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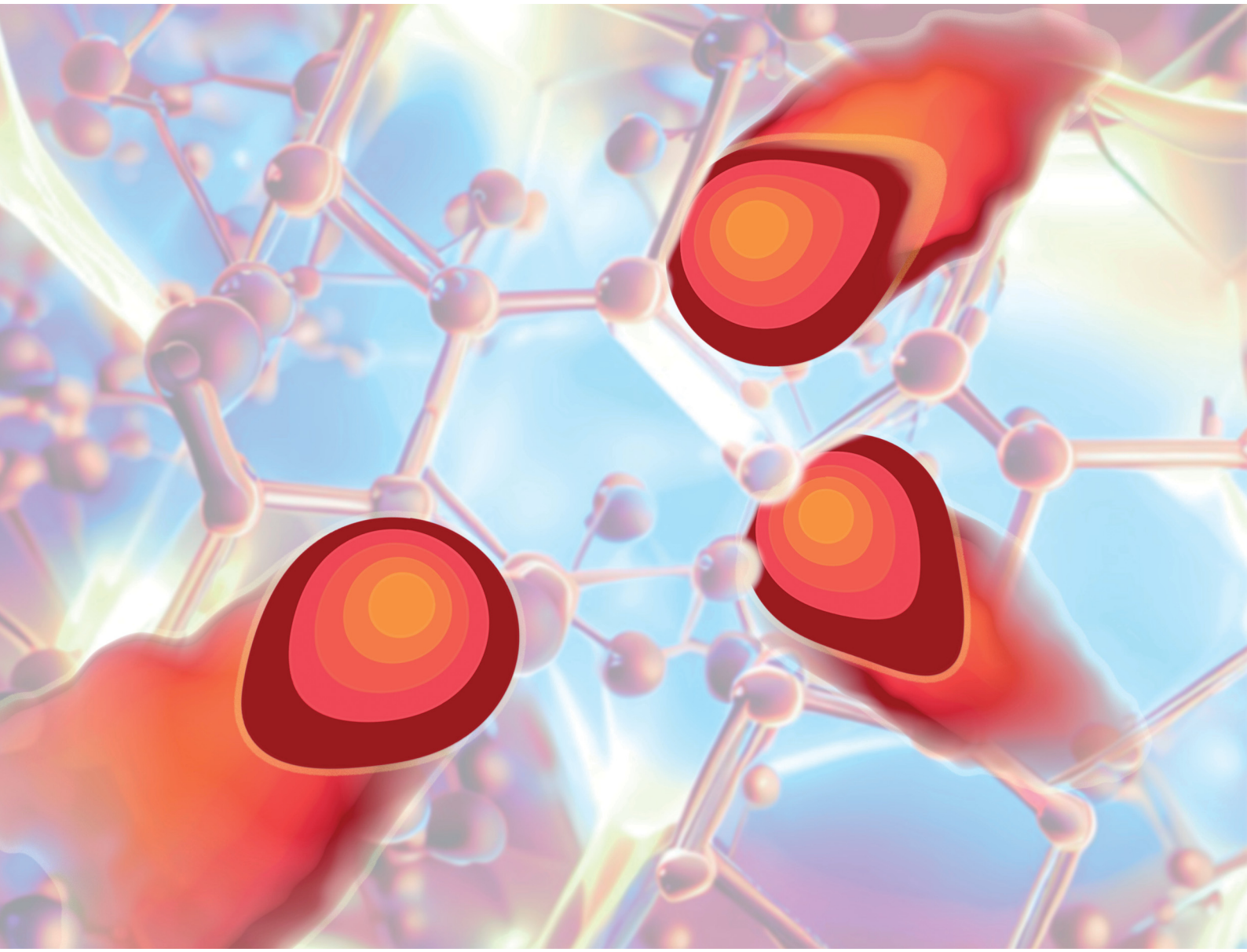

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Amorphous MOFs for next generation supercapacitors and batteries

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Metal–organic frameworks (MOFs) are porous materials comprised of metal nodes and organic linkers, which feature highly tunable structures and compositions that can be tailored for energy storage applications. While MOFs research in this area has predominantly focused on the crystalline domain, amorphous MOFs have also attracted increasing interests. Amorphpus MOFs, which lack any long-range periodic order in the framework, exhibit several properties that are beneficial for energy storage such as isotropic conduction, higher ionic and electrical conductivity, increased defect sites and enhanced electrochemical stability. This perspective aims to highlight the recent developments in amorphous MOFs including amorphous discrete powder, glassy and composite forms for batteries and supercapacitors. Additionally, we will also provide prospective areas for the future development of amorphous MOFs in this field.

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Introduction

With the remarkable advancements in technology witnessed in the past century, there has been a substantial surge in the demand for energy and its consumption. Consequently, there has been a notable shift away from fossil fuels as society strives towards a cleaner energy future, driven by stringent environmental policies. Presently, various battery technologies, including supercapacitors, lithium-ion batteries (LIB), and lithium–sulphur batteries, have garnered considerable attention due to their exceptional energy storage capacities and conversion efficiencies. However, it is important to address the significant capacity and stability challenges faced by both the electrodes and electrolytes in these batteries, as they can result in performance degradation during operation. Therefore, there is an urgent need for further advancements and improvements in battery technology development.[19,20]

Metal–organic frameworks (MOFs) or porous coordination polymers belong to a class of hybrid compounds that combine metal ions or clusters with organic ligands. This unique combination imparts them with several advantageous properties such as high surface area, tuneable pore sizes, and ease of modification.[21] As a result, MOFs have found extensive utility in diverse fields, ranging from catalysis[22,23] to gas separation,[24–26] gas adsorption[26,27] and recently electrochemical applications.[28–31]

MOFs have emerged as promising materials in the field of energy storage, leveraging their high tunability to achieve enhanced electrical performance. For example, MOFs tuning allows for improved electron access to active centres and, consequently, enhances the utilization of these active sites on MOFs, leading to superior performance in many fields such as electrocatalysis.[32,33] Furthermore, tuning of the metals, ligands and pore structures of MOFs can also enable fast and unimpeded ion transport leading to improvements in the rate performance, cycling stability and power density of energy storage devices.[34,35]

