Metal–organic frameworks (MOFs) beyond crystallinity: amorphous MOFs, MOF liquids and MOF glasses†

Javier Fonseca,*a Tenghua Gong,a Li Jiaoa and Hai-Long Jiang b

The field of metal–organic frameworks (MOFs) has been incorrectly believed to be purely crystalline. However, non-crystalline MOFs (amorphous MOFs, MOF liquids, and MOF glasses) are starting to emerge as alternative materials, beyond the dictatorial domain of crystalline MOFs. Non-crystalline MOFs present many opportunities, either as novel functional materials themselves, or as vehicles to create other materials. In this extensive Review, we describe the two approaches to preparing amorphous MOFs: (1) the amorphization of crystalline MOFs and (2) the direct synthesis. Special attention is paid to the relationship between preparation method, properties and applications of amorphous MOFs. We also explore the field of MOF liquids and their applications, centering our attention to the phenomenon of melting. Finally, MOF glasses are explained. We highlight the properties and applications of the MOF glasses that are not usually found in crystalline MOFs. New related glass materials such as MOF-blends, flux melted MOFs, MOF crystal-glass composites, MOF and inorganic glass composites, and MOF glass membranes are also reviewed. We conclude the fields of amorphous MOFs, MOF liquids, and MOF glasses by presenting our thoughts on the possible future research directions.

1. Introduction

Based on the IUPAC definition, metal–organic frameworks (MOFs) are coordination compounds extending through repeating coordination entities in 2 or 3 dimensions, containing potential voids.1 Even though IUPAC recommendations do not include crystallinity as a requirement, most research in the field of MOFs is placed on the long-range order scope. A small but growing number of non-crystalline MOFs (amorphous MOFs, MOF liquids, and MOF glasses) are starting to challenge...
the overwhelming dominance of their crystalline equivalents (Fig. 1). However, to date, they are still underrepresented. Given the importance of amorphous, liquid, and glass phases of the three major material families (polymers, metals, and ceramics), we believe that the emerging research area of non-crystalline MOFs will step forward to playing a major role in the discovery of new MOF materials.

Non-crystalline MOFs hold the key to next-generation technologies such as plastic technologies, communications, catalysis, and display technologies. However, we are now required to work at the frontier of complexity. Regarding crystalline MOFs, the global structure also reveals the local structure. Conventional crystallographic methods of structural analysis are not sufficient in studying non-crystalline MOFs. In these materials, the local atomic environment (the short-range order) must be explored by local probes including X-ray absorption spectroscopy (XAS), pair distribution function (PDF), and solid-state nuclear magnetic resonance (ssNMR) spectroscopy. The difficulties in the characterization of non-crystalline MOFs may explain why this domain remains underrepresented. It must not be forgotten that the purpose of structural analysis is to relate the structure to the properties so that these can be understood from the atomistic point of view.

In this Review, we have divided non-crystalline MOFs into amorphous MOFs (aMOFs), MOF liquids and MOF glasses. The classification criterion is based on the different structure of these materials. The structural difference between non-crystalline solid MOFs (aMOFs and MOF glasses) and MOF liquids is clear in terms of intermolecular forces and arrangement of molecules. In addition, we structurally differentiate aMOFs and MOF glasses. A non-crystalline solid MOF is a MOF glass if it satisfies the condition:

$$\text{SRO(MOF glass)} = \text{SRO(MOF melted)}$$

where SRO is short-range order. Therefore, eqn (1) represents the condition on the structural state of a MOF glass. Conversely, aMOFs are non-crystalline solid MOFs which violate condition (1). In other words,

$$\text{SRO(aMOF)} \neq \text{SRO(MOF melted)}$$

Herein, we begin by describing aMOFs. The general principles of reported amorphization approaches are explained to understand the process of amorphization itself and provide insights into the processing of crystalline MOFs. Then, several related studies of aMOFs are summarized. Direct synthesis of aMOFs is also covered in detail. The aim is to study the preparation of aMOFs, paying special attention to the methods and the theories behind them, as they influence the properties of aMOFs and, in turn, their applications. We conclude this section by presenting our thoughts on viable future research directions for aMOFs.

Focusing on MOF liquids, the accessibility of MOFs to liquid state is explored. Firstly, the concept of MOF liquids is defined. 

Li Jiao is a graduate student in the Department of Chemical Engineering at Northeastern University. Her research focuses on the rational design of nanomaterials for electrocatalysis.

Dr Hai-Long Jiang is a Professor of Chemistry at the University of Science and Technology of China (USTC) and PI of Hefei National Laboratory for Physical Sciences at the Microscale. He received his PhD degree in Inorganic Chemistry from the Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences in 2008. He subsequently joined Prof. Qiang Xu’s group at National Institute of Advanced Industrial Science and Technology as a postdoctoral and JSPS fellow in 2008–2011. After a postdoctoral stint at Texas A&M University with Prof. Hong-Cai Joe Zhou, he joined the faculty of USTC in 2013.
A brief background of related porous liquids materials is also provided to contextualize the study of MOF liquids. We examine several studies of MOF liquids centering our attention to the phenomenon of melting. The opportunities in practical applications of MOF liquids are also detailed throughout the text. Finally, we indicate what we believe to be interesting prospects in the field of MOF liquids.

We finish by examining MOF glasses. We explore glasses prepared from crystal MOFs by melt-quenching and other methods. Attractive properties, as well as applications of the MOF glasses that are not usually found in crystalline MOFs, are highlighted. New related material categories are also explained, including MOF-blends, flux melted MOFs, MOF crystal–glass composites (MOF–CGCs), MOF and inorganic glass composites, and MOF glass membranes. We concluded by predicting possible future directions for MOF glasses.

The aims of this extensive Review are (1) challenge the dominance of the crystalline MOFs and (2) motivate others to move into the emerging area of non-crystalline MOFs. Materials with properties rarely achieved in the crystalline domain are expected to emerge in this new field. We look forward to seeing how the field of non-crystalline MOFs expands. These are exciting times ahead.

2. Amorphous MOFs

2.1. Introduction

aMOFs are inorganic nodes (clusters or metal ions) connected by organic ligands extending in either two or three dimensions with potential for porosity. aMOFs retain the basic building blocks and connectivity of their crystalline counterparts, and consequently possess a lower entropy than true glasses. However, they display no long-range periodic order within the structure. Therefore, aMOFs exhibit only diffuse scattering from X-ray or neutron diffraction. In contrast, poorly crystalline MOFs still show Bragg peaks, which may be broad or badly defined.

aMOFs combine properties that are usually found in crystalline MOFs including outstanding thermal and chemical stabilities, high surface areas, excellent porosities, and tunable pore sizes, shapes and chemical functions, with the unique properties of the amorphous domain such as isotropy, absence of grain boundaries, abundant defects and active sites, and flexibility. Moreover, aMOFs are usually prepared under mild conditions, which facilitates large-scale applications of these materials.

Only 28 aMOFs has been reported until 2014. Today, this number has quadrupled, but it is still considerably lower in comparison to other classes of materials. Most aMOFs have been prepared by applying stress to a crystalline framework. To date, both static and hydrostatic pressures, heating, mechanical stress (ball milling, grinding, and so on), radiation, and electrical discharge have been applied to crystalline MOFs to induce their collapse and amorphize them. Chemical treatment has also led to crystal failure. In a minority of cases, aMOFs have been formed from direct synthesis (Fig. 2). It is likely that aMOFs have been synthesized and subsequently discarded without further investigation. In fact, high-throughput computational screening (HTCS) software identifies but discards aMOFs.

Amorphization is an entropy driven process that can be described as follows (Fig. 3):\(^1\) 11

1. When stress is applied, defects accumulate in the lattice becoming progressively more difficult to maintain long-range order. Stress raises the enthalpy (\(\Delta H_{\text{stress}}\)) and the entropy (\(\Delta S_{\text{stress}}\)) of the crystal.

2. When \(\Delta H_{\text{stress}}\) is equal to the overall enthalpy increase from the perfect crystal to the amorphous phase (\(\Delta H_{\text{a}}\)), all the amorphous configurations become equally accessible to the system. At that critical level, the atoms are not constrained to maintain long-range orientation and they can rotate and rearrange themselves locally to create a structure where the short-range order is preserved. Therefore, the number of ways that the atoms can arrange themselves with a certain degree of short-range order increases. The availability of many amorphous states that are isenthalpic with the stressed crystal abruptly increases \(\Delta S_{\text{stress}}\).

3. Thus, for a fixed degree of short-range order, there are many more microstates corresponding to a macroscopic amorphous state than microstates are corresponding to a damaged crystalline state. Namely, the configurational entropy of the amorphous phase is much higher than that of the stressed crystalline phase. If all states of equal enthalpy are equally accessible to the system, the system will find itself most often in the macrostates of the greatest entropy, i.e., the...
amorphous state. In other words, the probability of finding the system in any given macrostate is proportional to the entropy of the microstate, which is related to the number of equivalent microstates.

In the following sections of this Review, synthesis approaches of aMOFs are summarized. The aim is to study the synthesis of aMOFs paying special attention to the method, as they influence aMOFs applications. For every synthesis approach, the general principle is described. Then, several related comprehensive studies of aMOFs are summarized, focusing on the preparation and promising applicabilities of those materials (Table S1†). We also provide our thoughts about the perspectives of aMOFs.

2.2. Pressure-induced amorphization

Pressure-induced amorphization (PIA) is a phenomenon that involves an abrupt transition from a crystalline material to an amorphous solid through the application of pressure at temperatures below the melting point or glass transition range. It modifies the physical and chemical properties as well as the performance of porous materials. PIA achieves structural alteration which includes changes in pore size, opening and geometry, channel shape and internal surface area. Subsequently, these pressure-induced changes will affect the sorption selectivity, capacity and access to the binding sites of the porous materials. Additionally, pressure-transmitting fluids can generate new materials and phases not accessible through conventional synthesis or other stresses. Pressure-transmitting fluids can even induce porosity in conventionally nonporous materials. This is an area worth investigating further, since external high pressures are commonplace in industrial applications (i.e. during shaping or formulation).

The three mechanical processes that emerge when porous solids are subjected to pressure or shock must be mentioned: (1) compaction (squeezing out void space between crystals through deformation of crystals), (2) compression (reduction of the internal porosity of porous crystals with the partial collapse of free pore volume), and (3) cataclysmic ductile collapse (further collapse of the pore structure, fracture of the compacted crystals, and amorphization of the resulting solid).

2.2.1. Static pressure-induced amorphization. Chapman et al. initiated a new type of non-crystalline MOF system through the amorphization of an existing crystalline MOF. They investigated the impact of pressure on the structure and porosity of ZIF-8 (Zn(MeIm)₂, MeIm = 2-methylimidazolate). An irreversible structural amorphization was produced beyond 0.34 GPa. The amorphized ZIF-8 (aP-ZIF-8, aP = amorphization by pressure) remained porous, although the sorption and catalytic properties were altered. The nitrogen isotherms reflected changes in the pore dimension and sorption properties. It was hypothesized that the pressure disrupted the long-range translational symmetry of ZIF-8 while retaining its local structure, framework connectivity, and porosity (Fig. 4). This speculation was demonstrated by PDF analysis. It provided insight into the structural features that were retained in the amorphous ZIF-8 framework. While the short-range order which corresponds to the Zn–imidazolate–Zn links, was preserved in aP-ZIF-8, the well-defined longer-range order of crystalline systems was destroyed in the amorphous material. It was also studied the effect of pressure amorphization of ZIF-8 for gas retention and storage. I₂-loaded ZIF-8 was amorphized, thus minimizing the release of I₂. PDF analysis indicated that the local structure of the captive I₂ (the short-range I–I and I–framework interactions) was retained upon amorphization of the framework. Therefore, mechanically modified MOFs were proved to be promising interim storage of radioisotopes before incorporation into...
a long-term waste.\textsuperscript{18} ZIF-8 was also examined at pressures up to \(~39\) GPa by infrared (IR) absorption spectroscopy.\textsuperscript{19} At the highest pressure of 39.15 GPa, the IR profile was a broadened pattern, indicating the transformation to the amorphous structure. Upon complete decompression, the spectrum of the recovered sample was that of the sample at around 4 GPa. However, upon compression to 1.6 GPa followed by decompression, ZIF-8 was found to be reversible.

Therefore, structural modifications were reversible in a low-pressure region but irreversible in a high-pressure region.\textsuperscript{19} The dynamic deformation of ZIF-8 under compression was directly observed by \textit{in situ} transmission electron microscopy (TEM).\textsuperscript{17} ZIF-8 was compressed to pressures as large as 1.9 GPa, which produced an irreversible morphological transition and amorphization upon the release of applied pressure. At low pressures (<0.8 GPa), ZIF-8 was transformed from rhomboic dodecahedra to irregular blocks. Particle fracture occurred at 1.9 GPa. The Brunauer–Emmett–Teller (BET) specific surface area decreased from 1340 m\(^2\) g\(^{-1}\) to 253 m\(^2\) g\(^{-1}\) after treatment at 1.9 GPa, showing that the amorphous ZIF-8 remained partially porous. Methanol-solvated ZIF-8 was less deformable than the desolvated framework.\textsuperscript{17} A molecular dynamics study showed that the PIA of ZIF-8 is triggered by the mechanical instability of the framework under compression, due to the shear mode softening of the material.\textsuperscript{20}

MOF-5 (Zn\(_4\)O(BDC))\(_2\), BDC = 1,4-benzene dicarboxylate) was irreversibly amorphized by employing a compressing pressure of 3.5 MPa. A very small surface area (about 6 m\(^2\) g\(^{-1}\) was shown by amorphized MOF-5.\textsuperscript{21} Porous MOF-177 Zn\(_4\)O(RTB)\(_2\), RTB = benzene tribenzoate) was mechanically compressed to prepare monoliths with bulk densities more than three times its crystallographic density.\textsuperscript{22} When MOF-177 crystals were subjected to compressive stress, they underwent a crystal to amorphous phase transition. While the monoliths with densities below 0.51 g cm\(^{-3}\) were found to be crystalline, those with densities above 0.51 g cm\(^{-3}\) were amorphous. The progressive collapse of MOF-177 crystals to an amorphous phase decreased the micropore volume of monoliths while increasing the density. Consequently, the excess gravimetric hydrogen storage capacity of MOF-177 decreased with increasing density. However, the maximum excess volumetric hydrogen storage uptake at 77 K of the monolith with a density of 25.7 ± 1.2 g L\(^{-1}\) increased 80% of the theoretical value predicted based on the material's crystallographic density. It was also a \(~78\%\) increase in the volumetric hydrogen storage capacity of the starting material. Further increase in the density lowered the excess volumetric capacity which was attributed to the progressive depreciation of excess gravimetric uptake.\textsuperscript{22}

Upon external compression of UiO-66 Zr\(_6\)O\(_4\)(OH)\(_4\)(BDC)\(_6\) at 1.9 GPa, the effective number for Zr-O coordination bonds between Zr\(_\{\text{v}\}\) ions and carboxylate groups decreased from 4.0 to 1.9. Irreversible amorphization of UiO-66 was observed due to the endothermic bond breakage. The BET surface area of the framework dramatically decreased, from 1050 m\(^2\) g\(^{-1}\) to 76 m\(^2\) g\(^{-1}\) after compression at 1.9 GPa. XAS was employed to examine the local coordination environment around Zr\(_\{\text{v}\}\) ions. After pressure treatment at 0.4 GPa, the effective number of Zr-O\(_\text{COO}\) bonds and Zr···Zr scatterers decreased to 3.0 and 2.5 per Zr\(_\{\text{v}\}\) ion, respectively. At 1.9 GPa, the effective number of Zr-O\(_\text{COO}\) bonds and Zr···Zr scatterers dropped to 1.9 and 2.1 per Zr\(_\{\text{v}\}\) ion, respectively (Fig. 5). Therefore, the long-range order of UiO-66 was maintained, but the local coordination environment around Zr\(_\{\text{v}\}\) was partially changed upon compression. The absorbed energy per gram from the endothermic bond breakage of UiO-66 at compression at 1.9 GPa was estimated to be 2.1 kJ g\(^{-1}\). Therefore, substantial energy was irreversibly absorbed in UiO-66 during the collapse, comparable in magnitude to the energy released by typical explosives. Thus, Su \textit{et al.} have established the potential application of MOFs as mechanical energy absorbers for hydrostatic and shock compression.\textsuperscript{23} Subsequently, this research group examined the effects of shock on ZIF-8.\textsuperscript{24} Optical microscopic images taken before and after the impacts showed defined impact craters (Fig. 6). This framework was crushed after \(0.75\) km s\(^{-1}\) impacts (2.5 GPa). The shocked material had the same major diffraction peaks as the as-synthesized ZIF-8, but with significant broadening and loss of intensity. It must be noted that greater amorphization was observed after 2 GPa static compression. At velocities up to \(1.3\) km s\(^{-1}\) (5 GPa), ZIF-8 was fragmented and, thereafter, agglomerated. Consequently, complete amorphization of ZIF-8 crystals was achieved. These morphological changes were irreversible. High-speed emission spectroscopy revealed that 50 ns after

\begin{figure}[h]
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\includegraphics[width=\textwidth]{image.png}
\caption{After compression of UiO-66, the effective number of Zr–carboxylate oxygen (Zr–O\(_\text{COO}\)) bonds (shown in yellow) for each Zr\(_\{\text{v}\}\) ion decreased from 4 to \(~2\). Adapted with permission from ref. 23. Copyright 2017 The Royal Society of Chemistry.}
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\includegraphics[width=\textwidth]{image2.png}
\caption{Optical (a–d) and scanning electron microscopy (SEM) (e–h) images of ZIF-8 crystals after shock compression. (a, e) Without shock; (b, f) \(0.75\) km s\(^{-1}\) (2.5 GPa); (c, g) \(1.3\) km s\(^{-1}\) (5 GPa); and (d, h) \(1.6\) km s\(^{-1}\) (8 GPa). Adapted with permission from ref. 24. Copyright 2017 American Chemical Society.}
\end{figure}
impacts, an emission pulse was generated by ZIF-8 resulting from chemical bonds that were broken and subsequently reformed. Therefore, shock collapsed the nanopores of ZIF-8, cleaving the coordination bonds and perhaps other bonds of the framework. After the initial bond-breaking endothermic step, the chemically stored shock energy was released more gradually as broken bonds reform. Thus, it was proved the dissociation of shock wave energy through structural change (free volume collapse and endothermic bond breakage). There was a prior example of shock compression. Cu-BTC (BTC = 1,3,5-benzenetricarbonylate) with and without ferrocene (Fc) inclusion exhibited anisotropic structural collapse under shock loading. The shock resistance of Cu-BTC was enhanced through molecular inclusion of Fc into the pore structures. While Cu-BTC became amorphous at ~3.8 GPa, Cu-BTC-Fc turned into amorphous at ~5.8 GPa. Therefore, the structural integrity of a MOF material subjected to shock wave energy can be improved by hosting guest molecules. The surface areas and pore volumes of a$_p$-Cu-BTC and a$_p$-Cu-BTC-Fc were not explored.

### 2.2.2. Hydrostatic pressure-induced amorphization.

Spencer et al. investigated the pressure-dependent structural evolution of the three-dimensional (3D) zeolitic imidazolate framework (ZIF) [Zn$_2$(C$_3$H$_7$N$_2$)$_3$]$_n$ (α-phase). This ZIF, which crystallizes in the tetragonal space group I4$_1$cd, was found to undergo a transition to β-phase (tetragonal space group I4$_1$) within the moderate pressure range of 0.5–0.8 GPa. Thus, a previously unknown architecture (β-phase) was formed via pressure-induced conversion. The physical mechanism by which the transition occurred involved a complex cooperative bond rearrangement process. Although this material is a ZIF in terms of its topology, it contains no accessible pore volume. Moggach and coworkers presented the first hydrostatic-pressure study on a porous MOF, ZIF-8. At 0.18 GPa, the MOF increased in volume (from 4900.6 to 4999.6 Å$^3$), with an associated expansion of pore volume (2465 to 2556 Å$^3$). The hydrostatic media was compressed into the large nanopore, thus increasing the pore size and the cell volume. The MOF underwent a single-crystal to single-crystal phase transition at 1.47 GPa. Although the imidazolate ligands twisted and reoriented to increase the accessible pore volume, the new high-pressure phase (ZIF-8-II) still maintained the I43m space-group symmetry. The cell volume increased on undergoing the transition. Noteworthily, ZIF-8-II reverted to phase 1 at 0.82 GPa. Similarly, ZIF-4 (Zn[Im]$_2$, Im = Imidazole) was reported to suffer reversible PIA between 0.35 and 0.98 GPa.

The effect of pressure on MOF-5 with diethyl formamide (DEF) as the pressure-transmitting medium was explored in another study. Initial compression to 0.8 GPa resulted in solvent being forced into the pores, making the framework resilient to compression. At pressures about 1.3 GPa, the solvent was evacuated from the pores. Increasing the pressure to 3.2 GPa resulted in a gradual amorphization of the sample. At pressures above 3.2 GPa the sample became completely amorphous. In contrast to these investigations, an ab initio simulation study of the high-pressure behavior of MOF-5 reported that the amorphization of MOF-5 occurs at 2 GPa. The difference between the simulation conditions and experimental conditions was probably responsible for this discrepancy. During the simulations, MOF-5 was subjected to a gradually increased hydrostatic pressure. It was proposed that the reversible crystal-to-amorphous phase transition at 2 GPa was originated by the local distortions without breaking bonds in the framework. According to PDF results, amorphous MOF-5 (a$_p$-MOF-5) displayed well-defined short-range order and the lack of long-range correlations. Large-scale molecular dynamics simulation on MOF-5 resolved the structural mechanism for the deformation of MOF-5 under uniaxial compression. The deformation was primarily attributed to the structural collapse of the 001 plane, which involves slip along the (100) direction, facilitated by the flexible metal to ligand bonds.

Systematic exploration of zinc cyanide (Zn(CN)$_2$) upon mechanical pressure revealed new phases: four crystalline and one amorphous. The pressure-induced transitions were driven by including fluid molecules in Zn(CN)$_2$ in order to generate metastable open frameworks. Consequently, the framework expanded instead of densifying as expected under pressure. It provided a mean to transform dense interpenetrated frameworks into new porous materials. The transition depended principally on the pressure-transmitting fluid. The irreversible amorphization of Zn(CN)$_2$ was found beyond ~3 GPa, when exposed to X-rays but not without, being isopropanol the pressure-transmitting medium. a$_p$-Zn(CN)$_2$ was a nonporous phase.

Structural studies of a scandium terephthalate MOF (Sc$_2$(BTC)$_3$) and its nitro-functionalized analogue (Sc$_2$(NO$_2$-BTC)$_3$) at high pressures in the presence of different hydrostatic liquids that are either non-penetrative (Fluorinert-77) or adsorbing (methanol) have been reported by Graham et al. In Fluorinert-77, Sc$_2$BTC$_3$ underwent a reversible crystalline-to-amorphous phase transition at 0.4 GPa. The local structure of Sc$_2$BTC$_3$ in the amorphous phase was retained according to Raman spectroscopy. Upon immersion of Sc$_2$BTC$_3$ in methanol without added pressure, the unit cell expanded as methanol diffused into the framework. It expanded further at 0.3 GPa, as a result of additional methanol going into the porous material. Cell volume decreased from 1.1 GPa up to 3.0 GPa. Amorphization of Sc$_2$BTC$_3$ in methanol took place above 3.0 GPa. On the other hand, direct compression occurred on Sc$_2$(NO$_2$-BTC)$_3$ from ambient to 0.3 GPa using Fluorinert FC-77. Sc$_2$(NO$_2$-BTC)$_3$ underwent a phase transition (C2/c to Fdd2) to a denser but topologically identical polymorph on increasing pressure further to 0.8 GPa. Above that pressure, the cell volume decreased. The sample underwent an irreversible amorphization above 2.6 GPa, which was a much higher pressure than that for Sc$_2$BTC$_3$. It was in accordance with the stabilization effect of the presence of the bulk nitro group. Using methanol as hydrostatic liquid, Sc$_2$(NO$_2$-BTC)$_3$ cell volume decreased from ambient pressure up to 3.3 GPa. Amorphization of this framework took place above that pressure. The surface areas and pore volumes of the amorphous phases were not explored.

The flexible NH$_2$-MIL-53(In) (NH$_2$-In(OH)BDC) framework showed much higher resistance to amorphization than any
reported MOF.\textsuperscript{44} A slight decrease in the X-ray diffraction intensity along with a broadening and a shift to higher degrees was observed upon increasing the hydrostatic pressure over NH$_2$-MIL-53(In) in the presence of non-penetrating fluids. The crystallinity of the structure was maintained in pressure as high as 23 GPa. The textural properties (surface area, pore volume, pore size distribution, etc.) of the amorphous phase were not investigated. The compression of NH$_2$-MIL-53(In) was fully reversible up to 15 GPa. In the presence of a penetrating fluid, at relatively low pressures (1 GPa), the structure expanded to NH$_2$-MIL-53(In)$_p$ (from the \textit{Cc} to the \textit{Imma} space group). No further changes were observed, proving the high stability of NH$_2$-MIL-53(In) and evidencing that penetrating fluids enhanced the stability of the framework. Therefore, it was demonstrated that framework flexibility is not a limitation for MOF processing.\textsuperscript{44}

The piezochromic MOF Co$_2$(BDC)$_2$DABCO-4DMF·H$_2$O (DABCO = 1,4-diazabicyclo[2.2.2]octane, DMF = dimethylformamide) reduced its tetragonal symmetry at about 0.7 GPa. At that pressure, the crystal changed its color from blue to purple. At the pressure of 1.9 GPa, the crystal underwent an amorphization process, which was obvious by the reduced intensity of X-ray reflections. The purple crystals were transformed into a red amorphous phase above 1.9 GPa. At the mentioned pressure, there were no reflections above 2\(\theta\) = 3.5°. It indicated distortion of the crystalline structure of the sample; although some short-range translations were retained. The amorphization mechanism implicated distortions of the BDC linkers and Co(II)-coordination schemes. In doing so, the crystal field around the cations and their optical absorption were affected, resulting in a color change. In other words, the compression affects the light absorption of this piezochromic framework, generating their changes of color (Fig. 7). These results open new possibilities for developing environment-monitoring sensors and for designing new multifunctional and intelligent materials.\textsuperscript{35} The textural properties were not reported in this study.

