Metal-Organic Framework and Inorganic Glass Composites

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Metal-organic framework (MOF) glasses have become a subject of study due to their novelty as an entirely new category of melt quenched glass and their potential applications in areas such as ion transport and sensing. In this paper we show how MOF glasses can be combined with inorganic glasses, in order to fabricate a new family of optically transparent materials, composed of both MOF and inorganic glass domains. Here, we present the design rules for this family of materials, use an array of experimental techniques to propose the bonding between inorganic and MOF domains, and show that the composites produced are more mechanically pliant than the inorganic glass itself.
Introduction

Metal-organic frameworks (MOFs) are a class of porous three-dimensional framework materials produced from the self-assembly of inorganic nodes and organic linkers. High throughput synthesis techniques have resulted in over 80,000 reported crystalline MOF structures, in a broad variety of network architectures. Accessible pore volumes may exceed 5.02 cm$^3$g$^{-1}$, and thus compare favourably with both activated carbons and inorganic zeolites. These high internal volumes have led to proposed applications for crystalline MOFs in e.g. gas storage and separation, catalysis, water harvesting, and low-$\kappa$ dielectric applications.

Research into MOFs has traditionally focused on the crystalline domain. There has however been a growing impetus towards the synthesis and characterization of non-crystalline structures. In particular the zeolitic imidazolate frameworks (ZIFs) are a sub-family of MOFs of composition $M$(Im)$_2$, where $M$ is a tetrahedrally coordinated divalent metal cation, typically Zn$^{2+}$ or Co$^{2+}$, and Im is an imidazolate ($C_3H_3N_2^-$) derivative. Several structures have been shown to have an accessible liquid state, formed by heating the crystalline solids to approx. 450 $^\circ$C.

Inorganic glasses typically consist of multiple components, which help prevent crystallisation through introducing geometric frustration. These inorganic materials possess the chemical, thermal, and mechanical robustness required to be a structural component for applications involving mechanical cycling with large stresses. The high mutual solubility of inorganic glasses allows easy production of new materials with properties intermediate between two end-members, e.g. borosilicates, mixed-alkali glasses and aluminosilicates. This ability to tune physical properties is highly advantageous in industrial and technological applications, for example, in order to achieve specific mechanical performance. In similar ways, organic polymer glasses may also be ‘blended’ to produce new, homogeneous amorphous materials with intermediate and industrially relevant properties. We have previously applied similar methodologies to MOFs, showing that glass forming ZIF systems can be mixed in the liquid state to produce a structure with sub-micrometre scale domains, where the glass transition temperature is tuneable between that of the end-members.

Motivated by the relative advantages of MOFs, and inorganic glass materials families, here we detail the fabrication and characterization of an unconventional class of composite materials, containing domains of both inorganic- and MOF- glasses. Specifically, we exploit liquid phase mixing between a liquid MOF and an inorganic melt, in order to create a composite material which incorporates the mechanical, thermal and chemical properties of inorganic glasses while maintaining the chemical versatility of the metal-organic framework component.

Results

Materials Selection

To maximise the available temperature region for composite synthesis ZIF-62, $[\text{Zn(Im)}_{1.75}(\text{bIm})_{0.25}]$ (Im = $C_3H_3N_2^-$ and bIm = $C_7H_5N_2^-$), (Figure 1a) was chosen as the glass-forming MOF component. This is because of the large temperature range between the melting point offset $T_m$ (approx. 437 $^\circ$C) and the onset of thermal decomposition (approx. 600 $^\circ$C). A key factor in the selection of the inorganic glass component is the possession of a glass transition temperature $T_g$ close to the $T_m$ of ZIF-62. This is to enable good mixing between the two liquid phases and therefore promote formation of strong interfacial bonding between the components. Another important consideration is the avoidance of chemical reactions leading to the decomposition of the organic linkers. We therefore selected the...
inorganic glass series, with composition \((1-x)[(Na_2O)_2(P_2O_5)]-x[(AlO_{3/2})[AlF_3]]_y\) (Table S1) in the same glass family as reported in the literature\(^{22}\), which possess \(T_g\) in the range 310 – 450 °C, and because previous literature indicated the chemical compatibility of phosphate groups and imidazole in hybrid inorganic systems\(^{23}\).

Figure 1: Structural chemistries 2D representations of a. the structure of ZIF-62, showing ZnN\(_4\) tetrahedra connected by imidazolate (Im) and benzimidazolate (blm) organic ligands and b. the local structure of the \((1-x)[(Na_2O)_2(P_2O_5)]-x[(AlO_{3/2})[AlF_3]]_y\) glass series, composed of varying lengths of phosphate tetrahedra chains and Al(OP)\(_4\)F\(_2\) octahedra with Na\(^+\) as the counter cation. Key: N – light blue, Zn – purple, C – dark grey, P – blue, O – red, Al – light grey, F – orange, Na – green, H – omitted for clarity. Inorganic structure adapted from Le et al.\(^{22}\). with permission.

Phosphate glasses are a widely explored family of inorganic glasses due to their low melting temperatures and biocompatibility\(^{24}\). The \((1-x)[(Na_2O)_2(P_2O_5)]-x[(AlO_{3/2})[AlF_3]]_y\) glass is comprised of two major domains: (i) chains of phosphate tetrahedra connected through bridging P–O–P linkages, with some terminal non-bridging oxygens (NBOs) associated with sodium (P–O–Na\(^+\)), and (ii) islands of Al(OP)\(_4\)F\(_2\) octahedra, which are strongly bonded to the phosphate chains through Al–O–P bridging bonds (Figure 1b)\(^{25}\). Three \((1-x)[(Na_2O)_2(P_2O_5)]-x[(AlO_{3/2})[AlF_3]]_y\) compositions were prepared, and analysed by energy dispersive spectroscopy (EDS) (Supplementary Figure 1). The chemical compositions of these glasses are given in (Supplementary Table 1), in accordance with this the resultant glasses are referred to as the base, Na-deficient and Al-rich compositions.

