A metal-organic framework with ultrahigh glass-forming ability

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Glass-forming ability (GFA) is the ability of a liquid to avoid crystallization during cooling. Metal-organic frameworks (MOFs) are a new class of glass formers (1–3), with hitherto unknown dynamic and thermodynamic properties. We report the discovery of a new series of tetrahedral glass systems, zeolitic imidazolate framework–62 (ZIF-62) [Zn(Im)2−x(bIm)x], which have ultrahigh GFA, superior to any other known glass formers. This ultrahigh GFA is evidenced by a high viscosity η (105 Pa·s) at the melting temperature Tm, a large crystal-glass network density deficit (Δρ/ρg)network, no crystallization in supercooled region on laboratory time scales, a low fragility (m = 23), an extremely high Poisson’s ratio (ν = 0.45), and the highest Tg/Tm ratio (0.84) ever reported. Tm and Tg both increase with benzimidazolate (bIm) content but retain the same ultrahigh Tg/Tm ratio, owing to high steric hindrance and frustrated network dynamics and also to the unusually low enthalpy and entropy typical of the soft and flexible nature of MOFs. On the basis of these versatile properties, we explain the exceptional GFA of the ZIF-62 system.

INTRODUCTION

Glassy materials are formed in many ways (4), among which the most common is to quench a liquid from above the liquidus temperature (Tm) to below its glass transition temperature (Tg) at a rate sufficiently fast to avoid crystallization (5). Melt-quenched (MQ) glasses are classified by bonding: covalent, ionic, or metallic. Resistance to crystallization of the melt in the supercooled state can be regarded as a measure of glass-forming ability (GFA), which is commonly inversely associated with the liquid fragility m (corresponding to the activation energy of viscosity η at Tg) (4, 5). GFA is also measured by the ratio Tg/Tm; that is, a liquid with higher Tg/Tm has a higher GFA. Originally empirically defined as the Kauzmann “2/3 Law” (5, 6) and justified for molecular systems (7), extending this to other MQ glasses (1) reveals considerable variability in Tg/Tm. Systems with Tg/Tm > 2/3 have a high GFA because they are increasingly viscous throughout the reduced supercooled state, which inhibits crystallization. In some instances, crystallization is completely absent on laboratory time frames, notably for B2O3 glass (8), where there is a significant crystalline-glass density difference Δρ/ρg, but also for acrylic glasses such as poly(methyl methacrylate) (PMMA) (9), where crystallization is blocked by the random orientation of side and pendant groups (atacticity).

The structural rules for glass formation are well established (5) and, for oxide glasses, result in Zachariasen’s continuous random network (CRN) model of corner-sharing cation polyhedra, recently confirmed through transmission electron microscopy images (10). Subsequently, a simplified model based on a topological optimization of the non-crystalline network was introduced (11), which has been reduced to a purely mathematical condition for the formation of infinitely large, topologically disordered networks of arbitrary dimensionality (12) and explored in detail for metallic and oxide systems (13).

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Fig. 1. Structural units and calorimetry of ZIF-62. (A) Similarity between tetrahedra in silicate glasses and ZIF-62 Im/blm networks. (B) \(C_p\) and mass loss versus \(T\), heated at 10 K min\(^{-1}\), following desolvation to eventual melting at \(T_m = 708\) K. (C) \(C_p\) upscans of ZIF-62 glass quenched from above \(T_m\) showing a clear glass transition (\(T_g = 595\) K), yielding \(T_g/T_m (0.84)\). Inset: Optical image of a transparent MQ glass.

RESULTS

Figure 1B shows the isobaric heat capacity (\(C_p\)) curve obtained during the first DSC upscan, where we can observe the enthalpy response to the solvent release and the melting process (characterized by \(T_m\)). Figure 1C exhibits the \(C_p\) curves obtained during the second and third DSC upscans, where we can see the glass transition (characterized by \(T_g\)). The \(T_g/T_m\) is found to be 0.84, which is significantly higher than the empirical “2/3 rule.” The MQ ZIF-62 is transparent and fully noncrystalline after soaking for 24 hours close to \(T_m\) (Figs. 1C, inset, and 2A and fig. S1). X-ray photoelectron spectroscopy (XPS) bands for Zn, N, and C orbitals of ZIF-62 crystal and MQ glass overlap almost perfectly (fig. S2), implying no obvious electronic structural differences. The total scattering x-ray diffraction (XRD) atomic radial distribution functions \(D(r)\) for ZIF-62 and the derived MQ glass share virtually the same intratetrahedral correlations and amplitudes, chiefly from Im, confirming common geometries and rigidity (Fig. 2B). However, the interatomic correlations become weaker and broader in the MQ glass, indicative of tetrahedra and bridging angle disorder analogous to long-range order in CRN oxide glasses, which seldom persists beyond 2 nm (5). In addition, the Raman data for ZIF-62 and MQ glass reflect nearly the same frequencies and strength of intratetrahedral vibrations (Fig. 2C), endorsing the integrity of organic linkers being retained in the MQ glass, consistent with the simulation results for ZIF-4 (19). However, there are some changes from crystal to glass: (i) The Zn-N stretching mode (21) becomes non-Gaussian and increases in frequency, and (ii) the C-N mode (22, 23) decreases in frequency. Both effects indicate small adjustments in the glass tetrahedral dynamics compared to ZIF-62, consistent with network disorder and flexibility.