Although MOFs research in the energy field have predominantly focused on the crystalline domain, amorphous MOFs have also garnered increasing attention. This is because amorphous MOFs exhibit a relatively high energy state, possess abundant defect sites, and can offer isotropic ion conduction pathways.[13,36,37] For example, Zhang *et al.* found that amorphous MIL-88B (Fe_3O $[C_6H_4(CO_2)_2]_3OH{\cdot}nH_2O$) has better rate and cycle performance in lithium–sulphur battery compared with its crystalline counterpart.[38]

Hitherto, there has been limited reviews focusing on amorphous MOFs for energy storage, despite their significant potentials in this area.[20,39,40] Given the recent developments on amorphous MOFs in energy storage (Fig. 1), we aim to highlight and provide our perspectives on these materials, which encompasses discrete amorphous MOF powders, melt-quenched MOF glasses and amorphous MOF composites. We will focus on two specific energy storage fields, including supercapacitors and

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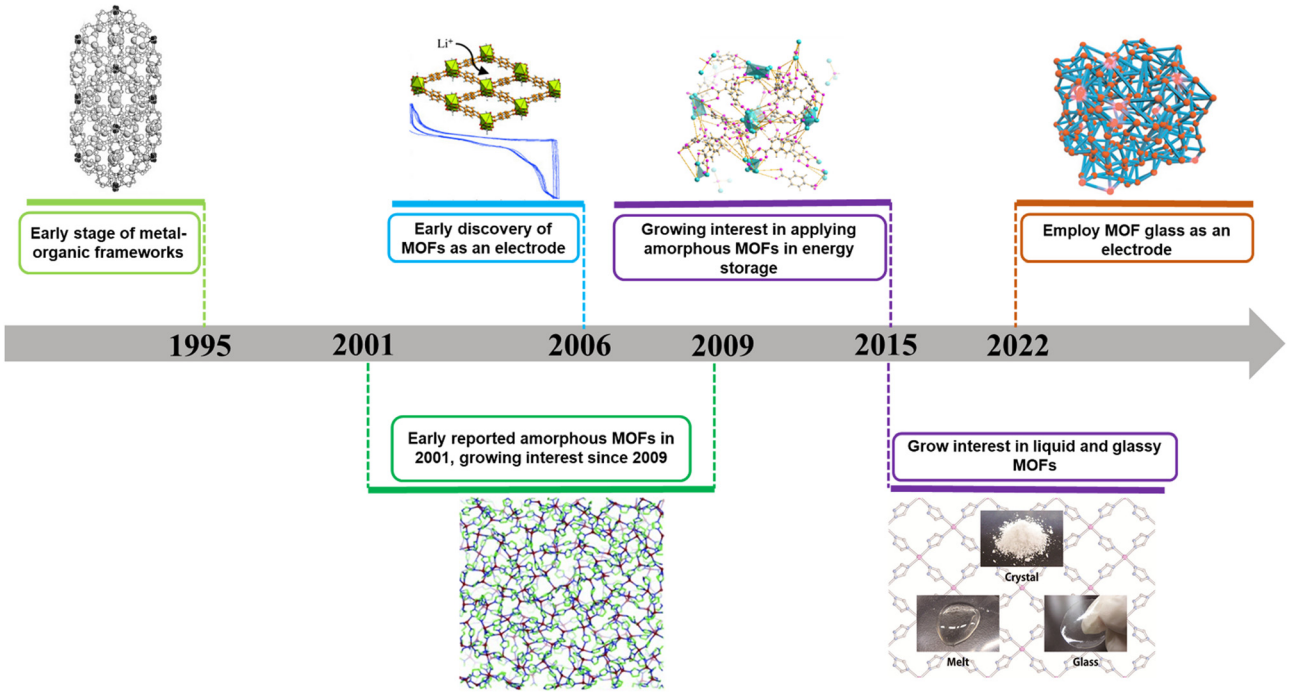

Fig. 1 Roadmap of development of amorphous MOFs and its application in batteries and supercapacitors.[1–11]

batteries (lithium-ion batteries (LIB), lithium–sulphur batteries *etc.*). Furthermore, we will provide future prospects of amorphous MOFs in this field. It is envisioned that this perspective will provide useful insights into the development of amorphous MOFs and their composites for energy storage.

Amorphous MOFs for energy storage

What are amorphous MOFs?

Majority of MOFs research including the energy storage area has focused on the crystalline domain. Crystalline MOFs have well defined and ordered structures. In other words, metal ions and organic ligands are arranged in repeated continuous patterns, featuring both long-range and short-range orders. Therefore, crystalline MOFs structures can be characterised by X-ray diffraction analysis and differentiated by the positions of diffraction peaks. Normally, crystalline MOFs are fabricated *via* solvothermal or hydrothermal approaches. Mechanochemical milling can also fabricate crystalline MOFs, but it is likely to introduce amorphous phases.[41,42]

In contrast to crystalline MOFs, non-crystalline MOFs, also called amorphous MOFs, feature a random distribution of metal ions and ligands within the framework, lacking any long-range order (Fig. 2). Consequently, amorphous MOFs display only diffuse scattering in X-ray or neutron diffraction patterns.[12]

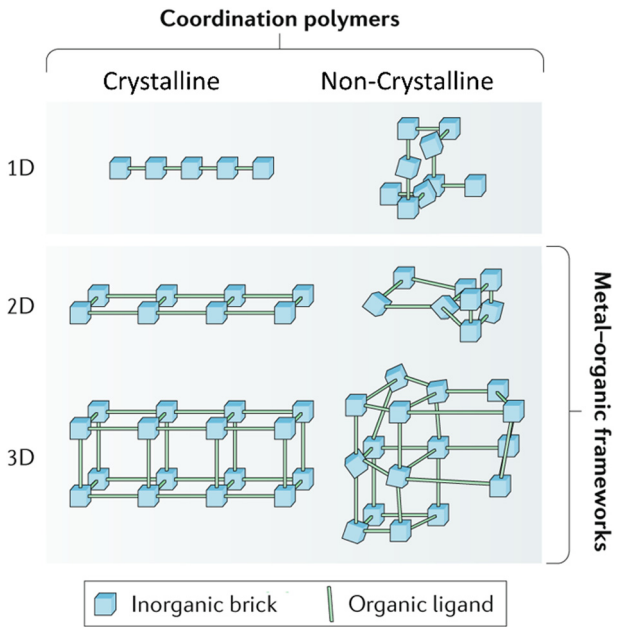

Fig. 2 Crystalline *vs.* non-crystalline. Reproduced from ref. 12 with permission from Springer Nature, copyright 2018.

