-8, we probed the possible decomposition products by conducting TG–MS analysis. TG–MS experiments were performed on bulk IL and IL@ZIF-8 composites with LT and HT heating conditions. As for the decomposition of bulk EMIM [TFSI], it was previously found that elimination and nucleophilic substitution are major mechanisms of decomposition. At high temperatures (over 350 °C), decomposition of the anion to more nucleophilic groups such as NH₂ and F, and the subsequent attack of cation methyl and ethyl groups resulted in the occurrence of different decomposition products in isothermal and scanning TG-MS experiments (in order to minimize the progressive effect of such reactions on the cyclic C₆ scans performed on quenched IL@ZIF-8 glasses, Fig. 2d, the upper limit of these scans was set at 360 °C; on the other hand, a further reduction of the scanning range would compromise accurate assignment of the glass transition region). According to the results shown in Supplementary Fig. 9, almost all mass to charge ratios, m/z, coming from IL@ZIF-8 match the masses detected from the bulk IL at LT and HT conditions. Assignment of m/z values to decomposition products has been reported previously. Moreover, TG–MS shows that detection of masses occurs in the isothermal segments of LT and HT heating conditions. This agrees with mass losses observed in TGA experiments (see Supplementary Fig. 8).

Digested liquid ¹H NMR was also performed on ZIF-8, IL, IL@ZIF-8, a_4(IL@ZIF-8-LT), and a_4(IL@ZIF-8-HT) samples to ascertain the stability of the ZIF-8 linker and of the IL; the spectra are discussed in the Supplementary Information. The results suggest large-scale decomposition of the IL and some linker decomposition within the glass, as also indicated by the darkened color in the optical images (Fig. 3).

The top of Fig. 4 compares the ¹H–¹³C cross-polarization (CP) NMR spectra for ZIF-8, IL@ZIF-8, a_4(IL@ZIF-8-LT), and a_4(IL@ZIF-8-HT). CP experiments result in much higher signal/noise (S/N) than single-pulse experiments, but also only allow observation of solid-like carbons (¹H T₁ times must be longer than the time needed for ¹H–X polarization transfer). There are three main carbon peaks highlighted with blue boxes from the mlm linker of ZIF-8: CH₂ (C₇), CH (C₉), and C (C₈) at 14.26, 124.67, and 151.66 ppm; the peaks from pure ZIF-8 are sharp with widths of 0.2–0.3 ppm indicating crystallinity. In comparison, a broad shoulder emerges in a_4(IL@ZIF-8-HT) and almost all sharp peaks are absent in a_4(IL@ZIF-8-LT), agreeing with the XRD results displayed in Fig. 2a. Although these NMR experiments only probe short-range interactions, the broadness and sharpness of the peaks are clear indications of the degree of crystallinity, allowing for assignment of the peaks to amorphous and crystalline features in Fig. 4. The variety of electronic environments found in broad NMR peaks is assumed to be from varying bond angles and bond lengths, and strongly indicates a system without long-range order. This loss of crystallinity is confirmed for the a_4(IL@ZIF-8-LT), and a_4(IL@ZIF-8-HT) by both XRD and pair distribution function (PDF) measurements, as well as by single-pulse ¹³C NMR (Supplementary Figs. 16–18).

For a more thorough discussion of the ¹H–¹³C spectra, we turn to the fits of the C (C₇), CH (C₉), and CH₃ (C₈) peaks, respectively, in Fig. 4b. Upon IL addition, the three main carbon peaks remain mostly unchanged, yet, a substantially shifted second peak emerges downfield (higher ppm) of the CH₃ (C₈) and CH (C₉) peaks. Since the intensity of CP peaks in liquids is very low (as can be seen for pure EMIM peaks in IL@ZIF-8 in Fig. 4a and in Supplementary Fig. 22), these new peaks in the IL@ZIF-8 in Fig. 4 correspond to ZIF-8 interacting with the IL. Moreover, Supplementary Fig. 24 confirms the appearance of a new peak at ~15.4 ppm in IL@ZIF-8 that does not exist in either pure IL or ZIF-8. Finally, IL@ZIF-8 interactions are further corroborated by the different chemical shifts of IL vs. IL@ZIF-8 in Supplementary Fig. 23.

