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Author/s:
Lin, Z;Richardson, JJ;Zhou, J;Caruso, F

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Direct synthesis of amorphous coordination polymers and metal–organic frameworks

Zhixing Lin[1,2], Joseph J. Richardson[1,2], Jiajing Zhou[1] and Frank Caruso[1,†]

[1]Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria, Australia.

[2]These authors contributed equally: Zhixing Lin, Joseph J. Richardson

[†]e-mail: fcaruso@unimelb.edu.au

Toc Blurb

Amorphous coordination polymers and metal–organic frameworks can be directly synthesized under mild conditions using a broader range of metals and ligands than their crystalline and crystal-derived counterparts, and therefore exhibit different physicochemical properties. This Review discusses the direct synthesis of amorphous coordination polymers, as well as their characterization, properties and applications.

Abstract | Coordination polymers (CPs) and their subset, metal–organic frameworks (MOFs), can have porous structures and hybrid physicochemical properties that are useful for diverse applications. Although crystalline CPs and MOFs have received the most attention to date, their amorphous states are of growing interest as they can be directly synthesized under mild conditions. Directly synthesized CPs can be constructed from a wider range of metals and ligands than their crystalline and crystal-derived counterparts and demonstrate numerous unique material properties, such as higher mechanical robustness, increased stability and greater processability. This Review examines methods for the direct synthesis of CPs and MOFs, as well as their properties and characterization routes, and offers a perspective on the opportunities for the widespread adoption of directly synthesized CPs.

[H1] Introduction

Coordination polymers (CPs) and their higher-dimensional and potentially porous subset, metal–organic frameworks (MOFs), are supramolecular materials comprised of metal nodes and organic ligands[1,2]. CPs in the crystalline state have been the primary focus of the field over the past three decades, mainly because of their defined structures, high internal surface areas and potential for crystal engineering[3–5]. For example, the periodic spacing of metals and ligands has allowed for fundamental research on controlling pore size and surface area, as both properties have been correlated to achieving enhanced performance in various applications[6–9]. However, processing these crystalline materials for practical applications can be challenging owing to issues with maintaining accessible pore volumes, integration into existing infrastructure and safety concerns arising from the frequent use of toxic precursors and solvents[10–13]. Primarily, these issues arise from the synthesis conditions and the rigid, brittle and often unstable nature of crystalline CPs[14–16] (Box 1). Many such materials contain some amorphous domains, which often increase the pore size as well as the mechanical and chemical robustness of the material, thereby improving functionality[17–20]. There has thus been increased attention directed towards amorphous CPs over the past decade[21,22], as their study raises fundamental questions about the rational design of amorphous materials, and their potential applications in areas such as catalysis and biomedicine are promising[23,24] (Box 1).

Two distinct routes currently exist for synthesizing amorphous CPs, namely direct synthesis from precursors and the amorphization of pre-synthesized crystalline materials[25,26]. Although amorphization can generate materials with specific advantages[23,27] (such as a high diffusion barrier, owing to structural collapse, which enables sustained drug release[28]), it is often energy intensive, requires the synthesis of the crystalline material and can sometimes lead to non-porous materials[29]. Alternatively, direct synthesis involves control of the coordination kinetics to generate amorphous materials under mild, ambient conditions[30,31] that are more energy efficient and environmentally friendly than those used in amorphization. The direct synthesis of amorphous CPs has also received renewed interest because it leads to unique morphologies and allows for facile tuning of the functional properties, often without the need for organic solvents[30]. The coordination kinetics can be controlled during direct synthesis through the choice of precursors (flexible and asymmetric organic ligands, seeding agents or templates) and/or through control of the synthesis conditions (such as different precursor concentrations, precursor ratios, solvents or reaction time) (Fig. 1). The general ease of synthesis and the wide range of available building blocks make amorphous CPs of interest for fundamental structure–property–function investigations of metal–organic systems. Fundamental studies and applications of amorphous CPs are expected to lead to a convergence of ligands, morphologies and techniques for the engineering and application of these materials[24,26], and this Review provides impetus in that direction.

In this Review, we focus on the direct synthesis of amorphous CPs and MOFs, as well as the characterization and properties of the resulting materials. Comparisons with crystalline CPs are provided when possible to highlight the unique properties and performance of amorphous CPs; however, there is a scarcity of direct comparisons in the current literature. We conclude with our perspective on potential future aims and directions for these amorphous materials.

[H1] Direct synthesis of amorphous CPs and MOFs

Although the amorphization of crystalline CPs is possible[23,32], going straight from precursors to amorphous CPs during synthesis offers advantages in terms of milder synthesis conditions, a wider range of applicable building blocks and the formation of products with enhanced physicochemical properties. Various approaches can be used to generate coordination defects, which minimize the kinetic or thermodynamic energy of the metal–organic complexes at the particle–solution interface and, thus, prevent crystallization (either permanently or temporarily) during CP formation[33,34]. Thus, most amorphous CPs are spherical when synthesized in solution and can be highly adherent when synthesized at interfaces, which can have benefits in applications ranging from drug delivery to photonics[35]. In the following sections, we discuss the different approaches used to directly synthesize amorphous CPs from precursors under ambient conditions.

[H2] Flexible and/or asymmetric ligands

Natural and synthetic flexible and/or asymmetric ligands with functional groups that can strongly coordinate to metal ions (such as phenolic and phosphonate moieties) can be used to form amorphous

CPs under ambient conditions, as the intramolecular rotation of the ligands, lack of symmetry planes and the relatively strong cumulative chelation strength of the functional groups can prevent or slow crystallization[36,37] (Fig. 2). With the direct synthesis approach, water is often used as the solvent, which requires the interaction between the metal and ligand to be comparable to or stronger than the interactions between the metal and water, and the resulting amorphous CPs are therefore often stable in a wide range of polar and nonpolar solvents, in contrast to many classes of crystalline and amorphized CPs, which are not stable in polar solvents (such as water)[16]. Moreover, the radius of the metal is not a major concern when directly synthesizing amorphous CPs, unlike when synthesizing crystalline coordination materials given that the size of the ion can change or interfere with the crystal structure. Therefore, a wide range of metals can be used with flexible and/or asymmetric ligands without notable changes to the experimental protocol[38–40].