How to obtain amorphous MOFs

Amorphous MOFs can be obtained through amorphization of crystalline MOFs, which is an entropy driven process. The amorphization process can be described as the following three steps (Fig. 3): Firstly, stress is applied to the crystalline MOFs. This causes the long-range order to be gradually lost due to accumulation of defects within the stressed MOFs' lattice. Meanwhile, entropy and enthalpy also increased due to the stress applied (State 1). When the increase in enthalpy caused by stress (ΔH_{stress}) is equal to the enthalpy of transition from perfect crystalline to amorphous phase (ΔH_{Ca}), the long-range

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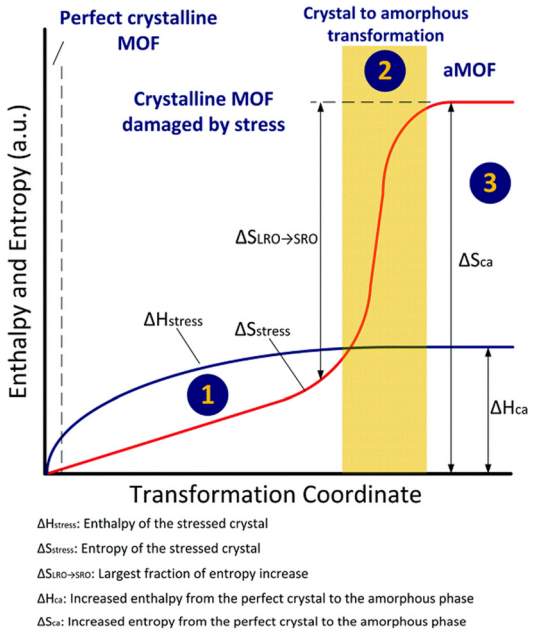

Fig. 3 Schematic representation of amorphization. Reproduced from ref.13 with permission from Royal Society of Chemistry, copyright 2021.

configuration of the atoms is no longer constrained. All atoms rotate and rearrange locally to the amorphous configuration where only short-range order exist. It is important to note that the crystal to amorphous transformation might be isenthalpic in some cases where there is a sudden and dramatic increase in entropy (State 2). In the final stage, no significant change in entropy or enthalpy is seen (Stage 3).[13]

Amorphization can be achieved through two routes, namely the top-down synthesis route and bottom-up synthesis route. Top-down synthesis involves the application of an external stimulus such as pressure, heat or radiation on pre-synthesized crystalline MOFs. This results in a change, loss or damage in the MOFs' lattice, porosity, channels, geometry, and connection.[5,43–45] Long-range order cannot be maintained and the MOFs gradually lose their crystallinity. The outcome is a disordered, amorphous MOFs with an abundance of defect sites. On the other hand, bottom-up synthesis represents the direct synthesis of amorphous MOFs from metals and ligands precursors, which is regulated by the choices of precursors and synthesis conditions.[46] There are three methods to control the direct synthesis of amorphous MOFs. The first method is to use flexible and/or asymmetric ligands that have strong connection with metal ions, such as amino acids and nucleotides, to directly fabricate amorphous MOFs.[47,48] Apart from ligands, templates and seeding agents can also be used to increase the local concentration of metal ions or ligands, which can help to form amorphous MOFs.[49–51] Lastly, synthesis conditions are also an important parameter that regulates MOFs' crystallinity. Solvent, reaction time, pH, type of metal salt precursors, metal to ligand ratios and concentration can all impact the crystallinity of MOFs.[52]

A synthesis route that is only applicable to a subgroup of amorphous MOFs is melt-quenching. This process requires the MOFs to have an accessible melting temperature that is below its decomposition temperature. This means that the covalent bonds within the ligands have to be stronger than the coordinative bonding between metal nodes and ligands to avoid decomposition.[44,53] Upon heat treatment, a transition from solid to liquid phase can be observed at the melting temperature (T_m). Subsequent rapid cooling of the melt, otherwise known as quenching, can avoid re-crystallisation and form an amorphous solid called melt-quenched MOF glass (MQG). The presence of a glass transition temperature (T_g) in this amorphous solid is required to classify it as a glass.[44] The ability of a glass-forming liquid to resist crystallisation during cooling to form glass is called the glass forming ability.[54,55] Generally, low GFA melting liquid will require faster quenching rate to overcome crystallisation and *vice versa*. The Kauzmann "2/3" law denotes that the T_g of a glass is empirically about 2/3 of its melting point (T_m), and thus a melt with a T_g/T_m ratio higher than 2/3 is considered to have a high GFA. It is commonly accepted that GFA is also associated with liquid fragility, crystal density, glass density and viscosity at T_m.[7]

Compared to crystalline MOFs, amorphous MOFs and MOF glasses tend to have lower porosity and surface area, but they feature higher ionic and electrical conductivity and more defect sites.[12,56,57] The use of amorphous MOFs in the MOF composites can provide new order–disorder structural configurations, thereby expanding the variety of composite structures and properties in the energy storage field. Moreover, amorphous MOFs have also been demonstrated to act as a suitable host matrix for a variety of functional guest materials.[58–60] This paper will mainly discuss amorphous MOFs in discrete powders form including its sub-family of melt-quenched MOF glass (referred as MOF glass in the following content). In addition, we will also discuss composites based on amorphous MOFs.