\subsection*{2.3. Heat-induced amorphization}

Heat-induced amorphization (HIA) is a phenomenon that involves an abrupt transition from a crystalline material to an amorphous solid through application of temperature below that of the melting point or glass transition range. Normally, HIA of MOFs is based on the fast removal of the solvent from the pores of the framework. It provokes the collapse of the material by the action of the internal forces in the liquid–gas meniscus. It is worth noting that the temperature of amorphization (\(T_a\)) decreases as the heating rate is reduced.

An example of HIA of MOF was reported by Masciocchi \textit{et al.}\textsuperscript{3} Amorphous Cu(Im)$_2$ ($a_T$-Cu(Im)$_2$, \(a_T\) = amorphization by heating) was formed by heating solid [Cu(HIm)$_2$(CO$_3$)$_2$]·H$_2$O at 110 °C for 20 min in an oven. The following decomposition reaction was confirmed by TGA:

\[
\text{[Cu(HIm)$_2$(CO$_3$)$_2$]·H$_2$O} \rightarrow \text{Cu(Im)$_2$} + 2\text{H$_2$O} + \text{CO}_2 \quad (3)
\]

Later, this research group proved that M\textsuperscript{n} imidazolate-containing complexes (M = Ni, Pd, and Pt) are decomposed upon heating to give the M[Im]$_2$ species.\textsuperscript{36} Amorphous Ni(Im)$_2$ ($a_T$-Ni(Im)$_2$) was created by heating [Ni(HIm)$_2$(Im)(CH$_3$COO)] at 130 °C for 4 h. Similarly, amorphous Pd(Im)$_2$ ($a_T$-Pd(Im)$_2$) was formed by heating Pd[HIm]$_2$(Im)$_2$ under nitrogen at 150 °C; and amorphous Pt(Im)$_2$ ($a_T$-Pt(Im)$_2$) was synthesized by heating Pt[HIm]$_2$(Im)$_2$ at 250 °C.\textsuperscript{37} $a_T$-Ni(Im)$_2$, $a_T$-Pd(Im)$_2$, and $a_T$-Pt(Im)$_2$ were found to be stable up to 420 °C, 400 °C and 450 °C, respectively. Moreover, $a_T$-Ni(Im)$_2$ was also reported to be formed by thermal decomposition of Ni(acac)$_2$(HIm)$_2$ (acac = acetylacetone) complex at 260 °C. According to IR absorption patterns, the three amorphous complexes presented square-planar coordination geometries.\textsuperscript{36} The textural properties of $a_T$-Cu(Im)$_2$, $a_T$-Ni(Im)$_2$, $a_T$-Pd(Im)$_2$, and $a_T$-Pt(Im)$_2$ were not reported.

A thermally stable MOF was synthesized after a crystalline-to-amorphous-to-crystalline (CAAC) phase transition. Interpenetrated [ZnI$_2$(TPT)$_2$·5.5(C$_6$H$_5$NO$_2$)(H$_2$O)] (TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) was amorphized to phase 2 at 550 K. A transformation from amorphous phase 2 to ‘hidden’ intermediate amorphous phase 3 was found at 570 K. Further heating caused a new crystalline phase [ZnI$_2$(TPT)$_2$]$_2$ (phase 4) to appear at 600 K (Fig. 8). This new porous framework was remarkably robust and thermally stable (up to 673 K).\textsuperscript{37} Phase 2 returned to phase 1 when it was immersed in nitrobenzene, indicating reversible amorphization. There was a molecular reorganization from the double interpenetrated 3D network in

\begin{figure}
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\includegraphics[width=\textwidth]{Fig7}
\caption{Single crystal of Co$_2$(BDC)$_2$DABCO-4DMF·H$_2$O changing color under the pressure. Hypochromic effect in the VIS spectra. Adapted with permission from ref. 35. Copyright 2017 The Royal Society of Chemistry.}
\end{figure}
phase 1 to the non-interpenetrated saddle-type 1D network in phase 4. Therefore, solid memory of \( \text{[ZnI}_2\text{(TPT)}_2\text{]} \cdot \text{5.5(C}_6\text{H}_5\text{NO}_2\text{(H}_2\text{O)} \) to form \( \text{[ZnI}_2\text{(TPT)}_2\text{]}_n \) must persist in the amorphous phases. According to extended X-ray absorption fine structure (EXAFS) analysis on the Zn K-edge, the tetrahedral coordination geometry was preserved upon the transformation from 1 to 2 and 4. In agreement with this result, the PDFs of phase 1, phase 2, and phase 4 were almost identical up to approximately 5.5 Å, indicating that the local structure environment around Zn was common to all three phases. PDF of phase 1 and phase 4 showed long-range ordering due to crystallinity. In contrast, the PDFs of phase 2 and phase 3 showed only short-range ordering, with intensity decreasing at high r. The PDF of phase 3 was different from others. It was observed elongation and broadening of the Zn–I bonds, suggesting that Zn did not have a regular coordination environment in phase 3.\(^{38}\) The resulting saddle-type network (phase 4) can be used for S\(_3\) and P\(_4\) trapping.\(^{39,40}\) This work demonstrates that amorphous phases play a key role in some fascinating crystalline network formations. In a similar work, isostructural interpenetrated metastable coordination networks, \( \text{[[ZnBr}_2\text{(TPT)}_2\text{]}_n \cdot \text{5(C}_6\text{H}_5\text{NO}_2\text{(H}_2\text{O)} \) and \( \text{[[ZnCl}_2\text{(TPT)}_2\text{]}_n \cdot \text{5.5(C}_6\text{H}_5\text{NO}_2\text{(H}_2\text{O)} \) have been studied at elevated temperatures.\(^{41}\) Upon heating to 573 K, \( \text{[[ZnBr}_2\text{(TPT)}_2\text{]}_n \cdot \text{5(C}_6\text{H}_5\text{NO}_2\text{(H}_2\text{O)} \) exhibited crystalline-to-amorphous-to-crystalline (CAC) phase transformation to \( \text{[[ZnBr}_2\text{(TPT)}_2\text{]}_n \cdot \text{(H}_2\text{O)} \). Thus, after nitrobenzene guest removal and molecular rearrangement, a double interpenetrated network was obtained. It was suggested that the molecular reorganization involved cleavage and formation of coordination bonds, which can be explained by the formation of the amorphous phase. Similarly, \( \text{[[ZnCl}_2\text{(TPT)}_2\text{]}_n \cdot \text{5.5(C}_6\text{H}_5\text{NO}_2\text{(H}_2\text{O)} \) underwent CAC phase transformation involving bond-breaking and bond-forming to yield \( \text{[[ZnCl}_2\text{(Cl)}_n][\text{ZnCl}][\text{TPT}][\text{Cl}]]_n \).\(^{44}\) These studies proved that the solid-state reactions have different reaction conditions to those in the solution state. New MOFs, that are difficult (if not impossible) to be obtained directly using traditional synthetic methods, with interesting physicochemical properties may be created via an amorphous phase. The surface area and pore volume of a\(_T\)-\( \text{[ZnI}_2\text{(TPT)}_2\text{]}_n \), a\(_T\)-\( \text{[ZnBr}_2\text{(TPT)}_2\text{]}_n \) and a\(_T\)-\( \text{[[ZnCl}_2\text{(Cl)}_n][\text{ZnCl}][\text{TPT}][\text{Cl}]]_n \) were not explored.

Bennet et al. discovered that ZIF-4 amorphized when heating to 300 °C.\(^{42}\) The amorphous structure was reported to be a continuous random network analogous to that of amorphous silica [a-SiO\(_2\)].\(^{43,44}\) Subsequently, a\(_T\)-ZIF-4 underwent an amorphous-to-crystal transition when heated to 400 °C. This dense crystalline phase (ZIF-3ni), which had the same composition as ZIF-4, was stable up to around 500 °C, whereupon thermal decomposition took place. ZIF-4 was recoverable from a\(_T\)-ZIF-4 at ambient conditions. According to PDFs results, the tetrahedral Zn coordination environment and the bridging coordination motif of the imidazolate ions were identical to ZIF-4, a\(_T\)-ZIF-4 and ZIF-3ni. There was some broadening of the peaks in the PDFs with increasing temperature which is consistent with increased thermal motion.\(^{45}\) It is worth mentioning that in situ thermal amorphization of ZIF-4 has been followed by in situ far-IR spectroscopy, which provided information about lattice dynamics of ZIF-4.\(^{44}\) Likewise, ZIF-1 (\( =\text{Zn(Im)}_2 \), ZIF-3 (\( =\text{Zn(Im)}_2 \) and Co-ZIF-4 (\( =\text{Co(Im)}_2 \) underwent amorphization to a\(_T\)-ZIF (a\(_T\)-ZIF-1, a\(_T\)-ZIF-3 and a\(_T\)-Co-ZIF-4, respectively) and recrystallization to ZIF-3ni at similar temperatures to that of ZIF-4.\(^{45}\) Amorphization from ZIF-1, ZIF-3 and Co-ZIF-4 was found to occur at 300 °C. Continued heating to above 400 °C resulted in the formation of the dense ZIF-3ni. The PDFs from the four a-ZIFs showed excellent agreement (Fig. 9). Each pattern displayed the same sharp features below the metal–metal distance of ca. 6 Å and similar broad features above the...
largest differences were found in the Co-ZIF-4 due to the different scattering factors of Zn and Co. The textural properties of aT-ZIF-4, aT-ZIF-1, aT-ZIF-3 and aT-Co-ZIF-4 were not reported. A near-perfect continuous random network model for aT-ZIF with periodic boundaries obtained through the conversion of amorphous SiO2 model has been constructed by Adhikari et al. The radial distribution function was in good agreement with measurements for aT-ZIF-4. The electronic structure and bonding of aT-ZIF and crystalline ZIF-4, ZIF-3, and ZIF-8 were reported to be very similar, reaffirming the identical short-range ordering. Recently, models of amorphous MAF-7 (Zn(mt2)), mtz = 3-methyl-1,2,4-triazole), amorphous LiB-ZIF-4 (LiB(Im)4), and amorphous LiB-MAF-7 have also been constructed based on the aforementioned model of aT-ZIF.

Although amorphization of ZIF-8 has been realized via ball-milling or compression, this framework has not been amorphized by heating, since ZIF-8 undergoes a direct phase transition to ZnO upon thermal treatment. However, ZIF-8 was reported to be amorphized under a relatively slow heating rate and a prolonged thermal treatment thanks to the protection of a surrounding polyimide polymer (Matrimid®) which prevented the full oxidation of ZIF-8. The crystalline structures of the ZIF-8 nanoparticles embedded in the Matrimid® matrix amorphized at temperatures above 250 °C. It was assumed that the Matrimid® might provide thermochemical protection for the embedded ZIF-8. The BET surface area and total pore volume of amorphous ZIF-8 embedded in the Matrimid® decreased up to 16 cm² g⁻¹ and 0.09 cm³ g⁻¹. The long-range periodic ordering was lacking in the amorphous ZIF-8. However, they retained the basic building blocks and the connectivity of crystalline ZIF-8 as confirmed by the combined XRD, Fourier transform IR spectroscopy-attenuated total reflectance (FTIR-ATR) and electron diffraction results. In addition, the thermal treatment also covalently bonded ZIF-8 and the polymer and induced an oxidative cross-linking of the matrix. It resulted in novel amorphous mixed matrix membranes (MMMs) with increased stability or plasticization resistance at pressure up to 40 bar. These MMMs boosted the gas separation performance to the highest CO2/CH4 selectivities ever reported to date for membranes based on commercial polymers, marking a new milestone for challenging natural gas purification. Similarly, ZIF-7 (Zn(PhIm)3, PhIm = benzimidazolate) loaded MMMs showed high selectivity for CO2/CH4 separations. MMM prepared from pre-amorphized via ball-milling ZIF-8 failed to achieve high CO2/CH4 selectivity in comparison to the cross-linked MMMs prepared via in situ thermal-oxidative treatment. This work uncovers the applicability of amorphized MOFs for gas or liquid membrane separations.

A new type of electrically bistable MOF, CuI[CuIII(pdt)] (pdt = 2,3-pyrazinedithiolate), has been developed. The physical properties of the framework were reversibly modulated by crystalline-to-amorphous transformation. Microporous CuI[CuIII(pdt)] was transferred into its amorphous non-porous phase aT-CuI[CuIII(pdt)] by heating at 120 °C for 2 h. CuI[CuIII(pdt)] was recovered after soaking amorphous aT-CuI[CuIII(pdt)] into acetonitrile (CAN) for 6 h. Therefore, the reversible transformation was closely related to the removal and adsorption of CAN. Both crystalline and amorphous phases were stable at room-temperature (RT) and standard pressure. Surprisingly, the conductivity of amorphous aT-CuI[CuIII(pdt)] was 130% higher than that of crystalline CuI[CuIII(pdt)]. aT-CuI[CuIII(pdt)] exhibited a semiconducting behavior. It is worth mentioning that the conductivity of most semiconductors significantly decreases from their crystalline to their amorphous phase. The structural transformation from CuI[CuIII(pdt)] to aT-CuI[CuIII(pdt)] started from the distortion of N-Cu-N bonds. Besides the rearrangement of Cu-N bonds, according to EXAFS, the coordination number of Cu increased because of the generation of new Cu-S bonds. The electron donor-acceptor pair for conduction was conserved along the amorphization, and the new Cu-S bonds generated additional means for electron moving. Therefore, the new coordination can explain the unusual enhanced conductivity of aT-CuI[CuIII(pdt)] compared with CuI[CuIII(pdt)]. This work opens the door to design and prepare electrically bistable semiconductors from MOFs for applications in memories, displays, switches, sensors and quantum computation.

Mn-MIL-100 (MnBTC) was found to undergo a crystal-to-amorphous transition to aT-Mn-200 at 200 °C. The amorphous phase was maintained until 250 °C (aT-Mn-250). On further increasing the temperature to 350 °C, aT-Mn-250 became crystalline MnOx. The pore size distribution of Mn-MIL-100 showed micropores (1.3 nm) and mesopores (2.6 nm, 5.3 nm), aT-Mn-200 had a broad pore size distribution in the range of 2–5 nm, mainly centered at 2.58 and 3.54 nm. Moreover, aT-Mn-250 displayed less density of pores than aT-Mn-200. Therefore, the increased temperature collapsed the pore channels. In line with these results, the BET surface areas were 1147, 15.6, and 4.0 m² g⁻¹ for Mn-MIL-100, aT-Mn-200, and aT-Mn-250, respectively. aT-Mn-250 exhibited higher catalytic activity for CO oxidation than Mn-MIL-100 and aT-Mn-200, although it had a smaller specific surface area. In addition, aT-Mn-250 showed excellent catalytic stability. Therefore, the surface area was not the key factor governing the catalytic performance. The good catalytic activity of aT-Mn-250 was figured to be related to high lattice oxygen mobility and good low-temperature reducibility. In a similar investigation, a ZIF-67 (Co(Im)3) hollow sphere (HS-ZIF-67) was treated at 200 °C for 3 h.
260 °C to prepare an amorphous structure (α-T-HS-ZIF-67).\textsuperscript{31} Subsequent crystallization to CoO4 occurred at 270 °C (Fig. 10). Due to the collapse of the ordered microporous structure during the amorphization of HS-ZIF-67 to α-T-HS-ZIF-67, the BET surface area decreased from 611.4 to 315.2 m\(^2\) g\(^{-1}\). Moreover, the BET surface area of CoO4 was 149.3 m\(^2\) g\(^{-1}\). Accordingly, the total pore volume was reported to be 0.42, 0.41 and 0.40 m\(^3\) g\(^{-1}\) for HS-ZIF-67, α-T-HS-ZIF-67 and CoO4, respectively. α-T-HS-ZIF-67 was found to exhibit significantly better oxygen evolution reaction (OER) catalytic activity in basic electrolyte than crystalline CoO4. α-T-HS-ZIF-67 was not stable. It evolved to CoO4 nanoparticles after 1000 catalytic cycles, which resulted in a decrease of the electrocatalytic activity. Moreover, α-T-HS-ZIF-67 also displayed better catalytic activity for nonenzymatic glucose sensing than CoO4. Therefore, α-T-HS-ZIF-67 provided more active sites during electrochemical reactions than CoO4. This phenomenon was attributed to α-T-HS-ZIF-67 having a larger specific surface area and more structure defects at the molecular level than crystalline CoO4.\textsuperscript{31} These publications serve as examples of the considerable attention that amorphous materials have received in catalysis during the last few years.\textsuperscript{54-56}

In a recent study, Orellana-Tavra et al. have examined a biocompatible bismuth-based MOF, CAU-740 (Bi(BTB)) as a drug delivery system (DDS).\textsuperscript{29} CAU-7 was loaded with the cancer drugs sodium dichloroacetate (DCA) and α-cyano-4-hydroxycinnamic acid (α-CHC) both capable of modifying cancer metabolic pathways. CAU-7 was able to retain its crystalline structure after loading. CAU-7 showed progressive discharge of the drugs, achieving time release up to 17 days and 31 days for DCA and α-CHC, respectively. To delay the delivery of guest molecules, CAU-7 loaded with the cancer drugs was either mechanically or thermally amorphized. The theory behind mechanical milling-induced amorphization will be covered in detail in the next section of this Review. While ball-milling (mechanical amorphization process) on the loaded CAU-7 generated am\(_m\)-CAU-7 (am\(_m\) = mechanical milling amorphization), temperature-based amorphization (180 °C) produced the α-T-CAU-7. The drug release profiles differed for both drugs and amorphization processes. For DCA, am\(_m\)-CAU-7 replicated the profile of crystalline CAU-7, with a small decrease in the total amount released. α-T-CAU-7 liberated DCA much faster, with total release at 4 days. It was reasoned that the fast release was triggered by water molecules dragging DCA from the pores during the thermal treatment. Both am\(_m\)-CAU-7 and α-T-CAU-7 reproduced the same profile of crystalline CAU-7 for the liberation of α-CHC, even though the release was significantly slower. Between days 0 and 4, the difference in the amount released was 32% lower from α-T-CAU-7 and 19% for am\(_m\)-CAU-7 compared to crystalline-CAU-7.\textsuperscript{29} Logically, the slower release was related to the sluggish diffusion in the amorphous frameworks. It must be noted that amorphous CAU-7 loaded either with DCA or α-CHC had higher therapeutic efficiency compared with the free drug approach.

### 2.4. Mechanical milling-induced amorphization

Mechanical milling stresses beyond the elastic limits of MOFs cause irreversible, plastic deformation. Large plastic deformation induces high defect density, which produces partial or complete loss of crystallinity and porosity with the accompanying distortion and changes to local bonding structure.\textsuperscript{60} The kinetics of phase transformations induced during mechanical milling depend on the energy transferred to the powder by a shearing action or impact of the high-velocity balls. According to the large amount of experimental results available in the field of ball milling, it is evident that the nature and kinetics of phase transformations are responsive to the milling conditions. In other words, the energy transfer is governed by parameters such as the type of mill, milling speed, ball/powder weight ratio, dry or wet milling, and the duration of milling.\textsuperscript{61} Amorphization of MOFs during mechanical milling is usually attributed to the defects. Neither the increase in free energy nor the number of defects have been investigated systematically. It must be mentioned that mechanical milling can produce a variety of materials in the simplest possible way. Thus, it is a promising technique for solid-state processing, being able to synthesize a variety of equilibrium and non-equilibrium phases which are difficult to produce in a conventional manner.

Bennett et al. prepared amorphous ZIFs by mechanical stress.\textsuperscript{62} ZIF-1, ZIF-3 and ZIF-4 were ball-milled without solvent for 30 min at RT. Those crystalline ZIFs were irreversibly amorphized to nonporous am\(_m\)-ZIFs (am\(_m\)-ZIF-1, am\(_m\)-ZIF-3 and am\(_m\)-ZIF-4). Ball-milling amorphization of ZIFs was easy and fast, compared with heating or hydrostatic pressure. Milling crystals of ZIF-1, ZIF-3 and ZIF-4 did not result in ZIF-ze formation. However, ZIF-ze was observed upon heating the am\(_m\)-ZIFs to 450 °C, as found with the α-T-ZIFs and was mentioned in the previous section. According to PDF results, very similar amorphous materials were produced from both mechanical milling and thermal stresses. Moreover, these am\(_m\)-ZIFs did not show nanoporosity. They displayed surface area and N\(_2\) uptake similar to the dense ZIF-ze prepared by solvothermal reaction. It is worth noting that am\(_m\)-ZIF-1 (11 m\(^2\) g\(^{-1}\)), am\(_m\)-ZIF-3 (21 m\(^2\) g\(^{-1}\)) and am\(_m\)-ZIF-4 (10 m\(^2\) g\(^{-1}\)) had greater BET specific surface areas than α-T-ZIF-4 (1 m\(^2\) g\(^{-1}\)). It was also reported the ball-milling amorphization of nanocrystalline porous ZIF-8 (nanoZIF-8). nanoZIF-8 was also ball-milled without solvent for 30 min at RT. The stable amorphous product (am\(_n\)-nanoZIF-8) was not nanoporous and showed a BET specific surface area of 56 m\(^2\) g\(^{-1}\).\textsuperscript{61} In a complementary study, the mechanical amorphization of nanoZIF-8 (ref. 63) was also investigated.\textsuperscript{48} The irreversible amorphization of ZIF-8 via ball-milling was studied for varying amounts of time. It was completely amorphized in 20 min. Upon further milling for up to 300 min, there were no observable changes in the sample. Unsurprisingly, the local chemical environment and chemical composition were held upon ball-milling as found by PDF analysis. The resultant amorphous ZIF-8 (am\(_n\)-ZIF-8) possessed higher density than its crystalline counterpart. There was an initial rapid density increase from 1.45 g cm\(^{-3}\) to 1.50 g cm\(^{-3}\) after 30 min of milling, followed by a slower increase to 1.52 g cm\(^{-3}\) after 300 min. The rapid increase in density at short times was due to the conversion from the crystalline to the amorphous form. The increase in density at longer times was attributed to a further loss of free volume. am\(_n\)-ZIF-8 also showed a lower porosity than its
crystalline counterpart. Micropore volume decreased from 0.6715 to 0.0048 cm$^3$ g$^{-1}$ in the first 30 min. Accordingly, the BET specific surface areas dropped from 1583 to 55 m$^2$ g$^{-1}$ after 30 min of ball-milling. A decrease in thermal stability upon amorphization was also evident. The decomposition temperature ($T_d$) reduced from 486 °C for crystalline ZIF-8 to 418 °C for am-ZIF-8 (30 min), and was further lowered to 350 °C for am-ZIF-8 (300 min). Recently, the effect of amorphization on the dynamics of the MFeIm linkers in ZIF-8 has been investigated. According to $^1$H solid-state NMR spectra, the type of motion of the linkers was preserved after amorphization. In contrast, variable temperature $T_1$ and $T_2$ measurements of am-ZIF-8 revealed that the amorphization could significantly change the rotational angle, the activation barriers, and the rate constants for the original modes of motions in ZIF-8. Furthermore, a new librational mode appeared in am-ZIF-8, which could not be observed in the crystalline phase. 

Baxter et al. reported a comparative study on the time dependence to induce amorphization via ball-milling at 20 Hz, for the porous ZIF-4, ZIF-8 and CdIF-1 (Cd(MeIm)$_2$) and the dense phases ZIF-zni and BIF-1-Li (LiB(Im)$_4$), which is the lithium/boron analogue of ZIF-zni. It was found that rates of amorphization increased with decreasing density and increasing porosity. Thus, dense ZIF-zni (4.66 nm$^2$) amorphized slower than ZIF-4 (3.68 nm$^2$) and, in turn, this framework underwent structural collapse slower than ZIF-8 (2.45 nm$^3$). The presence of solvent within the pores of the ZIFs and zeolites was found to reinforce the materials against ball-milling compared with their desolvated counterparts. It was also reported that the isostructural frameworks ZIF-8 and CdIF-1 amorphized in 30 and 20 minutes, respectively. The greater stability of the zinc compound compared with its cadmium analogue was primarily ascribed to the M–N bond strength. The shorter Zn–N bonds in ZIF-8 (1.987 Å) compared with the Cd–N bonds in CdIF-1 (2.199 Å) were expected to be stronger. On the other hand, while ZIF-4 (4.66 nm$^2$) amorphized within 120 minutes, its isostructural frameworks BIF-Li-1 (5.49 nm$^3$) still retained some crystallinity after 7 hours of ball-milling. The stability showed a correlation with their framework density. Amorphous ZIF-zni was structurally indistinguishable from amorphous ZIF-4 with both structures retaining the same short-range order that was present in their crystalline precursors. However, the local environment of amorphous CdIF-1 was not the same as that in the crystalline phase. Some rearrangement of the bonding around the cadmium took place during the milling process. In addition, the zeolites Na–X [Na$_{16}$Si$_{23}$Al$_{18}$O$_{80}$], Na–Y [Na$_2$Si$_{17}$Al$_{26}$O$_{88}$] and Na-ZSM-5 [Na$_{1.92}$Al$_{1.92}$Si$_{22.08}$O$_{68}$] were also studied. ZIFs were far less resistant to structural collapse than zeolites. While the least stable zeolite (Na–X) amorphized after 240 minutes, the most stable solvated ZIF (ZIF-8) required 60 minutes to lose its crystallinity. The results were consistent with the shorter and stronger bond lengths and the greater density in Na–X.