Nucleic acids are flexible biopolymers with a strong affinity for metal ions and can be readily used to prepare amorphous CPs; indeed, most of the metal–nucleic acid CP literature relates to amorphous CPs[41,42]. Owing to the flexibility of the ligands, synthesizing nucleic acid-based crystalline CPs is challenging and requires precise synthesis conditions, whereas amorphous CPs can be readily prepared by mixing the precursors in water at room temperature[43,44]. Although different nucleotides share many features, only nucleotides with certain structures can form CPs with specific metals that are easy to reduce, such as gold (ref.[45]). Moreover, the metal, nucleotide and number of phosphates on the nucleotide have a notable role in determining the type of amorphous CP formed (such as particle or gel), their subsequent interaction with other molecules[43], and their optical, magnetic and catalytic properties[44,46].

Amino acids also have an affinity for metal ions through their termini and often through their side chain. Furthermore, peptides and proteins can adopt various conformations and therefore tend to form amorphous CPs rather than crystalline CPs upon chelation with metals[47,48]. Synthetic approaches have been developed to tune the amino acid sequence and to incorporate disulfide bridges (from peptides) into the final amorphous CPs, which can allow for the formation of redox-responsive amorphous CPs that disassemble in the presence of chelating agents[49]. Moreover, self-assembled peptides with complex architectures, such as disks, can be further assembled into hollow spheres through the addition of metal ions[50] without the loss of structure, which implies that their function is also maintained.

Many hydroxy-rich biopolymers can also be used to synthesize amorphous CPs, with representative ligands including chitosan, alginate, cyclodextrins, phenolics and cellulose[37,51–53]. The resulting amorphous CPs tend to be highly biocompatible and biodegradable, and, owing to the incorporation of protonatable chelators, undergo reversible interactions in response to external stimuli[38]. Amorphous CPs constructed from hydroxy-rich small natural molecules (such as gallic acid and tannic acid) can have metal-dependent disassembly profiles owing to the multivalent interactions of the ligands **[Au:OK?]** and can be covalently cross-linked to change their stability and porosity[30,38]. Cellulosic materials and chitosan are also commonly used to form amorphous CPs owing to their large size and flexibility, which make the formation of crystalline CPs more challenging[54,55].

Phosphonates (natural or synthetic) are a class of small molecules that can have short-range order, but it is challenging to order them on the longer length scales needed to generate crystalline materials owing to their strong and fast chelation[56], although microwave synthesis can facilitate crystallization[57]. Phosphonates are thus regularly used to directly synthesize amorphous CPs[52]. Surfactants and evaporation-induced self-assembly can be used to facilitate the formation of amorphous phosphonate-based CPs[58,59], which can be synthesized in different shapes, such as two-dimensional (2D) materials[60] and hollow capsules[61].

In addition to natural ligands, a wide range of synthetic flexible and/or asymmetric small-molecule ligands can be used to directly synthesize amorphous CPs. For example, replacing a rigid ligand that forms crystalline CPs with a chemically similar flexible ligand can result in amorphous CPs[35], and by mixing asymmetric and symmetric ligands, amorphous, semi-crystalline and crystalline CPs can be formed, depending on the ratio between the ligands[62]. Flexible ligands with different symmetry, geometry and arm number have been used to form different tubular amorphous CPs, demonstrating that ligand morphology influences particle shape, even in amorphous materials[63]. Interestingly, small rigid ligands with specific geometries can also be used to form amorphous CPs through self-limited growth, as the rigid structure of the ligand impairs subsequent chelation steps and epitaxial growth[64].

Flexible polymeric synthetic ligands have a high degree of chemical tunability and can be used to form crystalline or amorphous CPs[65], depending on the spacer length between the chelating groups on the side chain. Specifically, spacers that are too short or too long lead to amorphous materials, which generally lack the porosity of some crystalline polymer-based CPs[66]. Alternatively, chelating groups can be added to the termini of polymers to preserve the functionality of the polymers themselves, which can result in the formation of highly stable amorphous materials[67].

In summary, using flexible and/or asymmetric ligands is a common approach to directly synthesizing amorphous CPs under mild, ambient conditions, although some restrictions exist in terms of the applicable building blocks as many of the reported ligands conventionally used to synthesize CPs are rigid and symmetrical. Nevertheless, the flexibility and/or asymmetry of the ligands means multiple functionalities can be incorporated into the building blocks prior to synthesis. Finally, it is important to note that although many flexible and/or asymmetric ligands readily lead to amorphous CPs, there is growing interest in crystallizing CPs composed of such ligands[65].

[H2] Templates and seeds

Templates and seeding agents can be used to induce the formation of amorphous CPs by locally increasing the concentrations of the metal and/or organic ligand[68] (Fig. 3). This approach therefore allows for synthesis at lower concentrations of the precursors (up to several orders of magnitude)[55] and in different solvents (such as water) than commonly used for crystal synthesis. However, the formation of amorphous CPs on templates generally requires interactions between the ligand and the surface of the template, and therefore the chemical properties of the ligand must be taken into consideration[30]. By contrast, seeding agents generally only need to act as a sink for the metals[30].

Templates can be used to concentrate ligands that form metal–organic complexes and the use of functional or cargo-loaded templates also offers a high degree of control over the functionality of the resultant core–shell materials[69–71]. For example, some adhesive ligands, such as phenolics and phosphonates, can adsorb onto templates while chelating metals. These concurrent processes locally increase the concentrations of both precursors, which leads to the formation of amorphous CP coatings, sometimes in a matter of seconds[30]. Strongly chelating organic ligands and aqueous synthesis conditions are generally used with the templating method, leading to increased water stability of the resultant CPs[72–74]. The coordination interactions within amorphous CP coatings are comparable to that of metal ions to water molecules, thus they are sufficiently robust to avoid disassembly in the presence of water and, therefore, can be used for a wide range of aqueous-based applications (such as drug delivery). Sacrificial templates can be selectively removed in specific solvents and can therefore be used to form hollow and mesoporous amorphous CP replicas of different template geometries[30,69] (Fig. 3a,b).

Phenolics strongly adhere to many surfaces, which allows for the formation of surface-confined amorphous CPs, termed metal–phenolic networks (MPNs), on various nanoscopic and macroscopic templates[30,69] (Fig. 3c). The ability to form MPNs using different metals and ligands enables the porosity and responsiveness to external stimuli (such as pH, solvent and temperature) to be tuned[30,38,69]. The diverse interactions between the phenolic ligands themselves, as well as between the ligands and the metals and templates (such as hydrogen bonding, π interactions, electrostatics, chelation and hydrophobic effects) facilitate the rapid formation and deposition of MPNs[33]. Moreover, these diverse interactions impart water stability to MPNs, and the disassembly properties can be tuned through judicious choice of the metal ions. More than 8,000 phenolic molecules with different functions (for example, anticancer and neuroprotective effects) have been discovered in nature to date, and given the synthesis of phenolic polymers[75], the field of MPNs should continue to grow.