Regarding \(\Delta p/\rho_0\), the MQ ZIF-62 glass is slightly denser than its original crystalline state (17), as the case of zeolites (5, 14). However, there are considerable differences between the internal pore volume fraction for ZIF-62 (27%) (17) and that for the MQ glass (6%), which was revealed by positron annihilation lifetime spectroscopy (PALS) (figs. S3 and S4 and table S2) (24). This large difference indicates that the density of the network surrounding the pores in ZIF-62 is far higher than the equivalent CRN network enveloping the fewer pores in the glass, pointing to a far more diluted and disordered topology of the glass than the parent crystal (see the Supplementary Materials).

Another very important contributory factor to the ultrahigh GFA of MQ ZIF-62 glass is its unusually high viscosity \(\eta (10^{5.1}\) Pa·s) at \(T_m\) (fig. S2), which is a first insight into MOF-liquid viscosities. Interpolated from fitting the MYEGA equation (25), this is comparable to that of silica at \(T_m\) (10^{5.5}\) Pa·s) (25). The fragility index \(m\) of liquid ZIF-62 obtained from DSC is 23 (fig. S5), a small value comparable to that of silica (\(m = 20\)) (26), confirming the exceptionally strong nature of supercooled ZIF-62 and with the high \(\eta(T_m)\) and explaining, for instance, why sintering powdered samples do not achieve appreciable flow until \(T_m\) is exceeded (fig. S6).

To suppress crystallization below \(T_m\), the cooling rate must be significantly faster than the crystal growth kinetics. For strong liquids such as silica and ZIF-62, viscous flow and crystal growth are fully coupled (26). Silica has one of the lowest growth rates \(U_{\text{max}}\) close to \(T_m\) over 24 hours, leading to micrometer crystallites being readily detectable optically. The absence of detectable crystallization when ZIF-62 glass is held close to \(T_m\) for similar periods (Fig. 2A) indicates even lower \(U_{\text{max}}\), commensurate with its superior GFA. This resistance to recrystallization is consistent with the diffusing units in ZIF-62 being much larger than in oxide systems so that their migration is mutually conficted.

The effects of framework composition on the microstructure and thermodynamic properties of the ZIF-62 systems and MQ glasses were
inspected by nuclear magnetic resonance (NMR) spectroscopy. Solution NMR spectra of the dissolved samples (fig. S8 and table S3) showed that \( \text{bIm/(Im + bIm)} \) ratios for crystals and glasses were equal (Fig. 3A), demonstrating that no decomposition or volatilization occurred during melting and that Zn-N and N-Zn-N constraints and linker conformation survived melting. \(^1\)H-\(^13\)C cross-polarization magic-angle spinning (CPMAS) solid-state NMR spectra distinguish the signals that belong to the different C sites of bIm and Im in crystal-line ZIF-62 systems and reflect the structural evolution with increasing \( \text{bIm/(Im + bIm)} \) ratio (Fig. 3B and figs. S10 and S11). More demanding carbon-detected \(^1\)H spin-diffusion NMR spectroscopy confirmed that bIm and Im linkers were intimately mixed within nonstoichiometric ZIF-62 frameworks (that is, the framework with compositions deviating from that of standard ZIF-62) and indicated that, with the increasing bIm content, not only tetrahedral nodes with one bIm and three Im linkers but also tetrahedral nodes involving two bIm linkers start to appear (figs. S12 and S13). This is an indirect implication that the substitution of bIm for Im takes place in a random manner, without bIm clustering.

