

### Metal–Organic Frameworks

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## A New Dimension for Coordination Polymers and Metal–Organic Frameworks: Towards Functional Glasses and Liquids

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There are two categories of coordination polymers (CPs): inorganic CPs (i-CPs) and organic ligand bridged CPs (o-CPs). Based on the successful crystal engineering of CPs, we here propose noncrystalline states and functionalities as a new research direction for CPs. Control over the liquid or glassy states in materials is essential to obtain specific properties and functions. Several studies suggest the feasibility of obtaining liquid/glassy states in o-CPs by design principles. The combination of metal ions and organic bridging ligands, together with the liquid/glass phase transformation, offer the possibility to transform o-CPs into ionic liquids and other ionic soft materials. Synchrotron measurements and computational approaches contribute to elucidating the structures and dynamics of the liquid/glassy states of o-CPs. This offers the opportunity to tune the porosity, conductivity, transparency, and other material properties. The unique energy landscape of liquid/glass o-CPs offers opportunities for properties and functions that are complementary to those of the crystalline state.

#### 1. Introduction

Coordination polymers (CPs) are defined as coordination compounds with repeating coordination entities extending in one, two, or three dimensions.<sup>[1]</sup> CPs with two- (2D) and three-dimensional (3D) structures are called CP networks and offer a variety of useful properties. Early inorganic CPs (*i*-CPs) included cyanide complexes, Prussian blue, and Hofmann clathrates.<sup>[2]</sup> Three significant developments made in the last few decades have greatly influenced the direction of research trends (Figure 1). The first development was the



**Figure 1.** Chronological progression of coordination polymers (CPs). There have been four major advances in the development of *o*-CPs<sup>[8]</sup> the construction of *o*-CPs and determination of their X-ray structure (first generation (1G)), permanent porosity by gas adsorption (second generation (2G)), soft crystal, such as crystal-to-crystal, transformation upon application of chemical/physical stimuli (third generation (3G)), and liquid and glassy states of *o*-CPs and metal-organic frameworks (MOFs) derived from crystalline states (fourth generation (4G)).

discovery of organic-ligand-bridged structures. Applying organic ligands to CPs expanded the chemistry in terms of the modularity and designability, which resulted in numerous new compounds. Single-crystal X-ray analysis has been essential for characterizing these structures. The first organicligand-bridged CP (o-CP) characterized by X-ray crystallography was constructed from the d10 metal ion Cu<sup>+</sup> and adiponitrile.<sup>[3]</sup> Only several decades later were further such structures reported. Square-grid (1986),<sup>[4]</sup> diamond (1989),<sup>[5]</sup> and honeycomb (1992)<sup>[6]</sup> networks of copper ions have been made, which was followed by those with other  $d^{10}$  metal ions (Cd<sup>2+</sup>,  $Ag^+$ , and  $Zn^{2+}$ ) in the mid-1990s.<sup>[7]</sup>

The second noteworthy progression was the development of *o*-CPs with robust and permanent porosities by gas adsorption,<sup>[9]</sup> which opened up a new direction for the chemistry of

porous materials. The discovery of porous *o*-CPs led to the generation of functional porous materials through design principles. Since then, a large number of these porous crystals have been synthesized, which are now also called metal-organic frameworks (MOFs)<sup>[7b]</sup> or porous coordination polymers (PCPs). For the sake of consistency, we will refer to these porous materials as MOFs. The third development was the demonstration of the intrinsic flexibility and dynamic properties of the MOF structures.<sup>[10]</sup> This involves both the transformation of the entire crystal structure as well as local molecular motion in crystals and is triggered by chemical stimuli (gas sorption and substrate inclusion) or physical

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stimuli (temperature, pressure, light, and electric fields).<sup>[11]</sup> The flexibility and dynamics of these structures as well as their bistability with porosity has distinguished them from other conventional porous solids, such as carbons, zeolites, phosphates, and mesoporous silica. The dynamics of the coordination bonds and the multistability of phases of o-CPs are relevant not only to the crystal-to-crystal transformation, but also to the crystal-to-liquid/glass transformation, which is the main topic in this Minireview. We previously summarized the structure and function of next-generation MOFs through "HAD" attributes: 1) hierarchy and hybrid, 2) anisotropy and asymmetry, and 3) disorder and defect.<sup>[8b]</sup> The observation and control of disorder and defects in MOFs are important for investigating metastable characteristics in the structures, and examining their functions as catalysis, their conductivity, etc.<sup>[12]</sup> Currently, a fourth development is taking place that is related to (3): namely, the melting and vitrification of crystals of a family of o-CPs, including MOFs.

The chemistry of *o*-CPs has developed together with crystallography. However, the three major material families—polymers, metals, and ceramics—show both crystalline and noncrystalline states. The noncrystalline states include liquids and glasses, and both states are indispensable for discovering new properties and the development of materials. In contrast, there have been relatively few studies on the liquid or glassy states of *o*-CPs, because of the difficulty of both their synthesis and characterization. The emergence and control of liquid/glassy states of *o*-CPs provides new scientific directions in this field. From this perspective, we discuss

liquid/glassy states of *o*- and *i*-CPs through their melting and vitrification behaviors, their structures, and their functionalities.

# 2. Discovery of the Melting and Vitrification of o-CPs

#### 2.1. History

It has been challenging to obtain a liquid state by heating *o*-CPs, because they transform irreversibly into different materials.<sup>[13]</sup> The resulting products are often porous carbons, metal oxides, metal nanoparticles, and their composites, all of which serve as functional materials.<sup>[14]</sup>

In recent years, several *o*-CP crystals have been discovered that show melting and vitrification behaviors (Figure 2).<sup>[15]</sup> This means the components (metal ions, bridging ligands) are neither vaporized nor reacted in the liquid state.