For the HT condition, a_4(IL@ZIF-8-HT), there are at least three types of carbon peaks (Fig. 4b). The first type of peak, very slight retention of the sharp ZIF-8 and IL-associated sharp ZIF-8 peaks, is in simple agreement with the XRD results. We note that the LT condition shows the same trends (Supplementary Fig. 21). Like the IL-associated carbon peaks, the broad peaks (Fig. 4b) are found downfield of the sharp peaks, indicative of interactions with IL and/or strain of ZIF-8 linkers. The third type of peak is located upfield (lower ppm), identified as free ZIF-8 linkers which are unbonded to Zn²⁺. Overall, the spectral regions representing amorphous features and the free linker are very wide and sometimes contain more than one clear peak; these large ppm ranges represent the many different types of chemical environments and bonding which exist after heating. Returning to more quantitative single-pulse ¹³C NMR, in Supplementary Fig. 25, we find that for the C₂ carbon in the LT sample roughly 21, 58, and 21% can be identified as crystalline, amorphous, and free linker, respectively.
Simultaneously, in Fig. 5a and Supplementary Fig. 23, we also find a large increase in S/N for the IL peaks in a_{IL@ZIF-8-LT} and a_{IL@ZIF-8-HT}, indicating that much more of the IL is now immobilized and behaving like a solid. This result is unsurprising in consideration of the collapse of the pores as evidenced by the dramatic differences in the out-of-plane bending and C=N stretches in the IR after heating (see Supplementary Tables 1 and 2). The most substantial changes in chemical shifts, i.e., electronic environments, are observed for the Cd:C H2 and Ca:C H3 carbons in EMIM (see Supplementary Fig. 23). In the heat-treated samples, we further observe the formation of imidazole, highlighted in gold, confirming the loss of ethyl and methyl from EMIM observed in 1H NMR results. Finally, for the a_{IL@ZIF-8-HT} sample, the signals from Ch in the IL cation and C1 in imidazole are very broad. This is in line with our 1H NMR and literature data which reveals this hydrogen to be the most reactive and likely to interact with other molecules in the material.46,47

The 1H–15N CP NMR spectra for ZIF-8, IL@ZIF-8, and a_{IL@ZIF-8-LT} are provided in Fig. 5b, perfectly matching the trends of 1H–13C CP NMR, Fig. 4a. Upon heating, a broad shoulder appears downfield along with a broad peak upfield identified again as free-linker. The free-linker peak position represents a much different environment than that of the original ZIF-8 linker. This is expected, given that the nitrogen of the ZIF-8 linker bonds directly to the Zn^{2+} metal center: the shift direction suggests the formation of Zn–H bonding as the imidazole peak is found at −171.6 ppm in DMSO.48 This general increase in shielding, i.e., electron density, on the nitrogen of the mIm applies for the carbon atoms of the ZIF-8 linker as well, as all the assigned free-linker peaks have lower chemical shifts than their corresponding intact framework peaks. Comparing to 1H-15N CP NMR of a_{IL@ZIF-8-LT}, the sharp peak which would be evidence for a crystalline phase is not detected in 1H–15N CP NMR of a_{IL@ZIF-8-HT}, shown in Supplementary Fig. 26, which is in agreement with XRD data in Fig. 2a.
According to the literature, strong interionic interactions occur between [EMIM] and [TFSI] within the IL. 49 Moreover, it has been shown that IL ([BMIM][TFSI]) interacts with ZIF-8 via the N or S atoms of the IL anion and Zn sites in ZIF-8. 35 Although ILs are composed of charged ions, they also are molecules with substantial intermolecular hydrogen bonding 50. For example, the S = O group in trifluoromethanesulfonic acid has been found to form a hydrogen bond with a CH carbon in an imidazole ring 31,32. Surprisingly to most chemists, several studies show the protons attached to sp3 carbons (methyl and ethyl groups) of EMIM forming H-bonds with halogens and nitrogen 33,50. We are unsure of the strength of the interaction between CH3 and an H-acceptor such as S = O, but our 1H-13C CP NMR agrees: the interactions between ZIF-8 linker hydrogens and IL ions explain the reason that only the ZIF-8 linker CH (C1,3) and CH2 (C2) carbons are affected by the incorporation of IL, while the ZIF-8 linker C2 or lone C is mostly unaffected by IL incorporation. Furthermore, hydrogen bonding results in positive shifts (deshielding) of carbon peaks in conjugated ring systems, just like our emerging peaks in IL@ZIF-8 in Fig. 453. Thus, we believe the IL anion to interact with the ZIF-8 mIm linkers via H bonding as shown in Fig. 6a.

