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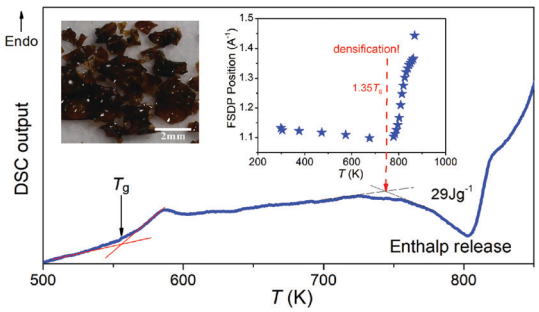

Structural evolution in a melt-quenched zeolitic imidazolate framework glass during heat-treatment Q2

Jiayan Zhang, Louis Longley, Hao Liu, Christopher W. Ashling, Philip A. Chater, Kevin A. Beyer, Karena W. Chapman, Haizheng Tao, David A. Keen, Thomas D. Bennett* and Yuanzheng Yue*

A pronounced enthalpy release occurs around 1.38T_g in the prototypical metal–organic framework glass formed from ZIF-4 [Zn($C_3H_3N_2$)$_2$], but there is no sign for any crystallization (*i.e.*, long-range ordering) taking place. Q4

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A pronounced enthalpy release occurs around 1.38T_g in the prototypical metal–organic framework glass formed from ZIF-4 [$Zn(C_3H_3N_2)_2$], but there is no sign for any crystallization (*i.e.*, long-range ordering) taking place. The enthalpy release peak is attributed to pore collapse and structural densification.

Metal–organic frameworks (MOFs) consist of metal clusters or ions linked by organic ligands into large open-networks with various pore architectures.[1,2] Amongst these, the zeolitic imidazolate frameworks (ZIFs) are of interest due to their excellent chemical stabilities.[3] The M–Im–M (M – transition metal, Im – imidazolate, $C_3H_3N_2^-$) angle in ZIFs is analogous to the Si–O–Si bond angle in zeolites, and so many ZIFs adopt zeolitic tetrahedral network topologies.[4,5] Thermal[6] and pressure-induced[7] amorphization of the crystalline state is observed, with one structure, ZIF-4, melting to form a 'liquid-MOF' at *ca.* 860 K.[8] Quenching this liquid yields a glass with a continuous random network of corner-sharing $Zn(Im)_4$ tetrahedra.[9] Given the structural similarities to conventional SiO_2 glass, this presents opportunities to study MOF-glasses in the context of existing inorganic glass materials.[10–12]

In particular, the dynamic properties of the glasses upon heating should be investigated, given the rich behavior of the structural evolution upon heating of other supercooled liquid families.[13–15] Motivated by an initial study on the glass formed by melt-quenching ZIF-62 $[Zn(Im)_{1.75}(bIm)_{0.25}]$ (bIm – benzimidazolate $C_7H_5N_2^-$), which demonstrates ultrahigh stability against crystallization,[16] here we investigate the effect of heat-treatment upon a melt-quenched zeolitic imidazolate framework glass, formed from ZIF-4 $[Zn(Im)_2]$. Consistent with prior literature, the ZIF-liquid quenched back to room temperature at a rate of 10 K min^{-1} is referred to as a_gZIF-4.[17]

Differential scanning calorimetry (DSC) experiments were performed on a crystalline sample of ZIF-4, and show desolvation, amorphization, recrystallization (to the dense ZIF-zni phase, also of composition $Zn(Im)_2$), and subsequent melting events. These are labelled features A–D respectively, in the black dashed curve in Fig. 1, and are consistent with previous results.[9] In a second experiment, a sample of ZIF-4 was heated to 853 K, *i.e.*, above the melting temperature, T_m, and quenched back to room temperature at a rate of 20 K min^{-1}, which is twice as fast as the quench rate used for previous ZIF-4 glass samples. The resultant material is termed fq-a_gZIF-4 (fq – fast