 $[Zn(HPO_4)(H_2PO_4)_2](imH_2)_2$  (Figure 3A,  $imH_2 = mo$ noprotonated imidazole) is a one-dimensional (1D) *i*-CP of Zn<sup>2+</sup> ions and phosphate chains with intercalated imidazolium cations (Figure 3A).<sup>[15a]</sup> Differential scanning calorimetry (DSC) shows the compound has  $T_m = 168$  °C and the liquid state transforms into a glassy state upon cooling to 25 °C. The behavior is an indication of the potential melting and vitrification of *o*-CPs. Two *o*-CPs were subsequently reported to show crystal-to-liquid transitions: 2D layer [Zn(1,2,4triazole)<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>] (Figure 3B),<sup>[16]</sup> and a 3D network [Zn(i-



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**Figure 2.** Snapshots of schematic structures of crystal, glass, and liquid states of *o*-CPs. The blue cores and red bars represent metal ions and bridging organic ligands, respectively. According to the current knowledges, we propose: 1) glassy states have middle-range order as a result of metal–ligand connectivities forming networks, 2) the first coordination spheres of metal ions in the three phases are nearly identical according to X-ray absorption studies, 3) the liquid state has more fragmented (but not completely) metal–ligand networks.

midazolate)<sub>2</sub>] (Figure 3 C).<sup>[15c]</sup> Metal phosphates commonly show melting and glassy states, but their  $T_{\rm m}$  values are much higher because of the lack of organic species. [Zn(1,2,4triazole)<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>] ( $T_{\rm m}$  = 180 °C) has stacking layers consisting of Zn<sup>2+</sup> and 1,2,4-triazole as well as H<sub>2</sub>PO<sub>4</sub><sup>-</sup> coordinated to Zn<sup>2+</sup> ions at axial positions. [Zn(imidazolate)<sub>2</sub>] (Zn-ZIF-4,  $T_{\rm m}$  = 593 °C) comprises Zn(im)<sub>4</sub> tetrahedra and shows an orthorhombic porous structure.<sup>[17]</sup>

To characterize the melting phases of an o-CP and elucidate the mechanism, the crystal structures of the o-CPs below the  $T_{\rm m}$  value need to be identified. The composition of both the liquid/glassy and crystalline states should be identical in as far as we regard these phase transformations to be "melting" or "vitrification". There are many reports on amorphous (or even glassy) o-CPs, including gels and metallopolymers, where the crystalline states could not be identified. They are out of the scope of this Minireview. Phase transitions are determined by DSC to clarify the melting and vitrification behaviors.

A variety of analytical techniques have been established to identify the structures and dynamics of liquid/glassy states in glass/liquid research.<sup>[18]</sup> X-ray absorption fine structure spectroscopy (XAFS) is widely used to establish short-range



**Figure 3.** *i*-CPs and *o*-CPs with their melting temperatures ( $T_m$ ). Crystal structures of A) 1D [Zn(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>](imH<sub>2</sub>)<sub>2</sub> (im-H<sub>2</sub> = monoprotonated imidazole) and B) 2D [Zn(1,2,4-triazole)<sub>2</sub>-(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>]. C) Two crystal structures of 3D [Zn(imidazolate)<sub>2</sub>] (Zn-ZIF-4 and ZIF-zni). Gray C, blue N, pink O; light blue polyhedra: phosphates, gray polyhedra: tetrahedral Zn<sup>2+</sup>.

order, especially the coordination structure around metal centers. Neutron and/or X-ray total scattering<sup>[19]</sup> are frequently used with the pair distribution function (PDF) to evaluate middle-range correlations. Molecular dynamics (MD),<sup>[20]</sup> density functional theory (DFT),<sup>[21]</sup> and/or reverse Monte Carlo simulations<sup>[22]</sup> have been used with the abovementioned experimental data to determine the structures. Solid-state NMR, IR, and Raman spectroscopy are also good methods to obtain information on chemical structures and their dynamics. The comprehensive use of these methods has enabled the melting phenomena of *o*-CP crystals to be characterized and their melting and glass states defined.

The temperature of the decomposition  $(T_d)$  must be higher than the  $T_m$  value for the melting of the *o*-CP crystals to be observed. The strength of the coordination bond and the ionization tendency of metals are key to ensure  $T_m < T_d$ . Combinations of metal ions and ligands suitable for the construction of melting *o*-CPs have been investigated, but one could refer to the chemistry of either the molten salt or ionic liquid. Anti-crystal engineering to design ionic liquids has been reported,<sup>[23]</sup> whereby the cations and anions are available for constructing *o*-CPs.

The reported *o*-CPs showing melting or vitrification are listed in Table 1. Considering these examples as well as the structures of known ionic liquids, suitable building blocks for *o*-CPs are azolate/azole, nitriles, and inorganic anions such as  $H_2PO_4^-$ , SCN<sup>-</sup>, and dicyanamide (N(CN)<sub>2</sub><sup>-</sup>).<sup>[24]</sup> The total energy required for melting *o*-CPs also depends on the dimensionality of the crystal structures. Considering that the

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Table 1: o-CPs and i-CPs with organic molecules as counterions or terminal ligands that show melting and/or vitrification behaviors.<sup>[a]</sup>