We know from DSC that melting of the composite occurs well before the substantial mass loss (381 °C vs. 410 °C). Given the evidence of amorphization and formation of free linkers from the solid-state NMR, alongside the proposed mechanism of melting in ZIFs, 49 we suggest that upon dissociation from the Zn2+ metal centers, the 2-methylimidazolate linkers are stabilized by electrostatic interactions with the IL ions (or partially decomposed IL molecules), which leads to a stable liquid (see Fig. 6b, c).

After incorporation into ZIF-8 and subsequent heating at LT and HT conditions, mass spectroscopy and solution 1H NMR tell us that much of the IL anion is lost and that the IL cation loses some of its methyl/ethyl groups upon heating. The leaving groups and percentages of each, based on the area under the TG–MS curves, are shown in Fig. 7a. The mass loss curves were also used to calculate the elemental composition of the final LT and HT samples, in Fig. 7b, c, respectively. The general trends are that zinc remains, while fluorine, oxygen, and sulfur content decrease substantially in the LT sample and are absent entirely in the HT sample. Commensurately, the carbon and nitrogen concentrations also increase, however, they do so in an unexpected fashion: the increase in nitrogen content is more than double that of the carbon content. Indeed, the many possible decomposition products from the IL make it challenging to discern the exact structure of the resulting glass after further heating. Nevertheless, one possible structure for the LT sample is depicted in Fig. 7b, where some of the original IL cation and anion can be found, as some F, S, and O remains, but where there are also new molecules, such as imines (ketimines, aldimines, sulfimyl imines, and fluoro-substituted amines), which contain the elements known to remain, and are liquids at RT and fairly stable in the absence of water (expected from our Brunauer–Emmett–Teller (BET) measurements in Supplementary Fig. 32 and Supplementary Table 9), especially in the case of hexafluoroacetone, (CF3)2CNH.

In the HT sample, only Zn, C, N, and H remain in the material, yet again the increase in N content is notably high. Consequently, we believe only imines (ketimines and aldimines) without fluorine substitution remain, which are stabilized by interactions with the Zn2+ sites, as has been shown with silver in the literature 54. In fact, if the R’ group is not H, these molecules are specifically known as Schiff bases when they act as negatively charged ligands to form metal complexes 55. For example, such an R’ group could be resulting from one of the ethyl/methyl groups that are lost from the EMIM cation, as shown by both the solution 1H NMR and 13C SSNMR. Although the exact composition of the partially decomposed IL and ZIF-8 mixture is hard to determine, the mass loss from the ZIF-8 linkers is low and the net result is the formation of a glass.

We investigated the removal of IL residues from the a IL@ZIF-8-HT and a IL@ZIF-8-LT samples by conducting post-process washing experiments in acetone. Details are provided in the Supplementary Information, Supplementary Fig. 29–32, and Supplementary Table 9 for the obtained results. In short, washing
amorphization of IL@ZIF-8 at 381 °C. Orange and green bonds represent Zn²⁺–N⁻ bonding and H bonding between IL and ZIF-8, respectively. For a schematic view of the whole pore, see Supplementary Fig. 27.

results in a significant reduction of the brownish tint (which we have assigned to the decomposition products) and notably enhanced gas adsorption performance by partially removing the unreacted or decomposed compounds from the glass matrix. TGA-DSC scanning of post-washed ag(IL@ZIF-8-HT), Supplementary Fig. 31, confirmed that the glassy nature of the sample is preserved during washing. Gas adsorption experiments using N₂ or CO₂ (Supplementary Fig. 32) reveal a fourfold increase of the glass' total porosity after washing; in particular, the washed a₇(IL@ZIF-8-LT) sample which contains a major fraction of crystalline ZIF-8 (being only partially amorphized) exhibited improved CO₂ uptake compared to the adsorption capacity observed for other MOF glasses such as a₇(ZIF-8)ₜ₂(ZIF-62)₀.5. While outside of the scope of the present study, future exploration of LT-type composite materials containing crystalline ZIF-8 in a partially melted IL@ZIF-8 matrix phase may be beneficial towards the application of these materials, for example, in gas adsorption and separation.