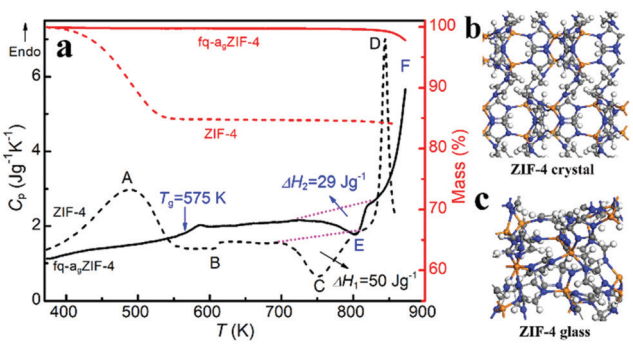

Fig. 1 (a) C_p measurements (black) and thermogravimetric analysis (red) of as-synthesized crystalline ZIF-4 (dashed line) and a_gZIF-4 (solid line), at a heating rate of 10 K min^{-1}. A: desolvation; B: amorphization; C: recrystallisation to ZIF-zni; D: melting; F: decomposition. T_g: glass transition temperature; ΔH_1: enthalpy released during crystallization of ZIF-zni; ΔH_2: enthalpy released during the exothermal peak E. (b) Unit cell of ZIF-4 crystal and (c) atomic configuration of the melt-quenched a_gZIF-4 from ref. 10. Zn – orange, N – blue, C – grey, H – white.

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quenched) for clarity. Reheating fq-a$_g$ZIF-4 (under argon) in the DSC, revealed a glass transition in the region of 565–595 K with the glass transition temperature (T_g) of 575 K (black solid curve in Fig. 1). Curiously, after the glass transition, a broad exothermic peak (marked as E) occurs at *ca.* 725–820 K. The enthalpy released during this process is 29 J g^{-1}, lower than that of the formation of the crystal ZIF-zni (50 J g^{-1}). Decomposition of the liquid of ZIF-4 glass is then evident at *ca.* 840 K (point F), which is 30 K lower than the decomposition temperature of the liquid of ZIF-zni, without quenching back to room temperature.[9]

In poor inorganic glass formers, crystallization above the glass transition is common, which causes a narrow and sharp exothermic peak, due to energy release during fast nucleation and crystal growth.[18,19] To determine whether this occurs here, isothermal heat-treatments were performed on fq-a$_g$ZIF-4, at varying treatment temperatures (T_h), for times (t_h) of 5 and 30 minutes, in the region of the exothermic peak E. PXRD measurements of the resultant material show no sharp Bragg peaks, implying that long-range ordering (LRO) does not occur, *i.e.*, the samples did not recrystallize (Fig. 2a). This behavior is in contrast with many other glass systems where an exothermic response occurred during heat-treatment is representing LRO.