Entry	<i>T</i> <sub>m</sub> [°C]	<i>Τ</i> <sub>g</sub> [ <sup>°</sup> C]	Functions in glassy state	Ref.
$\label{eq:constraint} \begin{split} & \overline{\textbf{o-CPs}} \\ & [M(1,2,4\text{-triazole})_2(H_2PO_4)_2] \\ & (M = Zn^{2+}, \ Cd^{2+}, \ Cr^{2+}, \ Mn^{2+}) \\ & [Zn(im)_2] \ (ZIF-4) \end{split}$	<b>o-CPs</b> 184 (Zn <sup>2+</sup> ) 593	<b>o-CPs</b> 32 (Zn <sup>2+</sup> ) 79–90 <sup>(b)</sup> (Cd <sup>2+</sup> ) 62 (Cr <sup>2+</sup> ) 90 (Mn <sup>2+</sup> ) 316 (LDA) 292	<b>o-CPs</b> anhydrous H <sup>+</sup> conductivity	<b>o-CPs</b> [15b, 28] [15c]
		(HDA)		
[Zn(im) <sub>1.75</sub> (bim) <sub>0.25</sub> ] (Zn-ZIF-62) [Zn(im) <sub>2-x</sub> (bim) <sub>x</sub> ]	437	318	kinetic separation of propylene/propane <sup>[c]</sup>	[29]
[Co(im) <sub>1.70</sub> (bim) <sub>0.30</sub> ] (Co-ZIF-62) [Co(im) <sub>2-x</sub> (bim) <sub>x</sub> ]	432	290		[29b, 30]
[Zn(im) <sub>1.62</sub> (5-Clbim) <sub>0.38</sub> ] (ZIF-76) [Zn(im) <sub>1.33</sub> (5-mbim) <sub>0.67</sub> ] (ZIF-76-mbim)	451 471	310 317	gas uptake of $\rm CO_2$ and $\rm N_2^{[d]}$	[31]
Cu(isopropylimidazolate)	185	NA		[32]
<i>i-CPs</i> [Zn(HPO <sub>4</sub> )(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ](imH <sub>2</sub> ) <sub>2</sub>	160	30	anhydrous H <sup>+</sup> conductivity	[15b]
$[Zn_3(H_2PO_4)_6(H_2O)_3] \cdot bimH$	164	NA		[15b]
$[Zn_3(H_2PO_4)_6(H_2O)_3] \cdot H(2Mebim)$	97	NA		[15b]
[Zn <sub>2</sub> (HPO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> PO <sub>4</sub> ) (5ClbimH) <sub>2</sub> ](H <sub>2</sub> PO <sub>4</sub> ) (MeOH)	148	72	gas uptake (H $_{\rm 2}O$ and methanol vapor) and anhydrous H $^+$ conductivity	[33]
$[Cd_3(SCN)_2Br_6(C_2H_9N_2)_2]$	142	NA		[34]
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	187 138 217 203	68 59 71 72		[24b]
(1-butyl-4-methylpyridinium)[Cu(SCN) <sub>2</sub> ]	80	NA		[24a]

[a] im = imidazolate, bim = benzimidazolate, 5-Clbim = 5-chlorobenzimidazolate, 2Mebim = 2-methylbenzimidazolate,  $C_2by = 1$ -ethyl[4,4'-bipyridin]-1-ium,  $C_4by = 1$ -butyl[4,4'-bipyridin]-1-ium, Phbpy = 1-phenyl[4,4'-bipyridin]-1-ium, 3-Pybpy = [3,1':4',4''-terpyridin]-1'-ium, NA = not available. [b]  $T_g$  depends on the time of the ball milling processes. [c] Gas uptake is reported for glasses with  $[Zn(im)_{2-x}(bim)_x]$ , where x = 0.05, 0.17, and 0.35. [d] Gas uptake is observed for  $[Zn(im)_{1.0}(5-Clbim)_{1.0}]$  and  $[Zn(im)_{0.93}(5-mbim)_{1.07}]$ .

glassy and liquid states are composed of fragmented coordination networks, 3D structures require higher energy than 1D or 2D structures to dissociate coordination bonds and melt. The thermal stability of the liquid state is another important parameter. To stabilize the liquid state, an appropriate electrostatic interaction between the metal ions and ligands is required to avoid vaporization.

Several previous studies suggested the possibility of melting o-CPs. For example, the 2D layer structure of [Ag(1,3,5-tris(3-ethynylbenzonitrile)benzene)-

 $(CF_3SO_3)]$ ·2 benzene shows a degassed state (crystal structure unknown), which melts at 169 °C according to its TGA/DTA profile (TGA = thermogravimetric analysis, DTA = differential thermal analysis).<sup>[25]</sup> Further examples of *o*-CPs that undergo melting can be found in the crystal structure database.<sup>[26]</sup> Research into inorganic molten salts or metal-

containing ionic liquids is related to the chemistry of *o*-CPs.<sup>[27]</sup> Most metal-containing ionic liquids are discrete, but some are regarded as *o*-CPs.

#### 2.2. Structures of Liquid and Glassy States

Investigation of the structures of the liquid and glassy states of o-CPs is important for understanding the phase transition and functionality of these materials. The melting behavior and glass structure of 1D  $[Zn(HPO_4)(H_2PO_4)_2]$ - $(imH_2)_2$  (*i*-CP, Figure 3A) have been studied. X-ray structural analysis and solid-state NMR spectroscopy have shown that the intercalated imidazolium starts to undergo in-plane rotational motion below the  $T_m$  value at 75 °C (Figure 4A). Such crystals that undergo local rotational motion of the