Phosphonate-based amorphous CPs can coat various substrates, and the resultant films are generally more stable than phenolic-based coatings when using the same metal, owing to phosphonates being stronger electron donors[72]. The rapid chelation and formation of metal–phosphonate complexes means that phosphonates readily form amorphous structures when interacting with metals in water, particularly for tri- and tetravalent metals[76], and the strong hydrogen bonding between the phosphonic acid groups and water molecules endows phosphonate-based amorphous CP coatings with high water stability and superhydrophilicity[72].

Notably, the use of templates can often lead to amorphous CPs with ligands that might otherwise yield crystalline CPs in the absence of templates[68,77]. This outcome is likely due to the metal–organic coatings being too thin for sufficient rearrangement to produce long-range order and/or the high curvature of the templates[78,79]. For example, when palladium nanoparticle templates were used, a transition from an amorphous coating to a crystalline coating was seen during zinc-based CP film growth over 4 h, which is directly correlated with the thickness of the coating increasing over time[80]. The surface chemistry of the template is also important in helping to achieve uniform coatings: surface modification, such as through functionalization with carboxylate groups or coating with chitosan, can facilitate the deposition of uniform amorphous CP coatings[81].

Similar to the templating of amorphous CPs, seeding agents such as synthetic polymers and biomolecules can locally increase the concentration of precursors to rapidly generate amorphous materials at low precursor concentrations and in aqueous conditions that are generally not favourable for preparing large complexes (Fig. 3d,e). Seeding agents can therefore expedite the complexation process, hinder crystallization and produce coordination defects[77] (Fig. 4). Engineering defects into CPs, whether with seeding agents or otherwise, allows for control of the amorphousness, as increasing the size and number of defects decreases the crystallinity. Synthetic polymers such as polyvinylpyrrolidone and biomolecules ranging from cellulose nanocrystals to chitosan and proteins have been used as seeds for amorphous coordination materials with different ligands, often leading to enlarged pores and sometimes higher surface areas compared with those prepared without seeding agents[82–85].

In summary, templates and seeding agents are commonly used for generating amorphous CPs from building blocks that are routinely used to synthesize crystalline materials. This approach can allow for synthesis in aqueous, ambient conditions, as well as the facile loading of functional cargo by using the cargo as templating agents or seeds[38,75,82]. Moreover, multiple different forms or sizes of cargo can be readily integrated during synthesis, which would normally prove challenging for crystalline CPs owing to their specific and narrow pore sizes. Notably, sacrificial templates can enable the generation of complex and hierarchical amorphous CPs from relatively straightforward synthesis approaches. Additionally, the use of templates and seeding agents can decrease the quantity of precursors needed, which could have commercial advantages for the subsequent amorphous CPs.

[H2] Synthesis conditions

Specific synthesis conditions are important in controlling the formation of amorphous CPs versus crystalline CPs. Conditions that cause amorphous particles or precipitates to form from precursors commonly used to prepare crystalline materials can be harnessed to directly synthesize amorphous CPs and MOFs (Fig. 5). Overall, the solvent, reaction time and environmental conditions (pH, temperature, pressure and ionic strength) during synthesis, together with the ligand-to-metal ratios and concentrations, and even the metal salts used as precursors, are interrelated in dictating whether amorphous or crystalline CPs form[86] and allow for control of the final structure and properties (that is, morphology, crystallinity and porosity) of CPs.

As an example, the impact of synthesis conditions on crystallinity has been widely studied for imidazolate-based MOFs[87,88]: during synthesis, amorphous intermediates regularly occur at the early stages of formation, and the amorphous MOFs can then be converted into crystalline MOFs by washing in organic solvents, ageing or other post-treatments[89,90]. Indeed, most coordination materials are amorphous during the early stages of the reaction and then crystallize over time (if they crystallize at all), depending on the environmental conditions (such as temperature and pressure)[34,91–94]. Seeding agents can also induce crystallization[51,95–97]. Solvothermal techniques that involve elevated temperature and pressure are commonly employed for the synthesis of crystalline MOFs, whereas ambient conditions are regularly used for amorphous MOFs[98]. Generally, higher temperatures lead to higher crystallinity or expedite crystallization[99,100]. Amorphous CPs synthesized with flexible ligands, such as phenolics and phosphonates, can convert into crystals under appropriate solvothermal treatment[101,102], but often only specific pH and concentrations yield pure crystals, with the exact conditions required for crystallization dependent on the metal used[68,103,104].

Many amorphous CPs can be directly synthesized in water even though water interacts strongly with the metal ions[30,72]. This strong interaction can lead to unsaturated metal sites that propagate defects and decrease long-range order in the complexes[33]. Alternatively, amorphous materials can be precipitated by dissolving metal–organic complexes in a solvent in which they are highly soluble, followed by rapid introduction of a solvent in which they are insoluble[25]. Interestingly, organic solvent additives can inhibit or promote the formation of crystals depending on the system studied, and amorphous CPs can sometimes be produced by adding a co-solvent to water[105]. In addition, for the same precursors, the use of different solvents can produce crystalline or amorphous materials. For example, in the synthesis of hollow MOF nanocages, switching from *N*,*N*-dimethylformamide (DMF) to *N*,*N*-dimethylacetamide led to the formation of amorphous MOFs[106]. Moreover, in the synthesis of MOF nanopolyhedra, using triethylamine (TEA) as an additive to DMF led to amorphous MOF particles, whereas adding both TEA and hexane to DMF led to crystalline MOF particles[107]. A dynamic solvent-induced crystallization–amorphization process was observed in the synthesis of infinite CP microparticles: solvent exchange between pure pyridine and pyridine mixed with another solvent resulted in dissolution or formation of CPs, respectively, and could also be used to transition between amorphous and crystalline CPs, depending on the choice of the additional solvent[25,108] (Fig. 5). Amorphous CPs can also be synthesized in one solvent and then crystallized in another solvent upon subsequent heating[109], which highlights the importance of amorphous CPs as intermediates to crystalline materials.