The ability of ZIF-8, ZIF-69 (Zn(cPhIm)mnIm), cPhIm = chlorobenzimidazolate, nlm = 2-nitroimidazolate) and ZIF-mnIm (Zn(mnIm)$_2$, mnIm = 4-methyl-5-nitroimidazolate) to trap I$_2$ via amorphization induced by ball milling has been evaluated. The I$_2$-containing crystalline ZIFs were ball-milled for 30 min at 25 Hz. Crystalline I$_2$-filled ZIF-69 started to lose guest at 90 °C, whereas amorphized ZIF-69 (am-ZIF-69) started to lose I$_2$ at 200 °C. At that temperature, crystalline ZIF-69 contains almost no I$_2$. However, complete guest loss from am-ZIF-69 occurred around 350 °C. Therefore, amorphization retarded the onset of I$_2$ loss by over 100 °C and delayed complete guest loss by 150 °C. In ZIF-8 and ZIF-mnIm, the difference in the onset of mass loss between crystalline and amorphous frameworks was also around 100 °C. Upon reaching the holding temperature of 200 °C, both amorphous ZIFs (am$_m$-ZIF-8 and am$_m$- ZIF-mnIm) lost very little I$_2$. It should be pointed out that am-ZIF-8, which has been detailed in the previous section, continued to lose I$_2$ at a holding temperature of 200 °C, whereas am$_m$-ZIF-8 did not. It is likely related to the difference in porosity between am$_m$ ZIFs and ap$_p$ZIFs. While the latter possess some residual porosity, the former is not porous. The retention effect reported in this study highlighted the irreversibly trapping of guest molecules by ball-milling-induced amorphization of the frameworks. 

Building on the concept of trapping guest molecules by irreversibly collapsing porous networks around occluded species, it was reported the loading of a therapeutic agent (calcein) in UiO-66 followed by its structural collapse by ball-milling. Ball-milling on the loaded UiO-66 at 20 Hz for 30 min amorphized the framework to loaded am$_m$-UiO-66. While UiO-66 released all the calcein within 2 days, am$_m$-UiO-66 prolonged the delivery time up to 30 days. Moreover, after 1 h, the crystalline and amorphous frameworks released 36 and 3.5% of calcein, respectively. After 5 h, these amounts increased to 68 and 16% for UiO-66 and am$_m$-UiO-66, respectively. am$_m$-UiO-66 still retained 33% of calcein after 10 days. Amorphous am$_m$-UiO-66 was not only able to extend the release time of calcein but to penetrate the cells while maintaining the kinetic of delivery. This study on controlled drug release was extended to the family of Zr-based MOFs. It was analyzed the loading and release of calcein and the anticancer drug 5-CHC in UiO-66, UiO-66-Br ([Zr$_6$O$_{4}$(OH)$_4$(BDC-Br)$_6$]), UiO-66-NO$_2$ ([Zr$_6$O$_{4}$(OH)$_4$(BDC-NO$_2$)$_6$]), UiO-66-NH$_2$ ([Zr$_6$O$_{4}$(OH)$_4$(BDC-NH$_2$)$_6$]), MIL-140B ([Zr$_6$O$_{4}$(OH)$_4$(nbd)$_6$]), nbd = 2,6-naphthalenedicarboxylic acid), MIL-140C ([Zr$_6$O$_{4}$(OH)$_4$(bdpc)$_6$]), bdpc = [1,3-biphenyl]-4,4’-dicarboxylic acid), [Zr$_6$O$_{4}$(OH)$_4$L$_7$]$_n$ (L = 4,4’-(1,2-diazadienyl) bis-benzoic acid), and [Zr$_6$O$_{4}$(OH)$_4$L$_8$]$_n$ (L = 4,4’-(1,2-ethenediyl)bis-benzoic acid). These loaded MOFs were amorphized via ball-milling at 20 Hz for 30 min to control the delivery of guest molecules. Crystalline MOFs loaded with calcein released this molecule in approximately 2–3 days presenting a burst effect during the first hours. Amorphous UiO-66-Br and UiO-66-NO$_2$ (ap$_p$-UiO-66-Br and ap$_p$-UiO-66-NO$_2$) trapped calcein molecules, and only a fraction of the total loaded amount, 63 and 68 wt%, respectively, was released. Amorphous UiO-66-NH$_2$ (ap$_m$-UiO-66-NH$_2$) progressively released calcein for 15 days. There was no different release profile between crystalline and amorphous MIL-140B and MIL-140C. Likely, either the porosity of those MOFs was not completely blocked after the ball-milling or the loaded calcein increased their stability. On the other hand, crystalline MOFs loaded with 5-CHC presented
a burst effect during the first hours of release, delivering α-CHC in ~1 day. Crystalline UiO-66-NO₂, as an exception, reached 94 wt% release after 3 days. There was no significant difference between the crystalline and amorphous patterns. Therefore, amorphization did not contribute to any significant improvement in the delivery time. Either the pores were not obstructed to avoid the diffusion of α-CHC, or the stability of the MOFs increased due to the loaded molecules. These results highlight the necessity of a compromise between the pore size of the MOF and the size of the guest molecules to accomplish a controlled release via mechanical ball-milling.

In another study, UiO-66, MIL-140B and MIL-140C were collapsed upon ball-milling at 20 Hz during 10, 15 and 20 min, respectively. Consequently, the aMOFs: am-Uio-66, am-MIL-140C and am-MIL-140B*, were generated. The asterisk denotes the retention of some Bragg peaks in the diffraction pattern of MIL-140B after milling. The PDFs of am-Uio-66 and UiO-66 are very similar below 6 Å. It confirmed the presence of the Zr₆O₄(OH)₄ structural building unit in am-Uio-66. According to the reduction in intensity and severe broadening of the peaks at longer distances, am-Uio-66 lost the long range-order of the framework. However, the presence of some intensity suggested the partial retention of the structural linkage (Fig. 11a and b). According to PDFs of MIL-140B and am-MIL-140B*, the nearest Zr–Zr distance in the inorganic backbone, moved from 3.3 Å to 3.5 Å upon amorphization. Moreover, the rigid ZrO inorganic chain did not remain intact. It was suggested that some Zr–O bonds were broken during the ball-milling process, causing the chain to twist. Above 15.9 Å, the PDF of am-MIL-140B* was featureless, in contrast to its crystalline counterpart (Fig. 11c and d). Similar differences were observed in the PDFs of MIL-140C and am-MIL-140C. The same movement of nearest Zr–Zr distances upon amorphization was observed. Similar reductions in the intensity of the peak belonging to nearest neighbor Zr–O correlations were also noticed (Fig. 11e and f). Therefore, while the inorganic Zr₆O₄(OH)₄ clusters of UiO-66 remained intact upon amorphization, the ZrO backbone of the MIL-140 frameworks underwent distortion. The different behavior was attributed to the larger interconnected nature of the inorganic clusters in UiO-66, where 24 Zr–O bonds hold the unit together. It contrasted with the ZrO chains of the MIL-140 frameworks, where in a unit containing the same number of Zr ions, only 16 Zr–O bonds hold the chain together. This study also included defective models of MIL-140B performed by density functional theory (DFT) calculations. Defects investigated included coordinated water to Zr centers combined with linker displacement. Those defective models provided better agreement with the experimentally observed structural cell parameters than the defect-free ones. These results shed light on the relationship between defects and amorphization. The textural properties of am-Uio-66, am-MIL-140B, and am-MIL-140C were not reported.

HKUST-1 [Cu₃(BTC)₂], UiO-66, Al-ndc, ZIF-8 and Zn-MOF-74 ([Zn₄(dhta)(H₂O)₆]·8H₂O, dhta = 2,5-dihydroxy terephthalic acid) were amorphized by ball-milling at 400 rpm and 1 h under an Ar atmosphere. According to EXAFS, HKUST-1, ZIF-8, Al-ndc, and Zn-MOF-74 showed identical profiles in their pristine and amorphous phases. In contrast, Zr-Uio-66 displayed distinct profiles. Therefore, the Zr₆O₄(OH)₄ clusters in the framework were significantly distorted by ball milling. The crystalline frameworks of Cu-HKUST-1, Zn-ZIF-8, Al-ndc, and Zn-MOF-74 were reconstructed by exposing the amorphous phases to saturated water or methanol vapor at 25 °C for 3 days. However, Zr-Uio-66 did not rebuild to a crystallized state. It was demonstrated that recrystallization depends on the amorphous
states and whether the coordination environment of the pristine state is preserved. While the amorphous phases did not display porosity, the recrystallized phases recovered over 80% of their porous capacity. Similarly, mixtures of Al-ndc and Ga-ndc with molar ratios ranging from 1 : 9 to 9 : 1 were amorphized and subsequently turned into crystalline states. Each crystallized state of a mixture had unique cell parameters because of the solid solution formation. The X-ray absorption near-edge structure (XANES) spectra of the amorphous and crystallized states of the 1 : 1 mixture were identical to the pristine, amorphous, and crystallized states of Ga-ndc. Therefore, the coordination environment of Ga$^{3+}$ in amorphous and crystallized states of the 1 : 1 mixture was retained to be octahedral. EXAFS analysis was consistent with the result of XANES. Scanning TEM-energy dispersive X-ray (STEM-EDX) measurements for amorphous and crystallized states of the 1 : 1 mixture presented a well dispersed distribution of Al$^{3+}$ and Ga$^{3+}$ ions (Fig. 12). Due to the mismatch in cell volumes of each framework, attempts to synthesize solid solutions of Al-ndc/In-ndc and Ga-ndc/In-ndc and subsequently form a crystallized state were unsuccessful. However, solid solution of MOF-74 and ZIF-8 was achieved. Therefore, this approach is available for the preparation of solid solutions of other MOF systems.

Muratović et al. explored the response of crystalline Ni-MOF-74 ([Ni$_2$(dht)$_2$](H$_2$O)$_2$)$_8$H$_2$O) and Zn-MOF-74 to mechanical stress. Solvent-free Ni-MOF-74 and Zn-MOF-74 were ball-milled at 30 Hz for 90 min to get the amorphous materials a$_{m}$Ni-MOF-74 and a$_{m}$Zn-MOF-74, respectively. While a$_{m}$Zn-MOF-74 was recrystallized in less than 3 min by milling with MeOH or water additives, the amorphization of a$_{m}$Ni-MOF-74 was irreversible. It proved that the mechanical behavior of MOF-74 strongly depended on the metal nodes. The magnetism of Ni-MOF-74 was found to be dominated by ferromagnetic exchange interaction ($J$ = 16 cm$^{-1}$) in the helical nickel-oxo chains and weaker antiferromagnetic interaction ($J$ = −3 cm$^{-1}$) between the adjacent chains. However, the amorphization profoundly modified the physical properties of Ni-MOF-74, resulting in a significant decrease of the bulk magnetization in a$_{m}$Ni-MOF-74. In other words, spin-crossover from the magnetic high-spin state with $S = 1$ to non-magnetic low-spin state with $S = 0$ occurred upon mechanical action. The surface areas and pore volumes of a$_{m}$Ni-MOF-74 and a$_{m}$Zn-MOF-74 were not explored.

Very recently, high sodium ion conductivity was introduced into ZIF-8 by impregnation with the sodium-salt-containing ionic liquid (IL) [Na$_{0.1}$EMIM$_{0.9}$]TFSI. This composite (S-IL@ZIF-8) was demonstrated to exhibit superionic properties.
with low activation energy. Structural collapse via ball-milling under an inert atmosphere was found to enhance the stability of S-IL@ZIF-8. The IL was partially expelled from the composite upon ball-milling for 60 minutes. However, the IL solution remained inside of the pores upon ball-milling for 15 min ($a_{\text{m}}(\text{S-IL@ZIF-8})=15$) and 30 min ($a_{\text{m}}(\text{S-IL@ZIF-8})=30$). Under these conditions, S-IL@ZIF-8 was only partially amorphized. The collapse exerted a disrupting effect on the interconnected conduction channels within ZIF-8. Consequently, for $a_{\text{m}}(\text{S-IL@ZIF-8})=15$ and $a_{\text{m}}(\text{S-IL@ZIF-8})=30$, ionic conductivity decreased, and activation energy increased as compared to the values of these properties for pristine S-IL@ZIF-8. Conductivities for both crystalline and amorphized samples decreased after exposure to ambient air ($T = 20 ^\circ\text{C}$, humidity $\sim 45\%$) from 2–20 days. The decrease in conductivity for the crystalline sample was up to 33% after 20 days, while partially amorphized samples showed a decrease of only 15% after the same period. After 2 and 20 days of exposure at 85 °C, the conductivity of S-IL@ZIF-8 was found to decrease by about 8 and 20%, respectively. For the partially amorphized samples, the decrease was only 6% after 20 days. In addition, at RT, the activation energy increased from 0.26 to 0.38 and 0.4 eV after 2 and 6 days of exposure, respectively. The activation energy in the partially amorphized composites remained unchanged after 2 days and increased slightly to 0.28 eV after 6 days. Therefore, the partial amorphization of the composite reduced IL discharge and exchange with ambient while superior ion conductivity was still maintained.\(^{73}\)

### 2.5. Irradiation-induced amorphization

The kinetic restrictions imposed on the MOF crystal by irradiation create the conditions for the thermodynamically unfavorable phase (the amorphous phase) to appear. The rate-limiting step to amorphization is the accumulation of enough radiation damage in the lattice of the framework. Radiation damage in crystals includes a decrease of diffraction intensity and resolution, displacement of atomic parameters, and site-specific structural damage.\(^{74}\) Logically, the more robust the framework, the greater the amount of local structural damage that must be accumulated to cause long-range disorder and, therefore, amorphization.\(^{13}\) Two connected processes explain amorphization. Primary processes, which include the interaction of neutron, ion and electron irradiation with the crystal, result in bond breaking, mainly, due to photooxidation. In addition, free radicals can emerge causing secondary radiation damage through subsequent chemical reactions (secondary processes).\(^{74}\) Whereas primary processes depend on the irradiation dose, secondary processes are temperature dependent.

The previously mentioned amorphization of Zn(CN)\(_3\) upon pressure ($\sim 3$ GPa) and X-rays irradiation is the first example of irradiation-induced amorphization (IIA).\(^{22}\) Subsequently, scanning electron beam has been reported to amorphize layered ZIF (ZIF-L).\(^{75}\) Scanning electron beam exposure at low magnification, and imaging/diffraction in the TEM at a minimal dose have no effects on the crystallinity of ZIF-L. Amorphization was caused by high magnification scanning electron beam at an electron dose of $1.1 \times 10^{-2}$ C cm\(^{-2}\) and an acceleration voltage of 5 kV. Amorphous ZIF-L ($a_1$-ZIF-L, $a_1$ = amorphization by irradiation) was drastically more stable in dissolution than its crystalline parent framework. While crystalline ZIF-L was completely dissolved in deionized water, $a_1$-ZIF-L remained intact in the same medium (Fig. 13). A similar phenomenon was observed for ZIF-8, Zn(PhIm)OAc and MIL-101 (Cr\(_3\)(H\(_2\)O)\(_2\)O(BDC)\(_3\),nH\(_2\)O). Scanning electron beam exposure at high magnification was also able to stabilize these frameworks in water. While polycrystalline ZIF-8 was created by exposing $a_1$-ZIF-L to MeIm vapor, crystallographically aligned ZIF-8 crystals (nearly single-crystal-like) were prepared by exposing crystalline ZIF-L to same linker.\(^{75}\) The textural properties of $a_1$-ZIF-L as well as amorphous ZIF-8, Zn(PhIm)OAc and MIL-101 ($a_1$-ZIF-8, $a_1$-Zn(PhIm)OAc and $a_1$-MIL-101, respectively) were not reported.

In another study, ZIF-4, ZIF-62 (Zn(Im)\(_{1.75}\)(PhIm)\(_{0.25}\)) and ZIF-zni were amorphized by synchrotron X-ray radiation.\(^{76}\) The rate of structural collapse varied strongly between the three frameworks. 50% of the initial diffraction intensity remained after cumulative exposure times of 6, 14, and 81 minutes for ZIF-4, ZIF-62, and ZIF-zni, respectively. The resistance to X-ray induced amorphization was mainly controlled by the elastic moduli of the ZIF structure, being in good agreement with their relative resilience under heat or pressure.\(^{76,42,45}\) Amorphous ZIF-4 ($a_1$-ZIF-4) was recrystallized to ZIF-zni by heating to 400 °C. It indicated that amorphization could primarily be caused by photooxidation of the Zn centers and subsequent breakage of Zn–N bonds. The amorphization rate accelerated with increasing temperature. It pointed at the presence of a thermally activated, secondary process in the course of amorphization.\(^{76}\)
The resistance under gamma irradiation of ZIF-8, UiO-66, HKUST-1, MIL-53 ([Al(OH)(BDC)], MIL-100 (AlBTC), and MIL-120 ([Al2(OH)6(C6O4H2)]) has been analyzed by Volkering et al. The different porous solids were subjected to doses up to 1.75 MGy. ZIF-8 was partially amorphized by irradiation doses between 1.25 and 1.75 MGy. The BET specific surface area of ZIF-8 exposed to a dose of 1.75 MGy (598 m² g⁻¹) was reported to be approximately half of that for the non-irradiated ZIF-8 (1328 m² g⁻¹). Moreover, under irradiation, the microporous volume of ZIF-8 decreased from 0.545 cm³ g⁻¹ to 0.198 cm³ g⁻¹. UiO-66 and HKUST-1 exhibited similar behavior to the gamma rays. Their structure decomposed after an irradiation of 1.75 MGy, as confirmed by the loss of porosity. The frameworks constructed with aluminum ([MIL-53, MIL-100 and MIL-120] remained intact by the gamma irradiation (up to 1.75 MGy). Surprisingly, the BET surface area of MIL-100 increased 215 m² g⁻¹ after irradiation. MIL-120 also experienced an increase of the specific surface of 273 m² g⁻¹. For both frameworks, the improvement of the porosity was assigned to the removal of species trapped within the pores. Alumina MOFs had a resistance to gamma irradiation comparable to at least 8 days under strong radio-active conditions during a nuclear accident. The stability was attributed to the low cross-section of aluminum, limiting the effect of gamma rays and the destruction of the frameworks. These results prove the applicability of aluminum MOFs in fields involving radiation environments such as nuclear plants, medicine or aerospace.

In parallel to the described IIa, the structural collapse via dielectric-barrier discharge has also been reported. MOF-5 was irreversibly amorphized to α-c-MOF-5 (α-c = amorphization by electrical discharge) using electrical discharge for a short time at ambient pressure and low gas temperature (around 120 °C). Either air or argon was directly employed as the plasma forming gas. Both flowing gases yielded nearly the same structural collapse. Whereas MOF-5 showed a BET surface area of 1702 m² g⁻¹, α-c-MOF-5 displayed a much smaller BET surface area (13.7 m² g⁻¹). Moreover, the total volume of the pores also decreased with the treatment. Therefore, the pores collapsed after dielectric-barrier discharge treatment.

2.6. Chemical treatment-induced amorphization

αMOFs prepared by applying stress to a crystalline framework have been previously presented. This section highlights the recent progress in the synthesis of αMOFs by chemical treatment. It includes amorphization via removing coordinated solvent, atmospheric water-induced amorphization, amorphization by ligand competition, and loading induced amorphization. In general, solvents, environmental gases, free organic ligands, and so on dispute the free space of the framework, which leads to the appearance of internal forces and sometimes provokes the collapse of the MOF.

2.6.1. Amorphization via removing coordinated solvent. An early example of amorphization by removing coordinated solvent was reported by Colodrero et al. This group synthesized a family of lanthanide-based carboxyphosphonate MOFs (LnHPA, Ln3([H6.75O3PCHOHCOO]+xH2O (x = 15–16)) which crystallized in the orthorhombic system. The lanthanide was either La, Ce, Pr, Sm, Eu, Gd, Tb, or Dy and the carboxyphosphonate ligand was 2-hydroxypentoxyacetic acid (H₄HPA). Two polymorphic LnHPAs were isolated: LnHPA-I and LnHPA-II. As an example, the polymorphic phase LaHPA-I was obtained for pH values below 0.8, whereas LaHPA-II phase was prepared at pH values of above 1. A mixture of phases was found at intermediate pH. For both polymorphs, the 3D frameworks resulted from the linkage of organic–inorganic layers by central lanthanide cations, which yielded trimeric units. Both LaHPA-I and LaHPA-II displayed no porosity. LnHPA MOFs underwent CAC transformations upon dehydration and rehydration cycles under vacuum at RT. For instance, polymorphic phase LaHPA-I became amorphous after 4 h of vacuum treatment, with the final pressure reaching ~2 × 10⁻⁴ mbar. Amorphous LaHPA-I was converted to crystalline LaHPA-II by rehydration. This CAC transformation resulted in a change of symmetry from Iba2 to Pcn. Under the same conditions, LaHPA-II amorphized upon dehydration and, subsequently, readsorbed water, leading to the same type of structure. It must be noted that loss and reuptake of water molecules were accompanied by clear changes in the photoluminescence spectra and lifetimes of the Eu analog (series II). Moreover, LnHPA MOFs showed proton conductivity. Particularly, GdHPA (series II) displayed the highest proton conductivity, σₜ = 3.2 × 10⁻⁴ S cm⁻¹, at 98% RH and T = 21 °C.

The topochemical conversion of the crystalline, insulating Cu³⁺Cl(ttcH₃)(ttc)₃⁻(ttcH₃)₅⁻ MOF into the semi-conducting amorphous Cu₁.₈⁺Cl⁻(ttc)₀₆(ttcH₃)₀₄ MOF has been described by Tominaka et al. Firstly, Cu³⁺Cl(ttcH₃) was dechlorinated in aqueous ammonia solution at pH 11.4, forming [H₂O]₀.₇[NH₄]₀.₅[Cu₁.₈(ttc)]⁻. Subsequently, this amorphous intermediate was dried at 130 °C under vacuum to yield a-Cu₁.₈⁺Cl⁻(ttc)₀₁(ttcH₃)₀₄ (a-Cu = amorphization by chemical treatment). According to the PDF results, a-Cu₁.₈⁺Cl⁻(ttc)₀₁(ttcH₃)₀₄ was similar to Cu¹⁺Cl(ttcH₃) from 1 to 3 Å. Therefore, the local structure was retained during the dechlorination reaction. The treatment changed the transparent orange Cu¹⁺Cl(ttcH₃) into shiny black a-Cu₁.₈⁺Cl⁻(ttc)₀₁(ttcH₃)₀₄ with retention of morphology (Fig. 14). It also increased the electrical conductivity from insulating to semiconducting. The conductivities of a-Cu₁.₈⁺Cl⁻(ttc)₀₁(ttcH₃)₀₄ were found to be 4.2 × 10⁻¹¹ S cm⁻¹ at 20 °C and 7.6 × 10⁻⁹ S cm⁻¹ at 140 °C. The surface area and pore volume of CuCl(ttcH₃), [H₂O]₀.₇[NH₄]₀.₅[Cu₁.₈(ttc)]⁻ and a-Cu₁.₈⁺Cl⁻(ttc)₀₁(ttcH₃)₀₄ were not explored. As already highlighted in previous examples, the amorphization proceeds under the influence of the structural constraints of the initial compound.

A crystalline and anionic Co⁹⁺-MOF ([Me₂NH₃]₀[Co₆(Me₂-NH₄)₀₂(OH)(SBDA)₀₂], H₅SBDA = 4,4′-sulfonyldibenzonic acid) has been reported by Tian et al. It was composed of C₅ symmetric Co⁹⁺ triangles as secondary building units. This framework underwent a phase transition from crystalline to amorphous upon removal of coordinated dimethylamine (DMA) and the ionic groups DMA⁺ and OH⁻ via thermal treatment and vacuum. The modification from crystalline and anionic framework to amorphous and neutral framework was accompanied by changes in the coordination geometry of Co⁹⁺ and magnetic...
exchange pathway. Whereas the crystalline MOF showed the coexistence of spin-canting, spin-flop and easy plane magnetic anisotropy behavior, the aMOF exhibited a much stronger spin frustration effect. Therefore, the structural amorphization via deionization improved the magnetic properties of the anionic MOF. The textural properties were not reported in this study.

2.6.2. Atmospheric water-induced amorphization. MOF behavior in humid environments is a critical topic when considering these materials for industrial applications. As most MOFs are hydrophilic, they often suffer partial or complete amorphization in the presence of water. As a representative study, the sulfonated PCMOF-17 framework \([\{\text{In}(5\text{-Hsp})_2\text{-Me}_{2}\text{NH}_2\}^\text{+}\cdot\text{DMF}\cdot(H_2O)_\text{0.4}]^{\text{+}}\cdot5\text{H}_2\text{sp} = 5\text{-sulfoisophthalic acid})\) was reported to amorphize at 60% or higher levels of relative humidity (RH). PCMOF-17 exhibited a high proton conduction value over \(10^{-3}\) S cm\(^{-1}\) at RT and low relative humidity (40% RH). Therefore, in a material with modest stability to water, the grain boundary contribution to proton conductivity was augmented by facile movement of ions through a more fluid interface. It should be mentioned that two archetypical MOFs (MOF-5 and Ni-MOF-74) were also artificially amorphized by exposing the frameworks to air at 40% humidity at RT from 0 to 24 h. The textural properties were not explored in these studies.

2.6.3. Amorphization by ligand competition. Recently, an aMOF nanocomposite [a-MOF-NC] has been synthesized by a ligand-competition amorphization pathway. MIL-88B (Fe\(^{1+}\)O(BDC-NH\(_2\))\(_3\), BDC-NH\(_2\) = 2-aminoterephthalic acid) with a nanorod morphology was treated in MeIm solution to induce amorphization and generate amorphous MIL-88B (a\(_{CT}\)-MIL-88B). The amorphization occurred due to the competition between BDC-NH\(_2\) and MeIm ligands. Subsequently, a-MOF-NC was obtained by further adding Co\(^{2+}\) into the reaction solution (Fig. 15). The a-MOF-NC possessed a core–shell nanorod@nanosheet architecture. The core–shell nanorod was structured into a Fe-rich Fe–Co-amorphous MOF core and a Co-rich Fe–Co-amorphous MOF shell. The nanosheets were amorphous Co(OH)\(_3\). The BET specific surface area of MIL-88B, a\(_{CT}\)-MIL-88B and a-MOF-NC was found to be 168.2, 66.2 and 46.8 m\(^2\) g\(^{-1}\), respectively. The a-MOF-NC exhibited excellent performance for OER with a low overpotential of 249 mV at 10.0 mA cm\(^{-2}\) and a Tafel slope of 39.5 mV dec\(^{-1}\) in 0.1 M KOH solution.