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6

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**Figure 4.** A) Crystal structures of  $[Zn(HPO_4)(H_2PO_4)_2](imH_2)_2$  at -30 °C and 75 °C. The imidazolium moieties rotate upon heating. The gray polyhedral represent tetrahedral  $Zn^{2+}$ . Monoprotonated imidazole are shown in light blue. B) Temperature dependence of selected bond distances of  $[Zn(HPO_4)(H_2PO_4)_2](imH_2)_2$ . Lindemann's rule empirically describes f = u/d, where u is the mean thermal atomic displacement of an atom, d is the bond length to the nearest-neighbor atom; f universally approaches 0.10 to 0.13 (area highlighted as red) near the melting temperature.<sup>[36]</sup>

molecules/ions are classified as plastic crystals.<sup>[35]</sup> When the temperature is further raised, the Zn<sup>2+</sup>–O bond in the 1D chain increases in length (Figure 4B) especially  $Zn^{2+}-O9$ reaches a critical value of f where the bond breaks and the structure melts (the  $T_{\rm m}$ ). Rotating imidazolium moieties are present in the vicinity of the Zn<sup>2+</sup>-O9 bond and form dynamic hydrogen bonds, and further fluctuation of the imidazolium group upon heating facilitates the melting. A structure similar to that of a melt-quenched glass (MQG) has been identified by X-ray diffraction. PDF analysis with total X-ray scattering shows the crystal and glassy states have a similar structural periodicity within 8 Å (Figure 5). The peak at 6 Å corresponding to the  $Zn^{2+}$ - $Zn^{2+}$  pair is maintained even in the glass. This indicates that the network domain is preserved in the glassy state. The glassy state shows a reversible glass-tocrystal transformation on application of a stimulus (annealing, scratching, and humidity). This indicates that rearrangement of the metal ions and ligands in the glassy state is a feasible means to reconstruct the crystalline state.

Although the structures of the liquid states of *o*-CPs have not been studied experimentally, the investigation of ionic liquids will be helpful in predicting the structure of the liquid



**Figure 5.** PDF analysis of the crystal and glassy state of  $[Zn(HPO_4)-(H_2PO_4)_2](imH_2)_2$ . G(r) is a reduced pair distribution function.

state of o-CPs. The structures of ionic liquids have been analyzed by combining X-ray scattering and simulation.<sup>[37]</sup> The parameters that define the structure include the degree of ion pair formation, hydrogen bonding, and the formation of ion clusters. In particular, the formation of a nonpolar alkyl domain has been discussed in relation to the length of the alkyl chain of ionic liquids (Figure 6A).<sup>[38]</sup> The liquid state of an o-CP would also have such a domain structure consisting of ligands and metal ions. Ligand polarity is an important parameter in the design of the domain structure of o-CPs. Rhythmic behaviors, such as the Zhabotinsky reaction, are also a topic of interest in regard to the melting process of o-CPs.<sup>[39]</sup> The self-oscillation of melting/recrystallization is of interest to understand melting behavior and dynamics. For example, the organic salt  $[C_4 mim]$ Br  $(C_4 mim = n$ -butyl-methylimidazolium) with a low  $T_{\rm m}$  value shows a continuous DSC signal indicating a small heat input/output when the measurement is recorded with a slow scan rate (Figure 6B). This is caused by the deprivation of heat from the partially melting domain and the resulting recrystallization. The melting process is dominated by slow dynamics (ca. 10 s); indeed,



**Figure 6.** A) Schematic representation of the domain structures of  $[C_n \min][PF_6]$  (n = 2, 4, 6, 8, 12). Red: anion + imidazolium ring. Green: alkyl chain. B) High-resolution DSC signal showing the continuous melting and recrystallization behavior of  $[C_4 \min]Br$ .

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multiple endothermic peaks are often observed at around the  $T_{\rm m}$  value during the melting of *o*-CPs by DSC, which suggests stepwise melting mechanisms dependent upon the crystal structure.

The thermal behavior and structure of 3D [Zn(imidazolate)<sub>2</sub>] (Zn-ZIF-4; Figure 3C, left) has been comprehensively studied.<sup>[15c]</sup> It displays  $T_{\rm m} = 593$  and  $T_{\rm d} = 602$  °C with multiple solid-liquid-solid transitions. The crystal relaxes to a stable low-density amorphous (LDA) state while maintaining network connectivity. The LDA state transforms to a disordered high-density amorphous (HDA) state through low-density liquid to high-density liquid (HDL) transitions, as characterized using DSC and small-angle X-ray scattering. On further heating, the HDL recrystallizes in the tetragonal nonporous Zn-ZIF-zni structure (Figure 3C, right)<sup>[40]</sup> before melting. PDF measurements indicate that the MQG and HDA states retain Zn<sup>2+</sup>-imidazolate connectivity similar to Zn-ZIF-4 up to 6 Å. The temperature dependence of the liquid and glass structures of Zn-ZIF-4 was studied by the combination of Xray and neutron scattering as well as first-principles molecular dynamics simulations (FPMD).<sup>[41]</sup> The structure exhibits liquid-like disorder on heating below the  $T_{\rm m}$  value; the computational approach estimates the enthalpy of fusion of Zn-ZIF-zni to be  $\Delta H_{\text{fus}} = 173 \text{ Jg}^{-1}$ , comparable with that of quartz  $(\Delta H_{\text{fus}} = 146 \text{ Jg}^{-1})$ .<sup>[42]</sup> FPMD gives diffusion coefficients for  $Zn^{2+}$  and imidazolate in the liquid state on the order of  $10^{-10} \text{ m}^2 \text{s}^{-1}$ , comparable with some conventional ionic liquids.<sup>[43]</sup> Reverse Monte Carlo modeling based on X-ray data at  $T_{\rm m} = 593$  °C found that 16.2 % of the porous volume in the liquid structure is accessible (Figure 7).



**Figure 7.** Distribution of the total pore volume in [Zn(imidazolate)<sub>2</sub>] (Zn-ZIF-4) with increasing temperature, as calculated by FPMD.