Discrete amorphous MOFs powders

The most common form factor of amorphous MOFs is discrete powders. Normally, MOF materials exhibit lower electrical conductivity with the loss of crystallinity due to the loss of porosity, lower surface area as well as the size imperfections.[61,62] However, amorphous MOFs can improve conductivity through other aspects, such as providing additional structural defect sites and unsaturated coordination sites that increase the active conductive surface area. This enables amorphous MOFs to be a promising candidate for energy storage purposes. For example, Yang *et al.* found that amorphous UiO-66 ($Zr_6O_4(OH)_4(BDC)_6$; BDC = 1,4-benzodicarboxylate) as illustrated in Fig. 4 has significantly higher specific capacitance (910 F g^{-1}) compared to crystalline UiO-66 (452 F g^{-1}). After 5000 cycles, the capacitance (610 F g^{-1}) of the amorphous phase remained high, which was over 1.5 times that of crystalline UiO-66. The improvement in performance was attributed to the increase in exposure of redox-active ligands resulting from the MOFs' metastable state and disorder within frameworks. Additionally, amorphous UiO-66 also exhibited higher thermal stability as indicated by the higher

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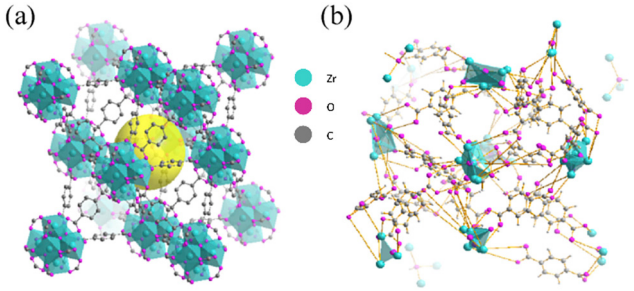

Fig. 4 Schematic representation of UiO-66 structures in the (a) crystal and (b) amorphous forms gained from reverse Monte Carlo (RMC) modelling. Amorphous UiO-66 has promising potential as a supercapacitor electrode material. Reproduced from ref. 6 with permission from Elsevier, copyright 2018.

decomposition temperature compared to the crystalline counterpart.[6]

Layered materials are also quite common in the energy storage field.[63] The application of amorphous MOFs with layered structures and large inter-sheet spacings can result in low diffusive resistance and high ion transport kinetics. Cui *et al.* fabricated amorphous Ni-pPD MOFs nanosheets (a-Ni-pPD, pPD = *p*-phenylenediamine) with large inter-sheet spacing of 1.6 nm induced by polarization. When coupled with an active carbon cathode, a-Ni-*p*PD showed a high gravimetric capacitance (259 F g^{-1}) and high areal capacitance (2.9 F cm^{-2}) at 2 A g^{-1} with a wide potential window of 2.85 V. High cycling stability was also observed where around 80% capacity was retained over 12 000 cycles.[64]

Amorphization can induce structural changes and bond rearrangement, so that new chemical bonding is likely to be introduced. New chemical bonding can generate new electron transport pathways and hence improve the electrical performance. Xiu *et al.* found that electrically bistable MOFs $Cu^{I}[Cu^{III}(pdt)_2]$ (pdt = 2,3-pyrazinedithiolate) can undergo reversible crystal-amorphous transformation upon external stimulation, and both forms (crystal and amorphous) can stably exist at ambient condition. After examination, they found that the reversible transformation was closely related to the adsorption and removal of acetonitrile (CAN). Interestingly, amorphous $Cu^{I}[Cu^{III}(pdt)2]$ exhibited 130% higher electrical conductivity compared to the crystalline form. The enhancement arose from conservation of functional groups in the structure and additional electron pathway (new Cu–S bonding) created during amorphization process.[65] This work opened the door for the application of amorphous MOFs as a switchable electrical conductor. Similar observations have also been made by Tomoinaka and co-workers, where amorphization created Cu–S–Cu bonding (CuS_x network) that improved electron transfer (Fig. 5). This turned crystalline $Cu^{I}Cl(ttcH_3)$ ($ttcH_3$ = trithiocyanuric acid) that was originally an insulator into an amorphous $Cu^{I}_{1.8}(ttc)_{0.6}(ttcH_3)_{0.4}$ semiconductor.[15]

Melt-quenched MOF glasses (MQG)

Glassy materials are known since the early days to be excellent ion conductors, such as glassy ceramics,[66] alkali silicate

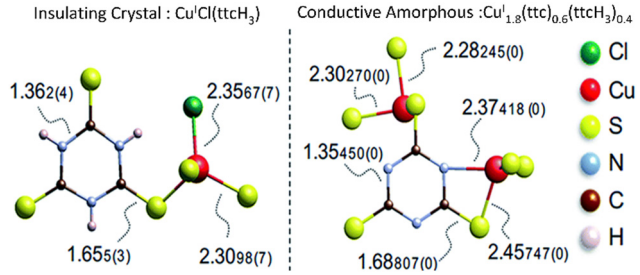

Fig. 5 Local structure and bond lengths of $Cu^{I}Cl(ttcH_3)$ and $Cu^{I}_{1.8}(ttc)_{0.6}(ttcH_3)_{0.4}$. Reproduced from ref. 15 with permission from Royal Society of Chemistry, copyright 2015.

glasses[67] and oxide glasses.[68] Due to the enhanced ion dynamics and the presence of isotropous conduction pathways, the glassy form of MOFs often exhibits superior ion conductivity over their crystalline phases, thereby improving the energy storage performances.[44,69,70] The heat treatment applied during the synthesis of MQG also serves as an activation step for solvent removal, which provides more active surface area and less potential solvent pollution with better processability than crystal. (Fig. 6)