Crystalline ZIF-62 was synthesised by a method adapted from the literature\(^{26}\) (Supplementary Figure 2). Then equal weights of ZIF-62 and each inorganic glass were ball-milled together. Consistent with previous literature on MOF blends and composites\(^{27}\), the full name for these physical mixtures takes the form (ZIF-62)(\((1-x)[(Na_2O)_2(P_2O_5)]-x[(AlO_{3/2})[AlF_3]]_y\) \(50/50\). We use the shortened naming convention (ZIF-62)(Inorganic Glass) \(50/50\) here, for readability and clarity.
**Thermal Characterization**

The three (ZIF-62)(Inorganic Glass) (50/50) samples were investigated using differential scanning calorimetry (DSC). Each of the samples in this series was heated above the melting endotherm to 450 °C and the mixtures were held for either 1 or 30 minutes at this temperature. Measurements on all samples were also made during a second heating ramp to 450 °C. The two different high temperature isothermal times were used in order to measure the effect of liquid phase mixing between the inorganic and the ZIF-62 on the structure of the resulting composite.

Samples of crystalline ZIF-62 were also subjected to the same heat treatments (i.e. holding for 1 and 30 minutes at 450 °C), in order to provide a point of comparison for the thermal behaviour of the composite samples. The initial heating curves of ZIF-62 samples showed a melting event, with an offset at approx. 434 °C. The second heating curve of these samples, i.e. after they were held at 450 °C for 1 or 30 minutes and then cooled, displayed clear glass transitions at 322 °C and 314 °C (Supplementary Figure 3), respectively, which is consistent with literature data on ZIF-62 and the resultant glass (termed a$_2$ZIF-62) $^{21}$.

The (ZIF-62)(Al-rich)(50/50) sample heated for 1 minute at 450 °C displayed melting of ZIF-62 ($T_m$(ZIF)), at 435 °C. This was followed by a rise in the baseline at approx. 440 °C (Figure 2a), which was assigned to the glass transition of the inorganic glass ($T_g$(Al-rich)) by comparing with a DSC scan of the pure Al-rich glass sample (Supplementary Figure 4). The second upscan showed two glass transitions; one assigned to Al-rich at approx. 440 °C, and the other assigned to a$_2$ZIF-62 at approx. 318 °C by comparing with that of the ZIF-62 control (Supplementary Figure 3). The (ZIF-62)(Al-rich)(50/50) sample heated for 30 minutes at 450 °C showed almost identical behaviour; the first upscan showed an endotherm from ZIF-62 melting at 428 °C followed by the inorganic glass transition. As with the "1 minute" sample, the second upscan contained two glass transitions, assigned to the inorganic, again at approx. 440 °C and a$_2$ZIF-62 at approx. 319 °C (Figure 2b).

![Figure 2. Glass transitions.](image)

The ZIF-62 melting endotherm was not evident in DSC experiments on the (ZIF-62)(Base)(50/50) and (ZIF-62)(Na-deficient)(50/50) samples due to the overlap of the glass transition of the inorganic glass component with the melting point of ZIF-62. However, the second heating cycle of the (ZIF-62)(Na-deficient)(50/50) and (ZIF-62)(base)(50/50) samples did contain separate a$_2$ZIF-62 and inorganic glass transitions irrespective of the length of time spent at 450 °C (Supplementary Figure 5 and 6). Thermo-gravimetric analysis (TGA) confirmed that none of the samples had any substantial mass loss upon heating to 450 °C (Supplementary Figure 7).
Bulk samples of the composites were then prepared in consideration of these DSC results, by heating pressed pellets (see methods) of the three [(ZIF-62)(Inorganic Glass)](50/50) powders in a tube furnace heated to 410 °C for 1 minute, and, in a separate experiment, for 30 minutes. This lower temperature, which is still greater than the onset of melting for ZIF-62, was used due to the much slower cool and therefore longer time that was spent at elevated temperatures for the tube furnace samples. The samples formed upon cooling in each case are referred to as \((a_2 \text{ZIF-62})_{0.5} \text{(Inorganic Glass)}_{0.5} - 1 \text{ min}\) and \((a_2 \text{ZIF-62})_{0.5} \text{(Inorganic Glass)}_{0.5} - 30 \text{ min}\) respectively (Table 1).

**Table 1: Sample terminology.**

| Inorg. Designation | Physical Mixture | Heat Treatment 410 °C 1 minute | Heat Treatment 410 °C 30 minutes |
|--------------------|-----------------|--------------------------------|---------------------------------|
| base               | (ZIF-62)(base) (50/50) | \((a_2 \text{ZIF-62})_{0.5}(\text{base})_{0.5}\) – 1 min | \((a_2 \text{ZIF-62})_{0.5}(\text{base})_{0.5}\) – 30 min |
| Na-deficient       | (ZIF-62)(Na-deficient) (50/50) | \((a_2 \text{ZIF-62})_{0.5}(\text{Na-deficient})_{0.5}\) – 1 min | \((a_2 \text{ZIF-62})_{0.5}(\text{Na-deficient})_{0.5}\) – 30 min |
| Al-rich            | (ZIF-62)(Al-rich) (50/50) | \((a_2 \text{ZIF-62})_{0.5}(\text{Al-rich})_{0.5}\) – 1 min | \((a_2 \text{ZIF-62})_{0.5}(\text{Al-rich})_{0.5}\) – 30 min |

**Surface Characterization**

Confocal microscopy was used to characterize the surface of the samples (Figure 3, Supplementary Figure 8). Clear evidence of flow in all cases was observed, with heat treatment for longer periods of time resulting in grain growth, reduction of interfaces and greater light transmittance through the samples. Additionally features indicating the action of surface tension were found, such as rounding of grains to form ‘islands’ and spheroidal bubbles. Large droplets lying on the surface, and, particularly, smooth surfaces over large areas are visible in the top-lit microscope images (Supplementary Figure 8).