 $[Zn(imidazolate)_{1.75}(benzimidazolate)_{0.25}]$  (Zn-ZIF-62) has the same network structure as Zn-ZIF-4 with 1/8 of the imidazolate moieties substituted by benzimidazolates. The partial ligand substitution decreases the  $T_m$  value to 437 °C and this provides a more stable liquid state. Zn-ZIF-62 releases guest solvents and forms an amorphous state above 337 °C, whereas an amorphous state melts on subsequent heating, without recrystallization to a dense phase, as in the case of Zn-ZIF-4. The Zn<sup>2+</sup>-Zn<sup>2+</sup> correlation peak at 6 Å is observed by PDF for its MQG, and the extended X-ray absorption fine structure shows unaltered Zn<sup>2+</sup>-N tetrahedra. Significant increases in both the elastic moduli (*E*) and hardness (*H*) are observed for the MQG prepared at 572 °C (135 °C higher than  $T_{\rm m}$ ) compared with a glass prepared at  $T_{\rm m}$ .

Considering these examples, a summary of the structures of liquids and glasses can be given. Most MQGs have the same first-sphere coordination geometry as their crystalline counterparts. PDF analysis shows that they preserve periodicity up to around 10 Å, which is often sufficient to claim metal-ligand-metal periodicity; however, this intensity is weak, and dynamics must also be considered. Advanced TEM techniques can observe the glass structure of *o*-CPs directly,<sup>[44]</sup> as has been successfully done for metal glasses.<sup>[45]</sup> Fast bond cleavage/reformation between metal ions and ligands occurs at around  $T_m$  and above. Solid-to-solid transition and melting are strongly influenced by the structure of the ligands in the system.

#### 2.3. Preparation of Glasses and Glass Composites

Glass is generally prepared by 1) cooling of the liquid state, 2) mechanical treatment of crystals, or 3) solution processes, such as the sol-gel method. Reported liquid states of o-CPs usually have high viscosities, and their MQGs are fabricated by cooling the liquid state at a normal rate. Most o-CPs do not have a stable liquid state, and this has prevented the development of glassy states. Mechanical treatments are available for the preparation of glassy states directly from crystals.  $[Cd(1,2,4-triazole)_2(H_2PO_4)_2]$  (Figure 8A) is an isomorphic 2D structure of [Zn(1,2,4-triazole)<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>], but it does not have a  $T_{\rm m}$  value, and MQG formation has not been reported. However, ball milling of the crystals can inject mechanical energy to obtain a glassy state.<sup>[28b]</sup> Mechanical treatment to generate a glass has been reported for various materials, ranging from hard metals to pharmaceuticals.<sup>[46]</sup> The applicability of milling-based vitrification for o-CPs is wide, but the mechanism remains unclear. For example, highly porous MOFs irreversibly change to an amorphous state (not to a glassy state) during milling and lose porosity as a result of shear-induced compression. In the case of the above-mentioned  $[M(1,2,4-triazole)_2(H_2PO_4)_2]$ , compounds with  $M = Cd^{2+}$ ,  $Cr^{2+}$ , or  $Mn^{2+}$  form a stable glassy state, but  $M = Zn^{2+}$ ,  $Fe^{2+}$ , or  $Co^{2+}$  do not form glasses upon milling. Unsuccessful cases show remaining powder XRD (PXRD) peaks and lower thermal stability upon milling.<sup>[28c]</sup> One of the parameters for successful vitrification by milling is the directionality of the coordination bonds, which depends upon the configuration of the d orbitals. In the vitrification process of  $[Cd(1,2,4-triazole)_2(H_2PO_4)_2]$  by milling, doping with molecules is also feasible.<sup>[28c]</sup> For example, the addition of 1,4-diazabicyclo[2.2.2]octane (dabco) during the milling of crystals leads to a glass containing homogeneously dispersed dabco molecules. 2D solid-state NMR spectroscopy indicates the doped dabco molecules exist within a distance of 5 Å to the glass network. The homogeneous distribution of the dopant allows a continuous change of the  $T_{\sigma}$  value depending on the amount of dabco. The doping perturbates the hydrogen bonds in the structure, thereby leading to higher H<sup>+</sup> conductivity. Interestingly, the volatile dabco is not released, even during heating of the glass composite, which indicates

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**Figure 8.** A) Crystal structure of  $[Cd(1,2,4-triazole)_2(H_2PO_4)_2]$  and the DSC profiles of glass samples obtained by mechanical ball milling for different lengths of time. Gray C, blue N, pink O; gray polyhedral: tetrahedral Zn<sup>2+</sup>. B) Composition-dependent progression of the  $T_g$  value for Zn-ZIF-4 and Zn-ZIF-62 blends.

that the glass can confine the small molecules. The ability of *o*-CP glasses to encapsulate guests is sufficient to allow the introduction of metal nanoparticles, organic polymers, etc. to fabricate multifunctional glass composites.

MOF glass blends are prepared by mixing the MOF candidates through ball milling followed by heating the physical mixture above the  $T_{\rm m}$  value.<sup>[47]</sup> For example, crystals of Zn-ZIF-4 and Zn-ZIF-62 are physically mixed and heated to the  $T_{\rm m}$  value of Zn-ZIF-62. The blend shows a single  $T_{\rm g}$ value at 306 °C, which is different from the individual  $T_{g}$ values of both Zn-ZIF-4 (292°C) and Zn-ZIF-62 (318°C). The  $T_{g}$  value of the blend can be tuned by altering the Zn-ZIF-62 content (Figure 8B). The long-range order of physical mixtures disappears on blending, and only short-range order below 6 Å is retained. Another blending of non-melting Co-ZIF-4 with Zn-ZIF-62 revealed heterogeneous mixing along with interlocked microstructures. The high viscosity of the system limits the complete homogeneity of the blend, and ligand swapping between phases results in interlocked domains. A further investigation of blends of Co-ZIF-62 and Zn-ZIF-62 was attempted using spatially resolved spectroscopy.<sup>[48]</sup> Analysis by electron energy loss spectroscopy during scanning transmission electron microscopy revealed intact azolate ligands with sharp interphases between the Co and Zn domains with widths of 200 nm to  $>1\,\mu\text{m}.$ 