2.6.4. Loading induced amorphization. Recently, an example of amorphization induced by loading nanoparticles has been reported by Zhang et al. Ag-based nanoparticles were uniformly dispersed on UiO-66. The framework structure was maintained at a loading of Ag of 2 wt%. However, UiO-66 amorphized at higher Ag loading (6, 10, and 14 wt%). The BET specific surface area of UiO-66 with 2, 6, 10, and 14 wt% of Ag loaded was reported to be 473, 11.5, 11.8, and 13.6 m\(^2\) g\(^{-1}\), respectively. The decrease of specific surface area from 473 to 11.5 m\(^2\) g\(^{-1}\) was suggested to be related to the amorphization of UiO-66. When Ag loading was 10 wt%, the catalytic performance for toluene oxidation was the best, likely, due to the lattice oxygen and surface Ag\(^0\) content. Toluene was catalytically converted to benzaldehyde and benzoic acid, eventually forming CO\(_2\) and H\(_2\)O. Therefore, a catalyst for toluene oxidation was successfully prepared, even though the framework collapsed.

2.7. Direct synthesis of amorphous MOFs

aMOFs have been mostly prepared in a top-down approach by applying stress and introducing disorder into the parent frameworks. In this section, bottom-up approaches for the synthesis of aMOF are described. However, this new paradigm is in its infancy. The design principles of bottom-up synthesis of porous aMOFs still need to be developed. However, it is anticipated that the combination of porous materials and soft matter sciences will lead to the discovery and development of many unexplored new materials and devices.

Lohe et al. reported the synthesis of an amorphous Fe-BTC aerogel \([\text{Fe}\text{[III]}\text{O}(\text{C}_{6}\text{H}_{4}\text{(COO)}_{3})_{3}]\text{NO}_{3}\) with impurities of water and ethanol. The MOF aerogel with permanent micro- and macroporosity was obtained in a sol–gel approach followed by supercritical CO\(_2\) drying. The BET specific surface area and total pore volume of the aerogel were reported to be 1618 m\(^2\) g\(^{-1}\) and 5.62 cm\(^3\) g\(^{-1}\), respectively. The air-dried powdered sample (xerogel) displayed a BET specific surface area and total pore volume of 1183 m\(^2\) g\(^{-1}\) and 0.71 cm\(^3\) g\(^{-1}\). Later, Klepper et al.
preformed thin films of amorphous organic–inorganic hybrid materials made from carboxylic acids (oxalic, malonic, succinic, glutaric, pimelic, suberic and sebacic acid) and trimethylaluminium (TMA) by atomic layer deposition (ALD).89 The carboxylic acid–TMA interactions were proposed to be of a bidentate type. As special cases, in the malonic, succinic, and sebacic acid–TMA systems, those interactions were suggested to be of both a bidentate and/or a bridging type. Recently, an amorphous Nd-based thin-film MOF (Nd-TP) has been synthesized by atomic/molecular layer deposition (ALD/MLD) from sublimated Nd(thd)₃ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) and BDC precursors at 200 °C.90 Nd-TP underwent an amorphous-to-crystalline phase transition upon RT humidity treatment (70% RH). A subsequent heat treatment completely removed the coordinated water molecules; however, the crystallinity was retained. The crystalline framework was able to reversibly adsorb and release water without losing crystallinity during several cycles. Nd-TP showed photoluminescence switching upon the amorphous-to-crystalline transition, having the emission intensity at 880 nm significantly higher for the amorphous film than for the crystalline film.91 Supersonic cold-spraying technique has also been used to deposit thin films. The technique is a high-rate coating method. It is based on the expansion of compressed gas through a convergent–divergent De Laval nozzle, thus creating a supersonic gas stream. Particles are injected into the mentioned gas prior deposition to the substrate. Those particles with supersonic velocities, possess enough kinetic energy to bond to the substrate upon impact (Fig. 16).91 By applying this technique, a-ZIF-8 films were directly obtained at high air pressure (exceeding 7 bars) which led to particle velocity of about 500 m s⁻¹.92 The loss in long-range ordering was attributed to the lattice strain in the compacted films. It is noteworthy that the cold-spray coating technique allowed preferentially oriented films. The cold-spray coating method enabled successful deposition of ZIF-8 films with (112)-oriented crystal structures in the presence of 20% DMF in the colloidal sol. Random polycrystalline ZIF-8 nanoparticles were deposited in the absence of DMF. Therefore, supersonic cold spraying is an excellent technique for manipulating the crystal structures and physical properties of MOF films.92

In their seminal work, Xin et al. prepared amorphous Zn(ICA)-2 MOF (a-Zn(ICA)-2) by direct addition of triethylamine (TEA) to the DMF solution of imidazole-2-carboxyaldehyde (ICA) and Zn(NO₃)₂·6H₂O at RT.93 The formation of amorphous phase was attributed to the direct addition of TEA. When TEA was added into the DMF solution, the reagents (Zn²⁺ and ICA) reacted immediately and formed a large number of coordination polymers (CPs). Those CPs formed irregular nanospheres with diameters of about 20 nm that, in turn, built a superstructure. Mesopores were randomly formed between the nanoparticles. The average mesopore diameter was calculated to be about 6–9 nm. Moreover, the BET surface area of a-Zn(ICA)-2 was 251 m² g⁻¹.93 Amorphous UiO-66 (a-Uio-66) has also been solvothermally prepared.94 a-Uio-66 was applied as the electrode material for supercapacitors. The specific capacitance of a-Uio-66 was as high as 920 F g⁻¹ at 10 mV s⁻¹, much superior to 452 F g⁻¹ of crystalline UiO-66. Moreover, the specific capacitance of a-Uio-66 was maintained up to 610 F g⁻¹ after 5000 cycles. The superior electrochemical performance of a-Uio-66, compared with crystalline UiO-66, was related to the metastable nature and the disorder of the amorphous framework which provided more active sites. In addition, the specific capacitance of a-Uio-66 was attributed to the faradaic reactions taking place at the surfaces and in the interior of the electrode, whereas for crystalline UiO-66, the specific capacitance was ascribed to the faradaic reactions taking place only at the surface of the electrode. Therefore, a-Uio-66 has a promising potential as a supercapacitor electrode material.94 A pH-responsive phase transformation from amorphous UiO-66-SO₃H to crystalline UiO-66-SO₃M (M = Li, Na, K) has been realized by neutralizing UiO-66-SO₃H with various alkali hydroxide solutions (LiOH, NaOH, KOH).95 The recovered crystallinity was attributed to bond breakage and metalation. Firstly, the hydrogen bonds among sulfonate acids were broken. Then, metalation occurred as well as the subsequent charge repulsion in UiO-66-SO₃M which expanded the collapsed framework and helped to recover crystallinity and porosity. It is worth mentioning that the initial amorphous UiO-66-SO₃H was directly synthesized using monosodium 2-sulfoterephthalate (SS-BDC) ligand. Whereas the BET specific surface area of amorphous UiO-66-SO₃H was only 11 m² g⁻¹, crystalline UiO-66-SO₃Li, UiO-66-SO₃Na and UiO-66-SO₃K exhibited a BET specific surface area of 148, 95 and 26 m² g⁻¹, respectively. The CO₂ uptake of crystalline UiO-66-SO₃K was 311% the capacity of amorphous UiO-66-SO₃H.95

Amorphous two-dimensional (2D) bimetallic Fe₃Ni₂(BDC-NH₂) MOF has been prepared by a mild RT solution phase method, and then physically deposited onto the Ni foam (Fe₃Ni₂(BDC-NH₂)/NF).96 The BET specific surface area of amorphous Fe₃Ni₂(BDC-NH₂) was reported to be 142.2 m² g⁻¹. The as-synthesized Fe₃Ni₂(BDC-NH₂)/NF was directly utilized as an efficient and robust OER electrocatalyst in alkaline medium (1.0 M KOH). It exhibited a low overpotential of 228 mV at a current density of 10 mA cm⁻² and a Tafel slope of 30.3 mV dec⁻¹. It also showed quite good operational stability in continuous electrolysis. Therefore, aMOFs possess great potential in the field of electrocatalysis.96 In another study,
A series of FeMn-MOF-74 MOFs (from amorphous to highly crystalline) were developed by temperature-controlled crystallization (Fig. 17). The amorphous FeMn-MOF-74 (a-FMM-120), prepared at 120 °C, showed a BET specific surface area of 42.55 m² g⁻¹. a-FMM-120 with optimal Fe/Mn radio possessed a saturation arsenic uptake capacity of 161.6 mg g⁻¹, which is the highest among MOF-based arsenic adsorbents. a-FMM-120 maintained the adsorption capacity during regeneration and reuse process, or in an anion-rich environment. These results were attributed primarily to the synergistic effect of homogeneous distribution of adsorption/oxidation sites and low-coordinated active centers. Therefore, the amorphous a-FMM-120 is a promising adsorbent for efficient arsenic-contaminated water remediation.

Amorphous Zr₁₀O₆C₆H₄₆N₄ MOF nanosheets with different surface charges have been synthesized by the addition of acetic acid (HAc) in the reaction system. Moreover, raising the amount of the HAc modulator also increased the size of the framework. The MOFs prepared with 0.1, 0.3, and 0.5 mL of HAc, named as CPPs-1, CPPs-3 and CPPs-5, displayed BET specific surface areas of 584.7, 522.4, and 587.5 m² g⁻¹, respectively. CPPs-1 showed maximum adsorption capacities for methylene blue (MB) and Congo red (CR) of 276.9 and 650.3 mg g⁻¹, respectively. CPPs-3 and CPPs-5 had adsorption capacities of 192.0 and 110.8 mg g⁻¹ for MB, respectively. The adsorption capacities of CPPs-3 and CPPs-5 for CR were 528.1 and 650.3 mg g⁻¹, respectively. Surprisingly, the adsorption capacity of CPPs-1 toward the anionic dye CR was much higher than that of CPPs-5, even though CPPs-1 had a negatively charged framework and CPPs-5 had a positively charged one. Therefore, amorphous CPPs-1 is promising in removal of dyes for water treatment. Similarly, amorphous Ni-pPD MOF nanosheets (a-Ni-pPD, pPD = p-phenylenediamine) were synthesized in water in the presence of NH₄OH and exposed to ambient air (Fig. 18). The BET surface area of a-Ni-pPD was 35 m² g⁻¹. It showed a large intersheet spacing of 1.6 nm, facilitating its ultra-fast and highly reversible intercalation reactions with tetraethylammonium cations (TEA⁺). When coupled with an activated carbon cathode in the organic electrolyte of ethylammonium tetrafluoroborate/acetonitrile (TEABF₄/CAN), the 230 μm-thick a-Ni-pPD anode showed a high gravimetric capacitance of 259 F g⁻¹ and a high areal capacitance of 2.9 F cm⁻² at a high discharging rate of 2 A g⁻¹ within a wide potential window of 2.85 V. It also displayed an excellent cycling stability for over 12 000 cycles. It resulted in an exceptionally high areal usable energy of 0.9 mWh cm⁻² for the full cell. According to in situ electrochemical AFM, high kinetics at high potentials are attributed to the increased intersheet spacing under large polarization.

A series of amorphous Zr-based MOFs have been synthesized by reacting carboxylic acid functionalized clathrochelates with ZrCl₄. Those rigid, large (up to 2.2 nm), and robust mono- and dinuclear clathrochelate complexes with up to five carboxylic acid groups were prepared by metal-templated reactions (Fig. 19). The carboxylic acid groups were oriented in a divergent fashion, with well-defined coordinate vectors. Amorphous Zr-MOF(23) and Zr-MOF(24) were obtained by reacting ZrCl₄ with carboxylic acid functionalized clathrochelates 2 and 4 (see Fig. 19a) in DMF, respectively. Similarly, amorphous Zr-MOF(25) and Zr-MOF(26) were created by the reaction of ZrCl₄ with carboxylic acid functionalized clathrochelates 13 and 15 (see Fig. 19b) in DMF, respectively. Those amorphous Zr-based MOFs displayed permanent porosity after solvent removal. The BET specific surface areas of Zr-MOF(23), Zr-MOF(24), Zr-MOF(25) and Zr-MOF(26) were found to be 410 m² g⁻¹, 955 m² g⁻¹, 535 m² g⁻¹, and 546 m² g⁻¹, respectively. It is worth mentioning that the surface area of Zr-MOF(24) was more than twice that of Zr-MOF(23). Therefore, it was possible to use the lateral oximato ligands for modulating the porosity of the MOFs.

Ueda et al. have fabricated an aMOF from organometallic ILs upon UV irradiation. The ILs [Ru(C₅H₅)[C₆H₄R]][B(CN)₄] (R = butyl, ethyl, octyl) exposed at UV light irradiation for 1 h, followed by removal of C₆H₄R group, generated the amorphous...
[\text{Ru}(\text{C}_5\text{H}_5)\{\text{B}((\text{CN})_4)\}]_n \text{ MOF (Fig. 20). The framework was formed due to coordination of the [B(CN)]^- to the Ru ion. Thus, the polycyano anion acted as a bridging ligand to form the 3D framework. The C_6H_5R ligands released during the reaction were removed by vacuum drying at 80 °C or by washing with methanol. Depending on alkyl chain length of the ILs, the BET surface area of a-[\text{Ru}(\text{C}_5\text{H}_5)\{\text{B}((\text{CN})_4)\}]_n ranged from 202 to 80 m^2 g^{-1}. The total pore volume was determined to be 0.27 cm^3 g^{-1}. Interestingly, the ILs were able to be recovered from a-[\text{Ru}(\text{C}_5\text{H}_5)\{\text{B}((\text{CN})_4)\}]_n by means of solvent treatment.\textsuperscript{101} Elsabawy \textit{et al.} have reported the synthesis of an amorphous Ni-based MOF (Ni\textsuperscript{++-1,3,5-tribenzyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione}) via microwave-assisted hydrothermal technique.\textsuperscript{102} The BET specific surface area of this aMOF was found to be 3181 m^2 g^{-1}. The carbon dioxide maximum uptake capacity for the amorphous-Ni-MOF was 118.2 mg g^{-1} at 30 °C and 27 bar.\textsuperscript{102} Recently, three amorphous (or poorly crystalline) MOFs A_0.25B-NiFe, A-NiFe and A_3C-NiFe (A = BDC, B = BDC-NH_2, C = 2-fluoroterephthalic acid = BDC-F) have been synthesized by ultrasonication at RT.\textsuperscript{103} TEA helped to deprotonate the carboxylic groups. The alkaline solvent also improved the reaction rate. It was reported that the electron-donating substitutes with low electronegativity increased the oxygen vacancies and enhanced the charge transfer, and consequently, improved the OER activity. Thus, A_0.25B-NiFe exhibited lower overpotential (237 mV at 10 mA cm^{-2}) and superior stability than its analogous frameworks.\textsuperscript{103}

Amorphous Co(MeIm)_2 (a-Co(MeIm)_2)\textsuperscript{104} has been used to encapsulate AuCo nanoparticles. AuCo-MeIm was synthesized by a self-template approach in which AuCo nanoparticles provided the Co(n) source to construct a-Co(MeIm)_2. Thus, AuCo cores were immobilized by a-Co(MeIm)_2 coatings. AuCo-
MeIm showed size-selective photocatalytic performance to remove Cr(VI) and MB. 82% and 84% of Cr(VI) were removed by AuCo and AuCo-MeIm, respectively. The great removal of Cr(VI) by AuCo-MeIm was attributed to the synergistic effect of AuCo cores and a-Co(MeIm)2 coatings. On the other hand, whereas AuCo degraded 78% of MB, AuCo-MeIm degraded only 57% of MB. Despite a-Co(MeIm)2 coatings increased contact between MB and catalyst, the degradation of MB decreased from AuCo catalyst to AuCo-MeIm catalyst. Therefore, a-Co(MeIm)2 coating offered resistance to the diffusion of MB. In addition, a-Co(MeIm)2 coatings also avoided the aggregation of AuCo particles. In a similar manner, amorphous Fe-ZIF-67 (a-Fe-ZIF-67) fibers have been used as a precursor to prepare sheet-like mesoporous nitrogen-doped graphene (MNG) with encapsulated CoFe alloy nanoparticles (MNG-CoFe). a-Fe-ZIF-67 was initially prepared by grinding of Co and Fe salts with MeIm-coated NaCl crystals. MNG-CoFe was subsequently obtained by carbonization in N2 flow, and posterior acid etching (Fig. 21). MNG-CoFe displayed high BET specific surface area as well as porosity within the mesoporous range. This catalyst exhibited a remarkable activity and stability for OER, oxygen reduction reaction (ORR), and hydrogen evolution reaction (HER), due to high electrochemical surface area (ECSA), active site density, and electron conductivity. Those performances were comparable and even superior to the benchmark platinum group metal (PGM) electrocatalysts.

The in situ packaging of enzymes in an amorphous ZIF (a-ZIF) at ambient conditions has been reported by Wu et al. The amorphous enzyme–ZIF nanocomposite was prepared by a one-step process, simply by mixing enzyme, metal ions, and organic ligands in an aqueous solution. The amorphous structure was produced by coordination defects between metal ions and organic ligands. a-ZIF with glucose oxidase (GOx) encapsulated (GOx-aZIF) exhibited 20 times higher activity than that in crystalline MOFs. Similarly, Candida antarctica lipase B (CALB) and catalase (CAT) in a-ZIF composites exhibited ~5 times higher activity than in corresponding ZIF-8 composites. Moreover, a-ZIF protected the encapsulated enzymes, displaying high stability. The delivery of GOx by a-ZIF enabled noninvasive detection of glucose in a single living cell, which discriminated cancerous from normal cells.

In another study, Lee et al. analyzed the morphological and structural evolutions of MOFs driven by different degrees of contribution of two organic linkers (BDC and isophthalate (IPA)) during the MOF construction. Highly crystalline porous MOFs with morphology of hexagonal rod were generated from the reaction of In3+ and BDC when the contribution of BDC linkers within the framework was dominant. However, when the contribution of the IPA linkers was superior, amorphous non-porous MOFs with spherical morphology were produced from the reaction of In3+ and IPA. Accordingly, whereas the BET surface area and total pore volume of the crystalline MOF were 1506 m2 g−1 and 0.73 cm3 g−1, respectively, the BET surface area and total pore volume of the aMOF were reported to be 69 m2 g−1 and 0.25 cm3 g−1, respectively. The morphology and porosity of MOFs constructed from the reactions of In3+ in the presence of both BDC and IPA were located somewhere between porous hexagonal rods and amorphous spheres (Fig. 22).

Gao et al. have proposed a strategy to construct amorphous coordination polymer microspheres. Such approach is based on distorting crystalline MOFs by introducing flexible building blocks during the solvothermal process. Specifically, bio-MOF-
100 (Zn\textsubscript{a}(ad)\textsubscript{b}(bpdc)\textsubscript{c}O\textsubscript{d}·4Me\textsubscript{c}NH\textsubscript{d}, ad = adeninate) was shown to collapse into amorphous coordination polymer microspheres by replacing rigid bpdc linkers by flexible SBDC linkers (SBDC = 4,4’-stilbenedicarboxylic acid). The amorphous coordination polymers spontaneously self-assembled into the microspheres to reduce surface energy. The microspheres possessed a Q factor as high as ~10\textsuperscript{4} and provide sufficient feedback for high quality single-mode lasing oscillations. The diameter of the microspheres was controlled by modulating the precursor concentration during the assembly process. Thus, the single or multi-mode lasing resonance was easily adjusted. This work opens a new way to construct flexible whispering-gallery-mode (WGM) based photonic components.\textsuperscript{108}

In a recent work from our research group, a liquid–liquid interface strategy to prepare mainly amorphous but also crystalline MOFs has been invented.\textsuperscript{140} The method was based on using a high electron-donating solvent and a complementary co-solvent to cushion basicity. The reaction medium consisted of two solutions with low miscibility, separated by an intermediate region. Under static conditions, metal ions and deprotonated ligands diffused into the intermediate segment where the synthesis of MOFs occurred.\textsuperscript{140} So far, up to 7 aMOFs have been synthesized by applying this approach. An amorphous Fe-based MOF, named as NEU-2, \{Fe(BPDI)\{Py\}\textsubscript{2}, BPDI = N\textsubscript{2}N\textsubscript{2}-bis(glycyl)pyromellitic diimide, Py = pyridine\} with multichannel pore systems was synthesized, and subsequently tested as class 1 sorbent by evaluating its CO\textsubscript{2} capture capacity.\textsuperscript{110} The BET specific surface area and total pore volume of NEU-2 were found to be 220.9 m\textsuperscript{2} g\textsuperscript{-1} and 0.554 cm\textsuperscript{3} g\textsuperscript{-1}. Amorphous NEU-3 (Zn(PMDA)\{Py\}\textsubscript{2}, PMDA = N\textsubscript{2}N\textsubscript{2}-pyromelliticidiimido-di-t-alanine) and NEU-4 (Fe(PMDA)\{Py\}\textsubscript{2}) were also synthesized by applying the aforementioned method.\textsuperscript{111} The BET specific surface area and total pore volume of NEU-3 were 94.2 m\textsuperscript{2} g\textsuperscript{-1} and 0.598 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. In NEU-4, the BET specific surface area and total pore volume were 293.8 m\textsuperscript{2} g\textsuperscript{-1} and 0.649 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. These MOFs along with NEU-1c (Zn(BPDI)\{Py\}\textsubscript{2}) and NEU-2 were smart guest-responsive materials due to their π Lewis acidic pore surface and framework flexibility. NEU-1c, NEU-2, NEU-3 and NEU-4 were reported to perform a variety of effects on adsorption and adsorptive separations. Specifically, NEU-4 showed ultrahigh benzene adsorption, recognition capability, selectivity for benzene over cyclohexane, dioxane, toluene, p-xylene and nitrobenzene, and high stability and regenerability.\textsuperscript{112}

In a subsequent study, we merged our liquid–liquid interface synthesis method and the metallolidigand approach to create a general method for the design and synthesis of bimetallic aMOFs.\textsuperscript{113} As proof-of-concept, NEU-5 \{[Zn(Fe\textted{Tpy}COO)\{PF\{}_2\textsubscript{2}\}\textsubscript{2}, NEU-6 \{[Zn(Ru(terpy)\textted{3})\{PF\{}_2\textsubscript{2}\}\textsubscript{2}, NEU-7 \{[Fe(Ru(terpy)\textted{3})\{PF\{}_2\textsubscript{2}\}\textsubscript{2} and NEU-8 \{[Ti(Ru(terpy)\textted{3})\{PF\{}_2\textsubscript{2}\}\textsubscript{2} were prepared. The BET specific surface area and the total pore volume of NEU-5 were 10.2 m\textsuperscript{2} g\textsuperscript{-1} and 0.027 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. In NEU-6, the BET specific surface area was 18.2 m\textsuperscript{2} g\textsuperscript{-1} and the total pore volume was 0.162 cm\textsuperscript{3} g\textsuperscript{-1}. In contrast with nonporous NEU-5 and NEU-6, NEU-7 and NEU-8 possessed a BET specific surface area of 174.2 and 244.2 m\textsuperscript{2} g\textsuperscript{-1}, respectively. In addition, the total pore volume of NEU-7 and NEU-8 was 0.262 and 0.305 cm\textsuperscript{3} g\textsuperscript{-1}, respectively. It must be mentioned that electro- and photoelectro-catalysts based on the controlled pyrolysis of those frameworks were developed for efficient catalysis toward HER, OER and ORR in both acidic and alkaline media. We anticipate that high-performance functional aMOFs for various applications will be created by these synthesis strategies.\textsuperscript{112}

Guan et al. have also prepared catalysts via the controlled pyrolysis, in this case, of amorphous coordination polymers as precursors.\textsuperscript{141} It should be highlighted that those catalysts were mixed metal oxides with multi-shelled morphology. Ni-Co coordination polymer spheres were synthesized and subsequently transformed into seven-layered Ni-Co oxide shells via rapid thermal oxidation (Fig. 23). That Ni–Co coordination polymer was synthesized by coprecipitation of Co\textsuperscript{2+} and Ni\textsuperscript{2+} ions in the presence of IPA at 160 °C for 4 h. Mn–Co, Mn–Ni, Zn–Mn, and Mn–Co–Ni oxide shells were also obtained by the thermal oxidation of amorphous mixed transition-metal coordination precursors. The multi-shelled Ni–Co oxide exhibited exceptional charge storage capability in aqueous electrolyte with high specific capacitance (~1900 F g\textsuperscript{-1} at 2 A g\textsuperscript{-1}), good rate capability, and ultrahigh cycling stability (93.6% retention over 20 000 cycles). A hybrid supercapacitor against graphene/multi-shelled mesoporous carbon sphere showed an energy density of 52.6 W h kg\textsuperscript{-1} at a power density of 1604 W kg\textsuperscript{-1}, as well as remarkable cycling stability.\textsuperscript{113}

It is worth mentioning those studies, which implicated aMOFs, performed with an end-goal, even though they did not explore the structural characteristics of the involved frameworks. As a representative work, the surface of Li(Li\textsubscript{0.17}Ni\textsubscript{0.20}Co\textsubscript{0.05}Mn\textsubscript{0.58})\textsubscript{2}O\textsubscript{2} has been coated with a homogeneous and amorphous Mn-based MOF layer with thickness of 2–3 nm.\textsuperscript{114} The crystalline structure of Li-rich layered oxide was maintained after the surface modification. As compared with the as-prepared material, Li(Li\textsubscript{0.17}Ni\textsubscript{0.20}Co\textsubscript{0.05}Mn\textsubscript{0.58})\textsubscript{2}O\textsubscript{2} modified with MOFs presented larger discharge capacity (323.8 mA h g\textsuperscript{-1} at 0.1C rate), high initial coulombic efficiency (91.1%), and good thermal stability without harming the cycle performance and high-rate capability. The improvement in electrochemical performance is mainly attributed to the good oxygen storage capability of the aMOF layer.\textsuperscript{114} Therefore, the surface modification of Li-rich layered oxides with aMOFs is a feasible and effective approach to enhance the discharge capacity for advanced lithium-ion batteries.