**Figure 3. Glass flow.** Side-illuminated z-scan digital microscopy images of the \((a_2 \text{ZIF-62})_{0.5}(\text{Inorganic Glass})_{0.5}\) compositions heat treated for 1 minute (a-c) and 30 minutes (d-f).
Laser scanning microscopy was used to measure the roughness profile parameters (Supplementary Figure 9), the arithmetical mean deviation of the primary profile decreases with heating time in all sample compositions, in accordance with the optical results. Given the sensitivity of nanoindentation to surface roughness, the surface profiles of (a₉ZIF-62)₀.₅(Na-deficient)₀.₅ and (a₉ZIF-62)₀.₅(Al-rich)₀.₅ (Supplementary Table 2) confirmed that they were unsuitable for the technique, however the (a₉ZIF-62)₀.₅(base)₀.₅ samples were examined using nanoindentation (Figure 4). The (a₉ZIF-62)₀.₅(base)₀.₅ results show clear heterogeneity in the sample, even on the 100 µm scale, with regions of high, and low hardness (H) and modulus (E). Stiffness values for pure samples of a₉ZIF-62 and the base inorganic glass are approx. 6.6 GPa²⁹ and 51 GPa respectively. The results show a significant decrease in heterogeneity in the samples heated for 30 minutes, in agreement with the surface profile parameters. This is accompanied by a decrease in the average E, suggesting a more compliant structure is formed upon mixing MOF and inorganic glass.

![Mechanical properties variation](image)

**Figure 4** Mechanical properties variation. Modulus (E) and hardness (H) contour maps together with wide-field confocal microscopy images of the area mapped across the surface of the (a₉ZIF-62)₀.₅(base)₀.₅ compositions heat treated for 1 minute (a–c) and 30 minutes (d–f).

**Structural Investigations**

**Spectroscopy**

¹H nuclear magnetic resonance (NMR) spectroscopy was carried out, and exhibited no appreciable changes in the organic linker ratio upon heating the (a₉ZIF-62)₀.₅(Inorganic Glass)₀.₅ samples for 1 minute. However, in the (a₉ZIF-62)₀.₅(Inorganic Glass)₀.₅ – 30 min samples the [bIm]/[bIm+Im] ratio was 0.3% higher, implying a common equilibrium state independent of the inorganic composition (Supplementary Figures 10—12, Supplementary Tables 3—9).
$^{31}$P MAS NMR spectroscopy was also carried out to investigate changes in the phosphate component of the inorganic glass. Peaks in the $[^{1}H](a_{g}$ZIF-62)$_{0.5}$(Inorganic Glass)$_{0.5} – 1$ min and – 30 min samples were found at higher chemical shifts than their respective pure inorganic glasses (with the exception of the Na-deficient – 1 min composition). Substantial new intensity in the $^{31}$P spectra appeared in the region 5 to −15 ppm, and increased proportionally with heat treatment time (Figure 5). This is consistent with literature values for the shifts of $^{31}$P in $\text{PO}_3\text{N}$ and $\text{PO}_2\text{N}_2$ species at −10 and 0 ppm, respectively$^{30}$, indicating the possibility of $\text{P—N}$ bond formation between the phosphate tetrahedra and Im ring. $^{31}$P($[^{1}H]$) cross polarization (CP) NMR measurements were performed of the same samples to further interpret this additional intensity. CP NMR experiments measure the proximity of nuclei in space; the efficiency of the transfer of magnetization is mediated by the dipolar coupling of heteronuclear spins (which has an $r^{-3}$ dependence)$^{31}$. Thus, $^{31}$P($[^{1}H]$) CP NMR experiments (Figure 5) shed light on these new peaks found in the 1d $^{31}$P spectra (highlighted by the residuals), specifically they reveal that the new intensity in the 1d $^{31}$P spectra can be assigned to phosphorus atoms with protons nearby. Despite no discernible intensity in the corresponding 1d $^{31}$P spectra, there is a peak centred at approx. 12 ppm in the CP spectra, which is in the ppm range of a phosphate tetrahedra without any bridging $\text{P—O—P}$ bonds. The efficiency of magnetization transfer from $^{1}H$ to $^{31}$P (as evidenced by increased intensity in the CP spectra) is commensurate with the proximity and number of nearby protons, thus, this new peak at approx. 12 ppm may reflect that an isolated phosphate tetrahedra is more mobile within the composite, and therefore, is found close to the protons of the imidazolate or benzimidazolate rings. All of the samples exhibit an increase in the intensity of the peaks in the $^{31}$P($[^{1}H]$) CP NMR spectra as a function of heat treatment time, including the peak located at circa 12 ppm (Supplementary Figures 13-17).

Figure 5 NMR spectroscopy. $^{31}$P SS NMR and $^{31}$P($[^{1}H]$) CP NMR of the inorganic glass (base) and the composites ($[^{1}H]a_{g}$ZIF-62)$_{0.5}$(base)$_{0.5}$ heat treated for 1 min (left) and 30 min (right).

Infra-red (IR) spectroscopy confirmed the integrity of the $a_{g}$ZIF-62 component within the composites (Supplementary Figure 18-21). There were however consistent small changes in the approx. 700 and 1450 cm$^{-1}$ peaks which have been assigned to out-of-plane bending and ring stretching, indicating some added deformation due to the presence of inorganic glass.

Raman spectra for $a_{g}$ZIF-62 – 1 min and – 30 min samples were nearly identical (Supplementary Figures 22 and 23), aside from a slightly larger redshift of the $\text{Zn—N}$ peak at approx. 175 cm$^{-1}$ in the 30 min sample. Raman spectra for the $[^{1}H](a_{g}$ZIF-62)$_{0.5}$(Inorganic Glass)$_{0.5}$ – 1 min and – 30 min samples contained similar features, ascribed to the $a_{g}$ZIF-62 component (Supplementary Figure 24). The most significant change was in the low frequency $\text{Zn—N}$ region (approx. 175 cm$^{-1}$) where a second, peak
emerges at approx. 145 cm \(^{-1}\) (Supplementary Figure 25). The \((a_2\text{ZIF-62})_{0.5}(\text{Inorganic Glass})_{0.5} – 30\) min samples also converge to a consistent C—N peak position (approx. 1175 cm \(^{-1}\)), red-shifted relative to the \(a_2\text{ZIF-62} – 30\) min control (Supplementary Figure 26). No discernible features arising from the inorganic glass were however able to be unambiguously determined.