The concentration, ratio and type (such as choice of metal salt) of precursor all have a role in determining the crystallinity of CPs. Lowering the ligand-to-metal ratio can cause irregular coordination when using rigid ligands, as the excess metal ions disrupt the long-range ordering of the coordination network and cause defects, thereby leading to amorphous CP formation[82]. The irregular coordination can lead to relatively large and inhomogeneous pores in amorphous materials compared with the pores observed in crystalline CPs or amorphized CPs. Similar trends are observed with biomolecule-seeded materials, for which lower ligand-to-metal ratios result in highly stable amorphous CPs, whereas higher ratios produce amorphous materials that readily dissolve and reform as crystals[89]. Additionally, the concentration of the seed itself can play a part in determining the amorphous nature of the final material, as higher concentrations of biomolecule seeds can lead to higher temperatures being required to crystallize the product because of the defects that can occur with seeding agents[84]. Similarly, fixed ratios, but lower concentrations of precursors can produce amorphous MOFs when templated on nanowires[78]. Excessively high concentrations of either precursor can lead to fast chelation and cross-linking of metal–organic complexes and impede their further rearrangement into an ordered structure, resulting in amorphous CPs[110]. Collectively, these examples highlight that the design space for amorphous CPs is larger than that of crystalline CPs.

The formation of amorphous materials can also be promoted by the use of mixed metals, owing to mismatches in their radii and valency causing defects and hindering long-range order, even when using solvothermal methods[111]. Additionally, specific organic metal salt precursors can be used during synthesis to stabilize the metal ion and prevent oxidation or reduction and modulate the formation process[112]. For this reason, metal acetate salts are often used for synthesizing amorphous CPs because they dissolve at higher pH and relative basicity compared with many other metal salt precursors, which allows for synthesis to occur at higher pH, and they can act as modulating counter ions for regulating the ordered coordination modes between the metal ions, the solvent, and competing organic ligands[105].

In summary, controlling the synthesis conditions offers a route to engineering amorphous CPs. It is often easier to synthesize amorphous CPs than it is to synthesize their crystalline counterparts, and therefore less troubleshooting is generally required when targeting amorphous materials.

[H1] Choosing whether to crystallize CPs

When designing CPs for various applications, an important question is whether crystalline or amorphous materials should be used. This choice not only determines the selection of the building blocks, but more importantly properties of the CP, including those related to their application, such as water stability and ability to coat substrates (Table 1). For example, density functional theory calculations have indicated that some amorphous zeolitic imidazolate frameworks (ZIFs) and ZIF analogues have higher dielectric constants than their crystalline counterparts[113]. Experimentally, a difference in the electric properties was found for other MOF types: amorphous bimetallic terephthalate MOFs had lower (more desirable) charge transfer resistance (~2.3 Ω) than their crystalline counterparts (~4.8 Ω)[114]. It is therefore crucial to weigh up the pros and cons of each form of a CP, and ideally amorphous and crystalline forms should be characterized when both are synthesized (whether by design or chance), as experimental comparisons between compositionally identical (or nearly identical) crystalline and amorphous CPs are still limited.

A class of amorphous CPs regularly compared against their crystalline counterparts are phosphonate CPs owing to the relative ease of making both types of coordination materials. This comparison allows for a better understanding of structure–function relationships. For example, iron–nickel-based amorphous phosphonate CPs achieved nearly 100% photocatalytic water oxidation versus only 40% for their crystalline counterparts[102]. Similarly, cobalt–iron-based amorphous phosphonate CPs exhibited better catalytic performance than their crystalline forms, as observed by the lower overpotential (278 vs 322 mV, respectively)[101], which is likely owing to the abundant surface defects and lattice dislocations. Besides phosphonate CPs, the solvothermal crystallization of amorphous MOFs can allow for useful comparisons. For example, amorphous zirconium-based MOFs had considerably lower overpotential in oxygen evolution reactions compared with their crystallized forms[98].

Moreover, enzyme-loaded directly synthesized amorphous MOFs exhibited 5–20 times higher catalytic activity than chemically identical enzyme-loaded crystalline MOFs, because the larger pore size in the amorphous materials resulted in a lower diffusion barrier, thus facilitating the diffusion of substrates[82] (Fig. 4). Similarly, with amorphous iridium-based CP coatings, access to the underlying template was retained and, therefore, the catalytic ability of the template material was preserved[79], which was not the case for analogous crystalline coatings. Although directly synthesized amorphous CPs regularly differ in their performance from crystalline CPs, they can also differ from CPs amorphized from a crystalline state, especially in regard to pore access and catalytic performance[82,115]. For example, amorphous MOFs prepared through direct synthesis using seeds featured expanded pores and a lower diffusion barrier[82] than the same amorphous MOFs prepared by amorphization of crystalline MOFs[115].

The physical structure of CPs can also have a notable role in determining potential applications. For example, owing to the reduction in scattering losses due to the elimination of hard edges, spherically shaped amorphous MOF microcavities prepared from flexible ligands exhibited superior microlaser performance than their crystalline counterparts prepared from rigid ligands[35]. In another example, the packing density of MPNs was controlled through various routes, such as the use of oxidizing metals, high concentrations of precursors and different solvents or pH, to tune the pore size between <1 nm and >100 nm (refs.[70,116,117]) and thus modulate the permeability, offering a higher degree of control compared with crystalline phenolic MOFs[118]. Crystalline and amorphous forms of the same MOF can have similar pore volumes and surface areas[109], although amorphous MOFs with flexible ligands might have lower surface areas than their rigid-ligand crystalline counterparts owing to pore collapse[62]. Nevertheless, amorphous CPs prepared from high seed concentrations of polyvinylpyrrolidone exhibited surface areas as high as ~500 $m^2 g^{-1}$, which is comparable to that of many crystalline CPs and MOFs, and showed higher anionic dye adsorption (~1,000 mg of dye per g of CP) than many crystalline materials owing to a combination of more unsaturated metal sites and better accessibility to hydrophobic regions[119]. Other amorphous MOFs have exhibited a higher CO_2 absorption capacity (0.8 mmol CO_2 per g) than their crystalline form (0.1 mmol CO_2 per g)[120] or have an adsorption capacity for lanthanides and other heavy metals that is nearly twice that of the crystalline forms[100,121,122].