A disordered phase has a relatively higher potential energy than an ordered crystalline phase. As MOF glass is in a metastable state with high potential energy, the structure can be easily affected by the insertion/extraction of Li^+ during the charge/discharge cycles, which can increase the size and number of conduction pathways. The formation of these additional and larger channels can benefit lithium-ion diffusion and storage (Fig. 7).[9] Furthermore, the presence of structural defect sites in MOF glass such as broken bonds and unsaturated coordination sites, coupled with the MOFs glass' higher active surface area for electrochemical reaction, can also enhance the performance. In contrast, the energy storage performance of crystalline MOFs might be restricted by their anisotropic properties, low degree of depolymerisation and low concentration of structural defects.[9]

Compared with other amorphous MOFs, MOF glasses have higher degree of disorder, even in short range. Increasing disorder can effectively shorten the diffusion distance of ions, which can help to promote ion transport kinetics and ion

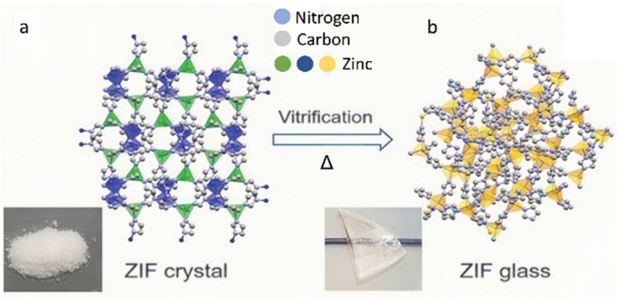

Fig. 6 Schematic representation of ZIF-62 structures in the (a) crystal and (b) glass forms. Reproduced from ref. 14 with permission from The American Association for the Advancement of Science, copyright 2020.

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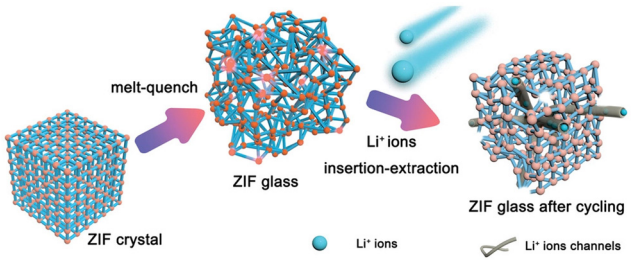

Fig. 7 Schematic indication of how ZIF-62 (Co) glass enhance the performance. Reproduced from ref. 9 with permission from John Wiley and Sons, copyright 2022.

intercalation within the material.[9,14,71] Gao *et al.* investigated the use of crystalline, amorphous and glassy states of cobalt-ZIF-62 $(Co(Im)_{1.75}(bIm)_{0.25}$, where Im = imidazole, bIm = benzimidazole) as anodes in a lithium-ion battery. It was observed that the lithium storage performances such as capacity, rate capability and cycling stability followed the order of glassy state > amorphous state > crystal state.[9] The enhancement in performance was attributed to the increase in distortion and local breakage of Co–N bonding which made Li-ion intercalation more accessible. Generated transfer channels exhibit enhanced stability, allowing a capacity increase of up to 1500 cycles. Furthermore, these channels also facilitate Li^+ ion diffusion and storage.[9]

Amorphous MOFs in MOF composites

Advantage of MOF composites in energy storage field. Researchers have investigated the incorporation of electronically conductive materials into MOFs to create MOF composites. This raises the question of whether the energy storage performance is enhanced in these composites compared to the original materials. The majority of MOFs are generally regarded as poor electrical conductors due to several factors, such as the presence of a wide bandgap, redox-inactive organic ligands, and limited pathways for low-energy electron transfer. These intrinsic barriers pose challenges for the practical utilization of MOFs as conductive media and therefore compositing can be a potential solution.[72]

Researchers have discovered that certain Fe-based MOFs possess favourable redox activity and lithium-ion mobility, leading them to be used as electrodes as early as 2007. However, the electrical performance of these MOFs was found to be relatively modest.[11] Subsequently, numerous researchers have endeavoured to employ MOFs as electrodes. Unfortunately, these attempts have often resulted in significant performance degradation, low capacity, and inherent mechanical brittleness.[73–75]

A prevalent observation with crystalline MOFs during the lithiation/delithiation process is their tendency to undergo structural collapse and irreversible amorphization due to their limited structural stability.[18,76] As a consequence, it may no longer be suitable for use as an electrode. However, in contrast, MOF composites may benefit from the lithiation/delithiation process. For example, Gao and his co-workers fabricated

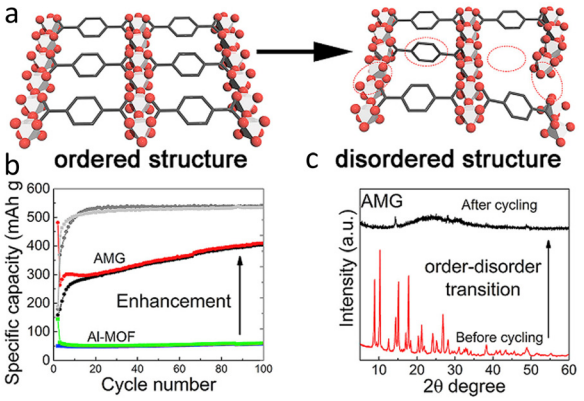

Fig. 8 (a) Structural change of AMG from crystal state to amorphous state during operation of lithium-ion battery. (b) Performance enhancement of AMG after amorphization (c) XRD result of AMG before and after cycling. Reproduced from ref. 17 with permission from Elsevier, copyright 2019.

graphene/Al(OH)$[O_2C–C_6H_4–CO_2]$ composite (also called AMG in Fig. 8) and found that the lithiation/delithiation process resulted in more open channels in MOFs for Li^+ ions migration and storage, and hence result in enhanced conductivity and lithium ion storage capacity.[17] Meanwhile, the introduction of graphene exhibit additional advantages arising from the synergistic effects. Graphene sheets can help to facilitate the interconnection of MOFs particle in composite and promote the Li^+ migration on the solid-electolyte interface (SEI) as well as charger transfer reaction during operation.[17]

Although MOF composites are actively being used for energy storage purposes, the diversity of MOF composites remains rather limited. Secondary materials incorporated into MOFs usually need to have desirable properties such as high electrical conductivity, good chemical compatibility as well as high stability and excellent mechanical strength. Only a limited number of guest materials have been used so far, with carbon nanotubes (CNTs),[77] graphene (G),[17,78,79] graphene oxide (GO),[80] reduced graphene oxide (rGO)[81–83] and conductive polymers[84,85] being the main guest materials of choice. For MOFs, the metal ions are usually transition metals such as Fe, Mn and Ni, while organic ligands are normally based on carboxylates, N-donor groups, sulfonates, phosphonates, or heterocyclic compounds.[76,86,87] Further exploration of MOF composites beyond the crystalline form towards amorphous MOF based composites can offer a potential solution to expand the diversity and performance of these materials in energy storage applications.