**DISCUSSION**

The retention of Zn nodes with mixed linkers through melting to vitrification (Fig. 2) contrasts with the breakup of stable tetrahedral arrangements when some CP systems melt (2). The additional steric hindrance of mixed linkers in nonstoichiometric ZIF-62 contributes to the extraordinarily high \( \eta(\text{Tm}) \) and keeps the similar topology of the hybrid network frozen into the glass. Both \( \text{Tm} \) and \( \text{Tg} \) rise with increasing bIm (Fig. 3C and fig. S9); however, \( \text{Tg}/\text{Tm} \) ratios remain constant (0.84), confirming the ultrahigh GFA of MQ ZIF-62 glasses (Figs. 1 and 2). The rising trends of \( \text{Tm} \) and \( \text{Tg} \) with increasing bIm indirectly confirm that the added bIm linkers uniformly and randomly substitute the Im linkers in the tetrahedral network, and hence, the Zn-linker tetrahedron becomes larger, leading to stronger steric hindrance.

The entropy and enthalpy of fusion of nonstoichiometric ZIF-62 (\( \Delta S_m \) and \( \Delta H_m \), respectively) also rise linearly with increasing bIm/(Im + bIm) (see table S2). \( \Delta S_m \) increase illustrates how bIm ligands enhance the number of configurational states at \( \text{Tm} \) (Fig. 3D). It is also comparable to the configurational entropy \( S_{\text{config}} \) retained in silica at its glass transition (see the Supplementary Materials) (28), reflecting the softer structure of MOFs. Likewise, the increase of \( \Delta H_m \) demonstrates that the bulkier linker demands more thermal energy to initiate structural reconfiguration at the onset of melting. Nevertheless, \( \Delta H_m \) is over two decades smaller than that for quartz (see the Supplementary Materials). In addition, the rising of \( \Delta S_m \) and \( \Delta H_m \) with bIm/(Im + bIm) also implies that the added bIm linkers chemically participate in the structural network in a random manner.

Finally, GFA in terms of \( \text{Tg}/\text{Tm} \) for ZIF-62 is compared in Fig. 4 with that for 50 other glasses. With \( \text{Tm} \)’s ranging more than 1800 K, traditional glasses fall on either side of 2/3 value for glass formation (5, 6). It
shows that \( T_g / T_m \) (0.84) of ZIF-62 is the highest of the 50 glasses, indicating its ultrahigh GFA. \( T_g / T_m \) of water is adopted as 0.5 in Fig. 4, and \( T_g \) is explained in table S4 (29, 30). In contrast, ZIF-4 has a \( T_g / T_m \) of 2/3 and amorphizes before crystallizing to ZIF-ze and subsequent melting but has a similar \( \Delta \rho / \rho_g \) value to that of water. Ranked below ZIF-62 but with \( T_g / T_m > 2/3 \) are the following glass formers: CP with weakly interacting linear chains has transitory GFA, very low \( \eta(T_m) \), and reversible crystallization and melting (2); SiO₂ glass with high \( \eta(T_m) \), but with low \( \Delta \rho / \rho_g \) weakly recrystallizes close to \( T_m \) (26); both PMMA and B₂O₃ glasses show no signs of recrystallization but for different reasons. The structure of PMMA sterically hinders periodic arrangement (9), whereas B₂O₃ with its boroxol ring structure is topologically remote from any candidate crystal, leading to a huge \( \Delta \rho / \rho_g \) (8). These metrics factor into the ultrahigh GFA discovered for ZIF-62 glasses with their uniquely high \( T_g / T_m \) and will influence the search for other MQ glasses that resist crystallization on laboratory time scales. Randomly distributed bulky linkers, such as bIm, inhibit recrystallization, as does the large network density deficit \( \Delta \rho / \rho_g \) network, making \( \eta(T_m) \) comparable to that of SiO₂ (28), traditionally the most viscous and strongest of inorganic liquids.

Because melting of ZIF-62 must involve complementary processes that lead to the enhanced GFA, three aspects of the melting mechanism emerge: (i) The central tetrahedral node acquires Lindemann kinetic energy (~\( k_B T_m \)), which weakens Zn-N coordination bonds, breaks crystalline periodicity, shrinks pores, eliminates channels, and generates and randomizes clusters, chains, and rings; (ii) flowing nanosized structural units experience strong steric hindrance, resulting in viscous cooperative transnational motion; (iii) the equilibrium between Zn-N bond deconfiguration and reconfiguration and altered conformation of linkers leads to a much expanded network compared to the porous ZIF-62. All of these suggest that a compromise between porosity, flexibility, and...
viscosity in MOF liquids may be necessary to facilitate applications involving guest separations in sintered MOF glass bodies.