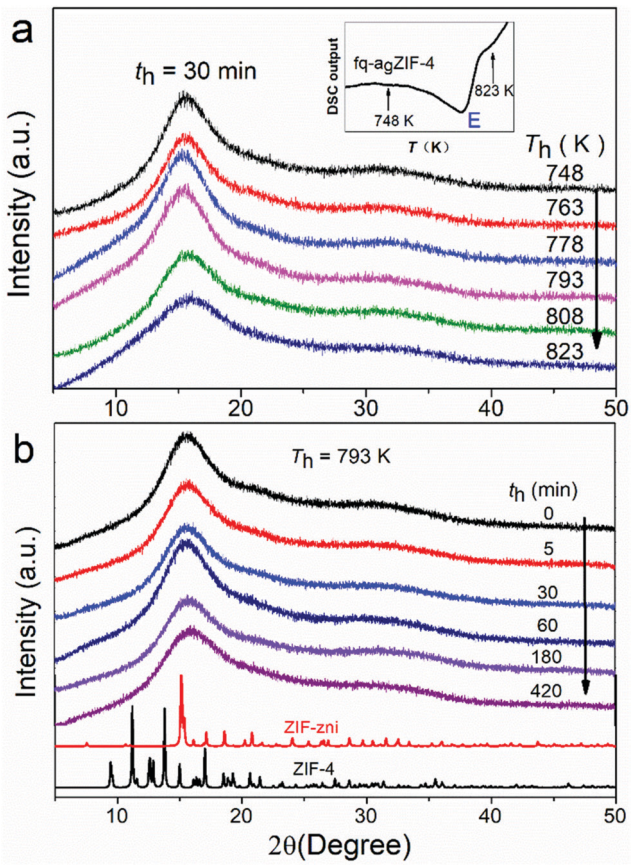

Fig. 2 (a) Powder X-ray diffraction (PXRD) patterns of fq-a$_g$ZIF-4, heat-treated at different temperatures for 30 min. Inset: DSC curve of fq-a$_g$ZIF-4, showing the range of T_h. (b) PXRD patterns of ZIF-4, ZIF-zni, and fq-a$_g$ZIF-4 heat-treated at T_h = 793 K for various durations from 0 to 420 min. t_h: heat-treatment duration; T_h: heat-treatment temperature.

Even prolonged heating of fq-a$_g$ZIF-4 at T_h = 793 K for 420 min, did not result in sharp Bragg diffraction (Fig. 2b). This temperature was chosen due to its location at the top of exothermic peak E (Fig. 2a inset). The absence of Bragg diffraction confirms that peak E is not associated with a crystallization process, *i.e.*, LRO, but instead must be attributed to a lowering of enthalpy of the system, and hence, causes the exothermic response, *i.e.*, the release of 29 J g^{-1} energy.

Samples of fq-a$_g$ZIF-4 were also heat-treated for 5 minutes at temperatures ranging from 748 K to 823 K, before cooling to room temperature (Fig. S1, ESI†). DSC experiments show T_g to be largely unaffected, *i.e.*, both long-range disorder and the glass network connectivity remain unchanged. Heat-treatment at 823 K however resulted in disappearance of the glass transition peak (Fig. S2, ESI†). A sample of fq-a$_g$ZIF-4 was heat-treated at 793 K for 420 min, and the product is hereby referred to as ht-fq-a$_g$ZIF-4 (ht – heat-treated), for clarity. DSC experiments confirmed that the exothermic peak E is present in both fq-a$_g$ZIF-4 and ht-fq-a$_g$ZIF-4 (Fig. S3, ESI†). SEM images show little difference between the two samples, though optical photographs show a distinct darkening in colour after heat-treatment (Fig. S4, ESI†). ^{13}C liquid NMR spectroscopy measurements were carried out (Fig. S5 and S6, ESI†) and, as expected, the two ^{13}C signals for the glass remain unchanged with increasing T_h, indicating that the local chemical environments of C-1 and C-2 on the imidazolate ring are unaltered during heat-treatment. Pycnometric density measurements demonstrated an increase in density during melt-quenching and heat-treatment. Densities of ZIF-4 crystal, fq-a$_g$ZIF-4 and ht-fq-a$_g$ZIF-4 were recorded as 1.25, 1.67 and 1.76 g cm^{-3}, respectively.

Fourier transform infrared (FTIR) spectra using the KBr disc technique were obtained. The full spectra of mid-IR region for the samples of ZIF-4, fq-a$_g$ZIF-4 and ht-fq-a$_g$ZIF-4 are shown in Fig. S7, ESI.†. The peaks located at 1681–1475 cm^{-1} are characteristic of C=C, C=N and imidazolate ring stretching.[20,21] Both the decreased absorption of the peak near 1680 cm^{-1} and the increased absorption of the associated weak peak near 1600 cm^{-1} indicate possible distortion of the imidazolate rings in the ZIF-4 glass upon melt-quenching and heat-treatment. This is further confirmed by the noticeable change of the C–H bending peak near 1387 cm^{-1}. The peak at around 530 cm^{-1} is assigned to imidazolate ring out-of-plane bending.[21,22]