Amorphous MOF composites *vs.* Crystalline MOF composites

Amorphous MOFs have several advantages over their crystalline counterparts, making them highly desirable for composite applications. Firstly, amorphization can increase and expose active metal sites of MOFs to secondary materials, which can promote better delivery of electrons and interfacial contact with conductive medium.[13,36] Furthermore, the higher energy state and disorderly structure of amorphous MOFs make them more amenable to functionalization, providing increased

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opportunities for chemical modification.[53](Fig. 3) This flexibility allows for tailoring of the material properties to meet specific application requirements. Additionally, amorphous MOFs tend to exhibit superior mechanical and thermal stability compared to their crystalline counterparts,[36] which can be useful in composite applications where these properties are important. Lastly, some amorphous MOF layers can exhibit oxygen storage capability. The stored oxygen in MOFs could help to mitigate issues caused by oxygen loss in electrodes such as Li-rich layered oxide, which can provide enhanced performance and stable operation.[88]

In a composite, enhancements in performance can arise from improved interfacial contact and interactions between MOF and secondary material. The amorphization process can help to increase and expose the active metal sites of MOFs to secondary materials for improved delivery of electrons. Lin *et al.* composited amorphous Ni-MOFs nanowires with conductive Ni carbon cloth (Ni/CC) to form a fisher-net superstructure. (Fig. 9) The composite featured abundant active sites and significantly increased pore volume, specific surface area and conductive surface area, which synergistically promoted electrical conduction and ion transportation within composite.[18] Another similar example was shown by Zhao *et al.*, where silver nanowire was composited into a 2-D amorphous MOF to form a conductive nanocomposite (a-CoL/Ag NC). The fabricated composite exhibited a higher specific capacitance, rate capacity, and long-term cycling stability compared to the parental materials when used as electrode. This was due to the enhanced interfacial interactions between composite and electrolyte, which facilitated ion and electron transport.[89] Zhao and co-workers also suggested that amorphous MOFs can achieve better interfacial interaction with secondary materials compared to the crystalline counterpart due to the higher energy state of amorphous materials.

In addition, some amorphous MOFs also showed unique properties which can be beneficial in a composite material for energy storage purposes. In a pioneering work by Qiao and co-workers, an amorphous Mn-based MOF layer (2–3 nm thickness) was coated on a crystalline Li-rich layered oxide. The composite exhibited an increased discharge capacity (323.8 mA h g^{-1} at 0.1C rate), high initial Coulombic efficiency (91.1%), and good thermal stability without impacting the cycling performance and high-rate capability. The observed enhancement was attributed to the oxygen storage ability of the amorphous MOF layer. This opens a new avenue of research by using amorphous MOFs for surface modification to achieve higher discharge capacity in lithium-ion battery.[88]

Furthermore, MOF as a host matrix can also be used to protect guest materials from external stimuli and limit internal alterations *via* confinement.[90] However, structural compatibility is always an issue during compositing. Poor compatibility is likely to lead to problems such as poor stability and pore blocking.[91] The use of amorphous MOFs, particularly MOF glass, is a good option for compositing as the high chemical reactivity of the liquid state upon melting can promote better binding with the secondary materials. In addition, structural disorder can facilitate higher ion conductivity and enhanced ion dynamics.[58,92,93] Nozari *et al.* composited sodium-containing ionic liquid (sodium bis(trifluoromethylsulfonyl)imide) into ZIF-8. Although the fabricated composite showed good ionic conductivity and low activation energy, it had relatively poor stability at ambient condition. Further partial amorphization of the composite by ball milling resulted in significant improvements in stability compared to the crystalline structure. (Fig. 10) The induced structural disorder reduced the pore size, which hindered ionic liquid exudation and prevented them from contact with the atmosphere. There was only a 6% decrease in performance after 20 days compared to 20% for the crystalline ZIF-8 composite. In terms of the activation energy, it remained almost unchanged for the partially amorphized composite with only a slight increase to 0.28 eV after 6 days of exposure, while there was an approximately 58% increase for the crystalline composite from 0.26 eV to 0.4 eV. Although amorphization also disrupted the interconnected conduction channels in MOF, the composite still

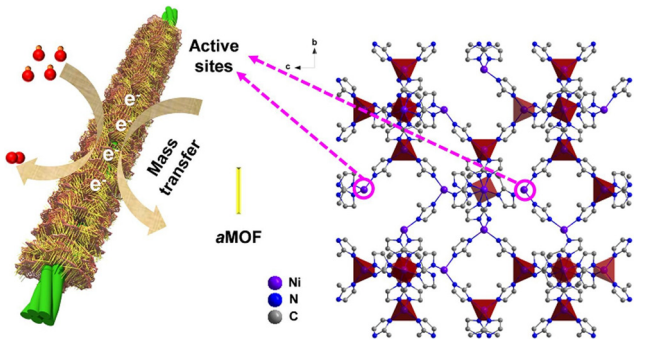

Fig. 9 Schematic of fishnet-like composites of amorphous Ni-MOFs nanowires grown on conductive Ni carbon cloth (Ni/CC). Reproduced from ref. 18 with permission from Elsevier, copyright 2020.