In another study, silver nanowires (Ag NWs) have been introduced into an amorphous 2D MOF nanolayer (a-CoL NL) by one-step solution agitation method at RT.\textsuperscript{115} In doing so, an amorphous 2D layer architecture (a-CoL NL) was constructed. It must be mentioned that a-CoL NL was previously synthesized via self-assembling. The BET surface area of A-CoL NL, Ag NWs, and A-CoL/Ag NW were reported to be 105.7, 24.1, and 83.6 m\textsuperscript{2} g\textsuperscript{-1}, respectively. Conductive a-CoL/Ag NW provided good contact between electrode materials and electrolyte ions and facilitated the transport of ions and electrons. It resulted in high specific capacitance, high output potential, great rate capacity at high current density, and long-term cycle stability. A-CoL/Ag NW electrode reached up to 1467 mF cm\textsuperscript{-2} at 1.0 mA cm\textsuperscript{-2}, and 1060 mF cm\textsuperscript{-2} even at 10.0 mA cm\textsuperscript{-2}. The A-
Activated carbon asymmetric supercapacitor (AC ASC) displayed a maximum energy density (110 W h kg\(^{-1}\) at 760 W kg\(^{-1}\)) and maximum power density (6410 W kg\(^{-1}\) at 63 W h kg\(^{-1}\)) in 3.0 M KOH. Moreover, the solid-state A-CoL/Ag NW//AC ASC had a broad operating potential window within 0–1.6 V, long cycle life (95.2% after cycling 7000 cycles), delivering an energy density of 151 W h kg\(^{-1}\) (at 790 W kg\(^{-1}\)), and a power density of 7972 W kg\(^{-1}\) (at 70 W h kg\(^{-1}\)).

Fischer et al. have prepared the first anionic aluminum MOF constructed from tetrahedral AlO\(_4\) SBUs (Al-Td-MOF-1, Li\([\text{Al(C}_6\text{H}_4\text{O}_2\text{)}_2]\]).\(^{116}\) It was synthesized in a two-step approach passing through an intermediate specie (an amorphous aluminate framework). While the BET surface area of Td-MOF-1 was reported to be 656 m\(^2\) g\(^{-1}\), the amorphous aluminate intermediate framework displayed a BET surface area of 52 m\(^2\) g\(^{-1}\). RT Li\(^+\) conductivity of 5.7 ± 1.9 × 10\(^{-5}\) and 0.7 ± 0.2 × 10\(^{-5}\) S cm\(^{-1}\) was found for Al-Td-MOF-1 and the amorphous aluminate intermediate framework, respectively. It was suggested that the amorphous aluminate intermediate framework had more dead-end pathways or defects which reduced the effective number of mobile charge carriers.\(^{116}\)

A one-dimensional (1D) super-long single-crystal Co-MOF nanotube (Co-MOF-74-NT, [Co\(_2\)(dhta)(H\(_2\)O\(_2\))\(_2\)×8H\(_2\)O]) has been fabricated by recrystallization of amorphous MOF-74 nanoparticles (a-Co-MOF-74-NP).\(^{117}\) Co-MOF nanotube was larger than 30 μm, with an average diameter of 66.8 ± 13.8 nm, corresponding to an aspect ratio larger than 400. The BET surface area of Co-MOF-74-NT was 848.8 m\(^2\) g\(^{-1}\). Co-MOF-74-NT was employed as a highly efficient nano column for the separation of large dye molecules such as MB and rhodamine B in aqueous solution. Co-MOF-74-NT was also an excellent precursor for preparing carbon nanostructures. An N-doped 3D hierarchical dendrite with carbon nanofiber trunks and carbon nanotube branches (NCo@CNT-NF) was created by the carbonization of Co-MOF-74-NTs in the presence of a secondary carbon and nitrogen source (dicyandiamide). NCo@CNT-NF exhibited excellent electrocatalytic activity for ORR, and exceptional applications in rechargeable Zn-air batteries.\(^{117}\)

Li et al. have uniformly coated a hollow sphere made of silica-supported Ni-based nanoparticles (Ni/SiO\(_2\)) with a-Ni-MOF-74.\(^{118}\) The released Ni\(^{2+}\) ions from the Ni nanoparticles interacted with a solution of dhta to form a-Ni-MOF-74 shell. This achieved a controlled spatial distribution of Ni nanoparticles at the interface between the SiO\(_2\) support and uniform a-Ni-MOF-74 shell. The developed Ni/SiO\(_2\)@a-Ni-MOF-74 catalyst was tested for tandem imination of nitrobenzene with benzaldehyde (Fig. 24). This catalyst exhibited 91.2% selectivity toward valuable imine product at 100% conversion of...
2.8. Perspectives in amorphous MOFs

As reviewed, distinct aMOFs can be obtained from the same starting MOF by different methods such as electrical discharge, mechanical milling, pressure, etc. Aside from the differences in the adsorption performance of the resulting aMOFs, another important question is determining their structural differences. This subjects to defining and comparing the short- and intermediate-range structure of those aMOFs. However, determining the structures of aMOFs is challenging due to the inability to make use of standard diffraction methods. aMOFs have generally been characterized by X-ray or neutron total scattering experiments.18,22,62 These techniques yield the total scattering function (\(S(Q)\)), which includes information on both Bragg and diffuse scattering. After suitable data reduction, the Fourier transform of \(S(Q)\) generates the PDF (\(G(r)\)). PDF describes the degree of local and intermediate ordering within amorphous solids.11 Although these are powerful techniques, they are not able to fully characterize an aMOF. In contrast, ssNMR spectroscopy can characterize the local structure and dynamics of aMOFs.120,121 This technique provides information that X-ray or neutron total scattering experiments cannot offer. Thus, we consider that ssNMR analysis is an essential tool in the characterization of aMOFs. In the coming years, we expect ssNMR to become the predominant characterization technique to determine the structural differences of aMOFs.

The main barriers to the application of aMOFs are the structure elucidation and the absence of porosity. Moreover, the distinction between true amorphous frameworks and those with poor crystallinity may be challenging.45 However, as the field of MOFs move to the amorphous state, new lines of research appear:

(1) Amorphized MOFs may achieve serious breakthroughs in natural gas purification. Specifically, amorphous MMMs have already been found to be highly stable and boost the gas separation performance to very high \(CO_2/CH_4\) selectivities.99 aMOFs are expected to successfully realize other similar adsorptive separations.111 The inherent flexibility and porosity of aMOFs will facilitate control over shape-selective adsorptions that preferentially retain compounds with specific dimensions.

(2) As reviewed, amorphized MOFs are proven to be promising materials to storage radioisotopes before incorporation into a long-term waste.18,66 They also have potential to delay the delivery of guest molecules.59,66 Both applications are based on the concept of trapping guest molecules by irreversibly collapsing porous networks around occluded species. To accomplish a controlled release of the guest molecules, it is required a compromise between the pore size of the MOF and the size of the loaded molecules.

(3) In water treatment, aMOFs are postulated to efficiently adsorb and remove heavy metals such as chromium and arsenic.97,104 In addition, they are also expected to remove dyes including MB and CR.96,99,104 Those presumptions are ascribed to the expected synergy between adsorption sites, which must be homogeneously distributed, and low-coordinated active centers in aMOFs.

(4) As-prepared aMOFs also possess great potential in the field of catalysis, which is in good agreement with the attention
that other related amorphous materials have received in this field during the last few years.\textsuperscript{122,123} Thus far, aMOFs-based catalysts have been prepared for toluene oxidation, OER and CO oxidation.\textsuperscript{85,86,90,103} The good catalytic activity of aMOFs is presumed to be related to their high density of active sites, which, in turn, may be connected to their density of defects at the molecular level. In addition, efficient electro- and photoelectro-catalysts based on the controlled pyrolysis of aMOFs and amorphous coordination polymers have been already developed.\textsuperscript{112} Therefore, it is expected that high-performance catalysts will be generated from the post-synthetic treatment of aMOFs.

(5) The development of sensors for humidity, pressure and other stimuli from aMOF is an attractive idea, even though is perhaps far at this stage. However, those aMOFs with piezo-chromism,\textsuperscript{35} displaying photoluminescence switching\textsuperscript{90} or with semiconductor behavior\textsuperscript{81} are a promising commencement.

(6) It is worth mentioning that stresses may lead to unique properties such as water stability,\textsuperscript{73} magnetism,\textsuperscript{81} etc. Besides, stresses may also induce porosity in conventionally nonporous materials.

(7) Notably, new multifunctional and intelligent aMOFs with physicochemical properties that are difficult (if not impossible) to be obtained in related materials will be created by overcoming the challenge of designing and constructing amorphous frameworks from molecular building blocks.\textsuperscript{109}

Synthesis approaches and promising applicability of aMOFs have been presented throughout this Review. It is anticipated that the field of aMOFs will attract further research in the coming years.

3. MOF liquids

3.1. Introduction

MOF liquid is defined as a liquid formed from the melting of a MOF, due to the retention of chemical configuration and coordinative bonding modes between the solid and liquid phases.\textsuperscript{124} Melting from a crystalline solid state to a liquid state is a common phenomenon in nature. In the framework of classical thermodynamics, melting of a solid occurs at a critical temperature at which Gibbs free energies of the solid and the liquid states are equal. From the chemistry viewpoint, melting of MOFs strongly depends on the interaction strength between the metal nodes and organic ligands.\textsuperscript{125} Usually, the coordinative interaction between metal nodes and linkers is stronger than the covalent bonding within the linkers.\textsuperscript{126} Therefore, thermal decomposition of the organic ligands typically happens before melting.\textsuperscript{127} However, a few MOFs have undergone melting prior to decomposition, which has been correlated to metal-ligand dissociation.

Lindemann criterion is widely used for predicting melting points ($T_m$), even though it is not thermodynamically sound.\textsuperscript{128} Lindemann’s rule (eqn (4)) to empirically forecast $T_m$:

$$f = \frac{u d}{T_m} \quad (4)$$

where $f$ is the Lindemann ratio, $u$ is the mean thermal atomic displacement (the square root of the Debye–Waller factor) of an atom, and $d$ is the bond distance to the nearest neighbor atom. Melting of inorganic systems has been observed when $f$ ranges from 0.10 to 0.13.\textsuperscript{129}

Eqn (5) quantified the dynamic behavior of a supercooled liquid.

$$m = \frac{d [\log(\eta)]}{d \left( \frac{T}{T_g} \right)} \quad (5)$$

where $m$ is the fragility index, $\eta$ is viscosity, and $T$ and $T_g$ are the temperature and glass temperature, respectively. $m$ measures the activation energy of the viscosity at the glass transition. In other words, $m$ quantifies the speed of the dynamical processes of a liquid as it approaches the glass transition temperature. $T_g$ is defined to occur when viscosity reaches $10^{12}$ Pa s. Fragilities for some low-density liquid (LDLs) fall between 12 and 14. They are super-strong liquids, the antecedents of perfect glasses.\textsuperscript{3}

In this section, background based on related porous liquid materials is firstly provided to contextualize the study on MOF liquids. Then, several related comprehensive studies of MOF liquids are summarized (Table S2†). We finish providing what we consider to be interesting prospects in the field of MOF liquids. Even though glass materials appear along this section, the theory behind glasses will be explained in the following one.

3.2. Discussion

In an early study, Giri et al. reported the first large, rigid organic cages to show measurable $T_m$.\textsuperscript{130} Rigid organic iminospherand cages were formed by imine condensation between four 1,3,5-triformylbenzene molecules and six functionalized-diamines (see Fig. 26). Below their $T_m$, (6) and (9) were amorphous, non-porous glass solids; (7) formed solvated crystals that became amorphous upon desolvation; and (8) was a crystalline cage that could be desolvated to generate permanent microporosity. The BET specific surface area of (8) was 289 m$^2$ g$^{-1}$. While analogous cages lacking alkyl chains decompose at $>300$ °C without melting, the alkylated cages had access to the liquid state. The melting point of cages (6), (7), (8) and (9) was shown to be 127 °C, 156 °C, 198 °C and 50 °C, respectively. There was an inverse relationship between chain length and melting point for cages with $n$-alkyl chains. The high melting point of cage 8 was related to its highly symmetrical and stable crystal packing. The cages were thermally stable in their liquid states below 300 °C. Above 60 °C, cage 9 was completely molten. It appeared fully newtonian above 80 °C. Thin glass fibres were processed from the molten state of 9.\textsuperscript{130}

The reversible solid-to-liquid phase transition of crystalline CPs have been explored by Umeyama et al.\textsuperscript{1} They showed that the thermal behavior of CPs was sensitive to slight alterations in the chemical composition. They selected [Zn(HPO$_4$)(H$_2$PO$_4$)$_2$]$_2$·2H$_2$Im to investigate the melting behavior. This CP melted at 154 °C. The supercooled state of [Zn(HPO$_4$)(H$_2$PO$_4$)$_2$]$_2$·2H$_2$Im was metastable at ambient temperature, whereas recrystallization was promoted at 100 °C (Fig. 27). It was found that the coordination bonds were cleaved at the melting point.
Therefore, liquid $[\text{Zn(HPO}_4\text{)}\text{(H}_2\text{PO}_4\text{)}_2\text{]}\cdot\text{2H}_2\text{Im}$ was an IL of zinc, phosphate, and imidazolium ions without a preserved coordination bond. However, according to PDF and XAS, the coordination bonds were reformed in the glass state. A thin film of $[\text{Zn(HPO}_4\text{)}\text{(H}_2\text{PO}_4\text{)}_2\text{]}\cdot\text{2H}_2\text{Im}$ with a thickness of 8 µm was fabricated by melting and recrystallization. This demonstrated improved performance due to flexible processability. In addition, recrystallization from the liquid state also provided a facile alignment of crystal orientation, and the growth of a monolith crystal.4

Temperature-based evolution of ZIF-4 was explored by Bennett et al.5 Firstly, ZIF-4 released DMF, which did not cause framework collapse. It was followed by the formation of a LDL at $T_m$, which corresponded to the low-density amorphous (LDA) phase. Above that temperature, LDL converted to a high-density liquid (HDL), which corresponded to the high-density amorphous (HDA) phase. HDL recrystallized to ZIF-zni upon further heating. LDL phase displayed a fragility of $m=14$, which is expected for super-strong liquids, while HDL had intermediate fragility ($m=41$). The HDA phase was formed when the HDL was cooled to RT, after completion of the liquid–liquid transition (LLT). Consequently, the glass transition during reheating of the HDA ($T_g=565$ K) was significantly lower than LDA ($T_g=589$ K). A bulk melt-quenched hybrid glass (MQG), virtually indistinguishable from the HDA phase, was formed by quenching from below the $T_m$. According to PDFs, the organic ligand and zinc tetrahedral coordination environments of ZIF-4 were retained in HDA and MQG.5

The melting of ZIF-4 was further studied by experimental and computational means. Heating of ZIF-4 above melting point (856 K) resulted in a significantly decreased Zn–Zn bonding, as well as loss of long-range order. It was found that the undercoordination of Zn$^{2+}$ increased dramatically when temperature increased. When approaching the melting point of ZIF-4 from a thermodynamic viewpoint, the main contribution to the free energy barrier was found to be energetic in nature, accompanied by a minor entropic stabilization. The porosity was maintained in the liquid phase. A large fraction of the void space in the ZIF liquid was accessible porosity. Specifically, 95% of the void space in the liquid was accessible at 1500 K, whereas only 74% in crystalline ZIF-4 was accessible at 300 K. Therefore, a neat porous liquid with intrinsic porosity was obtained from ZIF-4 (type 1 porous liquid).134,135 It was different from those porous liquids based on framework materials dispersed in a hindered solvent (type 3 porous liquid) and from those built from empty hosts dispersed or dissolved in a solvent that cannot penetrate the void of the cages (type 2 porous liquid).137–139 To provide further information for the reader, the types of porous liquids were deeply discussed in O’Reilly et al.’s article.140 The relationship between the synthesis conditions of ZIF-4 and $T_m$ and $T_g$ has also been investigated. It was found that whereas $T_m$ was maintained upon increasing the synthesis temperature ($T_s$), $T_g$ increased with $T_s$.141

First-principles molecular simulations have been performed to study the phenomenon of melting in ZIF-8, ZIF-4 and ZIF-zni, focusing on the influence of the topology of the crystalline MOF.142 Melting mechanism was found to be similar in all three frameworks. ZIF-8 was demonstrated to melt above its experimental temperature of decomposition. This was attributed to the high free energy barrier for the detaching of imidazolate linkers from the metal cations. It was hypothesized that while the ligands are stabilized by dispersive interactions in denser
ZIFs (ZIF-4 and ZIF-zni), they are very isolated in the intermediate state in highly porous MOFs (ZIF-8), and thus a high energetic barrier appears. Therefore, framework topology and density were reported to be important factors influencing melting.

The manipulation of the $T_m$ of a MOF via altering the chemistry of the crystalline state has been explored by Bennet et al. in their study of ZIF-4, ZIF-GIS (Zn(Im)$_2$, polymorphic structure with ZIF-4), TIF-$\gamma$ (Zn(Im)$_{1.8}$(mPhIm)$_{0.2}$, mPhIm = 5-methylbenzimidazolate), and ZIF-62.\(^{120}\) As previously mentioned, evacuated ZIF-4 amorphized to $\alpha_T$-ZIF-4 at 600 K, before recrystallization to ZIF-zni at 673 K, and subsequent melting at 863 K.\(^{42}\) After desolvation, ZIF-GIS, TIF-4 and ZIF-62 melted around 863 K, 740 K and 710 K, respectively. It is worth mentioning that $T_m$ may be reduced via replacing solvothermally produced ZIFs by those mechanochemically synthesized.\(^{146}\) All $T_g$ were found around 875 K. ZIF-4, ZIF-GIS, TIF-4, and ZIF-62 liquids were cooled back to RT, thus forming glasses ($\alpha_g$-ZIF-4, $\alpha_g$-ZIF-GIS, $\alpha_g$-TIF-4, and $\alpha_g$-ZIF-62, respectively) ($\alpha_g$ = glass state). The $T_g$ of $\alpha_g$-ZIF-4, $\alpha_g$-ZIF-GIS, $\alpha_g$-TIF-4 and $\alpha_g$-ZIF-62 was shown to be 565 K, 565 K, 591 K and 606 K, respectively. Therefore, alongside reducing $T_m$, the addition of successively larger organic ligands to the MOF structures increased $T_g$. ZIF-4, ZIF-GIS, TIF-4, and ZIF-62 liquids exhibited a fragility index of 39, 17, 23, and 35, respectively. ZIF-4 and ZIF-GIS liquids showed very different fragilities, even though they possessed the same chemical formula and melted at the same temperature. It was attributed to a remnant influence of the network architecture of the solid phase. Fragility was also observed to decrease with increasing organic ligand size. It must be mentioned that ZIF-GIS amorphized to $\alpha_T$-ZIF-GIS due to solvent removal. Similarly, solvent release from TIF-4 and ZIF-62 formed amorphous $\alpha_T$-TIF-4 and $\alpha_T$-ZIF-62, respectively. Whereas $\alpha_g$-ZIF-4 and $\alpha_g$-ZIF-GIS displayed glass-transition, $\alpha_T$-TIF-4 and $\alpha_T$-ZIF-62 did not. PDFs of these crystalline and MOF glasses were identical below 8 Å, with only small differences in peak intensities. In addition, PDFs were also similar to those of ZIFs amorphized. Logically, crystalline PDFs contained long range oscillations exceeding 20 Å. According to solid state $^{13}$C and $^{15}$N NMR, the organic linkers remained intact in the MOF glasses. The mechanical properties (the elastic modulus ($E$) and hardness ($H$)) of $\alpha_g$-ZIF-4, $\alpha_g$-ZIF-GIS, $\alpha_g$-TIF-4 and $\alpha_g$-ZIF-62 were also examined in this study.\(^{128}\)

The relationship between chemical composition and thermal properties of five isostructural ZIF-62 frameworks ZIF-UC-1a (Zn(Im)$_{1.7}$(PhIm)$_{0.6}$(mPhIm)$_{0.9}$), ZIF-UC-1b (Zn(Im)$_{1.66}$(PhIm)$_{0.2}$, mPhIm)$_{0.12}$, ZIF-UC-1c (Zn(Im)$_{1.63}$(PhIm)$_{0.17}$(mPhIm)$_{0.05}$), ZIF-UC-1d (Zn(Im)$_{1.59}$(PhIm)$_{0.27}$(mPhIm)$_{0.14}$), and ZIF-UC-1e (Zn(Im)$_{1.63}$(PhIm)$_{0.18}$(mPhIm)$_{0.21}$) has subsequently been studied by Rios Gómez et al.\(^{144}\) $T_m$ of ZIF-UC-1a, ZIF-UC-1b, ZIF-UC-1c, ZIF-UC-1d and ZIF-UC-1e was found to be 706 K, 691 K, 698 K, 693 K and 703 K, respectively. Therefore, $T_m$ of these frameworks was lower than that of ZIF-62, TIF-4 and ZIF-4.\(^{128}\) The inclusion of small amounts of PhIm was proved to decrease $T_m$ in non-stoichiometric variants of ZIF-62.\(^{145}\) It was attributed to an increase in structural disorder. $T_g$ of ZIF-UC-1a, ZIF-UC-1b, ZIF-UC-1c, ZIF-UC-1d and ZIF-UC-1e was reported to be 588 K, 578 K, 584 K, 583 K and 589 K. $T_g$ of these ZIF-62 frameworks was situated between that of ZIF-62 and ZIF-4.\(^{128}\) It is worth mentioning that the glasses ($\alpha_g$-ZIF-UC-1a-e) had the same chemical composition as their crystalline analogues. A probabilistic model was proposed to explain melting and the glass transition temperatures of the obtained glasses in terms of the structural disorder resulting from the incorporation of a third linker into the frameworks. Assuming a random distribution of the linkers, $T_g$ was predicted using the topological constraint theory (TCT) model.\(^{146}\) The results indicated a linear increment of $T_g$ as the amount of mPhIm increased in the frameworks (Fig. 28).\(^{144}\)

The effects of linker chemistry and crystal structure on MOF melting have been further explored by Bumstead et al.\(^{147}\) The thermal response of TIF-4 (Zn(Im)$_{1.8}$(mPhIm)$_{0.2}$, ZIF-UC-5 (Zn(Im)$_{1.6}$(cPhIm)$_{0.2}$), ZIF-UC-6 (Zn(Im)$_{1.4}$(cPhIm)$_{0.2}$), ZIF-UC-6 (Zn(Im)$_{1.2}$(PhIm)$_{0.2}$) and ZIF-76 (Zn(Im)$_{1.4}$(cPhIm)$_{0.2}$) was studied. Both TIF-4 and ZIF-UC-5 crystallized in an orthorhombic Pbcn space group and have the eag topology. $T_m$ was found to be 440 °C and 428 °C for TIF-4
and ZIF-UC-5, respectively. The lower $T_m$ of ZIF-UC-5 compared to TIF-4 was attributed to the electron withdrawing chlorine ligand which weakened the Zn–N coordination bond. In addition, the smaller van der Waals volume of cPhIm was claimed to cause a reduction in steric hindrance around the metal center, which facilitated linked dissociation during melting. $T_g$ for a$_g$ TIF-4 was reported to be 350 °C whilst that of a$_g$ZIF-UC-5 was 336 °C. The lower $T_g$ of ZIF-UC-5 compared to TIF-4 was ascribed to the smaller van der Waals volume of chlorine compared to the methyl group. The dispersion forces in TIF-4 were stronger and more energy was required for undergoing glass to liquid transition. $T_m$ of TIF-4 [Zn(Im)$_{1.8}$(mPhIm)$_{0.2}$] (440 °C)$^{147}$ was lower than that of TIF-4 [Zn(Im)$_{1.5}$(mPhIm)$_{0.5}$] (467 °C).$^{148}$ Moreover, $T_m$ of ZIF-UC-5 [Zn(Im)$_{1.8}$(cPhIm)$_{0.2}$] (428 °C)$^{147}$ was also lower than that of ZIF-UC-5 [Zn(Im)$_{1.72}$(cPhIm)$_{0.28}$] (432 °C).$^{148}$ Thus, decreasing the content of xPhIm reduced the $T_m$. Hence, the smaller steric hindrance of the zinc tetrahedra, when less xPhIm was present, favored melting. This study also

![Phase diagram for ZIF-62](image)

**Fig. 29** (a) $P–T$ phase diagram for ZIF-62. The stability field of crystalline ZIF-62 is shown in blue. Blue and red diamonds are the results of the phase transition analysis. Two amorphous phases with high and low densities relative to each other are shown in dark red (high $P$) and light red (high $T$), respectively. A dashed black line indicated the phase boundary between the two amorphous phases. The stability field of liquid ZIF-62 is shown in yellow. Crosses indicate high-$P$/high-$T$ conditions from which the samples were quenched for morphological analysis. SEM images of ZIF-62: (b) crystalline, as-synthesized; (c) high-$P$ amorphous, quenched from 440 °C, 5 GPa; and (d) high-$P$ molten, quenched from 420 °C, 3.4 GPa. Adapted with permission from ref. 151. Copyright 2019 Springer Nature.
demonstrated the importance of the crystal structure of the parent crystalline MOF for melting. Whereas ZIF-76-mPPhIm [Zn(Im)1.33(mPPhIm)0.67] (mixed phase) melted at 471 °C,149 pure phase ZIF-76-mPPhIm [Zn(Im)[mPPhIm]] did not melt.147 Therefore, the melting of ZIF-76-mPPhIm was assisted by impurities acting as a flux such as TIF-4. Similarly, ZIF-76 [Zn(Im)1.62(cPhIm)0.38] melted at 451 °C149 and pure ZIF-76 [Zn(Im)[cPPhIm]] did not melt before decomposition.147 Hence, the presence of a dense polymorph (ZIF-UC-5) was also essential in this case. Dense polymorphs are thought to melt first, and then act as a high temperature solvent for the remaining open pore frameworks.