Energy-dispersive X-ray Spectroscopy (EDS) was also used to investigate microstructure. The locations of the ZIF-62 glass domains were identified using the zinc signal, whereas those from the inorganic glass were determined by signals from aluminium and phosphorus. In each case the heaviest elements from each component, Zn(Im)\(_2\), NaPO\(_3\) and AlF\(_3\), were used to obtain the clearest signal. In all composite samples, distinct, segregated domains could be seen (Supplementary Figure 27-32).

**X-ray Diffraction and Microscopy**

Powder X-ray diffraction (PXRD) on \((\text{ZIF-62})(\text{Inorganic Glass})(50/50)\) samples confirmed that the crystal structure of ZIF-62 was intact prior to heat treatment (Supplementary Figure 33). The \((a_2\text{ZIF-62})_{0.5}(\text{Na-deficient})_{0.5} – 1\) min and \((a_2\text{ZIF-62})_{0.5}(\text{Al-rich})_{0.5} – 1\) min PXRD patterns appeared completely amorphous. The PXRD pattern of the \((a_2\text{ZIF-62})_{0.5}(\text{base})_{0.5} – 1\) min however contained a small number of low intensity Bragg peaks (Figure 6a). The position of these peaks, and in particular the most intense pair at approx. 15 ° 2θ, were found to match the reference pattern for ZIF-zni, a dense zinc imidazolate (Zn(Im))\(_2\) framework, reported in the literature\(^3\). The two Bragg reflections at around 15 °, which are ascribed to the \(\{400\}\) and \(\{112\}\) reflections from ZIF-zni, were also present in the PXRD patterns of the \((a_2\text{ZIF-62})_{0.5}(\text{Na-deficient})_{0.5} – 30\) min and \((a_2\text{ZIF-62})_{0.5}(\text{Al-rich})_{0.5} – 30\) min samples. In contrast to the diffraction pattern of \((a_2\text{ZIF-62})_{0.5}(\text{base})_{0.5} – 30\) min, appeared completely amorphous (Figure 6b).

![Figure 6 X-ray diffraction patterns and light microscopy. PXRD and light microscopy (inset) of a) \((a_2\text{ZIF-62})_{0.5}(\text{Inorganic Glass})_{0.5} – 1\) min and b) \((a_2\text{ZIF-62})_{0.5}(\text{Inorganic Glass})_{0.5} – 30\) min. Green check marks show positions of peaks in ZIF-zni\(^3\). White bar in each image is 1mm.](image)

**Pair Distribution Function Studies**

To further investigate the structure of the composites, total scattering experiments were conducted on the \((a_2\text{ZIF-62})_{0.5}(\text{Inorganic Glass})_{0.5} – 1\) min and \((a_2\text{ZIF-62})_{0.5}(\text{Inorganic Glass})_{0.5} – 30\) min samples, as well as the pure inorganic glasses and \(a_2\text{ZIF-62}\) controls. The total scattering structure factors, S(Q), of the \((a_2\text{ZIF-62})_{0.5}(\text{base})_{0.5} – 1\) min sample showed sharp features consistent with Bragg peaks from crystalline material. The Na-deficient glass and \((a_2\text{ZIF-62})_{0.5}(\text{Na-deficient})_{0.5}\) samples contained a single weak Bragg peak indicating a small amount of recrystallisation occurred on formation of the inorganic
glass, however outside of this the other samples appeared completely amorphous (Supplementary Figure 37-42). The corresponding pair distribution functions for the composites, obtained by Fourier transform of the total scattering data, contain peaks that, in the main, correspond to those found in the a$_2$ZIF-62 and inorganic glasses. (Supplementary Figure 43-48).

In order to identify whether the composites contained new correlations, a differential method was used (See Supplementary Methods$^{33,34}$. Briefly, the expected scattering intensity of a non-interacting mixture of a$_2$ZIF-62 and the relevant inorganic glass was calculated from the measured total scattering of each pure sample. This is then compared to the total scattering data collected on the composite samples, with the difference between them corresponding to scattering due to interaction between the a$_2$ZIF-62 and inorganic glass in the composite. The process reveals Bragg like peaks in the difference for the (a$_2$ZIF-62)$_{0.5}$(base)$_{0.5}$ – 1 min, (a$_2$ZIF-62)$_{0.5}$(Na-deficient)$_{0.5}$ – 30 min and (a$_2$ZIF-62)$_{0.5}$(Al-rich)$_{0.5}$ – 30 min samples (Figure 7a, Supplementary Figure 49-54), in line with those seen in the laboratory diffraction data. Interestingly this method also reveals weak remnant Bragg peaks in the (a$_2$ZIF-62)$_{0.5}$(base)$_{0.5}$ – 30 min sample (Figure 7b), which were not observable in the PXRD data due to the improved statistics of the synchrotron source. These features are obscured in the S(Q) due to the most intense Bragg diffraction peak coinciding with the first sharp diffraction peak (FSDP) from the a$_2$ZIF-62.