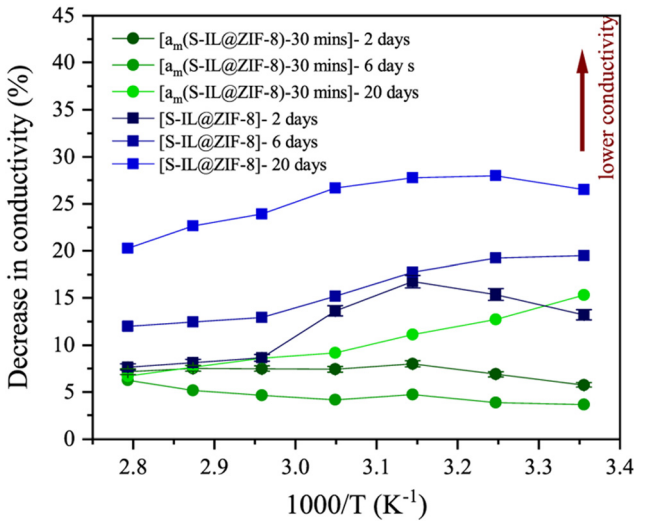

Fig. 10 Change in the ionic conductivity of crystalline (square) and amorphous composite (circle). Reproduced from open access journal ref. 16.

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maintained superionic behaviour.[16] Similar observations were also made by Qiao and co-workers.[88]

Conclusion and perspectives

As reviewed, amorphous MOFs have great potential applications in energy storage fields. However, due to limited understanding and relatively short-term investigations of disordered amorphous MOFs, its potentials are still uncovered. We hope the following perspectives can give researchers ideas and direction about the future development of amorphous MOFs in energy storage fields.

Development of MOF liquid/glasses

An interesting theoretical study that has been reported is that a large fraction of void space (95%) seems to be retained in ZIF-4 liquid at 1500 K, which is higher than its crystal counterpart (74%) at 300 K. This finding suggests the retention of porosity in MOF liquid even at high temperature. The larger pore volume of MOF liquid compared to the corresponding glassy state makes it particularly intriguing for energy storage under extreme conditions.[94] Nevertheless, there remains some bottlenecks for the development of MOF liquids. Firstly, majority of MOFs undergo decomposition (T_d) before reaching the melting temperature (T_m), which limits the diversity of this group of MOFs. In addition, the high melting temperature of meltable MOFs makes it difficult to stabilise them or perform experiments under this condition. For example, liquid ZIF-76 ($Zn(Im)_{1.62}(cPhIm)_{0.38}$) can only be obtained above its melting temperature of 451 °C and many characterisations, such as nuclear magnetic resonance (NMR), cannot proceed at such high temperature. In order to employ MOF liquids in the energy storage field, there is an urgent need to stabilise MOF liquids at ambient conditions for it to be practically feasible. Several efforts have already been made to lower T_m, such as ionic liquid incorporation and introduction of external pressure.[95–97] Efforts in these directions are vital to unlock the full potential of MOF liquids for energy storage applications.

MOF composites

Further efforts should be dedicated to investigating the synergistic effects between the parent materials in MOF composites to enhance their overall performance. Compatibility is the first thing to be considered, MOF glass emerges as a favourable candidate as a host matrix due to its high processability and chemical reactivity with functional materials during composite formation and melting. Moreover, by subjecting MOF glass composites to heat treatment, it is possible to regulate and eliminate interfacial defects, further improving their performance.[60] The utilization of MOF glass composites for energy storage purposes is currently in its nascent stages, with only a limited number of published papers focusing on anode applications.[9,98] Given the high moldability and excellent compatibility of glassy MOFs with guest materials, it has huge potential to be used as other energy storage components. Recent research has revealed that MOF glasses exhibit an even higher level of disorder compared to other amorphous MOF materials. This increased disorder can effectively shorten the diffusion distance of ions, thereby enhancing ion transport kinetics within the material.[9,14,71] As a result, we anticipate that in the future, we will witness a growing body of research on glassy MOF composites, exploring their application across a wider range of energy storage systems.

Additionally, it is crucial to acknowledge that the formation of MOF composites often leads to the disruption of the intrinsic organic–inorganic hybrid structure of MOFs. To ensure stable operation over extended periods, it becomes necessary to prioritize the preservation of the structural integrity of MOFs. This involves maintaining the active surface area and promoting good conductivity throughout the composite material. By preserving the original hybrid structure of MOFs, one can maximize their inherent properties and facilitate efficient charge transfer, leading to enhanced performance and long-term stability.[9,99,100] Strategies that promote the structural integrity of MOFs within composites should be explored to ensure their successful application in energy storage and other fields. This includes, but is not limited to, careful selection of guest materials, optimization of synthesis conditions, and the development of appropriate fabrication techniques that minimize structural damage while achieving desired composite properties.

Benefiting from structural disorder

Structural disorder is the main difference between crystalline MOFs and amorphous MOFs, and there are still promising potentials to be uncovered.[101] The abundance of unsaturated sites within amorphous MOFs offers opportunities for diverse applications alongside energy storage purposes, including their use as catalysts, which endows amorphous MOFs with multifunctionality. For instance, Zhang *et al.* employed amorphous MIL-88B ($Fe_3O[C_6H_4(CO_2)_2]_3OH{\cdot}nH_2O$) separator that can convert polysulfide to the non-soluble form in lithium sulphur battery.[38] By harnessing the abundant unsaturated coordination sites in amorphous MOFs, scientists can exploit their potential to achieve enhanced performance across a range of applications.

Meanwhile, the incorporation of structural disorder in MOF composites holds the potential to enhance the stability of energy storage devices. With the wide range of MOF composites already reported, there are ample opportunities to further enhance their performance stability by exploring amorphization. Establishing a clear relationship between the degree of amorphization and the resulting stability of the composite materials would be highly valuable, offering significant implications for advancements in the field of energy storage. By understanding and optimizing the extent of amorphization, researchers can unlock new strategies to improve the long-term stability and reliability of MOF composites in energy storage applications. However, this requires careful materials structure investigation to understand the gradual loss of the long-range order.