The technique of flux melting has been applied to melt ZIF-8,7 which does not possess an accessible liquid state in the pure form.144 Longley et al. prepared a mix of microcrystalline ZIF-8 and ZIF-62 (20/80 wt/wt ratio) referred to as (ZIF-8)(ZIF-62)(20/80). It should be remembered that Tm of ZIF-62 was reported to be 710 K.150 (ZIF-8)(ZIF-62)(20/80) was heated to 773 K, and then quenched back to RT. ZIF-62 amorphized at ~600 K, before melting at ~650 K. At that temperature, the liquid phase of ZIF-62 started the flux melting of ZIF-8. In doing so, a flux, melted MOF glass [aP{(ZIF-8)0.02(ZIF-62)0.08}] was produced. Tg of aP{(ZIF-8)0.02(ZIF-62)0.08} was found to be 607 K. According to PDF results, the short-range order of [ZIF-8](ZIF-62)(20/80) was maintained in aP{(ZIF-8)0.02(ZIF-62)0.08}. Similarly, aP{(ZIF-67)0.02(ZIF-62)0.08} was prepared by heating [(ZIF-67)(ZIF-62)(20/80)] at 770 K, and quenching. It is worth mentioning that Tg of aP of a pure sample of ZIF-67 was ~780 K.150 Flux melting is further explained in the section “Flux melted MOF glass”.

Widmer et al. have studied the stability field of the liquid phase of ZIF-62 and ZIF-4 at high-pressure and high-temperature conditions.151 They constructed a pressure vs. temperature phase diagram of ZIF-62 (Fig. 29). The phase stability of ZIF-62 ranged from ambient pressure to 8 GPa and from ambient temperature to 450 °C. ZIF-62 underwent a reversible amorphization at ~320 °C at ambient P. Similarly, ZIF-62 amorphized at ~5 GPa at RT. However, thermal amorphization was irreversible. It was found that high-pressure amorphous phase (aHP) had a higher density than high-temperature amorphous phase (aHT). The boundary between aHT and aHP was approximated by extrapolating the crystalline to aHP transition (c-aHP) boundary to higher pressures. At ambient P, ZIF-62 was reported to melt at ~430 °C. Tm at high pressures ranging from approximately 2 GPa to 3.5 GPa were visually determined. A melting curve with negative slope was found from ambient pressure to ~2 GPa. Therefore, aHT had lower density than the liquid phase. The melting curve was positive at pressure >2 GPa. Consequently, aHP exhibited higher density than the liquid phase. Similar experiments were carried out using ZIF-4. At ambient pressure, amorphization, recrystallization to ZIF-zni and melting occurred at ~250 °C, 320 °C and 580 °C, respectively. However, amorphization, recrystallization and melting temperatures were lowered by the application of pressure. Hence, this study shows how the stability field of the MOF liquids extend towards lower temperatures at increasing pressures.151

Very recently, Bumstead et al.152 have explored the thermal behavior of several different coordination polymer and MOF families. Tm of [(Co(μ-NCS)2(C5H4N2O2)(C5H4N2O2)]·C6H5N2O2, coordination polymer was reported to be 197 °C. The material also began to decompose at that Tm. Tg was found at 78 °C. The cadmium analogue coordination polymer, [Cd(μ-NCS)2(C5H4N2O2)]in, melted at 205 °C. Decomposition also occurred at Tm. However, it recrystallized at 144 °C upon cooling from 220 °C. Heating this sample back resulted in further recrystallization at 147 °C, before remelting of these recrystallized domains at higher temperature (Fig. 30). This research also examined the relationship between increasing disorder and propensity for glass formation. Tm and Tg of mechanochemically synthesized [Zn(Im)1.05(cPPhIm)0.05] were reported to be 366 °C and 296 °C, respectively. Mechanochemically synthesized [Zn(Im)1.05(cPPhIm)0.025(cPPhIm)0.025] exhibited a Tm of 356 °C and a Tg of 296 °C. Finally, [Zn0.8Co0.2(Im)1.05(cPPhIm)0.025(cPPhIm)0.025] was also mechanochemically synthesized. It was found that [Zn0.8Co0.2(Im)1.05(cPPhIm)0.025(cPPhIm)0.025] showed the lowest value of Tm (310 °C) currently known in the ZIF family. The Tg of this framework was reported to be 288 °C. All these ZIF frameworks suffered from partial loss of cPPhIm upon vitrification.152 The study of Bumstead et al. claims for an increase in standards of thermal characterization within the MOF literature. We support their demand.

So far, MOF melting based on reaching the thermal equilibrium has been reported in the Review. Kulachenkov et al. have studied ultrafast melting of [Cd(sdc)[L4]]·DMF [sdc = 4,4′-stilbenedicarbocxoylate, L4 = 1,4-di(1H-imidazol-1-yl)butane], [Cd[DMF][sdc][L6]]·DMF [L6 = 1,6-di(1H-imidazol-1-yl)
hexane), and [Zn(sdc)(L6)]:DMF via femtosecond (fs) IR laser pulses. \(^{1,2}\) These MOFs were exposed to 150 fs IR laser pulses with fluences of 10, 8, and 7 mJ cm\(^{-2}\). Two morphologically different particles were produced from [Cd(sdc)(L4)]:DMF: amorphized drops with metal–organic composition and homogeneous redistribution of the elements, and spherical particles whose internal structure can be described as core–shell. The shell was an amorphized organic phase and the core was a dendrite-like metal-oxide. Derivatives of irregular shape and amorphous phase with metal–organic composition were produced from [Cd(DFM)(sdc)(L6)]:DMF and [Zn(sdc)(L6)]:DMF. DFT calculations suggested that upon optical excitation, [Cd(sdc)(L4)]:DMF would undergo a controlled dissociation in the directions determined by the antibonding character of the delocalized conduction band minimum (CBM). A specific directionality of the crystal melting upon excitation cannot be expected neither in [Cd(DFM)(sdc)(L6)]:DMF nor in [Zn(sdc)(L6)]:DMF. Ultrafast melting of MOFs opens new perspectives for efficient postsynthetic processing of frameworks yielding materials with a rarely described combination of nonlinear optics, and potentially catalytic and energy storage applications.\(^{1,3}\)

3.3. Perspectives in MOF liquids

The requisite melting condition \(T_m < T_d\) is a starting criterion to recognize MOFs with, presumably, an accessible liquid state. \(T_m\) is strongly affected by the strength of ionic interaction between metal cation and organic anion, with lower interaction strengths favoring melting. \(T_d\) depends on several factors such as heating rate, atmosphere, chemistry of the material, particle size and so on. Therefore, further research is required to develop a set of rules for identifying those MOFs with available liquid phase. In addition, investigations to adjust \(T_m, T_g\) and \(T_d\) are still scarce.\(^1\)

We envisage the preparation of porous MOF liquids from the extensive library of existing MOFs. MOF liquids are an exciting field not simply for their novelty but also for their enhanced processability and manipulability in industrial settings. Liquid phase also facilitates the shaping of MOFs by providing a provisional state to mechanically and thermally stable MQG, or recrystallized product. Quenching high temperature MOF liquids may yield glasses with unusual properties or from which further processing may create materials with wide application potentials.

The utility of crystalline MOFs in gas adsorption, gas separation and catalysis is currently limited by the inability to process microcrystalline powders.\(^{1,2,3}\) MOF shaping has been approached by using binders, mechanical compression, or through the blending of active MOF components in polymeric substrates.\(^{1,2,3}\) However, these methods have often led to partial or complete collapse of the internal porosity, or pore blocking, preventing the access to the porosity.\(^{1,2,3}\) The challenge of shaping MOFs might be overcome by processing and manipulating MOF liquids without the use of a secondary component. It is anticipated that manipulation of MOF liquids and subsequent recrystallization shall be applied to develop monolithic MOF materials in the near future.

Future work will aim at the preparation of permanently porous liquids with large cavities, capable of binding complex molecules as guests. Thus, the size and shape selectivity of porous domains will be combined with the fluidity of liquids. In addition, porous MOF liquids are expected to be tunable through modification of inorganic clusters and ligand functionalization, in a similar manner to well-known crystalline MOFs. In doing so, porous MOF liquids will be designed and tailored for specific applications. Therefore, they offer opportunities for molecular separations, gas storage, ion transport, and extractions, due to their compatibility with existing industrial processes. Moreover, the reversibility of solid–liquid transitions in MOFs should also be explored. Phase-change MOFs may be interesting in memory and data storage applications.

MOF liquids are also promising in homogeneous catalysis. New homogeneous catalysts are expected to be developed by tailoring and tuning MOF liquids. Furthermore, these new catalysts are envisioned to open up new possibilities for reaction control and separation of the homogeneous catalyst from the reactants and the substrate.\(^{1,5}\)

The phenomenon of melting has been extensively examined throughout this Review. We hope this phenomenon extends and new research directions emerge.

4. MOF glasses

4.1. Introduction

Glasses can be broadly classified as inorganic, organic, and metallic, having ionic-covalent, covalent, and metallic bonds, respectively. A fourth family of glasses based on MOFs, which contain coordination bonds, have been recently reported. As previously mentioned, MOF glasses are amorphous solids mainly formed through rapid cooling of MOF liquids, avoiding crystallization (and the associated thermodynamic minimum). They maintain the disordered metal–ligand arrangement of MOF liquids. Therefore, MOF glasses preserve the integrity of both the inorganic and organic building units of the MOF liquids. MOF glasses undergo a transition to supercooled state at \(T_g\). Experimentally, \(T_g \approx 2/3T_m\) for most glass systems, known as Kauzmann “2/3 rule”.\(^{1,2,3}\)\(^{160,161}\) defining the practical limits of the supercooled state. Systems with \(T_g/T_m > 2/3\) have high glass-forming ability (GFA). They are increasingly viscous throughout the reduced supercooled state, which inhibits crystallization. Together with \(T_g/T_m\), activation energy of viscosity at \(T_g\) and liquid fragility \(m\) also measure the resistance to crystallization of the melt in the supercooled state and, therefore, the GFA. It should be noted that liquid fragility \(m\) and GFA are inversely associated.\(^{1,2,3}\) \(T_g\) of LDA phases is usually found to be significantly greater than that of HDA phases. LDA ultrastable (low entropy) glass phases are in the potential energy landscape (PEL) at similar potential energy to their crystalline equivalents. They have unique mechanical properties. By contrast, HDA phases that show the same composition as their perfect glass LDA counterparts, exhibit higher entropy as well as density, and are located higher in the PEL.\(^{3}\)

In the following sections of this Review, MOF glasses prepared from crystal MOFs by melt-quenching and, also, by
other methods are explored. Attractive properties and promising applications of the MOFs glasses are highlighted throughout the text. Subgroups of MOF glasses such as MOF-blends, flux melted MOFs, MOF-CGCs, MOF and inorganic glass composites, and MOF glass membranes are also explained (Table S2†). We concluded by providing our thoughts about the future directions for MOF glasses.

4.2. Glasses prepared by melt-quenching

Besara et al. revealed the ability of MOFs to exhibit glass behavior.163 1H NMR and specific heat ($C_p$) measurements were used to study phase transition in DMAZF ([[(CH$_3$)$_2$NH]$_2$Zn(HCOO)$_3$]). DMA'((CH$_3$)$_2$NH$_2$) moiety exhibited unique orientational dynamics with a decrease in the motional rate with temperature, resulting in an order–disorder phase transition at 156 K. Both the long-range and the short-range ordering behavior of DMAZF were probed to be related to unique motional dynamics of the DMA' moiety. At temperatures below 156 K, DMA' became more ordered, although DMA' still retained motion. Below 40 K, the rotational motions of the CH$_3$ groups also started to freeze, leading to multiple states with closely spaced energies. It resulted in a memory effect in the temperature dependence of the spin–lattice relaxation rate, which was a clear sign of glass-like behavior. The glass state was further confirmed by $C_p$ measurements. $C_p$ was unusually large at low temperatures, which indicated local ordering. The excess specific heat, which was indicated by a peak at about 25 K in the $C_p/T^3$ vs. $T$ curve, corroborated the presence of a glass phase.163

The studies of Umeyama et al. and Bennett et al., which have already been reviewed in MOF liquids section, are the earliest examples of glass CP and glass MOF, respectively. In both investigations, the local structure of the crystalline phase was maintained in the glassy phase. However, in a subsequent work of Umeyama et al., [Zn(H$_2$PO$_4$)$_2$(HTr)$_2$]$_n$ CP (Tr = 1,2,4-triazole) exhibited a network-to-molecular (2D-to-0D) transformation after glass formation.164 Air cooling at ambient temperature from the melted state of [Zn(H$_2$PO$_4$)$_2$(HTr)$_2$]$_n$ afforded the vitreous state, suppressing the recrystallization. $T_g$ was found to be 305 K. XAS results indicated that the arrangement around the zinc ions was distinct even at the nearest neighbors. It was postulated that the organization changed from octahedral to tetrahedral during the glass formation. PDF profile suggested that the building unit of glass

[Zn(H$_2$PO$_4$)$_2$(HTr)$_2$]$_n$ was a discrete molecule (0D). A molecular model for glass [Zn(H$_2$PO$_4$)$_2$(HTr)$_2$]$_n$ was built by changing the HTr molecules from bridging to monodentate ligands. Therefore, the geometry became tetrahedral while the chemical formula remained [Zn(H$_2$PO$_4$)$_2$(HTr)$_2$] (Fig. 31). The chemical diversity of coordination species and flexibility in coordination geometry were responsible for the unique glass formation, which was accompanied by a dynamic rearrangement in a coordination sphere.164

The porosities of ZIF-4, ZIF-zni and $a_{g}$-ZIF-4 (ref. 5) (Fig. 32) has been characterized by Positron Annihilation Lifetime Spectroscopy (PALS).165 In addition, a constructed structural model of $a_{g}$-ZIF-4 was applied to simulate the porosity of this glass MOF. Similarly, the porosity of ZIF-4 and ZIF-zni was simulated based on the crystallographic unit cells of these frameworks. According to PALS, ZIF-4 exhibited cavity sizes of 3.3 and 6.2 Å. However, the values calculated from the crystal structure were 3.3 and 5.1 Å. PALS yielded pores of 3.8 and 6.6 Å for ZIF-zni, whilst the crystal structure showed pores of 3.0 and 5.5 Å. Therefore, PALS slightly overestimated the pore sizes of the crystalline phases. PALS revealed cavity sizes of 2.6 and 6.9 Å for $a_{g}$-ZIF-4 which were in excellent agreement with cavities from simulation, 2.6 and 6.4 Å. Diffusion properties of $a_{g}$-ZIF-4 were also postulated based on the simulated model. It is worth mentioning that diffusivity ($D$) through amorphous materials has been related to the fractional free volume measured by PALS ($FF_{PALS}$):

$$D = A \cdot e^{-\gamma FF_{PALS}}.$$  

where $A$ is an empirical constant, which includes properties of penetrant and temperature; $\gamma$ is a geometric factor; and $\nu^*$ is the minimum volume required to allow diffusion. With all parameters held constant, diffusivity of $a_{g}$-ZIF-4 was calculated for $\nu^* (=1$ and $10 \text{ Å}^3$), equivalent to radii of 0.6 and 1.3 Å for small ions. The difference in diffusivity between two penetrants of different molecular volumes can be maximized with $a_{g}$-ZIF-4 and materials within the same range of $FF_{PALS}$. Zeolite MFI-100 and porous aromatic frameworks sits within this range. Therefore, $a_{g}$-ZIF-4 may be considered a promising candidate
for transport, sensing, capture, or release of small ions or molecules.\textsuperscript{165} It is worth mentioning that the effect of heat-treatment upon a\textsubscript{g}-ZIF-4 has been investigated by Zhang \textit{et al.} When holding at 793 K (1,387°C) for 420 min, a\textsubscript{g}-ZIF-4 was suggested to undergo structural densification, towards a lower energy state.\textsuperscript{169} In another study, the modulator 1-methylimidazole (1-Melm) has been introduced in the synthesis of ZIF-4 to explore the variation of particle size, size distribution, morphology, surface defects, phase transition, recrystallization, melting and glass formation. \textit{m}\textsubscript{1}-ZIF-4, \textit{m}\textsubscript{2}-ZIF-4, \textit{m}\textsubscript{15}-ZIF-4 and \textit{m}\textsubscript{4}-ZIF-4 (where \textit{m} corresponds to the molar ratio of 1-Melm : Im, \textit{m}\textsubscript{1} = 1 : 4, \textit{m}\textsubscript{2} = 3 : 2, \textit{m}\textsubscript{15} = 4 : 1, and \textit{m}\textsubscript{4} = 1 : 0) were synthesized. The corresponding glasses were obtained by melt-quenching. Upon the addition of 1-Melm, the peak temperature of the thermally induced amorphization gradually increased. The temperature range of the thermally induced amorphization process narrowed with the addition of 1-Melm. Importantly, the recrystallization process was similarly modified. Conversely, melting was less affected.\textsuperscript{170}

Qiao \textit{et al.} have reported the GFA of ZIF-62 (Zn(Im\textsubscript{2−x}PhIm\textsubscript{x})).\textsuperscript{171} The formation of a\textsubscript{g}-ZIF-62 has already been reviewed in the previous section.\textsuperscript{120} The \(T_g/T_m\) was found to be 0.84, which was higher than “2/3 rule”. This indicated the ultrahigh GFA of ZIF-62. The ultrahigh GFA was also evidenced by the extremely high viscosity (\(\eta = 105.1\) Pa s) at the \(T_m\) comparable to that of SiO\textsubscript{2}, traditionally the most viscous and strongest of inorganic liquids. The steric hindrance of mixed linkers in ZIF-62 contributed to the extraordinarily high viscosity. The fragility index \(m\) of liquid ZIF-62 was 23, confirming the exceptionally strong nature of supercooled ZIF-62. Large crystal-glass network density deficit (\(\Delta \rho/\rho_g\)) networks no crystallization in supercooled region on laboratory time scales, and an extremely high Poisson’s ratio (\(v = 0.45\)) confirmed the ultrahigh GFA. As increasing PhIm content, the \(T_g/T_m\) ratio was found to be retained but \(T_m\) and \(T_g\) both increased. The entropy and enthalpy of fusion of ZIF-62 (\(\Delta S_m\) and \(\Delta H_m\), respectively) also increased with rising PhIm content. PhIm ligands enhanced the number of configurational states at \(T_m\) and, therefore, increased \(\Delta S_m\). In addition, PhIm ligands required more thermal energy to initiate structural reconfiguration at \(T_m\), and, thus, increased \(\Delta H_m\).\textsuperscript{171}

Stepniewska \textit{et al.} have optimized the melt-quenching process of a\textsubscript{g}-ZIF-62 (Zn(Im\textsubscript{2−x}PhIm\textsubscript{x})\textsubscript{a}) to increase homogeneity, transparency, and size of ZIF-62 glass products. Large glass samples (>10 mm) with a certain degree of transparency and low bubble content were produced by quenching after melting for up to 5 min. The density of a\textsubscript{g}-ZIF-62 decreased with increasing melting time over 10 min. ZIF-62 glass foams were obtained when the melting lasted more than 30 min. The glass foams resulted from partial decomposition of a\textsubscript{g}-ZIF-62 during melting. \(T_g\) was found not to vary with melting time.\textsuperscript{171}

Zhou \textit{et al.} developed the first MQGs (a\textsubscript{g}-ZIF-76 and a\textsubscript{g}-ZIF-76-mPhIm) with permanent accessible porosity.\textsuperscript{149} Liquid ZIF-76 (Zn(Im\textsubscript{2−x}PhIm\textsubscript{x})\textsubscript{a}) was cooled to 451°C and liquid ZIF-76-mPhIm (Zn(Im\textsubscript{2−x}PhIm\textsubscript{x})\textsubscript{a}) was cooled to 471°C were cooled to produce a\textsubscript{g}-ZIF-76 and a\textsubscript{g}-ZIF-76-mPhIm, respectively. \(T_g\) of a\textsubscript{g}-ZIF-76 was found to be 310°C, whilst a\textsubscript{g}-ZIF-76-mPhIm possessed a \(T_g\) of 317°C. According to PDFs, the local Zn\textsuperscript{2+} environment (metal-linkage-metal connectivity) was near identical in ZIF-76, ZIF-76-mPhIm, a\textsubscript{g}-ZIF-76 and a\textsubscript{g}-ZIF-76-mPhIm. a\textsubscript{g}-ZIF-76 and a\textsubscript{g}-ZIF-76-mPhIm exhibited medium range order (MRO) in contrast with dense ZIF glasses.\textsuperscript{120} a\textsubscript{g}-ZIF-76 was found to show a single pore with a diameter of 5 Å. a\textsubscript{g}-ZIF-76-mPhIm presented two pores with diameters of 4.8 Å and 7.2 Å. The pores contracted upon vitrification. Optimized a\textsubscript{g}-ZIF-62 (Zn(Im\textsubscript{2−x}PhIm\textsubscript{x})\textsubscript{a}) and a\textsubscript{g}-ZIF-76-mPhIm (Zn(Im\textsubscript{2−x}PhIm\textsubscript{x})\textsubscript{a}) were porous to incoming gases (Fig. 33). a\textsubscript{g}-ZIF-76 and a\textsubscript{g}-ZIF-76-mPhIm adsorbed 4 wt% and 7.0 wt% of CO\textsubscript{2} at 273 K and 1 bar, respectively. a\textsubscript{g}-ZIF-76-mPhIm displayed superior textural characteristics compared to a\textsubscript{g}-ZIF-76. Likely, the methyl group helped to maintain the open network. Therefore, the inclusion of a bulky ligand was found to prevent close packing of the liquid state upon quenching. However, Im was still required to facilitate melting.\textsuperscript{149} Another example of
A permanently porous ZIF glass was reported by Frentzel-Beyme et al. The first microporous cobalt imidazolate glass was obtained from ZIF-62(Co) (Co(Im)_{1.70}(PhIm)_{0.30}), which is isostructural with ZIF-62(Zn). The glass framework was detected to decompose at \( T_m \) of ZIF-62(Co) was found to be 432 \(^\circ\)C. This liquid framework was then transformed into a paramagnetic ag-ZIF-62(Co) upon cooling to RT. According to PDF data, the short-range correlations up to 6 \( \AA \) (corresponding to the distance of neighboring Co\(^{2+}\) ions) were similar in the crystalline and glass states. ag-ZIF-62(Co) retained almost 50% of the porosity of the crystalline phase. Minor hysteresis was present during desorption of CO\(_2\). This indicated a well-connected, continuous network of micropores in the glass state.

ag-ZIF-62(Zn) has also shown to exhibit permanent porosity. ag-ZIF-62 was found to uptake 11 cm\(^3\) of CO\(_2\) g\(^{-1}\), 2.6 cm\(^3\) of CH\(_4\) g\(^{-1}\), and 0.7 cm\(^3\) of N\(_2\) g\(^{-1}\) at 293 K and 1 bar. The reduction in the adsorption capacity from crystalline to glass phase was much weaker for CO\(_2\) than for CH\(_4\) and N\(_2\). Therefore, much stronger affinity between CO\(_2\) molecules and the glass was suggested.

In addition, ag-ZIF-62 has been reported to kinetically trap a small amount of H\(_2\). The CO\(_2\) capacity of ag-ZIF-UC-1a and ag-ZIF-UC-1e compared to ag-ZIF-62 were reduced by the presence of mPhIm linkers. However, micro-porosity was observed to be retained. The CO\(_2\) uptake for ag-ZIF-UC-1a and ag-ZIF-UC-1e was 13% and 22% of that reported for ZIF-62, respectively. The adsorption–desorption processes were reversible, as demonstrated by the absence of hysteresis. Together with the potential advantages of MOF liquids/glasses in terms of processability and shaping, as well as their very high thermal \( T_d \), the permanent porosity of the MOF glasses paves the way for the application of such glasses in gas separation, energy storage and catalysis. We also envision the application of MOF glasses in composite membranes or even as free-standing glass membranes for technologically important separation processes.

Frentzel-Beyme et al. have synthesized and studied a series of M(Im)\(_{1-x}\)(PhIm)\(_x\) (with \( x = 0.02–0.35, \) M = Co or Zn) (Table 1). \( T_m \) of the M(Im)\(_{2-x}\)(PhIm)\(_x\) decreased from 440 \(^\circ\)C for \( x = 0.35 \) to 370 \(^\circ\)C for \( x = 0.03 \). Cooling the M(Im)\(_{2-x}\)(PhIm)\(_x\) liquids from 475 \(^\circ\)C to RT yielded their corresponding glasses.

Fig. 33 (a) CO\(_2\) adsorption isotherms of ag-ZIF-76-mPhIm. Labelling scheme: filled symbols = adsorption; empty symbols = desorption. (b) Calculated isosteric heats of adsorption (\( Q_{st} \)) for CO\(_2\) as a function of guest loading. Labelling scheme: orange = ZIF-76-mPhIm; blue = ag-ZIF-76-mPhIm. (c) Time-dependent CO\(_2\) uptake profiles (at 273 K and 5 Torr). (d) Pore size distributions calculated by nonlocal DFT (NLDFT) method from CO\(_2\) adsorption isotherms at 273 K. Adapted with permission from ref. 149. Copyright 2018 Springer Nature.
recrystallize to ZIF-zni(M) lied around $x = 0.05$ for M(Im)$_{2-x}$(PhIm)$_x$. PhIm linker was proved to suppress the recrystallization to the ZIF-zni(M) phase. $T_g$ of ag-M(Im)$_{2-x}$(PhIm)$_x$ (with $x \geq 0.03$) was reported to range from 290 to 320 °C when M = Zn and from 260 to 300 °C when M = Co. $T_g$ slightly increased with increasing PhIm concentration. According to these results, two requirements were suggested to melt ZIFs at lower temperatures, form stable liquid phases and transform them into porous glasses upon cooling:

(i) The ZIF must contain Im linkers and another imidazolate-type bulky linker/s.

(ii) $T_g$ of the bulky imidazolate-type linker/s must be higher than the $T_m$ of the framework.