Real space data, D(r)$^{\text{Diff}}$, were obtained by Fourier transform of the structure factor, S(Q)$^{\text{Diff}}$, corresponding to these intensity differences (Supplementary Figure 55-58). The D(r)$^{\text{Diff}}$ from (a$_2$ZIF-62)$_{0.5}$(Al-rich)$_{0.5}$ – 1 min and (a$_2$ZIF-62)$_{0.5}$(Na-deficient)$_{0.5}$ – 1 min samples are featureless above 3 Å indicating relatively little interaction between the inorganic and the ZIF-62 glass had occurred. The D(r)$^{\text{Diff}}$ of the (a$_2$ZIF-62)$_{0.5}$(Inorganic Glass)$_{0.5}$ – 30 min and the (a$_2$ZIF-62)$_{0.5}$(base)$_{0.5}$ – 1 min are all qualitatively similar as expected from the similar Bragg scattering observed in the S(Q)$^{\text{Diff}}$ (Supplementary Figure 53-54). Long-range order (LRO) was also evident in the (a$_2$ZIF-62)$_{0.5}$(base)$_{0.5}$ – 1 min, (a$_2$ZIF-62)$_{0.5}$(Na-deficient)$_{0.5}$ – 30 min and (a$_2$ZIF-62)$_{0.5}$(Al-rich)$_{0.5}$ – 30 min samples. However the D(r)$^{\text{Diff}}$ of (a$_2$ZIF-62)$_{0.5}$(Base)$_{0.5}$ – 30 min sample appeared flat at extended distances, which is due to the reduction in the size of the Bragg features in the S(Q)$^{\text{Diff}}$.  

![Figure 7](image-url)

*Figure 7 Experimental and calculated total scattering.* Experimentally measured (orange), calculated X-ray total scattering (blue) and difference (green) for a) (a$_2$ZIF-62)$_{0.5}$(base)$_{0.5}$ – 1 min and b) (a$_2$ZIF-62)$_{0.5}$(base)$_{0.5}$ – 30 min.
The $D(r)^{\text{diff}}$ of all the samples contain features due to the inorganic glass and ZIF-62 because of the difficulty of putting X-ray total scattering data on an absolute scale (See Supplementary Methods). In spite of this, a tentative attempt is made to assign the new correlations observed in the $D(r)^{\text{diff}}$. Raman and $^{31}$P NMR data indicated the presence of Na-N and P-N bonding in the composite samples, and so their expected bond distance ranges where measured from crystals of appropriate chemistry as between 2.4 – 3.0 Å $^{35,36}$ and 1.7 – 1.8 Å $^{37,38}$ respectively. It can be seen that there is a peak at approximately 2.6-2.7 Å consistent with Na-N in all (aN-ZIF-62)$_{0.5}$ (Inorganic Glass)$_{0.5}$ – 1 min samples. In the (aN-ZIF-62)$_{0.5}$ (Inorganic Glass)$_{0.5}$ – 30 min samples and in the (aN-ZIF-62)$_{0.5}$ (base)$_{0.5}$ – 1 min sample a peak at approximately 1.6 Å is observed, which is broadly in the range expected for a P-N correlation. However, the peak assigned as Na-N in the (aN-ZIF-62)$_{0.5}$ (Inorganic Glass)$_{0.5}$ – 30 min samples decreased in length to between 2.5-2.6 Å, which is in better agreement with an expected correlation from the pure inorganic glass (Supplementary Figure 55 and 57).

Discussion

$^1$H liquid NMR, IR, and TGA results confirm the integrity of the imidazolate and benzimidazolate linkers in all these composite materials. EDS results demonstrate no substantial overlap between separate domains of predominately zinc signal, originating from the ZIF-62, and areas with signal from both aluminium and phosphorous which originate from the inorganic glass phase. This agrees with the observation of two glass transitions in the DSC. The presence of inorganic glass and a$_n$ZIF-62 domains measured in EDS are also in good agreement with the variations in $E$ and $H$ measured by nanoindentation mapping. These results indicate a structure of separate a$_n$ZIF-62 and inorganic domains, which electron microscopy confirms are bonded into a single body.

The extent of interfacial mixing between the two phases is highly dependent upon the glass transition of the inorganic component. SEM of the (aN-ZIF-62)$_{0.5}$ (base)$_{0.5}$ ($T_g$(base) = 372 °C) samples showed a more homogeneous appearance than for those samples containing inorganic glasses with higher $T_g$. Indeed, the low degree of flow meant remnant particles were visible for (aN-ZIF-62)$_{0.5}$ (Na-deficient)$_{0.5}$ – 1 min ($T_g$(Na-deficient) = 414 °C) and (aN-ZIF-62)$_{0.5}$ (Al-rich)$_{0.5}$ – 1 min ($T_g$(Al-rich) = 449 °C). These results are intuitive, since the low temperature end of the glass transition can be described empirically as when a fluid has a viscosity of a solid (roughly $10^{15}$ Pa-s)$^{19}$, lower-$T_g$ inorganic glasses will have a lower viscosity at the same heat treatment temperature and therefore encourage a greater extent of intermixing between domains of different chemical compositions.

The X-ray diffraction experiments performed on a sample of (aN-ZIF-62)$_{0.5}$ (base)$_{0.5}$ – 1 min indicate recrystallization to ZIF-zni; small faceted crystals of which were also visible by SEM (Figure 8)$^{12}$. However, continued heating resulted in disappearance of these peaks, the (aN-ZIF-62)$_{0.5}$ (base)$_{0.5}$ – 30 min sample was completely amorphous. ZIF-zni is a dense, mono-linker imidazolate ZIF [Zn(Im)$_2$] that is reported in the literature as forming when ZIF-4 is heated to approx. 370 °C before melting at approx. 590 °C$^{21,40}$. ZIF-62 has not previously been reported to recrystallise on heating, with the absence of recrystallisation being explained by the bulkier benzimidazolate linker imposing added steric constraints on the ZnN$_4$ coordination polyhedra$^{21}$. Apart from the presence of the bulkier benzimidazole ligand in ZIF-62, ZIF-4 and ZIF-62 have closely interrelated structures: both crystallise in the $Pbca$ space group with the cag topology$^{41,42}$. Previous work has also shown that benzimidazole and zinc metaphosphate glass are miscible and react to form a clear solid material after heating at 160 °C for 24 hours$^{43}$. 