#### 2.4. Devitrification and Phase Diagram

The tendency of liquids to avoid crystallization during cooling is measured in terms of their glass-forming ability (GFA).<sup>[49]</sup> The MQG of Zn-ZIF-62 exhibits a  $T_g/T_m$  ratio of 0.84, higher than the empirical  $T_g/T_m = 2/3$  rule for various glass materials (Figure 9), which contributes to their high



**Figure 9.** Comparison of the  $T_g/T_m$  ratio of [Zn(imidazola-te)<sub>1.75</sub>(benzimidazolate)<sub>0.25</sub>] (Zn-ZIF-62) with glass-forming systems of water (black), organic materials (pink), metallic materials (blue), and oxides (orange).

GFAs. There are several steps in the crystallization of glass: 1) diffusion of atoms or ions, 2) generation of a crystal nucleus, and 3) growth or propagation of the nucleation site. The activation energy for crystal nucleation depends on the network connectivity between the metal ions and organic ligands in the *o*-CPs. 3D structures generally show a high GFA. Their MQGs preserve the coordination environment of the crystalline state and is denser, with a 20% reduction in the pore volume. Zn-ZIF-62 also shows high viscosity ( $\eta = 10^{5.1}$  Pas) at the  $T_{\rm m}$  value, which is comparable to a silica melt. The high viscosity and densification of the liquid state of Zn-ZIF-62, limit the flow behavior of ligands that avoids crystal growth and increase the GFA.

Control of the phase transition of crystals, glasses, and liquids in o-CPs through consideration of the phase diagram is important. As an example, PXRD studies have shown that the glassy state of  $[Cd(1,2,4-triazole)_2(H_2PO_4)_2]$  prepared by ball milling undergoes recrystallization at  $T_c = 111$  °C to return to its original crystal structure. When the total time of ball milling is increased, the  $T_c$  value of each glass also increases, as shown in Figure 8A, as a result of differing internal energies. On the other hand, the MQG of Zn-ZIF-62 and other 3D ZIFs do not return to their original crystal structures. The reversibility of the crystal-to-glass transformation depends on the randomness of the positions and interaction/dynamics of metal ions and ligands in the glassy state. In general, devitrification is not desired in glasses, but the reversible phase change has promising applications for

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nonvolatile memories through the switching of physical properties, such as electric conductivity or optical reflectivity/absorption.<sup>[50]</sup> Phase transition depends on pressure. As shown above,  $[Cd(1,2,4-triazole)_2(H_2PO_4)_2]$  has  $T_c = 111 \,^{\circ}C$  under ambient pressure but does not show a  $T_c$  value at a pressure of 4 GPa, even when heated to 153  $^{\circ}C$  (Figure 10 A). This behavior was confirmed by PXRD and in situ



**Figure 10.** A) Proton conductivity profiles for the glassy state of  $[Cd(1,2,4-triazole)_2(H_2PO_4)_2]$  under ambient and 4 GPa pressures. B) Experimental *P-T* phase diagram for Zn-ZIF-62.

measurement of the ion conductivity by AC impedance spectroscopy under various pressures using a diamond anvil cell. The movement of metal ions and ligands is suppressed by pressures, thus prohibiting recrystallization. More recently, a systematic investigation of the phase transition of Zn-ZIF-62 was conducted using in situ PXRD and SEM at variable pressures (Figure 10B).<sup>[51]</sup> The experimentally derived pressure-temperature phase diagram of Zn-ZIF-62 shows a negative slope for the melting curve between ambient pressure and 2 GPa. The external pressure promotes a lowering of the  $T_m$  value. In addition, a positive slope was found at pressures higher than 2 GPa. Two distinct amorphous phases play a key role in the phase diagram: one with a higher density than the liquid state and the other with a lower density than the liquid state.

#### 3. Properties of the Liquid and Glass States of o-CPs

#### 3.1. Porosity

One characteristic property of the crystalline state of o-CPs is their permanent porosity; typical examples are termed MOFs. The design of porous structures in MOF glasses or liquids presents a challenge. Methods based on spinodal phase separation (e.g. VYCOR<sup>®</sup> 7930), sol-gel approaches, sintering, and partial crystallization have been attempted to fabricate nanoporous inorganic glasses. Some of these techniques could be applied to MOF glasses, but simple melt-quench or mechanical milling can also directly produce porous MOF glasses. The porosity of MOFs in the glass/liquid states has been studied by both positron annihilation lifetime spectroscopy and theoretical calculations.<sup>[41,52]</sup> The partial retention of permanent porosity in ZIF-76-mbim MQG [Zn(im)<sub>0.93</sub>(5mbim)<sub>1.07</sub>] (5-mbim = 5-methylbenzimidazolate) has been studied experimentally.<sup>[31]</sup> Contraction of the pore volume from 0.17 to 0.12 vol % with a concomitant change in the pore size distribution occurs on vitrification of the crystalline state. Co-ZIF-62, with  $T_{\rm m} = 430$  °C, is also reported to be a precursor for a MOF glass.<sup>[30]</sup> The MQG of Co-ZIF-62 contains a few percent metallic cobalt and retains 50% porosity (CO<sub>2</sub> uptake is about 18 mLg<sup>-1</sup> at 100 kPa, 273 K) compared to the crystalline state.