Furthermore, ZIF-62 glass exhibits an ultrahigh Poisson’s ratio \( (\nu = 0.45) \), which is in strong contrast to that (0.15) of its counterpart, the ZIF-62 crystal. The two ratios are located on the opposite sides of the brittle-to-ductile transition (fig. S14) \((31)\), where the fracture energy scales abruptly. Physically, \( \nu \) distinguishes harmonic response where compression is compromised to retain shape \( (v \rightarrow 0) \) from incompressibility at the expense of shape \( (v \rightarrow 0.5) \). Accordingly, MQ ZIF-62 is far less compressible than ZIF-62. Such a large difference should be a contributing factor inhibiting recrystallization, either from the glass \( (v = 0.45) \) or from the supercooled liquid \( (v = 0.5) \).

**MATERIALS AND METHODS**

**Synthesis**

ZIF-62 was synthesized using Zn\((\text{NO}_3)\)\(_2\)·6H\(_2\)O (Zn; 99.99%) as the metal source, Im (99.5%) and bIm (99%) as the linkers, and \( \text{N}_2\text{N}’\text{-dimethylformamide (DMF); 99.9\%} \) as the solvent. The Zn (0.2 M), Im (1.5 M), and bIm (0.2 M) stock solutions were prepared by dissolving the above mentioned precursors in DMF. The appropriate volumes of the stock solutions were mixed together according to the reagent Zn/Im/bIm molar ratio of 1:13.5:1.5. The solutions were mixed in a 100-ml Teflon-lined autoclave, stirred for 1 hour, and then placed in an oven at 403 K for 96 hours. Subsequently, the Teflon-lined autoclave was cooled to ambient temperature. The solid was washed then placed in an oven at 403 K for 96 hours. Subsequently, the Teflon-lined autoclave was cooled to ambient temperature. The solid was washed and dried at 373 K for 4 hours. The crystalline nature of the as-prepared sample was confirmed by the XRD pattern. Moreover, to explore linker compositional effects on melting and glass formation, we changed the ratio between bIm and Im in ZIF-62 during synthesis according to the strategy outlined in table S1. The MQ ZIF-62 glass samples were obtained by heating the crystalline ZIF-62 powder to 773 K in argon in the DSC. The glass samples for mechanical tests were produced by using a melting-pressing approach in a vacuum furnace.

**Measurements**

**Calorimetric analysis**

The DSC characterizations of all the samples were conducted using a Netzsch STA 449 F1 instrument. The samples were placed in a platinum crucible situated on a sample holder of the DSC at room temperature. The samples were held for 5 min at an initial temperature of 313 K, heated at 10 K min\(^{-1}\) to the target temperature, and then cooled back to 473 K at 10 K min\(^{-1}\), thus forming the standard glass (32). After natural cooling to room temperature, the second upscan was performed using the same procedure. To determine the \( C_p \) of the samples, both the baseline (blank) and the reference sample (sapphire) were measured.

**Powder XRD**

Room temperature powder XRD data \((2\theta = 5^\circ \text{ to } 40^\circ)\) were collected with a Rigaku-RU 200B diffractometer using Cu K\(_{\alpha}\) \((\lambda = 1.540598 \text{ \AA})\) radiation.

**Viscosity**

The viscosity of ZIF-62 liquids was measured in the temperature range from 743 to 793 K above \( T_m \) in flowing nitrogen atmosphere on a rheometer (TA Discovery HR-2) with a parallel-plate geometry (diameter, 25 mm) at the strain of 0.1%. However, it was not possible to measure the viscosity data around \( T_g \) due to lack of a viscometer that could avoid the oxygen influence. On the other hand, it was easy to measure the \( T_g \) and the liquid fragility index \( m \). We combined the high-temperature viscosity data above \( T_m \) and the viscosity value \((10^{12} \text{ Pa} \cdot \text{s})\) at \( T_g \) and then fitted these data to the MYEGA viscosity model (25) to get the fragility index \( m \). Thus, we were able to extend the viscosity-temperature relation to the low-temperature range, in which the viscosity data were not available.

**Raman spectroscopy**

Raman spectra were recorded using a Thermo Nicolet Nexus spectrometer with a neodymium-doped yttrium aluminium garnet (Nd:YAG) laser (1064 nm), and the spectral resolution was 4 cm\(^{-1}\). A typical power of 0.1 W was used to record spectra in the range of 100 to 3500 cm\(^{-1}\).