Generally, compared with crystalline CPs, amorphous CPs have a wider pore size distribution with randomly interconnected pores; thus, processing methods are less likely to completely close, collapse or fill all the accessible pore volume. Control of the pore size and geometry during processing is key to achieving crystalline CPs with a high surface area, and improvements have led to an increase in the surface area of three orders of magnitude over the past two decades[4]. Pore size is often controlled over only a single order of magnitude (for example, between 1 and ~10 nm), as the pore size of crystalline materials is generally controlled by varying the ligand size or by using templates[123,124]. By contrast, the pore size of amorphous CPs can be additionally tuned by, for example, controlling the synthesis conditions and adding removable templates[69], allowing for control of the pore and void sizes over at least three orders of magnitude[70,116]. However, although the potential range of pore sizes is much larger, the ability to engineer narrow pore distributions can prove challenging in amorphous materials.

Although amorphous CPs show promising performance in specific applications, there are still notable gaps in understanding their limitations. For example, amorphous CPs that are responsive to force and temperature can be formed from flexible dendritic pyridyl ligands[125], but their integration into devices is yet to be achieved. Therefore, comparative studies between crystalline and amorphous CPs are necessary to understand which materials are better suited for specific applications, especially when considering real-world environmental factors such as humidity, pH changes, vibrations and impacts.

[H1] Characterizing directly synthesized amorphous CPs and MOFs

Structural characterization is important to distinguish CPs from other metal–organic materials that lack a network-like nature (such as organic polymers decorated with metal ions). Characterization is also crucial for comparing the physicochemical properties of different classes of amorphous CPs and for evaluating their performance in potential applications. We highlight five key features of amorphous CPs (namely, the formation, amorphous structure, coordination state, stability and porosity) and discuss the techniques used to analyse these. We summarize experimental characterization methods herein (Table 2), but it should be noted that computer simulations (such as molecular simulations and coarse-grained modelling) can be used in conjunction with empirical data to provide structural insight. There are methods that can be used to specifically characterize amorphous CPs, such as determining the pore size in liquids with fluorescent probes; however, many characterization methods can be used to study both amorphous and crystalline CPs. Although we focus on the characterization of directly synthesized amorphous CPs, we also highlight when compositionally identical materials will give different results with certain characterization methods based on their short-range or long-range ordering.

[H2] Direct formation

The formation of amorphous CPs can be a challenging process to study owing to their typically rapid formation, and thus highly specialized equipment is generally required[97,113]. Additionally, as described above, many crystalline CPs transition from an amorphous state, and therefore studies examining the formation and crystallization of crystalline CPs can also sometimes be considered to have examined the formation of amorphous CPs[93]. Formation can be observed through morphological changes using cryogenic or liquid cell transmission electron microscopy (TEM)[89,126] and light scattering[127,128], or by observing the molecular spacing and local environment using small- and wide-angle X-ray scattering (SAXS/WAXS) and diffraction[92,95,129,130], neutron scattering[131], gravimetric analysis[132], cryospray mass spectrometry[133] and extended X-ray absorption fine structure (EXAFS)[93,134]. In situ TEM can additionally allow for electron diffraction measurements to be taken at nearly the same time as imaging but requires customized equipment[89,126]. Similarly, EXAFS and SAXS are generally performed using a synchrotron X-ray source and therefore often require access or collaboration with beamline scientists. Notably, EXAFS can effectively probe the chemical environment at the earliest stages of formation, which cannot be generally achieved with other X-ray techniques[134]. Finally, widely used techniques such as scanning electron microscopy (SEM)[108,128,133] and ultraviolet–visible (UV–vis) spectrophotometry[30] can, respectively, enable monitoring of, for example, morphology changes and changes in turbidity[129] or colour (ligand-to-metal charge transfer (LMCT) bands) to determine the formation and growth in solution or on substrates. Understanding the formation mechanism is important for engineering specific properties into amorphous CPs. For example, it has been demonstrated that synthesizing MPNs from metal precursors that slowly transition into higher oxidation states, thereby slowing the formation of the MPN, produces thicker and more densely packed adherent amorphous CPs on substrates than those formed directly from oxidized metal precursors.

[H2] Amorphous nature

The lack of long-range order in amorphous CPs is relatively easy to confirm using various scattering techniques, but it can be challenging to study the short-range order and atomic positioning of the metals and ligands in amorphous CPs. The techniques used to monitor the formation of amorphous CPs can also be used to investigate the extent of their amorphous nature[134]. For example, the amorphous nature can be confirmed by X-ray diffraction (XRD), even though the absence of Bragg diffraction from amorphous CPs inhibits the identification of atom positions and the long-range structure of the materials[104,106]. However, the distribution of metal centres and the distances between atomic centres **[Au:OK?]** can be characterized by pair distribution function analyses, using a synchrotron X-ray source, to confirm the existence of metal–ligand–metal connectivity and to differentiate between crystalline and amorphous CPs in the same sample[97,99,130]. EXAFS can be used at different time points to demonstrate the time-dependent amorphous-to-crystalline transition of some CPs as this technique provides information about the metal–ligand distances and local configuration of atomic centres in amorphous and crystalline CPs[93,134]. The distribution of the organic linkers and the metals in amorphous CPs can also be investigated using spin-diffusion nuclear magnetic resonance (NMR) spectroscopy owing to changes in the ligand signals (often ^{1}H) and changes to the metal signature (such as ^{27}Al, ^{31}P and ^{113}Cd)[65,135]. Compared with the NMR spectra of crystalline materials, weaker metal peaks are often seen in the spectra of amorphous materials, and therefore NMR can be used to monitor the crystallization of amorphous CPs even when ^{1}H NMR shows no changes[136]. Similarly, the peaks of amorphous CPs in Fourier transform infrared (FTIR) spectra tend to shift to lower wavenumbers compared with those of crystalline CPs owing to the generally disordered and weaker bonds in the amorphous networks[7]. Electron microscopy such as TEM and SEM enables the observation of the morphology of amorphous CPs, whereby the amorphous nature is suggested by the lack of defined edges[108,128,136]. Moreover, electron diffraction can be performed in situ to confirm the amorphous nature. Thermogravimetric techniques can also be used to differentiate between crystalline and amorphous CPs, to some extent, because of the differences in thermal stability between crystalline and amorphous materials.