Preferential adsorption kinetics of propylene over propane is observed for the Zn-ZIF-62-bimx glass with increasing amounts of bulky benzimidazole ligands (x = 0.05, 0.17, 0.35). Kinetic sorption measurements showed faster diffusion rates for propylene than propane, with the rate also dependent on the imidazole/benzimidazole ratio (Figure 11). The effect is ascribed to a higher concentration of the bulky ligand resulting in narrower pores in the glass, which consequently slows down the diffusion of propylene, while no effect was observed for propane.

The zinc phosphate based 2D inorganic CP  $[Zn_2(HPO_4)_2-(H_2PO_4)(5ClbimH)_2](H_2PO_4)(MeOH)$  (5ClbimH = monoprotonated 5-chloro-1*H*-benzimidazole) contains guest  $H_2PO_4^-$  ions and methanol in the cavity. The degassed state of this compound shows  $T_m = 148 \, {}^{\circ}C.^{[33]}$  Its MQG shows both



**Figure 11.** Time-dependent propylene and propane sorption profiles of  $[Zn(im)_{2-x}(bim)_x]$  glasses with varying amounts benzimidazoles at the same equilibrium pressure.

10 www.angewandte.org

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Angew. Chem. Int. Ed. 2020, 59, 2-15

 $\rm H^+$  conductivity and porosity, which is attractive for protonmediated heterogeneous catalysis. MOF glasses without grain boundary properties could be applied as a new class of ceramic membrane for selective gas permeation.

The porosity in the liquid state of MOFs is also of interest. Both chemisorption and physisorption occur in the liquid state of MOFs. Discrete molecular systems such as ionic liquids and cage-type porous liquids are known to accommodate various gases through physical or chemical adsorption.<sup>[53]</sup> In the case of the liquid state of MOFs, the preorganization of the bond geometry of the metal ions and bridging ligands is key to affording large guest-accessible space and fast mass transport. The interaction of guests and metal ions could effectively be used for molecular recognition or separation.

#### 3.2. Ionic Conductivity

One typical physical property of glasses is ion conductivity.<sup>[54]</sup> In the glassy state, the ion pathway is isotropic and the structure has a lower density than the crystalline state, hence leading to a high ion conductivity. Several reports have discussed the enhancement of proton (H<sup>+</sup>) conductivity by the amorphization or glass formation of *o*-CPs.<sup>[55]</sup> The glassy state of [Cd(1,2,4-triazole)<sub>2</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>] obtained by ball milling shows H<sup>+</sup> conductivity several orders of magnitude higher  $(1.0 \times 10^{-4} \text{ S cm}^{-1} \text{ at } 125 \,^{\circ}\text{C})$  than the crystal state (Figure 12).<sup>[28b]</sup> Internal hydrogen bonds are made more dynamic



*Figure 12.* Temperature-dependent  $H^+$  conductivity for the crystal and glassy states of  $[Cd(1,2,4-triazole)_2(H_2PO_4)_2]$ .

by vitrification, and the 2D structure is maintained to a low degree. The H<sup>+</sup> conductivity in the glassy state drops once it reaches its  $T_c$  value because the structure returns to the crystalline state. The liquid state of  $[Zn(HPO_4)(H_2PO_4)_2]$ -(imH<sub>2</sub>)<sub>2</sub> dissolves various organic molecules. Its MQG is obtained by mixing it with trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H) in the liquid state, which leads to a H<sup>+</sup> conductivity several orders of magnitude higher  $(3.0 \times 10^{-4} \text{ S cm}^{-1} \text{ at } 110 \,^{\circ}\text{C})$  than the pristine state.<sup>[56]</sup> This is due to an increase in the amount of protonic carriers after doping. Nonetheless, a doping of 10 mol% shows a maximum enhancement of the H<sup>+</sup> conductivity. Thus far, H<sup>+</sup> conductivity has been shown to be dominant in the study of glasses of *o*-CPs, but other ion

species, such as Li<sup>+</sup> and Na<sup>+</sup>, are possible. One of the advantages of ion conductivity in glasses of *o*-CPs is the high transport number:  $t_+ = u_+/(u_+ + u_-)$ , where  $t_+$  is the transport number of cations (or anions) and  $u_+$  and  $u_-$  are the mobilities of cations and anions, respectively. In contrast to the discrete system, *o*-CP glasses have a network structure and the selective transport of cations (or anions) is expected. Moreover, the control of defects in the crystalline state of *o*-CPs and MOFs has been an important subject in recent years,<sup>[57]</sup> since defects affect the behavior of crystal melting and ion conductivity.<sup>[58]</sup>

#### 3.3. Optical Properties

Further promising materials properties of o-CP glasses are their transparency and moldability. We expect luminescence from various metal ions or ligands: the 1D structure of [Eu(hexafluoroacetylacetonato)<sub>3</sub>(1,4-bis(diphenylphosphorylethynyl)benzene)] exhibits red luminescence from the f-f transition derived from excited Eu3+ ions.[59] The crystal transforms to a glassy state and exhibits a characteristic twostep  $T_{s}$  transition. The quantum yield of the photoluminescence in the solid state can be as high as 86% at room temperature. The *i*-CP (1-butyl-4-methylpyridinium)[Cu- $(SCN)_2$ ] demonstrates luminescence and  $T_m = 91 \, {}^{\circ}C.^{[24a]}$  Upon cooling to the liquid state, it returns to its original crystal structure, a process confirmed by PXRD. Although the quantum yield of the luminescence is not high at room temperature, it shows detectable luminescence in the solid state below its  $T_{\rm m}$  value. In this system, SCN<sup>-</sup> works both as a bridging ligand to construct the CPs and a luminophore.