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In the context of energy storage, such as lithium-ion batteries, 2D materials are considered favourable options due to their ability to undergo intercalation, driven by covalent interactions within layers and van der Waals interactions between layers.[102] When it comes to 2D amorphous materials, the weakened interaction between layers facilitates diffusion, making them particularly promising for energy storage applications.[103] Additionally, 2D amorphous MOFs exhibit increased intersheet spacing under significant polarization, further enhancing their potential for energy storage purposes.[64] In the future, there is ample room for exploration and research on 2D amorphous MOFs, and even the development of MOF glass sheets, to unlock their full potential as versatile materials for energy storage applications.

Apart from varying dimensionality, scientists could also try to add electron withdrawing group. Hou *et al.* found that use of electron withdrawing group can weaken the organic–inorganic bonding, and the smaller van der Waals volume of the functional group can reduce steric hindrance around the metal node to facilitate its dissociation. The incorporation of electron withdrawing group into MOFs could be another possible strategy to improve conductivity. This is because easier breakage of organic–inorganic bonding and higher degree structural disorder caused by the introduction of electron withdrawing group could help to create new channels for ion diffusion and storage during the cycling process in batteries.[104] However, it is also necessary to investigate the stability of generated channels to fulfil long-term operation.

Notably, structural changes in amorphous MOFs are inevitable during operation and hence short-range order might be hard to maintain. However, there is currently no comprehensive comparison between short-range order and disorder in energy storage fields for MOFs. Even though MOF glasses, featuring higher degree of disorder, have shown better result in lithium battery application compared with other counterparts,[9,14] further investigations are still needed to gain deeper understanding of this phenomenon.

Fabrication of amorphous MOFs

In addition to traditional melting methods, a recently developed approach for melting MOFs involves the use of high-energy ultrafast femtosecond (fs) infrared (IR) laser pulses. Kulachenkov *et al.* successfully fabricated well-organized spheres comprised of a metal oxide dendrite core and an amorphous organic shell from MOFs, which have the potential for producing a new generation of materials.[94,105] Moreover, the ultrafast melting method can find application in fabricating melt-quenched MOF glasses. This could result in intriguing morphologies and the formation of larger glassy particles, further expanding the range of materials that can be explored for energy storage purposes.[94,105]

Direct synthesis of amorphous MOFs is still in its early stages and further development is needed. Direct synthesis generally does not require extreme condition, such as high pressure and temperature as is the case in top-down synthesis. Its mild and ambient synthesis condition can help to reduce the energy consumption and tends to be more environmentally friendly. Additionally, mild condition is especially beneficial for fragile materials, such as biomedical materials and drugs. Meanwhile, direct synthesis allows for relatively more control in coordination kinetics and amorphousness during fabrication, which could be helpful for scientists to investigate the optimum degree of amorphousness in energy storage applications.[46]

Understanding the properties and structure

Another important consideration prior to the application of amorphous MOFs is to obtain a fundamental and mechanistic understanding of these materials through proper characterisation. X-Ray or neutron total scattering experiments can be performed to yield the total scattering patterns, which feature information on both Bragg and diffuse scattering. Pair distribution function (PDF) can be calculated from the X-ray diffusion pattern which describes the degree of local and intermediate ordering.[36] In addition, solid-state nuclear magnetic resonance (SSNMR) can also provide information on the local structure and chemical bonding within amorphous MOFs. Furthermore, Fourier-transform infrared spectroscopy (FTIR) can provide additional information about the chemical bonding within MOFs, while Terahertz and Far-IR Spectroscopy (THz-FIR) can be used to further probe the metal-linker vibrations in the Thz region.[60,104] Another approach is to push characterisation to near or at atomic resolution. High-resolution transmission electron microscopy (TEM) and scanning TEM (STEM) imaging can be used to probe the interface, metallic centres and organic linkers. In addition, scanning electron diffraction (SED) can also be a powerful tool to characterise the regions of crystallinity/non-crystallinity in a MOF composite sample.[58,60,106]

At the moment, predicting the band structure of amorphous MOFs is a challenging task due to the disordered nature and large unit cell of these materials. The introduction of amorphous MOF composites further complicates computational calculations. As a result, there are practical limitations in terms of available computational methods and resources for accurately predicting the band structures of these materials.[33] Despite these challenges, ongoing research and advancements in computational methods hold the room for addressing these limitations and expanding our ability to predict the band structures of MOFs. Further development and refinement of computational algorithms, as well as improvements in computing power, will likely contribute to overcoming the current obstacles and enable more accurate predictions of the band structures of amorphous MOF composites.

Scalability and industrialization

Scalability is a crucial factor to consider in materials research, particularly when aiming for industrial-scale applications. The utilization of crystalline MOFs in such applications is often hindered by their relatively high cost and negative environmental impact resulting from the use of organic solvents during synthesis.[107] Even though mechanochemical synthesis

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shows promise in addressing these issues, the lack of comprehensive understanding in mechanochemistry often leads to partial amorphization of the samples. In contrast, the growing interest in amorphous MOFs offers a viable solution that completely circumvents the aforementioned challenges associated with mechanochemical milling. The shift in interest towards amorphous MOFs can effectively avoid these issues in mechanochemical milling. It is expected that the scale up of amorphous MOF materials is more easily achievable.

In order to practically use MOFs in the industry, scientists need to find a way of transferring MOF microcrystals into macroscopically shaped bodies which can fit the applications.[108] However, processibility is a major issue of crystalline MOFs that becomes a bottleneck towards industrialization.[109] In order to circumvent the issue of processability, one emerging group of amorphous MOFs called MOF glasses might be the solution. MOF glasses with an accessible liquid state upon heat treatment have much higher processability compared to their crystalline counterparts, which enables them to be easily shaped into different device configurations (Fig. 6).

Conflicts of interest

The authors declare no conflict of interest.

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