To further investigate, and compare, the structures of the crystalline and glassy composites, room temperature synchrotron X-ray total scattering experiments were conducted on the IL, ZIF-8, IL@ZIF-8, a₇(IL@ZIF-8-LT), and a₇(IL@ZIF-8-HT) samples. For comparison with the heat-treated samples, a₇(IL@ZIF-8-LT) and a₇(IL@ZIF-8-HT), a sample of ZIF-8 was amorphized (see Supplementary Fig. 33) via ball milling for 30 min at 30 Hz in a shaker-type grinding mill—as detailed in the Methods section. This ball-milled sample is herein referred to as am(ZIF-8), in accordance with prior nomenclature.

The structure factors, S(Q) in Supplementary Fig. 34a show Bragg peaks for the ZIF-8 and IL@ZIF-8 samples, in agreement with the XRD data collected in this work. The intensities of the Bragg peaks are reduced for the a₇(IL@ZIF-8-LT) sample (see Supplementary Fig. 34) but it is clear that the sample has not been fully amorphized. As expected, the S(Q)s for the IL and am(ZIF-8) samples show a noticeable absence of Bragg scattering, indicating their amorphous nature. The S(Q) for the a₇(IL@ZIF-8-HT) sample is most similar to the S(Q) of am(ZIF-8), both of which have a broad first sharp diffraction peak (FSDP) often described as a manifestation of intermediate-range order in glasses. In addition to this broad peak at ~1 Å⁻¹ in the S(Q) of a₇(IL@ZIF-8-HT), there is a small sharper peak at 0.52 Å⁻¹. This matches the scattering vector observed for the (011) Bragg peak in the PXRD of ZIF-8.

From the background-corrected X-ray total scattering data, the real space PDFs, G(r) could be extracted by Fourier transform and were subsequently converted to D(r) in order to emphasize the peaks at high r. These peaks correspond to atom–atom correlations in the sample, with the peak position determined by the interatomic distances between atom pairs and the intensity proportional to the product of the scattering factors from all of the atoms which correspond to a particular interatomic distance. As such, PDF analysis is a powerful tool for studying amorphous materials and glasses as the local short-range order can still be probed, but the presence of disorder and loss of structural coherence at longer length scales leads to the absence of peaks at this extended regime.