To probe any structural differences induced by heat-treatment, room temperature X-ray total scattering measurements were performed on fq-a$_g$ZIF-4 and ht-fq-a$_g$ZIF-4, and compared to previous data on a sample of ZIF-4 glass formed by natural cooling from 853 K, referred to as a$_g$ZIF-4 (Fig. 3).[8] The absence of Bragg diffraction in the structure factor $S(Q)$ of all samples confirms their amorphous nature and long-range disorder (Fig. 3a), while those for a$_g$ZIF-4 and fq-a$_g$ZIF-4 are near identical. The first sharp diffraction peak (FSDP) for ht-fq-a$_g$ZIF-4 appears to shift slightly to higher Q, which is in accordance with the higher density of this heat-treated sample. Pair distribution functions (PDFs) data were produced by a Fourier transform of these data. The short-range order (SRO) of the samples, *i.e.* correlations below 6 Å indicating local intra-imidazolate bonds and four local Zn–Im coordinating

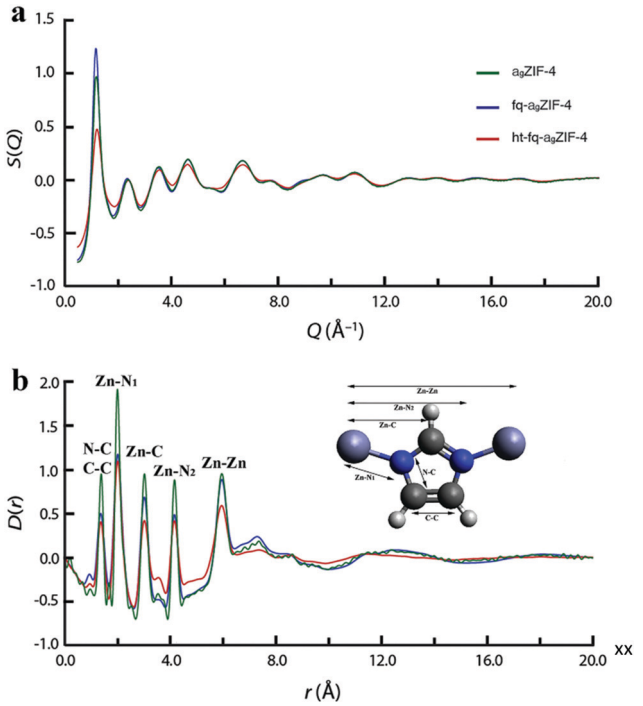

Fig. 3 (a) X-ray total scattering data $S(Q)$ and (b) corresponding X-ray pair distribution functions $D(r)$.

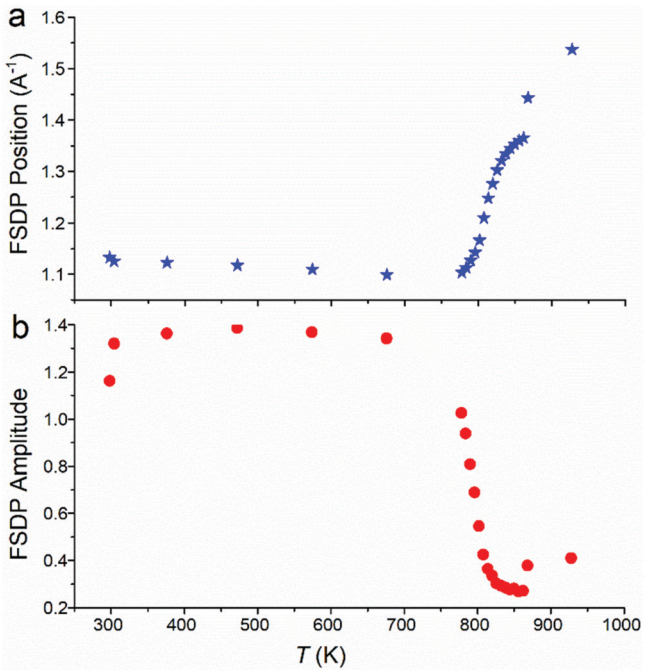

Fig. 4 Variable temperature synchrotron X-ray total scattering data $S(Q)$ showing changes in the (a) position and (b) amplitude of the first sharp diffraction peak (FSDP) with temperature. The two highest temperature points were collected during sample decomposition and above 900 K the pattern mostly consisted of that of the silica capillary.