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**Figure 8 Recrystallisation of ZIF-zi.** SEM Images of (a) ZIF-62 (80NaPO₃-20AlF₃)₀.₅ - 1 min at a) 200 times magnification and b) 500 times magnification. c) XRD pattern of (a) ZIF-62 (base)₀.₅ - 1 min in the tube furnace under Argon (red) and ZIF-zni reference pattern (blue). Inset XRD pattern of i) (a) ZIF-62 (base)₀.₅ - 1 min (red) ii) (a) ZIF-62 (Na-deficient)₀.₅ - 30 min (purple) iii) (a) ZIF-62 (Al-rich)₀.₅ - 30 min (cyan).

Therefore, supported by experimental results and consistent with the literature, the following is proposed to explain the observed formation of ZIF-zni:

1. Intimate mixing occurs between the inorganic glass and ZIF-62 upon heating and isothermal heat treatment above $T_m$(ZIF-62) and $T_g$(inorg).
2. This causes the depletion of benzimidazolate ligands in the ZIF-glass, leaving behind a defect-rich Zn(Im)$_2$ framework at the interface between the inorganic and ZIF liquids.
3. This imidazolate-rich region at the interface resembles a ZIF-4 structure, and thus undergoes recrystallisation to ZIF-zni.
4. The liquid ZIF promotes melting of the newly formed ZIF-zni phase; and so ZIF-zni melts on further heating.

In an apparent contrast, both (a) ZIF-62)₀.₅(Na-deficient)₀.₅ - 1 min and (a) ZIF-62)₀.₅(Al-rich)₀.₅ - 1 min samples were completely amorphous, though some recrystallization to the dense ZIF-zni (Zn(Im)$_2$) phase was observed in the corresponding samples heated for 30 minutes (Figure 8c inset). However, the inorganic glass in both these samples is expected to be more viscous due to higher glass transition temperatures. The delayed onset of ZIF-zni formation is therefore explained by the sluggish liquid mixing of the inorganic and ZIF components, which is necessary for reaction to occur.

The emergence of a large new peak at approx. 145 cm$^{-1}$ in the Raman spectra of the (a) ZIF-62)₀.₅(80NaPO₃-20AlF₃)₀.₅ - 1 min and all the (a) ZIF-62)₀.₅(Inorganic Glass)₀.₅ - 30 min samples, provides useful information on the reaction process. We link the reaction to the formation of new Na—N bonds, given similar peaks in sodium imidazolate-containing compounds at 161 and 136 cm$^{-1}$, and an as-purchased pure compound sodium imidazolide derivative (strong peak at 150 cm$^{-1}$) (Supplementary Figure 59).
$^{31}$P MAS NMR spectroscopy recorded for the $(a_2\text{ZIF-62})_{0.5}(\text{Inorganic~Glass})_{0.5}$ – 1 min and – 30 min samples have a noticeable peak shift to higher ppm when compared with their respective inorganic glasses (with the exception of $(a_2\text{ZIF-62})_{0.5}(\text{Na-deficient})_{0.5}$ - 1 min, which had an initial increase in the lower ppm region, approx. -26 ppm). In the literature, such shifts of $^{31}$P NMR peaks to higher ppm have generally been attributed to formation of terminal oxygens, causing a decrease in the average charge density on the phosphorus atoms\(^{16}\). However here the chemistry of the system and preparation method means that we do not expect the creation of new terminal oxygen bonds at high ppm. An alternative explanation is the formation of P—N bonds; we would expect P—N bonds to markedly shift the average $^{31}$P peak positions to higher chemical shift. Furthermore, in a $^{31}$P study of phosphorus oxynitride glasses, it was found that PO$_3$N and PO$_2$N$_2$ peaks appear at –10 and 0 ppm, respectively\(^{10}\). Secondly, the $^{31}$P{$^1$H} CP spectra detect protons in the proximity of these phosphorus atoms located in the high ppm region. Consequently, the formation of additional peaks at high ppm in the $^{31}$P NMR spectra and good agreement with the $^{31}$P{$^1$H} CP spectra points toward a significant interaction between the Im and bIm linkers and phosphorus in the inorganic glass via P—N bond formation.

We therefore tentatively propose the schematic (Figure 9) as one possible structure for the interface between the inorganic and ZIF glasses, in the composites formed here. The melting process of pure-phase ZIFs has previously been shown to involve Zn—N bond breakage at a critical temperature, which leaves both under coordinated Zn, and relatively electron-rich N sites\(^{14}\). Sodium is known to be relatively mobile in inorganic glasses, especially at temperatures near $T_g$, and would be expected to migrate to atoms with extra electron bond density. The Raman data here indicate that N—Na coordination happens very early, with the NMR data being consistent with the establishment of an equilibrium state involving P—N bond formation and/or creation of terminal oxygen. We note that the Na Kα edge (1.040 keV) and Zn Lα edges (1.012 keV) are too close in energy to observe simultaneously using EDS\(^{47}\), so we are unable validate the Raman data with elemental mapping.

Figure 9 Proposed Interface Structure. Schematic of the interface between inorganic glass and MOF glass domains, based on Raman, PDF and NMR spectroscopy.
These results describe a new class of inorganic–MOF glass composites, prepared by heating a mixture of a phosphate glass and ZIF-62. The composites formed upon cooling contain two distinct glass transition temperatures, implying an interlocked network structure of pure phase domains is formed. The extent of mixing is dominated by the inorganic glass transition temperature, which is itself linked to the chemistry of the glass. For those compositions involving inorganic glasses with the lowest glass transitions, mixing is so great that it enables a reaction of the inorganic and MOF components to occur. This results in a small degree of recrystallisation of ZIF-62 to form a dense ZIF-zni phase. This itself melts upon prolonged heating times and contact with the molten ZIF, leaving, coherent monolithic species containing both inorganic and MOF components.

The formation of materials containing interlocked inorganic glass and MOF glass will prove of great interest as prototypical examples of a new materials family, with mechanical properties intermediate between the two parent structures. Critically the emergence of this new class of composites implies the ability to alter the physical and chemical properties of the vast array of inorganic glasses currently used in e.g. display technologies and protective coatings.