The switching of the H<sup>+</sup> conduction by UV light using a MQG of [Zn(H<sub>2</sub>PO<sub>4</sub>)(HPO<sub>4</sub>)](imH<sub>2</sub>)<sub>2</sub> has been reported as a light-induced function.<sup>[56]</sup> Figure 13A shows that trisodium 8-hydroxy-1,3,6-pyrenetrisulfonate (pyranine) releases and recombines H<sup>+</sup> in response to UV light when used as a dopant. The H<sup>+</sup>-conducting MQG doped with 5 mol% pyranine shows reversible switching of H<sup>+</sup> conductivity upon irradiation with UV light. SEM and solid-state NMR spectroscopy confirm that pyranine is uniformly dispersed in the sample and contributes to the switching of long-range H<sup>+</sup> migration in the glass. Both the modulation of the composition and the transparency and moldability are essential considerations for application of the glasses in optically active materials. In this regard, the optical properties of Zn-ZIF-62 glass were studied (Figure 13B). A high transmittance (up to 90%) was found in the visible and nearinfrared wavelength ranges, comparable with that of many oxide glasses.<sup>[60]</sup> Although the observed refractive index (1.56) is similar to that of most inorganic glasses, it has a lower Abbe number (ca. 31).

#### 4. Perspectives

More examples are needed for a complete understanding of the general behaviors of melting and vitrification of this family of *o*-CPs, including MOFs. Scrutiny of both the

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11



Figure 13. A) Schematic illustration of the switching with UV light of the H<sup>+</sup> conductivity of an *i*-CP glass of  $[Zn(HPO_4)(H_2PO_4)_2](imH_2)_2$ doped with 8-hydroxy-1,3,6-pyrenetrisulfonate (pyranine). Gray C, blue N; light blue polyhedral: phosphates, gray polyhedra: tetrahedral Zn<sup>2+</sup>. B) Transmittance curve of the polished Zn-ZIF-62 MQG showing about 90% transmittance in the visible and near-infrared ranges.

crystallographic database and new syntheses are essential for this development. Computational approaches for predicting the stability of liquid states also contributes to the discovery of more examples. Aside from the design of melting/vitrifying structures, the current unanswered questions regarding the fundamental properties and functions of o-CPs are:

1) the length and structural periodicity of networks in liquid/ glassy states,

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- 2) the time scale of bond formation/cleavage of metal ions and bridging ligands in the liquid/glassy states,
- 3) the mechanical properties of the glass/liquid, and
- 4) the miscibility of the glass/liquid with other substrates.

There is an established background regarding conventional glasses including ceramics, metals, molecules, and organic polymers. Plausible unique features of the glassy state of o-CPs compared with these glasses are: the dynamic character of the coordination bonds, a high network connectivity through the use of secondary building units (SBUs) of metal clusters, and the combined properties of the coordination and hydrogen bonds with organic ligands, dispersion forces, as well as charge-transfer and electrostatic interactions. Figure 14 shows the processing-enabled formation of materials based on the glass and liquid states of o-CPs and the derived functions. Moldability and wide variability in the composition of the glass/liquid states enable the formation of various shapes and interfaces and the generation of promising materials.

Grain-boundary-free glass membranes can be used for selective gas permeation, while transparent films/monoliths can be used for photoconductivity or spectral conversion (luminescence and light-harvesting). The crystal-to-glass or crystal-to-liquid transformation is promising for heat storage, while the bistable resistivity is interesting for phase-change memory modules. Partial domain crystallization is feasible for the fabrication of glass ceramics. Large single crystals or glass fibers can be fabricated, and they can be used for internal reflection or optical transport. The soft and adhesive characters of glasses and liquids are important for engineering interfaces with other materials for energy devices (batteries, fuel cells). The 4G attributes (HAD) are important guidelines for creating functional materials based on the fundamentals of o-CPs.<sup>[8b]</sup> The glass and liquid states could be hybridized with other materials such as organic polymers, metal particles,



Figure 14. Materials and their functions obtained by the engineering of glass and liquid states of o-CPs/MOFs depending on the use of their glass and liquid states, and phase transformation.

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12

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or metal ions. These composites could be used as photocatalysts, electrocatalysts, storage media for reactive species, and phosphors. We also propose that the liquid state of *o*-CPs could potentially function as gas/ion transporters with fluid porosity as well as media for chemical reactions.

The processing capability of the glass and liquid states of o-CPs depends on the interaction between the metal ions and bridging ligands. The mechanical properties, particularly, the viscosity and working temperature, of glasses can be tuned by using different conditions during vitrification. In this regard, the mode of melting need to be understood. Sublattice melting and melting rhythms are often discussed for ionic liquids, molten salts, and eutectic solvents.<sup>[61]</sup> There is currently a huge library of metal ions and bridging ligands available for the construction of CP crystals. We should reinterpret this library from the viewpoint of phase control, which may enable the design of functional glasses and liquids of o-CPs, in particular MOFs.

#### Abbreviations

CP	coordination polymer
GFA	glass-forming ability
HDA	high-density amorphous
HDL	high-density liquid
<i>i</i> -CP	inorganic coordination polymer
LDA	low-density amorphous
LDL	low-density liquid
o-CP	organic-ligand-bridged coordination polymer
PDF	pair distribution function
MOF	metal-organic framework
MQG	melt-quenched glass
PCP	porous coordination polymer
$T_{\rm g}, T_{\rm m}, T_{\rm c}, T_{\rm d}$	glass transition, melting, crystallization, de-
-	composition temperatures

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#### **Conflict of interest**

The authors declare no conflict of interest.

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13

Minireviews

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Metal–Organic Frameworks

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Heart of glass: The liquid/glass states of coordination polymers (CPs) and metalorganic frameworks (MOFs) constitute a new class of amorphous materials and are related to ionic liquids and other ionic soft materials. The unique energy landscape and dynamics of liquid/glass CPs/ MOFs with coordination networks offer additional opportunities for properties and functions that are complementary to those of the crystalline state.

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15