[H2] Coordination states

The coordination state of amorphous CPs has a notable influence on their physicochemical properties (such as the pH-responsiveness, mechanical robustness and the availability of free metal sites), which in turn influences their subsequent application[33,70,116]. Understanding the coordination state is particularly relevant for some classes of amorphous CPs that contain different chelation states in the same material (for example, MPNs can exhibit bis and tris complexes), and these states can often be characterized by fluorescence spectroscopy[137] or by monitoring the LMCT bands using UV–vis spectrophotometry[30,51,138]. Moreover, shifts in binding energy as monitored by X-ray photoelectron spectroscopy and electron paramagnetic resonance spectroscopy can provide insight into the coordination state of the metal[78,139,140]. NMR spectroscopy can be used to confirm coordination through the deprotonation of the organic ligand or through changes in the coordination number and geometry of the metal[135,136]. FTIR spectroscopy can also demonstrate the deprotonation of the organic ligand[139] and is sensitive to the chelation state of phytate-based amorphous CPs[141]. More recently, it has been reported that the chelation complexes constituting amorphous CPs have specific buffering capacity, and therefore titration can also be used to determine the coordination state[116]. In most instances, the coordination state will help determine the overall stability of amorphous CPs, which is an important factor that governs their performance in various applications.

[H2] Stability

Many amorphous CPs are stable in water, a trait that can be challenging to engineer into crystalline CPs[142]. Studying their stability in different solvents, at different pH, when exposed to different chelating agents, and at different humidity and temperature is crucial for understanding and applying amorphous CPs in various fields. The coordination stability can be monitored with similar techniques to those used for studying the coordination state (such as UV–vis spectrophotometry, NMR spectroscopy and FTIR spectroscopy). Notably, changes in coordination state do not always correlate to disassembly in amorphous CPs; for example, MPN capsules can remain intact with different coordination states[116]. To study the overall stability of individual amorphous CP particles, flow cytometry can be used to count the particles over time or in different conditions[30]. Morphological characterization methods, such as atomic force microscopy[33], scattering[100], and optical and electron microscopy[38], can be used to monitor morphology changes and disassembly. For example, it was shown that amorphous iron–manganese-based MOFs were more stable than their compositionally similar crystalline counterparts using SEM and XRD[100]. Alternatively, disassembly can be monitored directly through the metal or ligand content being released from the amorphous CPs using techniques such as optical emission spectroscopy and mass spectrometry[38,69]. Indirect methods can also be used to study disassembly, such as monitoring the release of encapsulated cargo[49,143]. Additionally, thermogravimetric techniques can be used to study the stability of amorphous CPs at high temperatures[58].

[H2] Porosity

Several standard methods can be used to determine the porosity of amorphous CPs either in gas, using adsorption–desorption analyses[120,138], or in solution, using permeability tests with polymeric probes such as fluorescein–dextran or small-molecule dyes[116]. For example, the pores of azole-based amorphous CPs are sufficiently large to be detected by N_2 adsorption–desorption analysis, whereas the micropores of phenol or phosphonate systems are usually calculated by H_2 uptake owing to their smaller size[33]. Comparison of the pore sizes of amorphous and crystalline CPs and MOFs can provide insight into the origin of porosity; some amorphous materials have the same pore size as their crystalline counterparts, suggesting that in some cases, the pore size is derived from the precursor geometry regardless of the ordering[7]. Unsaturated metal sites can strongly bind solvents, such that activation of the pores or removal of the solvent is not always possible[144] and, therefore, the porosity has to be probed in solution. In these instances, pore size can be investigated by using different solvents or by using molecular probes, which can allow for the identification of gating mechanisms and pH-dependent porosity[33,116]. In addition, more advanced strategies such as cryo-TEM can be used to study the porous nature of amorphous CPs. For example, with biomolecule-seeded amorphous MOFs, the pores containing the biomolecule as well as those lacking the biomolecule could be visualized; Fourier transformation of the electron density scans enabled the accurate determination of pore sizes and distributions[82]. Similarly, complex techniques such as positron annihilation lifetime spectroscopy can be used to determine the pore sizes in amorphous CPs[145], although this technique has rarely been used for directly synthesized amorphous CPs.

[H1] Future perspectives

The direct synthesis of amorphous CPs has attracted interest because they demonstrate several unique material properties over their crystalline counterparts. The milder synthetic conditions (ambient temperature and pressure, and/or free from organic solvents) can generate emergent types of materials, including adherent materials, free-standing films, glasses and templated replica materials using a wide range of metals and a diverse ligands not commonly used for engineering crystalline materials. The amorphous structure also affords materials with tunable mechanical properties, exposed metal centres and greater processability, loading capacity and stability compared with their crystalline counterparts[146]. These advantages suggest that amorphous CPs might find use in various fields that require exposure to aqueous environments[38]. For example, amorphous CPs show particular promise in biomedical applications such as drug delivery, which involves exposure to complex media and biological triggers (such as the redox environment, pH, temperature and competitive chelators)[25,85,147]. Moreover, the ability to readily construct amorphous CPs from natural ligands and non-toxic metals reduces the risk of off-target effects and improves biodegradability, which are useful for biomedical and environmental applications[38,148,149].

A key advantage for future development is that the design and use of amorphous materials is not concerned with preserving delicate crystal structures and, therefore, the future of amorphous CPs is expected to be more expansive than for their crystalline counterparts. Although expanding the range of applicable ligands and metals is important for both crystalline and amorphous CPs, we emphasize two key aims for the future of amorphous CPs, namely improving the understanding of their formation, and studying their processability and integration into macroscopic functional materials.

Identifying how defects, disorder and the continuous random network arise during amorphous CP synthesis will allow for the rational design of amorphous structures and materials. This understanding is important, as it would enable more amorphous CPs to be synthesized under aqueous ambient conditions, which in turn would lead to more amorphous CPs that are stable in water[72,100,142]. In addition, this understanding will allow for better engineering of pores, exposed metal sites and side group accessibility of the ligands for separation and catalysis[33], and might also provide insight into how to make crystalline CPs more water stable. Insight into their formation could also be useful in understanding crystalline materials and determining why crystalline and amorphous CPs with the same composition but prepared using different synthetic routes can have different properties.

Amorphous CPs are generally more adherent and more mechanically robust than their crystalline counterparts, and therefore processing amorphous CPs and transforming them into functional macroscopic structures (such as thin films and monoliths) is more achievable. Theoretically, amorphous CPs can be used from a liquid state, which would allow for more accurate monitoring of material properties (for example, brittleness and transparency) than is possible for the solid state and for creating more complex nanostructured materials. Moreover, the ability to readily use amorphous CPs as coatings makes it easier to integrate them into composite materials than it is for crystalline materials; for example, amorphous CPs have been used as protective coatings for biological cells[150]. Furthermore, exploring properties (such as the pore size, metal density and ligand length) of amorphous CPs for the rational design of functional composite materials could provide unique opportunities for broad applications in diverse fields.