**Methods**

**Synthesis**

**ZIF-62.** Crystalline ZIF-62 was synthesised according to the following method: Zinc nitrate hexahydrate (1.65 g, 5.55 mmol), imidazole (8.91 g, 131 mmol) and benzimidazole (1.55 g, 13.12 mmol) were added to N,N-dimethylformamide (DMF) (75 ml). The mixture was then heated at 130 °C and stirred for 48 hours. The resultant product was washed with DMF (2 x 20ml) under vacuum to obtain a white crystalline powder (yield 42.6%). Before direct experiments on the ball-milled powder mixtures could be conducted, the powders were activated by soaking in dichloromethane (DCM) for 24 hours, followed by heating to 175 °C for 3 hours under vacuum. This was done to remove framework templating DMF from within the pores of the ZIF-62.

**Inorganic Glass Samples.** High purity reagents (optical grade) of NaPO₃ and AlF₃ were melted in a Pt crucible in an electric muffle furnace. Due to the known volatility of fluoride, care was taken to initially melt all mixtures at 800 °C for one hour to allow NaPO₃ to melt and dissolve the AlF₃ before higher temperatures were used for complete dissolution. Generally, longer melting times were preferred over higher melting temperatures when producing a homogeneous melt.

The base glass sample was melted at 800 °C for one hour before being taken up to 850 °C for half an hour before pouring. Higher amounts of AlF₃ required higher melting temperatures, with the Al-rich and Na-deficient glasses requiring 950 and 1000 °C to be completely homogeneous, respectively. Since the glasses were then to be pulverized and remelted, no attempts at annealing were conducted on the powders used for synthesis of the composites. Instead they were pulverized in a Retsch PM 100 grinder at 350 rpm with 1 min intervals for half an hour using ZrO₂ or Si₃N₄ balls (with roughly equal sample and ball volume). A bulk piece was saved from each composition to later be annealed for control measurements, such as elemental analysis and mechanical measurements. The annealing temperatures were 40—60 °C above the T_g of the inorganic phase; the glass specimens were then cut and polished to one micron.
To make 80 g of the base inorganic glass, 66.3 g of dry NaPO$_3$ powder and 13.7 g of AlF$_3$ powder were mixed thoroughly by hand before melting. The Na-deficient composition was made from 59.1 g of dry NaPO$_3$ powder and 20.9 g AlF$_3$, while the Al-rich used 51.6 g and 28.4 g, respectively.

**Composite Samples** \(\left[a_3\text{ZIF-62}\right]_{0.5}\left[\text{Inorganic}\right]_{0.5}\). Approximately 300 mg of crystalline ZIF-62 and 300 mg of inorganic glass powders were mixed together through ball-milling in a stainless steel jar (15 ml) for 5 minutes at 25 Hz with one 5 mm stainless steel ball bearing in a Retsch MM400 grinder mill. 200 mg samples of the ball milled powder mixture were placed in a 13 mm die and compacted into a pellet using 10 tonnes of pressure applied for one minute. These pellets were placed in a tube furnace (Carbolite 12/65/550) which was left to equilibrate under argon for one hour before heating to 410 °C at 10 °C/min and holding for either 1 or 30 minutes. All heating was done under constant argon flow. The heat treated pellets were left to cool under argon at the natural rate of the tube furnace; the samples were removed from the tube furnace at temperatures equal to or below 200°C.

### Thermal Characterisation

**Differential scanning calorimetry (DSC).** DSC characterisation was conducted using a Netzsch 214 Polyma. Approx. 10 mg of sample was placed in aluminium crucibles with a pierced concave lid. Heating and cooling steps were conducted under argon at a rate of 10 °C/min. Features in the DSC traces were processed by smoothing and analysed using the Netzsch analysis software, with glass transition temperatures \(T_g\) calculated using the midpoint.

**Thermo-gravimetric analysis (TGA).** TGA curves were recorded using a TA instruments Q-600 series differential scanning calorimeter. Approximately 10 mg powdered sample was placed in open alumina crucibles and heated at 10 °C/min under argon. The TGA data was analysed using the TA Universal Analysis software.

### Surface Characterisation

**Reflected light microscopy.** A Leica MZ95 microscope equipped with a Moticam camera with a resolution of 2 Mpixels was used to take reflected light microscopy images of the composite materials.

**Digital optical microscopy.** A Keyence VHX-6000 digital microscope equipped with VHCH2MK software and VHX-500 3D Viewer 1.02 was used to optically image the samples. The camera is a CCD detector with a resolution of 54 Mpixels. Images were generated by focal scanning along the z-axis and image stacking. Photos with different lighting (top-lit vs. side-lit) and magnifications (300X, 600X and 1000X) were taken.

**Confocal Laser scanning microscopy.** The roughness of the samples was measured using a Carl Zeiss Imager-Z1m LSM 700 confocal scanning microscope (CLSM) with an Ar$^+$ laser (488 nm) and an 11 μm pinhole. CLSM increments the sample stage in the z-direction and stitches together the series of ‘imaged’ layers, where surface height differences create bright (focused) and dark (unfocused) regions. An 20X/0.50 HD objective was used to scan a square area of 320 μm$^2$, whereas the z-axis range depended on the roughness of the surface. Roughness parameters were determined using the ZEN-black 2012 software. The error of the instrument is determined by the wavelength of the laser and pinhole size, which is expected to be on the order of 50 nm. Due to surface inconsistencies in our samples, i.e., large isolated, random divets, we chose a representative line profile and determined the 2d roughness for this line rather than a global 3d surface roughness.