As the X-ray atomic form factor is proportional to the atomic number, Z, the relatively light elements such as those in the IL component do not contribute as intensely as correlations with the heavier zinc atoms in ZIF-8. Additionally, the IL only accounts for a theoretical 35 wt% of the composite sample, so the overall contribution of the IL towards the PDF pattern of the IL@ZIF-8 composite is expected to be small. Even so, a comparison of the PDFs of the IL@ZIF-8 composite, along with its constituent components in Fig. 8a, shows that for correlations in which there are peaks in both the IL and ZIF-8 patterns (e.g., the peaks at ~1.4 Å), the intensity of the corresponding peaks in the IL@ZIF-8 composite is greater than in the pure ZIF-8 pattern. For peaks which only correspond to correlations in ZIF-8 (e.g., the peaks at 2.01, 3.01, 4.17, and 6.02 Å), the intensity is smaller than in pure ZIF-8 due to the reduced ZIF-8 content in the composite.
Long-range order was evident in the ZIF-8 and IL@ZIF-8 samples, with peaks in the \(D(r)\) extending out to 25 Å (see Supplementary Fig. 34b). However, the \(D(r)\) for the \(a_g(\text{IL@ZIF-8-HT})\) sample appears largely featureless at extended distances (>6.02 Å) which would be consistent with the vitrification of the ZIF-8 component. This loss of long-range order, alongside the retention of the local structure (short-range order), is consistent with glass formation, as has been observed for other glass-forming MOFs. The retained short-range order is very similar to that exhibited by the pure ZIF-8 sample (see Fig. 8b), suggesting that the secondary building block units (i.e., the Zn(2-MeIm)₄ clusters) of ZIF-8 are still intact, though, their arrangement at extended length scales is disrupted. The presence of this short-range order also suggests that the sample has not completely decomposed due to the heating procedure, or due to beam damage, consistent with the digestive \(^1\text{H} \text{NMR} \text{ data.} \) Finally, the PDF patterns of the \(a_g(\text{IL@ZIF-8-HT})\) sample and the \(a_m\text{ZIF-8, shown in Fig. 8b are remarkably similar which, together with the S(Q) only showing broad scattering features and very weak remnant Bragg scattering (Supplementary Fig. 34a), provides further evidence for the almost complete amorphization of the ZIF-8 framework within the composite. We conducted further investigations on the physical properties of the \(a_g(\text{IL@ZIF-8-HT})\) glass by examining optical absorbance as well as mechanical properties. Absorbance spectra taken of an \(a_g(\text{IL@ZIF-8-HT})\) glass film on a platinum substrate are presented.
in Supplementary Fig. 35 (experimental details are provided as Supplementary Information). The $a_g$(IL@ZIF-8-HT) glass is generally optically transparent but absorbing in the blue to the green part of the visible spectrum. This results in the brownish-red coloration observed in the microscope images presented in Fig. 3. Interestingly, the absorbance decreases towards the UV region, in the spectral range of ~500–360 nm (limit of the detector), which is a clear indicator for the absence of light scattering by crystal inclusions or other heterogeneities with a characteristic size corresponding to the wavelength of observation. Coloration aside, the obtained glass samples are highly transparent and possess no evidence of large-scale phase separation.

The mechanical properties of the $a_g$(IL@ZIF-8-HT) glass were studied through instrumented indentation testing using a nanoindenter (see Methods for details). The obtained depth profiles of hardness ($H$) and elastic modulus ($E$) are depicted in Supplementary Fig. 36. The indentation response displays a marked load dependence, which reflects in a continuous decrease of $H$ and $E$ with increasing displacement into the glass’ surface ($h$). This effect is more pronounced at small indentation depths and tends to level off as the indenter penetration increases, with the values of $E$ and $H$ eventually approaching the values of crystalline ZIF-8 reported in the literature ($H = 0.501$ GPa and $E = 3.10$ GPa)\textsuperscript{63}. Averaging the values of $E$ and $H$ between the upper 10% and lower 20% of each indentation depth profile resulted in mean values of $H = 0.730 \pm 0.136$ GPa and $E = 5.42 \pm 1.10$ GPa for $a_g$(IL@ZIF-8-HT). In a direct comparison with crystalline ZIF-8, we must emphasize that the mechanical stability may strongly vary as a function of the employed synthesis conditions: values of $H$ ranging from 0.501 to 0.643 GPa have been reported for crystalline ZIF-8. Likewise, $E$ was reported with values of only 3.10 GPa up to about 7.33 GPa\textsuperscript{63,64}. In this regard, the present $a_g$(IL@ZIF-8-HT) falls in the same category as other ZIF-type glasses, such as $a_g$ZIF-4 ($H = 0.676$ GPa and $E = 7.17$ GPa) or $a_g$ZIF-62 ($H = 0.656$ GPa and $E = 6.85$ GPa)\textsuperscript{65}.