**X-ray photoelectron spectroscopy**

XPS measurements were performed by an ESCALAB 250Xi x-ray photoelectron spectrometer using Al K\(_{\alpha}\) radiation. The spectra were calibrated by referencing the binding energy of carbon (C 1s, 284.6 eV).

**Solution NMR spectroscopy**

Solution \(^1\)H NMR spectra of digested samples \([\text{in a mixture of DCl (35\%)/D}_2\text{O (0.1 ml) and dimethyl sulfoxide–d}_6 (DMSO–d}_6 (0.5 ml)]\) of desolvated crystalline ZIF-62 samples and the ZIF-62 glasses (about 6 mg) were recorded on a Bruker Avance III 500 MHz spectrometer at 293 K. Chemical shifts were referenced to the residual proto-solvent signals of DMSO–d\(_6\). The spectra were processed with the MestreNova Suite.

**Positron annihilation lifetime spectroscopy**

PALS measurements were performed using an identical sample analysis methodology to that reported literature. The samples were measured on an EG&G Ortec fast-fast coincidence system using NaCl \((~1.5 \times 10^6 \text{ becquerel})\), which was sealed in a thin Mylar envelope. The samples in the form of powders were packed into a vacuum cell located 2 mm on each side of the positron source. The measurements were taken under vacuum \((1 \times 10^{-5} \text{ torr})\) at 298 K, and \(4.5 \times 10^{6}\) integrated counts per file for each sample were collected. A source correction of 1.48 ns and 3.033% was subtracted from each spectrum. The spectra were deconvoluted using the LT v.9 software. Each spectrum was fitted to four components, with the first two components fixed to 0.125 ns (para-positronium) and approximated to 0.4 ns (free annihilation). The third and fourth components were due to ortho-positronium \((\text{o-Ps})\) annihilation events indicating the presence of two distinct pore sizes within the materials. Table S2 lists the fitted parameters including \(\text{o-Ps}\) intensity and lifetime for each sample along with the calculated pore diameters and fractional free volume used.

**Solid-state NMR spectroscopy**

Solid-state NMR experiments were carried out on a 600-MHz Varian NMR system equipped with a 1.6-mm Varian HXY CPMAS probe. Larmor frequencies for \(^1\)H and \(^\text{13C}\) were 599.51 and 150.75 MHz, respectively, and sample rotation frequency was 40 kHz. For two-dimensional \(^1\)H MAS and \(^1\)H-\(^\text{13C}\) CPMAS measurements, \(^1\)H 90\(^\circ\) excitation pulse of 1.25 \(\mu\)s was used. The CPMAS experiment used ramped-amplitude (RAMP) CP block, with duration of 4 ms, and high-power X-inverse X (XiX) heteronuclear decoupling during acquisition; the number of scans was 6000, and repetition delay between scans was 1 s. For two-dimensional \(^\text{13C}\)-detected spin-diffusion measurements, the number of scans was 5000, number of increments in indirectly detected dimensions was 12, and repetition delay between scans was 0.5 s. The experiments used the Lee-Goldburg scheme during the 100-\(\mu\)s-long CP block and high-power XiX heteronuclear decoupling during acquisition. Frequency axes of \(^1\)H and \(^\text{13C}\) spectra were referenced to tetramethylsilane. Detailed information for calculating density deficit, entropy and enthalpy of fusion, and the analysis of NMR results and mechanical moduli can be found in the Supplementary Materials.
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SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/eaao6827/DC1

Supplementary Methods

fig. S1. Phase structure evolution with heating temperature.
fig. S2. Comparison of valence states between crystal and glass.
fig. S5. Determination of liquid fragility index (\(\eta\)).
fig. S6. The appearance change of the MQ ZIF-62 glass with heating temperatures.
fig. S7. XRD patterns of nonstoichiometric ZIF-62.
fig. S9. Influence of linker substitution on the s ratio of ZIF-62 crystal and glass.
fig. S13. Schematic representation of linker substitution.

REFERENCES AND NOTES


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samples and performed the DSC, XRD, Raman, liquid NMR, and XPS measurements and analysis, guided by T.D.B., G.N.G., H.T., and Y.Y. H.T. and A.Q. performed the viscosity study. C.M.D. and A.W.T. conducted the PALS experiments and analyzed the data. A.K. and G.M. performed the solid NMR study. J.C.M. facilitated the mechanical characterizations.

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