The ag$_2$Zn(Im)$_{2-x}$(PhIm)$_x$ were permanently porous against CO$_2$ as revealed by CO$_2$ sorption isotherms. The specific surface areas for ag$_2$Zn(Im)$_{2-x}$(PhIm)$_x$ materials, which were determined by nonlocal DFT (NL-DFT) fitting of the CO$_2$ adsorption isotherms, ranged between 235 and 269 m$^2$/g. Whereas small cavities (diameter $\approx$ 3.5 Å) were lost, medium sized cavities (diameter 5–6 Å) were preserved and even new larger cavities (diameter $\approx$ 8 Å) were formed upon melting and formation of ag$_2$Zn(Im)$_{2-x}$(PhIm)$_x$. Moreover, these microporous ZIF glasses were demonstrated to adsorb gaseous C$_4$ and C$_8$ hydrocarbons (i.e., propane, propylene, and n-butane). n-Butane (kinetic diameter 4.3 Å) isotherms exhibited significant hysteresis on desorption, in contrast to CO$_2$ (kinetic diameter 3.3 Å) isotherms. The adsorption kinetics were much faster for propylene than for propane and were also dependent on the content of PhIm. Therefore, the potential of these ZIF glasses for gas separation applications was demonstrated. In addition, we believe that the demonstrated low $T_m$ will open the door for incorporating temperature sensitive compounds (e.g., metal-organic or organometallic complexes, organic fluophores, etc.) into MOF glasses.$^{145}$

Recently, the synthesis, melting process and glass formation of ZIF-UC-2 (Zn(Im)$_{1.87}$(Cl-5-FPhIm)$_{0.13}$, 6-Cl-5-FPhIm = 6-chloro-5-fluorobenzimidazolate), ZIF-UC-3 (Zn(Im)$_{1.85}$(Cl-2-mPhIm)$_{0.19}$, 5-Cl-2-mPhIm = 5-chloro-2-methylbenzimidazolate), ZIF-UC-4 (Zn(Im)$_{1.66}$(FPPhIm)$_{0.34}$, FPPhIm = 5-fluorobenzimidazolate) and ZIF-UC-5 (Zn(Im)$_{1.72}$(cPhIm)$_{0.28}$) have been reported.$^{148}$ $T_g$ and $T_m$ of ZIF-UC-2, ZIF-UC-3, ZIF-UC-4, and ZIF-UC-5 were found to be 730 K and 679 K, 720 K and 663 K, 750 K and 694 K, and 750 K and 705 K, respectively. It was suggested that the electron-withdrawing groups on the PhIm ligand may weaken the Zn–N bond and, therefore, yield a reduction in the $T_m$ of the frameworks. In situ terahertz (THz)/far-IR studies provided evidence of a correlation between the ZIF $T_m$ and the thermal-induced Zn–N polyhedral deformation. The thermoinduced vibrational amplitude of the N atoms reached a critical point, leading the breaking of the Zn–N bond. Moreover, solid-state NMR demonstrated the formation of Zn–F bonding in the glass phase, implying a reduction in the overall network connectivity. Crystaline frameworks were heated above their $T_m$ and then cooled back to RT, yielding the glasses ag$_2$ZIF-UC-2, ag$_2$ZIF-UC-3, ag$_2$ZIF-UC-4 and ag$_2$ZIF-UC-5. The melting process was accomplished by a small thermal decomposition for the crystalline samples. $T_g$ was reported to be 523 K, 609 K, 563 K and 593 K for ag$_2$ZIF-UC-2, ag$_2$ZIF-UC-3, ag$_2$ZIF-UC-4 and ag$_2$ZIF-UC-5, respectively. PPDFs suggested the preservation of the short-range order in the glasses. Exploring the GFA via $T_g/T_m$ ratios, ZIF-UC-3 exhibited the highest ratio ever reported (0.92). This was ascribed to the presence of the sterically bulky 5-Cl-2-mPhIm ligand. The slightly lower GFAs of ZIF-UC-2 (0.77) and ZIF-UC-4 (0.81) were attributed to the formation of Zn–F bonds. All glasses showed reversible adsorption of CO$_2$, indicating the relatively rapid diffusion of guest molecules within these microporous frameworks. The presence of a fluorinm moiety within ag$_2$ZIF-UC-4 improved CO$_2$ uptake, compared with ag$_2$ZIF-62 and ag$_2$ZIF-UC-5. In addition, it was postulated that the presence of halogenated moieties on the PhIm-derived ligands can facilitate nonbonded interactions, which increase elastic modulus. ag$_2$ZIF-UC-4 and ag$_2$ZIF-UC-5 showed values of $E$ ≈ 9.4 and 9.3 GPa, respectively.$^{148}$

Nagarkar et al. have synthesized and shown the stable liquid and glass phases of the CPs: Cu$_2$(SCN)$_3$(bpy)$_2$(I)$_2$bpySCN = Table 1 Comparison of the molar Im : PhIm ratio and the corresponding $x$ values applied in the synthesis with the ratios and $x$ values found in the material (determined by $^1$H NMR spectroscopy). Adapted with permission from ref. 145. Copyright 2019 American Chemical Society

<table>
<thead>
<tr>
<th>ZIF</th>
<th>Ratio Im : PhIm (applied)</th>
<th>$x$ (applied)</th>
<th>Ratio Im : PhIm (found)</th>
<th>$x$ (found)</th>
<th>$T_m$</th>
<th>$T_g$</th>
<th>$T_g/T_m$</th>
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<tr>
<td>Zn(Im)$<em>{1.96}$(PhIm)$</em>{0.02}$</td>
<td>210 : 1</td>
<td>0.009</td>
<td>99 : 1</td>
<td>0.02</td>
<td>No melting. Partial recrystallization to ZIF-zni(Zn)</td>
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<tr>
<td>Zn(Im)$<em>{1.93}$(PhIm)$</em>{0.03}$</td>
<td>168 : 1</td>
<td>0.012</td>
<td>66 : 1</td>
<td>0.03</td>
<td>370</td>
<td>292</td>
<td>0.88</td>
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<tr>
<td>Zn(Im)$<em>{1.95}$(PhIm)$</em>{0.05}$</td>
<td>126 : 1</td>
<td>0.016</td>
<td>39 : 1</td>
<td>0.05</td>
<td>372</td>
<td>298</td>
<td>0.89</td>
</tr>
<tr>
<td>Zn(Im)$<em>{1.94}$(PhIm)$</em>{0.06}$</td>
<td>84 : 1</td>
<td>0.024</td>
<td>28 : 1</td>
<td>0.07</td>
<td>380</td>
<td>298</td>
<td>0.87</td>
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<tr>
<td>Zn(Im)$<em>{1.88}$(PhIm)$</em>{0.12}$</td>
<td>42 : 1</td>
<td>0.047</td>
<td>16 : 1</td>
<td>0.12</td>
<td>395</td>
<td>303</td>
<td>0.86</td>
</tr>
<tr>
<td>Zn(Im)$<em>{1.84}$(PhIm)$</em>{0.17}$</td>
<td>28 : 1</td>
<td>0.069</td>
<td>11 : 1</td>
<td>0.17</td>
<td>409</td>
<td>303</td>
<td>0.84</td>
</tr>
<tr>
<td>Zn(Im)$<em>{1.77}$(PhIm)$</em>{0.24}$</td>
<td>14 : 1</td>
<td>0.13</td>
<td>7.3 : 1</td>
<td>0.24</td>
<td>423</td>
<td>305</td>
<td>0.83</td>
</tr>
<tr>
<td>Zn(Im)$<em>{1.65}$(PhIm)$</em>{0.35}$</td>
<td>7 : 1</td>
<td>0.25</td>
<td>4.7 : 1</td>
<td>0.35</td>
<td>441</td>
<td>320</td>
<td>0.83</td>
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<tr>
<td>Co(Im)$<em>{1.98}$(PhIm)$</em>{0.02}$</td>
<td>210 : 1</td>
<td>0.009</td>
<td>99 : 1</td>
<td>0.02</td>
<td>No melting. Partial recrystallization to ZIF-zni(Zn)</td>
<td></td>
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<tr>
<td>Co(Im)$<em>{1.90}$(PhIm)$</em>{0.10}$</td>
<td>42 : 1</td>
<td>0.047</td>
<td>16 : 1</td>
<td>0.12</td>
<td>395</td>
<td>303</td>
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<td>Co(Im)$<em>{1.83}$(PhIm)$</em>{0.17}$</td>
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<td>278</td>
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<tr>
<td>Co(Im)$<em>{1.70}$(PhIm)$</em>{0.24}$</td>
<td>14 : 1</td>
<td>0.13</td>
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<td>0.24</td>
<td>423</td>
<td>305</td>
<td>0.83</td>
</tr>
</tbody>
</table>

$^a$ $x = 2 \times (c(\text{PhIm}) + c(\text{Im}))$, $c$ = molar concentration. $^b$ Absolute temperatures in K.
1-ethyl-[4,4′-bipyridin]-1-ium thiocyanate, Cu₂(SCN)₃(C₂bpy) (2) (C₂bpySCN = 1-butyl-[4,4′-bipyridin]-1-ium thiocyanate), Cu₄(SCN)₄(Phbpy)₄ (3) (PhbpySCN = 1-phenyl-[4,4′-bipyridin]-1-ium thiocyanate) and Cu(SCN)₂(3-Pybpy) (4) (3-PybpySCN = 4,1′,4′-terpyridin-1-ium thiocyanate) (Fig. 34). Tₘ of 1, 2, 3, and 4 was reported to be 187 °C, 138 °C, 217 °C, and 203 °C, respectively. Therefore, the melting was influenced by the substituent group on pyridinium ligands. Liquid 2 underwent a liquid to liquid transition at 160 °C. The liquid phases were stable for all CPs between 187–205 °C (1), 160–205 °C (2), 224–235 °C (3), and 203–250 °C (4). Glass CPs were prepared by cooling these liquid CPs to RT. Tₖ of 1, 2, 3, and 4 was found to be 68, 59, 71, and 72 °C, respectively. Consequently, the “2/3 rule” was followed by these glass CPs. Glass 1 was recrystallized by mechanical grinding. The glass CP maintained the local coordination environment, and partial metal ligand connectivity similar to the crystal structure. In another work, Inukai et al. have prepared a 2D porous proton-conductive CP, [Zn₂(HPO₄)₂(H₂PO₄)](Im)₁₋₀·₇(PhIm)₀·₃ for a g-Zn₁₋₀·₃(Im)₁₋₀·₇(PhIm)₀·₃ containing Co ions. The observed Mid-IR emission originated from d-d transition of Co ions. The Mid-IR luminescence intensity of the a₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-...
of Zn–Co-ZIF-62 (Zn$_{0.5}$Co$_{0.5}$(Im)$_{1.8}$(PhIm)$_{0.2}$) and a$_2$-Zn-Co-ZIF-62 using an open-aperture Z-scan technique. A NIR absorption band (1100 nm) was observed in a$_2$-Zn-Co-ZIF-62, which exhibited a strong NLO response with a high modulation depth of 63.85%. The NLO response was attributed to transient saturation of the $4T_1(4F)$ level of Co ions upon femtosecond laser excitation. The NLO response suggests the potential applications of a$_2$-Zn-Co-ZIF-62 in the photonics field for sensing and optical modulation.

The mechanical properties of MOF glasses are important for promising applications in protective coatings and display technologies, even though there is still little information about MOF glasses in this respect. Li et al. have investigated the mechanical behavior of a$_2$-ZIF-4, a$_2$-ZIF-62, a$_2$-ZIF-76, and a$_3$-[Zn(Im)$_{1.33}$(mPhIm)$_{0.67}$] to gain deeper insight into the mechanical properties of melt-quenched MOF glasses. Constant strain-rate nanoindentation experiments were carried out on those glass frameworks to characterize Young’s modulus and hardness. The strain-rate sensitivity, which describes the time dependence of deformation, was determined in nanoindentation SRJ tests and through classical constant load and hold (CLH) indentation creep experiments. Values of the strain-rate sensitivity of these MOF glasses were close to those values for glass polymers and Se-rich GeSe chalcogenide glasses (Fig. 35). Scratch experiments were also performed, for the first time, on a$_3$-ZIF-62 (a$_9$ = remelted glass). In another indentation study, Stepniewska et al. revealed the anomalous indentation cracking behavior of a$_3$-ZIF-62 by atomic force microscopy. Apparent shear bands on the indented faces with a sliding extent of ~35 nm were observed. The shear banding is in strong contrast to the cracking behavior of other types of fully polymerized glasses, which do not exhibit any shear bands under indentation. The anomalous cracking behavior was attributed to the easy breakage of the coordinative

Fig. 35 (a) Variation of Young’s modulus as a function of the indenter displacement in a$_2$-ZIF-4, a$_2$-ZIF-62, a$_2$-ZIF-76, and a$_3$-[Zn(Im)$_{1.33}$(mPhIm)$_{0.67}$]. (b) Correlation between the Young’s modulus and hardness. (c) Strain-rate sensitivity determined in nanoindentation SRJ tests plotted against the reduced temperature (testing temperature divided by $T_g$). (d) Relationship between the hardness and the indentation strain-rate during SRJ testing and CLH indentation creep experiments. At low strain-rates, whereas the more porous a$_2$-ZIF-76 and a$_3$-[Zn(Im)$_{1.33}$(mPhIm)$_{0.67}$] tend toward more viscous behavior, the dense a$_3$-ZIF-4 and a$_2$-ZIF-62 tend toward plastic behavior. Adapted with permission from ref. 181. Copyright 2019 American Chemical Society.
bonds (Zn–N), which are weaker than the ionic and covalent bonds in network glasses.183

In contrast to the two previous works,181,183 To et al. studied the fracture behavior of a\textsubscript{a}\textsubscript{g}-ZIF-62 using a non-indentation technique.184 Fracture toughness (\(K_{Ic}\)) of a\textsubscript{a}\textsubscript{g}-ZIF-62 was measured using single-edge pre-cracked beam (SEPB) method. \(K_{Ic}\) was determined to be \(\sim 0.1\) MPa m\(^{0.5}\), which was even lower than that of brittle oxide glasses. Molecular dynamics simulations using a reactive force field (ReaxFF)\textsuperscript{185} was also performed to understand the structural origin of the fracture behavior of

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**Fig. 36** (a) Structural representation of the crack propagation in the precracked ZIF-62 glass upon increasing strain (\(\varepsilon\)). Labelling scheme: C = red; N = green; H = gray; Zn = blue. (b) Zn–N bond before (left) and after breaking (right). (c) Experimental and theoretically predicted \(K_{Ic}\) for a range of materials. (d) Relationship between fracture surface energy and Poisson’s ratio for a range of materials. (e) Ashby plot of the relation between \(K_{Ic}\) and Young’s modulus (\(E\)) for a range of materials. Adapted with permission from ref. 184. Copyright 2020 Springer Nature.
Results of recent studies have probed the dynamic metal-linker bonding in MOFs. The recent work of Zhang et al. have discovered short-range polymorphism and amorphous phases instead of crystalline phases upon melt-quenching and the properties of the glasses obtained were characterized by various methods. The structural disorder between the MOF crystals and the corresponding glasses was also enhanced by the use of ReaxFF-based molecular dynamics simulations. The experimental trends were confirmed by these simulations.

Regarding computational analysis, ZIF-4, ZIF-8, and SALEM-2 (Zn[Im]2) glasses obtained via melt-quenching have been investigated by ab initio molecular dynamics simulations. Those MOF glasses were computationally explored at the quantum chemical level, which allowed to describe the coordination bonds breaking and forming. Both the substitution of the imidazole linker and the topology of the frameworks were found to affect the behavior upon melt-quenching and the properties of the glasses obtained (local order, average coordination, and porosity).

Andreeva et al. have probed the dynamic metal-linker bonding in MOFs with variable-temperature diffuse reflectance infrared Fourier transform spectroscopy (VT-DRIFTS) and ab initio plane wave density functional theory. The evidence of melting behavior in ZIFs was also observed for carboxylate-based MOFs by monitoring the redshifts of carboxylate stretches coupled to anharmonic metal-carboxylate oscillators. Although carboxylate-based MOFs were found to undergo structural distortions associated with melting, they decomposed before melting. The redshift of the carboxylate modes was attributed to a crystalline to amorphous phase transition. The authors suggest that the difference in melting between carboxylate-based MOFs and ZIFs is due to the metal nodes. While carboxylate MOFs are often made up multimetallic metal nodes, ZIFs contain individual metal ions. Upon dissociation from linkers, those multimetallic metal nodes, ZIFs contain individual metal ions.

As it has been reviewed, no structural difference in the short-range order between the MOF crystals and the corresponding glasses has been identified by PDF analysis, XAS, Raman spectroscopy, and 13C and 15N magic-angle-spinning (MAS) NMR. However, these results have been challenged by recent findings. Madsen et al. have discovered short-range disorder in Zn-based ZIF glasses using ultrahigh-magnetic-field 67Zn MAS NMR spectroscopy at 19.5 and 35.2 T. ZIF-4, ZIF-62, and ZIF-8-795 were found to contain two crystallographically distinct Zn sites at 1:1 ratio, one of which was a more distorted Zn[ligand] tetrahedron. However, upon melting and vitrification, the two distinct Zn sites characteristic transformed into a single tetrahedral site. Therefore, the scission and renewal of the Zn–N bonds upon melting resulted in structural reconstruction. The structural disorder of the Zn[ligand] tetrahedron in the glass state was higher than that in the crystalline phase. It is worth mentioning that the degree of short-range disorder was similar for all three ZIF glasses. The 67Zn NMR spectra of the ZIF glasses showed lower isotropic chemical shift compared with the crystalline frameworks. This suggested an increase in the average Zn–N distance in the glasses.

4.3. Glasses prepared by other methods

Glass prepared from crystals by melt-quenching has been reviewed so far. This technique can only be applied to MOF crystals with stable liquid phase. Chen et al. have reported a non-thermal method for the synthesis of the glass state of a 2D CP, CdTz [Cd(H2PO4)2(HTr)] (Tr = 1,2,4-triazole). The glass phase was prepared by solvent-free mechanical milling under an Ar atmosphere. Milling times were 40, 240, and 500 minutes, yielding ag-CdTz-40, ag-CdTz-240, and ag-CdTz-500, respectively. Tg and temperature of recrystallization (Tc) were found to be 79 °C and 104 °C, 85 °C and 126 °C, and 90 °C and 142 °C, for ag-CdTz-40, ag-CdTz-240, and ag-CdTz-500, respectively. Therefore, reversible crystal-to-glass transformation was obtained. According to XAS analysis and 113Cd NMR spectra, the local structural arrangement around Cd21 centers remained after the vitrification. PDF results suggested a deformed structure of the glass state. The Cd21 ions were proposed to coordinate with HPO42- and HT in a distorted octahedral arrangement. The proton conductivities of ag-CdTz were two orders of magnitude higher than those of CdTz. In addition, dielectric constant (\(\varepsilon\')) also enhanced after vitrification. The disorder and enhanced mobility of ligands in the glass structure yielded the superior proton conductivity and dielectric constant. In a subsequent study, Ohara et al. explored the mechanical vitrification of two 2D CPs: CrTz and MnTz. These CPs were ball milled under an Ar atmosphere. They found that the ball milling induced glass formation of CrTz and MnTz. Tg and Tc for glass CrTz and glass MnTz were reported to be 62, 90, and 81, 128 °C, respectively. By contrast, FeTz, CoTz, and ZnTz did not exhibit glass forming under ball milling. This was likely due to the higher bonding energies of FeTz, CoTz, and ZnTz compared to those of CrTz and MnTz. According to XAS and PDF analysis, the local coordination bonds of crystalline MnTz were preserved in glass MnTz, but the ligand orientations were distorted. Glass MnTz showed two orders higher H+ conductivity than MnTz at 25 °C, and even four orders higher at 86 °C, reaching 1.3 × 10–3 S cm–1 at that temperature. In addition, in this work, previously mentioned CdTz CP was doped with DABCO during the mechanical vitrification, resulting in tunable Tg and Tc and improvement of anhydrous H+ conductivity.
In another study, Zhao et al. developed an approach to obtain monolithic, transparent nanoporous MOF glasses by assembling metal nodes and organic struts and subsequent evaporation of a plasticizer-modulator solvent.\textsuperscript{191} Ti-oxo clusters (Ti$_6$O$_6$(OEt)$_{18}$) were reacted with 2,2-bis(4-hydroxyphenyl) propane (BPA) linkers in THF at reflux overnight. In doing so, the ethoxide ligands were replaced by phenolates to form a network. Then, the network was dissolved in m-cresol. Transparent orange monolithic glasses of Ti-BPA MOF were formed by evaporation of m-cresol at 140 °C (Fig. 37). The solvent removal decreased the configurational freedom of the large molecules in a solution, in a similar manner that cooling a liquid of fixed composition. During this process, the Ti-cresololate bonds were replaced by Ti–O–(BPA)–O–Ti bonds. The presence of Ti-oxo clusters in MOF glass was confirmed by XAS. In addition, IR spectroscopy proved the incorporation and integrity of the BPA linkers in the glass. Ti-BPP glass constructed with Ti-oxo clusters and 2,2-bis(4-hydroxyphenyl) propane (BPP) linkers was also synthesized by applying this approach. Ti-BPA glass and Ti-BPP glass exhibited an internal surface area of 330 m$^2$ g$^{-1}$ and 267 m$^2$ g$^{-1}$, respectively.\textsuperscript{191}

Li et al. have also attempted to develop new methodologies to fabricate bulk, homogeneous, and bubble-free MOF glasses.\textsuperscript{181} They explored (i) vacuum hot pressing and (ii) remelting routes to prepare bulk MOF glasses. (i) As a proof of concept, ZIF-62 was heated to 723 K under 15 MPa in vacuum. After 1 h, amorphous ZIF-62 was achieved, referred as a$_{\text{gp}}$-ZIF-62 (a$_{\text{gp}}$ = pressed glass). a$_{\text{gp}}$-ZIF-62 was found to be a mixture of a-ZIF-62 and a$_{\text{gr}}$-ZIF-62. Therefore, a heterogeneous bulk sample was obtained by vacuum hot pressing of ZIF-62. (ii) Herein, a$_{\text{gr}}$-ZIF-62 was firstly ball-milled at 25 Hz for 5 min to homogenize the particle size and subsequently pressed into a pellet. Then, a$_{\text{gr}}$-ZIF-62 pellet was remelted at 673 K (a temperature above $T_g$) to avoid the presence of bubbles in bulk. The presence of bubbles in glasses is considered a serious defect.\textsuperscript{182} The final glass, named as a$_{\text{gr}}$-ZIF-62, was free of bubbles. Therefore, a transparent and bubble-free bulk glass ZIF-62 was successfully fabricated by remelting. $T_g$ of both a$_{\text{gr}}$-ZIF-62 and a$_{\text{gr}}$-ZIF-62 was maintained at around 600 K.\textsuperscript{181}

Recently, Das et al. have investigated the crystal melting and vitrification behaviors of a 3D MOF, [Ag(pL2)(CF$_3$SO$_3$)$_2$]-2C$_6$H$_6$ (pL2 = 1,3,5-tris(4-ethylbenzonitrile)benzene).\textsuperscript{183} $T_m$ of the framework was found to be 271 °C. The liquid phase was transformed into a glass state by cooling to RT. $T_g$ was reported to be 161 °C. The vitrification was also obtained by mechanical hand-grinding in Ar atmosphere. $T_g$ of the hand-grinded glass was reported to be 107 °C. The hand-grinded glass MOF recrystallized at 117 °C. According to XAS, PDF, and FT-IR analysis, the coordination environment around Ag$^+$ was the same in crystalline and glass phases. The hand-grinded glass exhibited permanent porosity, as illustrated by the CO$_2$ adsorption isotherms. In addition, the hand-grinded glass MOF was found to recrystallize under benzene vapor.\textsuperscript{183} Similarly, the same research group have explored the melting and vitrification of a nitrile-based 2D CP, [Ag(mL1)(CF$_3$SO$_3$)$_2$]-2C$_6$H$_6$ (mL1 = 1,3,5-tris(3-cyanophenylethyl)benzene).\textsuperscript{184} The CP melted at 169 °C and had a wide liquid state temperature window of over 110 °C ($T_g$ = 280 °C), which is one of the largest for reported CP/MOFs. The crystalline phase transformed to glass state by melt-quenching or mechanical milling (hand-grinding). $T_g$ of the MQG CP was 68 °C. High thermal stability without crystallization or degradation was shown by the MQG CP. $T_g$ of the mechanical milled glass CP was also 68 °C. In contrast, the mechanical milled glass CP recrystallized at 102 °C. After performing hand-grinding over the MQG CP, the material allowed recrystallization at 130 °C. As determined by XAS, PDF, and FT-IR analysis, Ag$^+$ maintained the same coordination environment in crystalline and glass CPs. The mechanical milled glass CP exhibited permanent porosity as confirmed by CO$_2$ gas sorption studies. In addition, it was observed glass-to-crystal transformation upon exposure the mechanical milled glass CP to benzene vapor at 25 °C. A grain-boundary-free mechanical milled glass monolith was fabricated by a hot-press process. This monolith showed a $T_g$ of 71 °C and $T_c$ of 166 °C. Moreover, when the glass monolith was treated with benzene, surface crystallization was observed.\textsuperscript{184}

### 4.4. MOF-blends

MOF blends are a mixture of two glass-forming MOFs, created by heating to a temperature at which both frameworks are liquid and, subsequently, quenching. Longley et al. fabricated the blend (ZIF-4-Zn)$_{0.5}$(ZIF-62)$_{0.5}$.\textsuperscript{8} Firstly, ZIF-4-Zn and ZIF-62 were physically mixed in equal weight proportions by ball-milling. Subsequently, the mixture was isothermally treated for 2 min at 590 °C. Finally, the blend was formed by quenching. $T_g$ of (ZIF-4-Zn)$_{0.5}$(ZIF-62)$_{0.5}$ blend was reported to be 306 °C. $T_g$ of a further set of (ZIF-4-Zn)$_{1}$-(ZIF-62)$_{2}$, blends was also explored. The increase in $T_g$ with increasing ZIF-62 content was found to follow a linear relation. The blend (ZIF-4-Co)$_{0.5}$(ZIF-62)$_{0.5}$ was similarly prepared by quenching the physical mixture.
of ZIF-4-Co and ZIF-62 from 425 °C. $T_g$ of (ZIF-4-Co)$_{0.5}$(ZIF-62)$_{0.5}$ blend was found at 300 °C. PDF measurements were consistent with previous conclusions on near-identical short-range order between crystal and glass ZIFs. Electron energy loss spectroscopy (EELS) showed the presence of Co and Zn along with an interfacial region. EDX yielded more insight into the domain structure and interfacial bonding (Fig. 38). It was shown relatively sharp interfaces between Co and Zn domains. While some regions exhibited minor homogeneous mixing of Co and Zn, the majority were segregated into single-metal domains. The high viscosity of both molten phases prevented complete homogeneous mixing. In a subsequent study, Collins et al. reported a subwavelength spatially resolved physicochemical analysis of the electronic states at visible and UV energies in the blend (ZIF-4-Co)$_{0.5}$(ZIF-62)$_{0.5}$ by using EELS in STEM. Combined STEM-EELS and DFT calculations showed that domains less than 200 nm in size retained the electronic structure of the precursor crystalline ZIF phases. Consequently, the distinct mechanical properties observed in glass blends arose from interactions between domains in the glass.