Discussion

In summary, the incorporation of an IL into the pores of ZIF-8 makes this otherwise unmeltable compound melttable. Based on structural investigations, we hypothesize that melting is achieved by reducing the melting temperature of ZIF-8 to below its thermal decomposition temperature, using electrostatic interactions of the IL (or partially decomposed IL fragments) at the ZIF-8 pores’ interior surface in order to stabilize the rapidly dissociating ZIF-8 linkers upon heating. Although the methyl in mIm (ZIF-8 linker) likely changes the Zn$^{2+}$-linker bonding in ZIF-8 relative to meltable ZIF-4 (where only Im is present), the largest change is in topology: the sodalite ZIF-8 topology is over three times as porous as the cag ZIF-4 topology\textsuperscript{18}. The IL anion and cation interact strongly with the Zn$^{2+}$ and linker, respectively, and the IL is less constrained than the ZIF-8 linker; upon infiltration, it decreases the internal surface area of ZIF-8 (see Supplementary Fig. 32 and Supplementary Table 9 for surface area and pore volume analysis). Thus, the high porosity of ZIF-8, or the low mobility and isolation of its linkers no longer present a barrier to melting: the IL ions are immediately available to exchange with the rapidly dissociating Zn$^{2+}$-linker bond and prevent decomposition at elevated
temperatures. We note that similar hydrophobicity and high thermal stability of the IL are important factors determining the meltability of IL-incorporated MOF composites. More generally, we conclude that a suitable, i.e., strongly bonding, IL stabilizes ZIF (and potentially other MOF) melts by reducing the lifetime of unstable configurations via Zn\(^{2+}\)–N bonding and H bonding. The corresponding melt-quenched glass has a glass-forming ability which exceeds even those of previously reported super-strong glasses from conventionally meltable ZIFs.

This approach strongly broadens the variety of hybrid glass chemistries which may be derived from the MOF family. It offers exciting opportunities to melt other non-meltable crystalline MOFs, potentially enabling a broad range of hybrid glasses with a variety of physicochemical properties and corresponding applications, in particular, ones which are derived from MOF architectures with large pore sizes.

Methods
Preparation of IL@ZIF-8 composite. ZIF-8 and the IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [EMIM][TFSI] (>99%), were purchased from ACS-SYMAM Inc and IoLiTec, respectively. To remove moisture and volatile impurities, ZIF-8 was evacuated at 105 °C under vacuum overnight. IL@ZIF-8 composite was prepared using wet impregnation at a stoichiometric IL loading of 35 wt%, according to previous reports. Briefly, 0.55 g of IL was dissolved in 20 mL acetone and stirred for 1 h at room temperature in a sealed container to hinder acetone evaporation. Afterward, IL activated ZIF-8 (0.65 g) was added to the solution and the mixture was stirred at 35 °C for about 7 h under an open atmosphere until the acetone was evaporated. The resultant powder sample was dried overnight at 105 °C to remove the remaining acetone.

Glass samples. Approximately 25 mg of powder IL@ZIF-8 composite was placed in a platinum crucible and pressed by hand to provide better contact with the crucible. To facilitate an even heat transfer in the sample, a smaller platinum crucible that could fit inside the main crucible and gently pressed by hand to ensure good contact between the crucible and the powder sample. All measurements were performed under 20 mL min\(^{-1}\) of 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 5 °C min\(^{-1}\). To obtain the glass transition temperature (\(T_g\)), \(\alpha_2(\text{IL@ZIF-8-HT})\) in powder form was placed in a platinum crucible and heated to 400 °C with a 5 °C min\(^{-1}\) ramp rate. \(T_\alpha\), \(T_b\), and \(T_p\) are determined as the intersection of the starting baseline and the tangent to the DSC curve at the maximum gradient point.

Cyclic \(C_p\) scan. 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 good contact between the crucible and the powder sample. All measurements were performed under 20 mL min\(^{-1}\) of 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 5 °C min\(^{-1}\). To obtain the glass transition temperature (\(T_g\)), \(\alpha_2(\text{IL@ZIF-8-HT})\) in powder form was placed in a platinum crucible and heated to 400 °C with a 5 °C min\(^{-1}\) ramp rate. \(T_\alpha\), \(T_b\), and \(T_p\) are determined as the intersection of the starting baseline and the tangent to the DSC curve at the maximum gradient point.

Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were collected using a Thermo Scientific Nicolet iS10 model FTIR spectrometer in attenuated total reflection mode. Sixty-four and 128 scans were measured for background and sample spectra with 2 cm\(^{-1}\) resolution. Evaluation of the spectra was done using Fityk software.

Thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC). Thermogravimetric analysis (TGA) and DSC analysis 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 good contact between the crucible and the powder sample. All measurements were performed under 20 mL min\(^{-1}\) of 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 5 °C min\(^{-1}\). To obtain the glass transition temperature (\(T_g\)), \(\alpha_2(\text{IL@ZIF-8-HT})\) in powder form was placed in a platinum crucible and heated to 400 °C with a 5 °C min\(^{-1}\) ramp rate. \(T_\alpha\), \(T_b\), and \(T_p\) are determined as the intersection of the starting baseline and the tangent to the DSC curve at the maximum gradient point.