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Table 1 | **Applications and comparison of properties of crystalline and amorphous CPs**

Property	**Variable**	**Crystalline CPs**	**Amorphous CPs**	**Applications**[a]
Composition	Ligand	Rigid ligands; mostly synthetic	Flexible and/or asymmetric ligands; mostly natural	Bioactive flexible ligands (such as DNA and proteins) can be directly used for fabricating *a*CPs for drug delivery[41,47]
	Metal	Generally, ligand-specific; often requires metal-specific protocols	Relatively wide choice of metals; generalized protocols	Different metal ions can coordinate with the same ligand via generalized protocols to form *a*CPs for bioimaging (such as PET) and catalysis (metal-based)[38]
	Synthesis	Generally, solvothermal; relatively slow	Generally, aqueous; relatively rapid	The mild synthesis conditions of *a*CPs benefit biomedical applications, such as drug delivery[73]
	Cargo	Potential deformation after cargo integration; specific cargo size, shape and charge required for post-synthetic loading	Facile loading typically without deformation; wide choice of cargo size, shape and charge for pre- and post-synthetic loading	The wide selection of functional guests allows the synthesis and use of *a*CPs in broaderapplications[44]
Morphology	Particulate	Typically faceted polyhedral; wide range of sizes; higher chance of aggregation; generally, dispersible in only organic solvents	Generally, spherical; small range of sizes; lower chance of aggregation; typically, dispersible in various polar and non-polar solvents, including water	The spherical morphology of *a*CPs can reduce scattering losses and increase performance for miniaturized lasers[35]
	Planar (film)	Thin-film coatings require complex protocols and substrates; often discontinuous	Thin-film coating formation is facile and rapid within minutes on various substrates; often continuous	The ability to form thin-film *a*CP coatings is useful for applications requiring surface engineering, such as controllable drug release[73] and enhanced antigen recognition[74]
	Hydrogel	Additional cross-linkers required	Spontaneous hydrogel formation	Readily formed *a*CP hydrogels are useful for sensors[53] and drug delivery[148]
Coordination state	Saturation	Fairly saturated ligand and metal coordination	Often unsaturated coordination	The unsaturated ligands of *a*CPs can interact with and sequester dyes or heavy metals[119,122]
	Activity	Limited active metal centres depending on ligand geometry; bound solvent can sometimes be challenging to remove	Abundant active metal centres owing to the general lack of saturated sites; bound solvent can generally be removed	The high number of active metal centres of *a*CPs is expected to significantly benefit catalysis[101,102]
	Chelation state	Single chelation state; generally, static chelation state	Single or mixed chelation states; dynamic chelation states are common	The dynamic chelation states of *a*CPs can induce efficient intracellular drug delivery and subsequent endosomal escape[147]
Porosity	Pore size	Specific and predictable pore sizes; usually angstrom to nanometre;	Generally, nonspecific pore sizes; usually angstrom to micrometre; wide pore-size distribution	The larger pore sizes of *a*CPs compared with those of crystalline CPs can reduce diffusion barriers and increase the catalytic activity of the loaded cargo (such as enzymes)[82]

		narrow pore-size distribution		
	Pore-size control	Limited control over range of pore sizes (one order of magnitude)	Greater control over range of pore sizes (three orders of magnitude)	The greater control in engineering pore sizes within a wider range for *a*CPs (compared with crystalline CPs) benefits applications such as molecular separation[117] or enzyme-based catalysis[83]
	Accessibility	Often requires ‘activation’ and post-processing to vacate pores	Generally, does not require post-processing although solvent cannot easily be removed from some metal centres	The accessible porosity of *a*CPs is potentially useful for gas capture and separations[33]
Processability	Aqueous stability	Generally poor water stability	Often stable in water	The water stability of *a*CPs can be used for drug delivery[73] and heavy metal recycling[122]
	Coating	Difficult to form homogeneous coatings; adhesion to substrates can be challenging	Easier to form homogeneous coatings; adhesion to substrates is less challenging	*a*CPs can therefore coat desired substrates to be used for anti-fogging or prolonging fruit shelf-life[72]
	Composite	Difficult to be integrated into bulk materials (for example, monoliths) owing to the rigid and brittle nature	Relatively easy to integrate into bulk materials (for example, monoliths) owing to flexibility and tunable mechanical properties	The easy incorporation of *a*CPs with bulk materials benefits industrial applications such as adhesives or dynamic actuators[37,146]
	Thermal transformation	Well-studied thermal transformation; wide variety of derivatives (such as metal-doped carbon materials) studied	Thermal transformation not well studied; small number of derivatives studied	The study of the thermal transformation of *a*CPs is still at its early stages but can be potentially used for energy applications such as engineering supercapacitors[39]

CP, coordination polymer; PET, positron emission tomography.

[a] The unique properties of amorphous CPs, when compared with crystalline CPs, can give them better performance in the highlighted applications.

Table 2 | **Characterization of features and properties of amorphous CPs and MOFs**

Property	**Technique**	**Comments**
Formation		
Morphology and size	SEM, TEM, DLS, SLS, SAXS/WAXS, light microscopy	The formation of amorphous CP complexes or intermediates is typically fast and, therefore, relatively difficult to study.
Turbidity or colour	UV–Vis, light microscopy	
Molecular spacing and local environment	Scattering and diffraction[a], gravimetric analysis, MS	
Amorphous nature		
Crystallization degree or existence of amorphous structure	XRD, SAXS/WAXS, NMR, FTIR, TGA	The lack of long-range order in amorphous CPs is relatively easy to confirm, but it can be challenging to study the short-range order and atomic positioning of the metals and ligands in amorphous CPs.
Distances between metal centres and their local environments	PDFs obtained using synchrotron radiation, EXAFS	
Morphology and edges	SEM, TEM, electron diffraction	
Coordination state		
Chelation states	UV–Vis, titration, fluorescence spectroscopy	Multiple coordination states, which are difficult to quantify individually, often exist in the same amorphous CPs.
Coordination state of metal centres	XPS, EPR	
Deprotonation of organic ligands	NMR, FTIR	
Stability		
Coordination stability and disassembly	UV–Vis, NMR, FTIR, SEM, TEM, DLS, light microscopy	Many amorphous CPs are stable in water, but suitable morphological models (such as MPN capsules) might still be required to quantify their stability in aqueous ambient conditions.
Bulk stability	Flow cytometry, TGA, light microscopy	
Release of metal, ligand or cargo	OES, MS, CLSM	
Porosity		
Gas porosity	Adsorption–desorption analyses	Although the porosity of amorphous CPs can be controlled over at least three orders of magnitude, most amorphous CPs possess much wider pore-size distributions than their crystalline counterparts, making it challenging to quantify the pores using a single technique.
Porosity in solvents	Permeability tests using LC or CLSM	
Pore size	PALS, electron density scans, EM	