**Nanoindentation.** Modulus \(E\) and hardness \(H\) mapping was performed at room temperature using a KLA Nanoindenter G200 equipped with a three-sided Berkovich diamond indenter tip. The tip area
function and instruments frame compliance were calibrated prior to the first experiments on a fused silica reference glass specimen following the Oliver and Pharr method. Indentations with a depth limit of 500 nm were performed at a strain rate of 0.05 s⁻¹. In total, 121 indents were created across an area of 100 x 100 µm² with a spacing of 10 µm between individual indentation marks. The values of $H$ were calculated from the load divided by the project contact area of the indenter tip at the maximum load and the values of $E$ were derived from the reduced modulus $E_s = (1 - v_s^2)[1/E_r - (1 - v_i^2)/E_i]^{-1}$, where $E$ and $v$ are the Young’s modulus and Poisson’s ratio, respectively, of the indenter tip (subscript ‘i’) and the material tested (subscript ‘s’). Since the exact values of $v_s$ of the individual phases present in the composite materials are unknown, we defined the modulus as $E_s = E/(1 - v_s^2)$. Optical micrographs of the indented surface area were recorded using a Zeiss Smartproof 5 wide-field confocal microscope.

**Nuclear Magnetic Resonance (NMR) Spectroscopy**

**$^1$H NMR.** Approximately 6 mg of powder was digested in a mixture of DCl (20%)/D₂O (0.1 ml) and DMSO-d₆ (0.6 ml) and the spectra recorded using a Bruker 500 MHz DCH Cryoprobe Spectrometer. Processing and analysis was conducted in TopSpin.

**$^{31}$P MAS NMR.** $^{31}$P MAS NMR spectra were measured on a Bruker Avance III 400 (9.4 T magnet, 162 MHz for $^{31}$P) with a 4 mm MAS probe spinning at 12.5 KHz. All spectra were referenced to a non-spinning rotor filled with 85wt% H₃PO₄. Quantitative single-pulse experiments were conducted with a 60° pulse length (2—2.5 µs) and delay times between 150—400 s. In cases when insufficient sample was available, Teflon tape was used to ensure the rotor was full before spinning.

**Total scattering measurements**

X-ray data were collected at the I15-1 beamline at the Diamond Light Source, UK ($\lambda = 0.161669$ Å, 76.7 keV). Samples were loaded into borosilicate capillaries of 1.17 mm inner diameter. Data on the samples, empty instrument and capillary were collected in the region of $\sim 0.4 < Q < 26$ Å⁻¹. Corrections for background, multiple scattering, container scattering, Compton scattering, fluorescence and absorption were performed using the GudrunX program. For further details on the differential method, please see methods in the SI.

**X-ray Powder Diffraction**

Data was collected using a B3 (BB) Bruker D8 DAVINCI diffractometer using Cu Kα ($\lambda = 1.5418$ Å) radiation and a LynxEye position sensitive detector in Bragg–Brentano parafocussing geometry. A 5-40 ° 2θ angular range was used with a step size of 0.02 ° and a step time of 0.75 s.

**Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy**

Scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS) were conducted using a FEI Nova NanoSEM. Samples were mounted on steel stubs using carbon tape and sputter coated with gold using a current of 20 mA for 2 minutes. Spectra were analysed using the Esprit software created by Bruker.

For the inorganic glasses, EDS was performed using a desktop SEM Phenom ProX instrument at 10kV. The samples were fixed with an adhesive carbon tape on an aluminium sample holder.
Infra-red Spectroscopy

FTIR spectra of the powdered samples, approx. 5 mg, were collected on a Thermo Scientific Nicolet iS10 model FTIR spectrometer with an attenuated total reflection mode. All scans had a resolution of 2 cm⁻¹. A background scan was collected between each sample; almost no changes in the background were observed during collection.

Raman Spectroscopy

The samples were embedded in epoxy and polished to 1 micron. Spectra were collected on Renishaw inVia Raman microscope at 100x magnification using an excitation wavelength of 784 nm in a 180 scattering geometry; the resolution was 2 cm⁻¹ and the wavenumber region was 100—1500 cm⁻¹. The pure inorganic glasses were collected with higher laser power (100%) and long collection times (30 s) with a total of 6 scans. Similarly, the pure glassy ZIF controls were collected at 100% laser power, but due to fluorescence only 1 s collection time (180 scans) could be used without detector saturation; in the case of the 30 min heat treatment 30 s of bleaching was also required to prevent saturation. Longer bleaching times and more scans did not result in a better S/N ratio. The composite samples were significantly more fluorescent, therefore, requiring lower laser powers (5—10%) and longer bleaching times (up to 300 s was found to increase the S/N ratio). In general, lower $T_g$(inorg) composites needed the lowest laser powers and longest bleaching times, indicating the highest fluorescence. The technique was also found to be extremely sensitive to the surface quality with rough surface absorbing strongly. The resulting spectra were processed in Renishaw software WiRe 4.0.

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.

Acknowledgements

This project received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (ERC grant UTOPES, grant agreement no. 681652). T.D.B acknowledges the Royal Society for a University Research Fellowship (UF150021), and a research grant (RSG\R1\180395). He wishes to thank the University of Canterbury Te Whare Wānanga o Waitaha, New Zealand, for a University of Cambridge Visiting Canterbury Fellowship, and the Leverhulme Trust for a Philip Leverhulme Prize (2019). AFS acknowledges the EPSRC for a PhD studentship award under the industrial CASE scheme, along with Johnson Matthey PLC (JM11106). The authors gratefully acknowledge the provision of synchrotron access to Beamline I15-1 (EE20038-2), at the Diamond Light Source, Rutherford Appleton Laboratory, UK.

Contributions

LL and CC wrote the manuscript with the help of TDB and LW. Sample preparation and synthesis was done by LL and CC. X-ray total scattering measurements were carried out by LL, JMT, AFS, MFT and DSK. Interpretation of the PDF results and development of the differential PDF measurements was carried out by DAK and LL. Nano-indentation experiments were carried out by RL. Differential scanning calorimetry and thermo-gravimetric analysis were carried out by LL. X-ray diffraction was carried out by LL. Reflected light microscopy, energy-dispersive spectroscopy and scanning electron microscopy was carried out by LL. Raman and Infra-red spectroscopy was carried out by CC. Confocal microscopy
was carried out by CC and LW. NMR experiments and interpretation of the results were carried out by CC.

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Additional Information

The authors declare no competing interests.

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