Cyclic \(C_p\) scan. A Netzsch STA 449 F1 instrument was used to perform cyclic \(C_p\) scans. In these, the sample was heated up to 360 °C, then cooled to 200 °C, and heated again to 360 °C. All experiments used the identical heating rate of 20 °C min\(^{-1}\). The cooling rate between the first and the second upscan was varied from 10 °C min\(^{-1}\) to 15 °C min\(^{-1}\) and 20 °C min\(^{-1}\). For each cycle, a baseline and a sapphire reference scan were recorded prior to the sample scan using the same temperature program. A platinum crucible was placed for the inside the sample crucible was placed on the sample. To enhance the concentration of washed species in the filtrates, in particular, ones which are derived from MOF architectures with large pore sizes.

Ambient temperature X-ray pair distribution function (XPDF). Synchrotron X-ray total scattering data were measured at the Diamond Light Source, UK (E20038). Samples were hand-ground and loaded into borosilicate capillaries with a 1.17 mm inner diameter. The ZIF-8 and crystalline IL@ZIF-8 samples required the use of a beam filter due to detector saturation, giving a transmission factor of 0.519; all other samples were used without this beam filter. Data were collected for an empty capillary (used as a background) and for all samples to a Q value of 2.5 Å\(^{-1}\) (\(\lambda = 0.161669 \text{ Å}, 76.69 \text{ keV}\)) with a collection time of 10 min per sample. Data normalization, background subtraction, and subsequent Fourier transform was performed using the GudrunX program to obtain the PDFs for each sample. The atomic compositions used for this analysis were calculated from TG–MS data for the \(\alpha_2(\text{IL@ZIF-8-HT})\) and \(\alpha_2(\text{IL@ZIF-8-HT})\) samples.

Amorphization of ZIF-8 via ball-milling. About 50 mg of ZIF-8 was loaded into a 10 mL stainless steel jar with 2 mm \(\times\) 7 mm stainless steel ball bearings. The jar was then placed into a Retsch MM400 grinder mill operating at 30 Hz for 30 min. The successful amorphization was confirmed by powder XRD.

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Gas sorption and Brunauer-Emmet-Teller (BET) analysis. An Autosorb iQ instrument (Quantachrome) was used for BET surface area and pore volume analysis of ZIF-8, IL@ZIF-8, aIL(II)@ZIF-8-LT, and aIL(II)@ZIF-8-HT samples. To quantify the BET surface area, N2 adsorption was monitored at 77 K. Around 20 mg of sample material were used for each measurement. Samples were outgassed for 20 h at 10−8 mbar, 125 °C prior to measurement. For the relatively low surface areas for aIL(II)@ZIF-8-LT and aIL(II)@ZIF-8-HT samples, N2 and CO2 adsorption experiments at 77 and 273 K, respectively, were repeated using adjusted parameters (equilibrium times of 100 s, pressure tolerance of 2% with respect to P0, and degassing temperature of 150 °C).

Nanoindentation tests. Instrumented indentation experiments were carried out at room temperature using a nanoindenter (G200, KLA Co.) equipped with a Berkovich diamond tip (Synton-MDP Inc.). Samples were mounted in a thermosetting polymer (Araldite CY212, Arag Scientific Ltd.). The tip area function and the instrument’s frame compliance were calibrated prior to the first experiments on a fused silica reference glass (Corning Code 7980, Corning Inc.), following the method of Oliver and Pharr.69 Depth profiles of hardness H and modulus E were obtained from indentations conducted in the continuous stiffness method70. In total, 25 indents with a depth limit of 2000 nm were performed per sample at a strain rate of 0.05 s−1. Values of H were calculated from the load divided by the projected contact area of the indenter tip and values of E were derived from the reduced modulus71.

Data availability. The data that support the findings of this study are shown in the manuscript or supporting information, or available from the corresponding author on any request.

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L.W., V.N., and T.D.B. conceived of this study. Sample synthesis, preparation, thermal
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C.C., and L.W. V.N. and C.C. wrote the first draft of the manuscript with the help of
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Competing interests
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