[a] SAXS/WAXS, EXAFS, diffraction, neutron scattering. CLSM, confocal laser scanning microscopy; DLS, dynamic light scattering; EPR, electron paramagnetic resonance; EXAFS, extended X-ray absorption fine structure; EM, electron microscopy; FTIR, Fourier transform infrared; LC, liquid chromatography; MS, mass spectrometry; NMR, nuclear magnetic resonance; OES, optical emission spectroscopy; PALS, phase-analysis light scattering; PDF, pair distribution function; SAXS/WAXS, small- and wide-angle X-ray scattering; SEM, scanning electron microscopy; SLS, static light scattering; TEM, transmission

electron microscopy; TGA, thermogravimetric analysis; UV–Vis, ultraviolet–visible spectroscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

Fig. 1 | **Routes to directly synthesize amorphous CPs and MOFs.** Amorphous coordination polymers (*a*CPs) can be formed directly from flexible and/or asymmetric ligands of natural or synthetic origin, including nucleotides, proteins, polymers, polysaccharides and small molecules (part **a**). Moreover, *a*CPs can be grown in and around polymeric, biological, particulate and planar seeds and templates (part **b**). The synthesis conditions, such as the aqueous solution (pH, temperature and ionic strength), ligand-to-metal ratio, and ligand and metal concentration, can also be varied to directly synthesize *a*CPs rather than crystalline CPs (part **c**).

Fig. 2 | **Flexible and/or asymmetric ligands for directly synthesizing amorphous CPs and MOFs. a |** Examples of natural ligands that can be used to form amorphous coordination polymers (CPs) include amino acids, nucleotides, polyphenols, hydroxy-rich biopolymers, and phosphonates. **b |** Synthetic ligands used for the synthesis of amorphous CPs include small molecules and polymers with the chelating groups either in the backbone or at the termini. In each example, the functional groups that chelate to the metal ions are shown in blue.

Fig. 3 | **Templating and seeding strategies for the direct synthesis of amorphous CPs and MOFs. a–c |** Solid and porous particles, and macroscopic substrates can be used as templates to fabricate amorphous CP (*a*CP) capsules (part **a**), particles (part **b**) and films (part **c**). Scanning electron microscopy images (right, parts **a** and **b**) and a photograph (right, part **c**) of examples of the corresponding amorphous materials are also shown. **d,e |** Proteins and synthetic polymers can be used as seeding agents to endow functionality into *a*CPs (part **d**) or improve their stability (part **e**). Scanning electron microscopy (right, part **d**) and transmission electron microscopy (right, part **e**) images of the amorphous materials are also shown. Part **a** (microscopy image) reproduced with permission from ref.[30], AAAS. Part **b** (microscopy image) reproduced with permission from ref.[69], American Chemical Society. Part **c** (photograph) reproduced with permission from ref.[70], American Chemical Society. Part **d** (microscopy image) reproduced from ref.[82], CC BY 4.0 Part **e** (microscopy image) reproduced from ref.[85], CC BY 4.0 (http://creativecommons.org/licenses/by/4.0/).

Fig. 4 | **Controlling material properties of MOFs using seeding agents. a,b |** Molecular simulation of the structure of crystalline ZIF-8 (part **a**) and amorphous ZIF-8 (*a*ZIF; part **b**). The amorphous state exhibits enlarged pores. **c |** X-ray scattering data of simulated crystalline ZIF-8, amorphous ZIF (am), glucose oxidase-loaded amorphous ZIF (GOx-am), and GOx-loaded crystalline ZIF-8 (GOx-ZIF-8). The absence of Bragg diffraction in am and GOx-am confirms their amorphous nature. **d |** Density functional theory pore size distributions determined by N_2 adsorption and desorption at 77 K for ZIF-8, *a*ZIF and GOx-*a*ZIF. The pores of *a*ZIF and GOx-*a*ZIF are mesopores and larger than that of their crystalline counterparts (i.e., micropores). **e |** Enzymatic activities of enzyme-loaded ZIF-8 and enzyme-loaded *a*ZIF-8. The enzyme-loaded amorphous ZIFs exhibited 5–20 times higher catalytic activity than chemically identical enzyme-loaded crystalline ZIFs. CALB, *Candida antarctica* lipase B; CAT, catalase. Adapted from ref.[82], CC BY 4.0 (http://creativecommons.org/licenses/by/4.0/).

Fig. 5 | **Transitioning between amorphous and crystalline CPs through solvent choice. a |** The judicious choice of solvent enables the direct assembly and disassembly of salen-based amorphous CPs and crystalline CPs and their interconversion. Methanol likely coordinates to the metal ions, leading to rearrangement of the coordination network into an ordered structure. **b |** Scanning electron microscopy images show the amorphous (sphere) and crystalline (rods) CPs, as well as the intermediates that form during conversion upon addition of methanol to the solid amorphous spheres. Part **b** is adapted with permission from REF.[108], American Chemical Society.

Box 1 | **Challenges in crystalline CPs and MOFs and opportunities for amorphous analogues**

The periodic and ordered structure of crystalline coordination polymers (CPs) and metal–organic frameworks (MOFs) endow the materials with ultrahigh porosity and mechanical rigidity. This rigidity and accompanying brittleness make it challenging to process crystalline CPs and MOFs into functional macroscopic systems (such as thin films and monoliths), often leading to the loss of accessible pores. Moreover, many crystalline CPs and MOFs are synthesized at high temperature and pressure with organic solvents; this is an energy-intensive process, and the use of solvents might present environmental risks and affect downstream applications. **[Au:OK?]**

By contrast, the flexible and disordered nature of amorphous CPs and MOFs give rise to mechanical and chemical robustness. This robustness and accompanying processability make it easier to transform amorphous CPs and MOFs into functional macroscopic systems (for example, thin films, monoliths and hydrogels) with the added benefits of facile cargo loading and tunable release. Moreover, many amorphous CPs and MOFs are synthesized in ambient and aqueous conditions; therefore, they are more environmentally friendly than their crystalline counterparts and are generally stable in water.