bonds forming a tetrahedron are consistent with those witnessed for glass ZIFs previously.[23] Positions of the peaks belonging to the C–C/C–N, Zn–N, Zn–C, Zn–N and Zn–Zn distances at *ca.* 1.33, 2, 3, 4 and 6 Å are largely unchanged between samples. Specifically, correlations between 6 Å and 8 Å for ht-fq-a$_g$ZIF-4 are less distinct upon heat-treatment above T_g. The feature at 7.5 Å, which has previously been ascribed to a M–L–M–L interaction (*i.e.* between Zn and a nitrogen atom of the 2nd nearest imidazolate in this sample),[24] is less pronounced. The weaker degree of atomic pair correlations in this region is perhaps associated with structural relaxation (and the associated densification) upon heat-treatment.

To provide a firm structural origin for the exothermic peak E in the DSC scans, high temperature X-ray total scattering measurements, collected on a sample of a$_g$ZIF-4 at the APS synchrotron and published previously, were reanalysed.[8] These data were collected on heating a$_g$ZIF-4 at the Advanced Photon Source, US. Temperature intervals were roughly 100 K, from 298 to 778 K (Fig. S8 left, ESI†), and showed little change in the FSDP. However, those obtained in 6 K steps from 778 K to 862 K (Fig. S8 right, ESI†) demonstrated marked changes. A Pseudo-Voigt peak fit was applied to model the position, intensity and width of the FSDP as a function of temperature (Fig. 4). A sharp change at approximately 770 K (*i.e.* close to the onset of the exothermic peak E in Fig. 1a) was seen in all parameters reflecting structural changes in the glass at this temperature (Fig. 4 and Fig S9, ESI†). The increase in position and decrease in intensity qualitatively indicate a densification of the structure.

Hence, holding the as-quenched ZIF-4 glass at 793 K (1.38 T_g) for 420 min can lead to structural densification, towards a lower energy state (*i.e.*, 29 J g^{-1} lower). The energy released by this process is 3/5 of the energy released by LRO, *i.e.*, crystallization (Peak C in Fig. 1a). This type of relaxation has not been observed in inorganic network glasses. The degree of relaxation is driven by two structural factors of the ZIF-4 glass. First, the size of Zn[Im]$_4$ tetrahedron is much larger than that of SiO_4 tetrahedron since the Zn–Zn distance (5.9 Å) is much longer than the Si–Si distance (3.1 Å). Second, the coordinating bond between Zn and Im is significantly weaker than the Si–O bonds in oxide glasses. These two factors make the Zn(Im)$_4$ tetrahedron more 'floppy', and hence more distorted after melt-quenching, and therefore pose a higher thermodynamic driving force for relaxation.

Piecing the results together yields a complex picture of structural evolution in a$_g$ZIF-4. The absence of crystallization in the glass, even after heat-treatment at high T_h for a long duration, is encouraging for the development of future applications.

YY designed the project. JZ, TDB and YY wrote the manuscript with inputs from other co-authors. All samples were prepared by JZ. DSC, XRD, SEM, L-NMR and FT-IR experiments were performed by JZ and HL, analysed by JZ, YY, HT and HL. Ambient temperature PDF data was collected by LL, CWA, TDB, DAK and PAC. Analysis was performed by LL and DAK. Variable temperature PDF data was collected by TDB, DAK, KAB and KWC, and analysed by LL and DAK.

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Conflicts of interest

There are no conflicts to declare.

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