4.5. Flux melted MOFs

Flux melted MOFs are glasses made from a glass-forming MOF and a non-glass forming MOF. They are created by quenching from $T_m$ of the glass-forming component. To form flux melted MOFs, it is required an accessible and reasonably wide temperature region over which the liquid, and crystalline MOFs, are both stable. The two MOFs should obey the condition $T_{m1} < T_d2$, where $T_{m1}$ refers to the $T_m$ of the liquid-forming MOF, and $T_d2$ is the $T_d$, or upper stability limit, of the crystalline MOF.

As mentioned in the previous section – MOF liquids – the technique of flux melting has been applied to melt ZIF-8. A flux melted MOF glass ([ZIF-8]$_{0.2}$(ZIF-62)$_{0.8}$) was produced by heating (ZIF-8)(ZIF-62)(20/80) to 773 K, and then quenched back to RT. Similarly, a$_g$-[ZIF-67]$_{0.2}$(ZIF-62)$_{0.8}$ was prepared by heating (ZIF-67)(ZIF-62)(20/80) at 770 K, and quenching (Fig. 39). a$_g$-[ZIF-8]$_{0.2}$(ZIF-62)$_{0.8}$ and a$_g$-[ZIF-67]$_{0.2}$(ZIF-62)$_{0.8}$ were reported to adsorb CO$_2$ at 273 K and 1 bar. Analysis of the CO$_2$ isotherms yielded surface areas of 325 m$^2$ g$^{-1}$ and 202 m$^2$ g$^{-1}$ for (ZIF-8)(ZIF-62)(20/80) and a$_g$-[ZIF-8]$_{0.2}$(ZIF-62)$_{0.8}$.

Fig. 38 Chemical mapping of domain structures in (ZIF-4-Co)$_{0.5}$(ZIF-62)$_{0.5}$. (a) ADF-STEM image and corresponding EELS analysis. ADF-STEM image and corresponding EDX mapping for (b) a second and (c) a third glass particle. The orange boxes correspond to the regions analyzed for chemical mapping. Adapted with permission from ref. 6. Copyright 2018 Springer Nature.
respective. Surface areas of 218 m² g⁻¹ for (ZIF-67)(ZIF-62)(20/80) and 194 m² g⁻¹ for a g [(ZIF-67)₀.₂(ZIF-62)₀.₈] were also estimated from the isotherms. In addition, the diffusion of CO₂ in glass was found to be slower than in the crystalline precursor, which was consistent with the more constricted and tortuous pore network.⁷

Recently, the (ZIF-4-Co)₀.₅(ZIF-62)₀.₅ blend and the a g [(ZIF-67)₀.₂(ZIF-62)₀.₈] flux melted glass have been characterized by STEM-EDX tomography with absolute quantification.⁹⁶ The (ZIF-4-Co)₀.₅(ZIF-62)₀.₅ blend was revealed to consist of a Zn-rich domain and a Co-rich domain, which was in good agreement with the results of the previously reviewed study.⁹⁵ These observations were consistent with the high viscosity of liquid ZIFs. In a g [(ZIF-67)₀.₂(ZIF-62)₀.₈], a relatively phase-pure Zn region and a homogeneous mixing of Zn and Co in the Co-rich regions was observed. Therefore, significant miscibility was noted, which was in consonance with previous studies.⁷

4.6. MOF crystal-glass composites

MOF-CGCs are materials in which a crystalline MOF is embedded within a glass MOF matrix. To form MOF-CGCs, the T_d of the crystalline framework is required to exceed the T_m of the glass-forming matrix. In addition, flux melting should be avoided. In the earliest study of MOF-CGCs, Hou et al. synthesized MOF-CGCs comprised of MIL-53 or UiO-66 embedded within a_g-ZIF-62.⁶ The mixture ZIF-62 and MIL-53 (or UiO-66) was firstly homogenized by ball-milling (30 Hz, 5 min). It yielded [MIL-53]₀.₅[ZIF-62]₀.₅ or [UiO-66]₀.₅[ZIF-62]₀.₅, where X and Y are percentages by mass of each component. The mixtures were then heated at 450 °C (above T_m of ZIF-62) for 10 min and, subsequently, cooled back to RT. In doing so, (MIL-53)₀.₅(a_g-ZIF-62), or (UiO-66)₀.₅(a_g-ZIF-62), were obtained. T_g of (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ was found to be 310 °C. T_g of (UiO-66)₀.₂₅(a_g-ZIF-62)₀.₇₅ was not exactly determined due to the dehydroxylation of the UiO-66 inorganic cluster. Two separated phases in (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ and, also, in (UiO-66)₀.₂₅(a_g-ZIF-62)₀.₇₅ were revealed by STEM-EDX, which mapped the elemental distribution of the metal centers (Fig. 40). A fragment of (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ was reconstructed by STEM-EDX. Particles of MIL-53 of 30–300 nm in size were found to be embedded within the ZIF-62 glass. Similar results were also obtained with the (UiO-66)₀.₂₅(a_g-ZIF-62)₀.₇₅. The PDFs of (MIL-53)[ZIF-62]₀.₇₅ and (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ were very similar in their short-range order, below 7.5 Å. The PDFs also retained the longer-range oscillations due to Al-Al correlations in MIL-53. PDF of (UiO-66)₀.₂₅(a_g-ZIF-62)₀.₇₅ displayed weaker features above 6.4 Å compared to the PDF of (UiO-66)[ZIF-62]₀.₇₅. The stabilization of MIL-53-lp in (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ was also examined in this study. It should be remembered that the physisorption of water by open-pore MIL-53-lp causes a transition to a closed pore MIL-53-np, due to formation of framework-guest (water molecule) interactions.⁹⁹ According to XRD results, only MIL-53-lp was present in (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅. The H₂ uptake of (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ was 1.9 mmol g⁻¹ at 1 bar. Moreover, the CO₂ adsorption capacity of (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ approached the capacity of pure MIL-53. The stabilization of MIL-53-lp within the glass allowed a high CO₂ uptake even at low pressure conditions. Pores sizes of 5–6 and 11 Å were also calculated from Ar isotherms on (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅. In a subsequent work, the stabilization of MIL-53-lp upon encapsulation within a_g-ZIF-62 was further explored by Ashling et al.¹⁰⁰ They synthesized a series of (MIL-53)₀.₉(a_g-ZIF-62)₀.₁, where x = 0.2₅, and also 0.₃ ≤ x ≤ 0.₉ in 0.₁ increments. The maximum total loading capacity for MIL-53-lp stabilization was found to be between 60 and 70 wt% MIL-53 within a_g-ZIF-62. MIL-53-np emerged upon higher concentrations of MIL-53. The total CO₂ quantity adsorbed was found to increase from (MIL-53)₀.₂₅(a_g-ZIF-62)₀.₇₅ (1.06 mmol g⁻¹) to (MIL-53)₀.₆(a_g-ZIF-62)₀.₄ (2.55 mmol g⁻¹), in accordance with the increasing concentration of MIL-53-lp within a_g-ZIF-62. The maximum effective CO₂ adsorption capacity of the (MIL-53)₀.₉(a_g-ZIF-62)₁₋₋ series was at 80 wt% MIL-53.¹⁰⁰

4.7. MOF and inorganic glass composites

Longley et al. have combined MOF glasses with inorganic glasses producing composite materials of both glassy domains. ZIF-62 was selected as the glass-forming MOF component.
Three inorganic glasses with composition \((1 - x)[(\text{Na}_2\text{O})_x(\text{P}_2\text{O}_5)] - x[(\text{AlO}_{3/2})_x(\text{AlF}_3)_y]\) were chosen to prepare the composite. They were named according to their composition: base, Na-deficient and Al-rich. Importantly, \(T_g\) of these inorganic glasses, which ranged from 310 to 450 °C, was close to the \(T_m\) of ZIF-62 (437 °C). Equal weights of ZIF-62 and each inorganic glass were ball-milled together. Subsequently, the ball-milled mixtures (ZIF-62)(Inorganic Glass)(50/50) were held at 450 °C for 1 or 30 minutes and then quenched. Specifically, (ZIF-62)(Al-rich)(50/50) heated at 450 °C for 1 minute showed melting of ZIF-62 at 435 °C and glass transition of Al-rich at ~440 °C. In the second heating cycle, glass transitions were found at ~318 °C, which
corresponded to ag-ZIF-62, and at ~440 °C, which corresponded to ag-Al-rich. Almost identical behavior was found with (ZIF-62)(Al-rich)[50/50] heated for 30 minutes at 450 °C. ZIF-62 melting endotherm was not shown in DSC experiments on the (ZIF-62)(Base)[50/50] and (ZIF-62)(Na-deficient)[50/50] samples due to the overlap of the T_g of the inorganic glass component with the T_m of ZIF-62. However, T_g of ag-ZIF-62 and inorganic glass were found in the second heating cycle. These glass composites were referred to as (ag-ZIF-62)_{0.5}(Inorganic Glass)_{0.5}–1 min and (ag-ZIF-62)_{0.5}(Inorganic Glass)_{0.5}–30 min. A significant decrease in heterogeneity was found in the samples heated for 30 minutes. While the XRD patterns of (ag-ZIF-62)_{0.5}(Na-deficient)_{0.5}–1 min, (ag-ZIF-62)_{0.5}(Al-rich)_{0.5}–1 min and (ag-ZIF-62)_{0.5}(base)_{0.5}–30 min appeared completely amorphous, the patterns of (ag-ZIF-62)_{0.5}(Na-deficient)_{0.5}–30 min, (ag-ZIF-62)_{0.5}(Al-rich)_{0.5}–30 min and (ag-ZIF-62)_{0.5}(base)_{0.5}–1 min contained a small number of low intensity Bragg peaks. These peaks were found to match those of ZIF-62. These results indicated a small degree of recrystallisation to ZIF-62, which was further confirmed by SEM and PDF. In these composites, the glasses were found to bond at their interfaces. However, there was minimal overlap between glasses. The mixing of inorganic glasses and MOF glasses is expected to produce composites with mechanical, thermal, chemical and electrical properties of inorganic glasses while maintaining the chemical versatility of the MOFs.199

4.8. MOF glass membranes

The challenges that limit the fabrication and utilization of zeolite and MOF membranes, which are related to the presence of defects and unavoidable grain boundaries,200 are expected to be overcome by MOF glass materials. In other words, it is envisioned high-performance MOF glass membranes without grain boundary structures. The first MOF glass membrane was fabricated by melt-quenching treatment of an in situ solvothermally synthesized polycrystalline ZIF-62 membrane on a porous ceramic alumina support (Fig. 41).175 T_m was set to 440 °C and held for 15 min to guarantee the complete melting of the ZIF-62 solid to liquid. ZIF-62 liquid penetrated the nanopores of the alumina support via capillary extrusion. The ZIF-62 liquid turned into the glass state by cooling down to RT, forming the isotropic and free of grain boundaries ZIF-62 glass membrane. The molecular sieving ability of the membrane was enhanced via the vitrification. The selectivities for H_2/CH_4, CO_2/N_2 and CO_2/CH_4 were 50.7, 34.5 and 36.6, respectively. The excellent performances exceeded the corresponding Robeson upper bounds. The glass membrane also exhibited long-term and water stability.175 Very recently, Lin et al. have developed another MOF glass membrane via in situ melting and vitrification.201 Zn[(Im)_{1.95}(PhIm)_{0.05}]_{0.5} was used as the filler for polyimide 6FDA-DAM (6FDA = 2,2-bis(3,4-carboxyphenyl)hexafluoropropedianhydride, DAM = 2,4,6-trimethyl-p-phenylenediamine), which was the matrix. The composites, named as (Zn[(Im)_{1.95}(PhIm)_{0.05}])_{x}(6FDA-DAM)_{1−x} where x is the weight ratio of the ZIF, were treated at 390 °C in Ar to achieve complete melting of [Zn[(Im)_{1.95}(PhIm)_{0.05}]]. Subsequently, they were cooled down to yield (ag-Zn[(Im)_{1.95}(PhIm)_{0.05}])_{x}(6FDA-DAM)_{1−x}. The in situ melting within matrix effectively reduced the defects even at meso- and macroscale. The CO_2/N_2 separation performance of the membrane was measured in this study. (ag-Zn[(Im)_{1.95}(PhIm)_{0.05}])_{0.5}(6FDA-DAM)_{0.5} membranes had lower CO_2 permeability than that of the neat polymer membrane, but with a significantly enhanced selectivity. It is worth mentioning that the surface area (NLDFT) of [Zn[(Im)_{1.95}(PhIm)_{0.05}]]_{x} and ag-

![Fig. 41. Top-view SEM images of (a) polycrystalline ZIF-62 membrane and (b) ag-ZIF-62 membrane. (c) Scheme of the formation of the glass membrane. (d) XRD patterns. (e) EDXS mapping of ag-ZIF-62 membrane, including the membrane on the surface and the infiltration of the top layer of the alumina support. Labelling scheme: Zn = green. (f) Single-gas permeance as a function of the gas kinetic diameter. Ideal selectivity at 25 °C (inset). Separation performances of the glass membrane: (g) H_2/CH_4, (h) CO_2/N_2, and (i) CO_2/CH_4. Adapted with permission from ref. 175. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.]

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[Zn(Im)_{1.95}(PhIm)_{0.05}] was found to be 476 and 173 m^2 g^{-1}. Therefore, \( a_e[\text{Zn(Im)}_{1.95}(\text{PhIm})_{0.05}] \) retained significant micro-porosity. The surface area (NLDFT) of (\( a_e[\text{Zn(Im)}_{1.95}(\text{PhIm})_{0.05}] \))(6FDA-DAM)_{1-x} was not reported.201

4.9. Perspectives in MOF glasses

The development of a glass phase from a crystalline state is one of the principal areas of study in materials chemistry. Unique properties such as transparency, network dynamics, and mechanical flexibility may arise from this transformation. Particularly, the huge advantage of MOF glasses compared to the crystalline frameworks is based on their very high \( T_d \) and their liquid phase processability.

LDL-to-HDL transition has been reported in MOF glasses.5,206 Angell plots can be employed to quantify the large differences in viscosity of the glass-forming LDL and HDL phases (Fig. 42). The viscous behavior of new MOF glasses can be conveniently compared on such plot. When appropriate, the temperature dependence of the viscosity can be fitted with model equations such as Vogel–Fulcher–Tammann (VFT)207 or MYEGA.208

MOF glasses with accessible porosity are starting to emerge. These MOF glasses with intrinsic porosity can be considered a new class of porous hybrid inorganic–organic materials. They are more thermally stable than organic polymer glasses and have greater chemical functionality than microporous inorganic glasses.127 These glasses cannot compete with the ultra-high surface areas displayed by zeolites and crystalline MOFs, they must be seen in the light of their high thermal and mechanical stability, and ease of processing. An immense number of MOF glasses with porosity are predicted to be formed due to (1) the large number of known crystalline MOFs that can serve as potential precursors and (2) the tunability of those crystalline MOFs prior to melting.209 In addition, we presume that the elucidation of the mode and mechanism of MOF melting will promote the design of new MOF glasses with desired optical, electrical, and mechanical properties. Aside from the preparation of MOF glasses, the current questions are:

(i) The local structure of the MOF glasses when compared to that of their crystalline parents, and

(ii) The time scale of bond cleavage and subsequent formation.

MOF glasses are expected to be applied in the photonics fields for sensing and optical modulation. Moreover, the immersion of stimuli-responsive MOFs into the glass domain will lead to new, smart applications and a new era of glass technology.210 However, although the transparency of MOF glasses can be optimized, the potential of MOF glasses in transparent electronics remains hampered by their brittleness and low intrinsic electrical conductivity. MOF glasses are also promising for transport, sensing, capture or release of small ions or molecules. Moreover, the disorder, open network, and enhanced mobility in the glass state favor the ion conductivity. Consequently, ion conduction may be expected in MOF glasses.

Phase-change MOFs are promising materials for memory and data storage applications (Fig. 43).211 Phase-change devices are based on the reversible switching between crystalline and glass state.212,213 Amorphization (RESET-operation) of a bit occurs by melt-quenching, employing a precisely controlled amount of heat. The heat sources are either laser pulses or electrical pulses, depending on the application in optical or electronic data storage. The huge temperature difference between the confined melt and the surrounding material leads to high cooling rates. Thus, a melt-quenched glassy bit is formed. Crystallization (SET-operation) requires annealing of a glassy bit at a temperature above \( T_g \) and below \( T_m \). Low intensity (low current) pulses are used to distinguish between low and high reflectivity (conductivity) in order to determine whether a bit is amorphous or crystalline. Crystalline and glass phases often exhibit very different optical and electrical properties, thus providing the contrast to distinguish between logical states. Thus, phase-change materials, specifically phase-change MOFs, can be employed for rewritable optical and electrical data storage.

The challenges that limit the fabrication and utilization of zeolite and MOF membranes will be overcome by grain

Fig. 42. Angell’s fragility plot. Those systems obeying a strict Arrhenius dependence of \( \log \eta \) vs. \( T_g/T \) such as the archetypical liquid GeO\(_2\) are known as “strong”202. Those systems exhibiting a pronounced non-Arrhenius dependence such as liquid toluene are labeled as “fragile”.203 Water and Ge\(_{15}\)Te\(_{85}\) show anomalous behavior and cannot be described using a conventional as Vogel–Fulcher–Tammann (VFT) or MYEGA equation.204,205 Adapted with permission from ref. 206. Copyright 2019 Elsevier.

Fig. 43. Operation principle of phase-change devices.
boundary-free glass membranes. The absence of grain boundaries facilitates mass transport and gas permeability. Therefore, MOF glasses are promising candidates to construct high-performance grain-boundary-free membranes for gas separation, photoconductivity or spectral conversion (luminescence and light-harvesting). On the other hand, the mechanical properties of MOF glasses need to be understood to determine the suitability of these materials for promising applications in protective coatings and display technologies. There is a lack of knowledge of mechanical properties owing to the challenge in preparing large bulk glass samples for mechanical testing. We expect this issue to be overcome by preparing monolithic MOF glasses from crystalline frameworks by hot-pressing.  

Research into MOF-CGCs should be focused on improving the processing methods to incorporate larger amounts of the active MOFs. It is reasonable to propose the dispersion of various crystalline MOFs into a MOF glass to create a composite material. The optimum loading limits and the effects of crystalline MOF size should be also investigated. Moreover, the low $T_m$ of MOF glasses will allow the incorporation of temperature sensitive compounds such as organic fluorophores. In addition, CGC is expected to facilitate the assembly of crystalline MOFs into thermally and mechanically stable devices with various shapes. Regarding MOF blends, materials with exceptional mechanical properties may be accessed by blending process. Summarizing, research into MOF glasses will provide exciting opportunities for a great number of potential applications in the near future.

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>MOF</td>
<td>Metal–organic frameworks</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>PDF</td>
<td>Pair distribution function</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic-angle-spinning</td>
</tr>
<tr>
<td>ssNMR</td>
<td>Solid-state nuclear magnetic resonance</td>
</tr>
<tr>
<td>CGCs</td>
<td>Crystal-glass composites</td>
</tr>
<tr>
<td>aMOF</td>
<td>Amorphous metal–organic framework</td>
</tr>
<tr>
<td>HTCS</td>
<td>High-throughput computational screening</td>
</tr>
<tr>
<td>$\Delta H_{\text{stress}}$</td>
<td>Enthalpy of the stressed crystal</td>
</tr>
<tr>
<td>$\Delta S_{\text{stress}}$</td>
<td>Entropy of the stressed crystal</td>
</tr>
<tr>
<td>$\Delta S_{\text{LRO} \rightarrow \text{SRO}}$</td>
<td>Largest fraction of entropy increase</td>
</tr>
<tr>
<td>$\Delta H_{\text{ca}}$</td>
<td>Increased enthalpy from the perfect crystal to the amorphous phase</td>
</tr>
<tr>
<td>$\Delta S_{\text{ca}}$</td>
<td>Increased entropy from the perfect crystal to the amorphous phase</td>
</tr>
<tr>
<td>PIA</td>
<td>Pressure-induced amorphization</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>ZIF</td>
<td>Zeolitic imidazolate framework</td>
</tr>
<tr>
<td>MeIm</td>
<td>2-Methylimidazolate</td>
</tr>
<tr>
<td>a$_{\text{P}}$</td>
<td>Amorphization by pressure</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>Im</td>
<td>Imidazole</td>
</tr>
<tr>
<td>BDC</td>
<td>1,4-Benzenedicarboxylate</td>
</tr>
<tr>
<td>DEF</td>
<td>Diethyl formamide</td>
</tr>
<tr>
<td>BTB</td>
<td>Benzenetribenzoate</td>
</tr>
<tr>
<td>BTC</td>
<td>1,3,5-Benzenetricarboxylate</td>
</tr>
<tr>
<td>Fc</td>
<td>Ferrocene</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>DABCO</td>
<td>1,4-Diazabicyclo[2.2.2]octane</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>HIA</td>
<td>Heat-induced amorphization</td>
</tr>
<tr>
<td>$T_A$</td>
<td>Temperature of amorphization</td>
</tr>
<tr>
<td>a$_{\text{T}}$</td>
<td>Amorphization by heating</td>
</tr>
<tr>
<td>acac</td>
<td>Acetylacetone</td>
</tr>
<tr>
<td>CAAC</td>
<td>Crystalline-to-amorphous-to-amorphous-to-crystalline</td>
</tr>
<tr>
<td>TPT</td>
<td>2,4,6-Tris(4-pyridyl)-1,3,5-triazine</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>CAC</td>
<td>Crystalline-to-amorphous-to-crystalline</td>
</tr>
<tr>
<td>mtz</td>
<td>3-Methyl-1,2,4-triazole</td>
</tr>
<tr>
<td>FTIR-ATR</td>
<td>Fourier transform infrared spectroscopy – attenuated total reflectance</td>
</tr>
<tr>
<td>MMMs</td>
<td>Mixed matrix membranes</td>
</tr>
<tr>
<td>PhIm</td>
<td>Benzimidazolate</td>
</tr>
<tr>
<td>pdt</td>
<td>2,3-Pyrazinedithiolate</td>
</tr>
<tr>
<td>RT</td>
<td>Room-temperature</td>
</tr>
<tr>
<td>CAN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>HS</td>
<td>Hollow sphere</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>DDS</td>
<td>Drug delivery system</td>
</tr>
<tr>
<td>DCA</td>
<td>Sodium dichloroacetate</td>
</tr>
<tr>
<td>Z-CHC</td>
<td>$\alpha$-Cyano-4-hydroxyxianamic acid</td>
</tr>
<tr>
<td>a$_{\text{m}}$</td>
<td>Mechanical milling amorphization</td>
</tr>
<tr>
<td>nanoZIF-8</td>
<td>Nanocrystalline ZIF-8</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Decomposition temperature</td>
</tr>
<tr>
<td>cPhIm</td>
<td>Chlorobenzimidazolate</td>
</tr>
<tr>
<td>nIm</td>
<td>2-Nitroimidazolate</td>
</tr>
<tr>
<td>mnIm</td>
<td>4-Methyl-3-nitroimidazolate</td>
</tr>
<tr>
<td>ndc</td>
<td>2,6-Naphthalenedicarboxylic acid</td>
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<tr>
<td>bpdc</td>
<td>[1,1′-Biphenyl]-4,4′-dicarboxylic acid</td>
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<td>L7</td>
<td>4,4′-(1,2-Dienediy)bis-benzoic acid</td>
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<tr>
<td>L8</td>
<td>4,4′-(1,2-Ethenediy)bis-benzoic acid</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>dhta</td>
<td>2,5-Dihydroxyterephthalic acid</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near-edge structure</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>IIA</td>
<td>Irradiation-induced amorphization</td>
</tr>
<tr>
<td>a$_{\text{i}}$</td>
<td>Amorphization by irradiation</td>
</tr>
<tr>
<td>a$_{\text{e}}$</td>
<td>Amorphization by electrical discharge</td>
</tr>
<tr>
<td>H$_2$HPA</td>
<td>2-Hydroxyphosphonoacetic acid</td>
</tr>
<tr>
<td>ttcH$_3$</td>
<td>Thiotriocanuric acid</td>
</tr>
<tr>
<td>a$_{\text{CT}}$</td>
<td>Amorphization by chemical treatment</td>
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<tr>
<td>H$_3$SBDA</td>
<td>4,4′-Sulfonyldibenzoic acid</td>
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<tr>
<td>DMA</td>
<td>Dimethylamine</td>
</tr>
<tr>
<td>5-H$_3$sip</td>
<td>5-Sulfoisophthalic acid</td>
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<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>a-MOF-NC</td>
<td>aMOF nanocomposite</td>
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<tr>
<td>BDC-NH$_3$</td>
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</tr>
<tr>
<td>TMA</td>
<td>Trimethylaluminium</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>MLD</td>
<td>Molecular layer deposition</td>
</tr>
</tbody>
</table>
Conflicts of interest

There are no conflicts to declare.
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References


